Characterization of Inorganic Catalysts and Materials by Solid-State NMR

Aaron Rossini

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Characterization of Inorganic Catalysts and Materials 
by Solid-State NMR

by

Aaron J. Rossini

A Dissertation
Submitted to the Faculty of Graduate Studies 
through the Department of Chemistry and Biochemistry
in Partial Fulfilment of the Requirements for
the Degree of Doctor of Philosophy at the
University of Windsor

Windsor, Ontario, Canada

2010

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The Characterization of Inorganic Catalysts and Materials by Solid-state NMR

by

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Declaration of Co-Authorship / Previous Publications

The majority of the material contained within this document has been previously published in peer-reviewed journals. In accordance with regulations defined by the Faculty of Graduate Studies, this dissertation is presented in manuscript format. I was the principal investigator for all publications, excepting Chapter 8, which was a joint effort with the research group of Prof. Glen G. Briand (Mount Allison University). I had a significant role in the preparation of all manuscripts. I acknowledge my supervisor, Professor Robert W. Schurko, as a co-author in this work as he made significant contributions to the writing/editing of the individual manuscripts and chapters. Portions of the manuscripts upon which Chapters 2 and 8 are based, have been removed from the thesis because they were written by co-authors. Dr. Ivan Hung, a former graduate student in the research group acquired some of the $^{91}$Zr and $^{47/49}$Ti SSNMR spectra shown in Chapters 3 and 4. All other listed authors on manuscripts contributed through the synthesis of the materials studied, contribution of single crystal X-ray diffraction structures, or contribution of quantum chemical calculation data. The dissertation is based on the following publications:


I certify that I have obtained permission from the copyright owner(s) to include the above published material(s) in my thesis. I certify that this thesis, and the research to which it refers, are the product of my own work during my registration as a graduate student at the University of Windsor.
Abstract

This thesis demonstrates the application of solid-state nuclear magnetic resonance (SSNMR) spectroscopy to probe the structure of a variety of inorganic complexes and materials, many of which find applications in catalysis. Particular focus is given to SSNMR spectroscopy of “exotic” and unreceptive NMR nuclei. Complimentary characterization techniques such as quantum chemical calculations and X-ray diffraction experiments are also employed.

The initial focus of the thesis is on the characterization of crystalline molecular metallocenes by $^{35}$Cl, $^{47/49}$Ti and $^{91}$Zr SSNMR spectroscopy. All of these nuclei are considered to be unreceptive for NMR experiments due to a combination of low natural abundance, low resonance (Larmor) frequency and/or extreme broadening by anisotropic NMR interactions. It is demonstrated that with the combination of modern pulsed NMR techniques and high magnetic fields, SSNMR spectra of these nuclei in metallocenes can be rapidly acquired. Correlations are made between the symmetry and structure of the metallocene species, and the observed electric field gradient (EFG) and chemical shift (CS) tensor parameters extracted from the SSNMR spectra. Preliminary results from SSNMR studies of model heterogeneous metallocene catalysts are also presented.

$^{45}$Sc SSNMR spectroscopy of simple coordination complexes is investigated. Simple coordination complexes were investigated because most previous $^{45}$Sc SSNMR studies have been limited to extended systems with poorly defined structures. SSNMR experiments are also employed to investigate the molecular structure of a
heterogeneous scandium catalyst, microencapsulated Sc(OTf)₃.

²⁰⁷Pb SSNMR in conjunction with quantum chemical calculations are used to investigate the electronic structure of a series of lead(II) thiolate complexes. Frequently, lead(II) complexes possess stereochemically-active lone electron pairs. The observed and calculated ²⁰⁷Pb CS tensor parameters are utilized to probe the electronic configuration of the lead(II) complexes.

The utility of frequency swept WURST pulses for the acquisition of nuclear quadrupole resonance (NQR) spectra is investigated. The WURST pulses are demonstrated to be particularly useful for locating a NQR of unknown frequency and for acquiring wideline NQR spectra. The utility of WURST pulses for optimizing the configuration of NQR/NMR spectrometer systems is also demonstrated.
I would like to dedicate this work to Erin and my family for providing me with support during my post-graduate studies.
Acknowledgements

There are a large number of people who should be acknowledged for making many contributions to the work outlined in this thesis. First and foremost I would like to thank Professor Robert Schurko for affording me the opportunity to work in his research laboratory. Rob initially hired me as a second year undergraduate student to work in his laboratory for the summer. It seems that something piqued my interest during that first summer, as I would later stay on in Rob’s laboratory for the following eight years (three undergraduate and five post-graduate). Rob has always been a fair supervisor who has shown a keen interest in my work, even some of my crazier ideas, and has afforded me the chance to attend many scientific conferences.

Given the inordinate amount of time that one spends in the laboratory and office with their fellow graduate students, there are several co-workers who must also be acknowledged. In particular I would like to thank Ivan Hung, who in a way, was my primary supervisor when I first entered the lab. I learned a great deal from Ivan and I often find myself recalling lessons learned from him. In a similar vein, Andy Lo and Cory Widdifield were also more senior members of the laboratory who also taught me a great deal and were always willing to help with any experiments and problems that arose. I would also like to thank many of the other people I worked with over the years such as Joel Tang, Hiyam Hamaed, Bryan Lucier, Marcel Hildebrand, Ryan Mills and Graham Briscoe. I am especially grateful to Marcel for all of the work that he put into the work described in Chapter 7, which was initially his fourth-year Honours project. I would also
like to acknowledge two post-docs, Luke O’Dell and Kris Harris. I had a chance to work with both Luke and Kris towards the end of my graduate studies and I found working with them to be very intellectually stimulating.

In addition to the members of the Schurko group, there are many people at the University of Windsor who I would also like to thank. I am especially grateful to Professors Charles Macdonald and Samuel A. Johnson for both agreeing to serve on my PhD. committee. Both of them have also provided a great deal of advice over the years in matters of synthetic chemistry and crystallography. They are both very patient and were willing to answer any questions regarding synthesis and handling of compounds, no matter how naive my questions were. I would also like to thank the members of the Macdonald group, Benjamin F.T. Cooper, Greg Farrar, Chris Allan and Rajoshree Bandyopadhyay. We shared lab space with the Macdonald group and all of them provided advice and help to me at some point. I would also like to thank the two NMR managers who ran the solution NMR facility, Mike Fuerth and Matt Revington. Mike and Matt both helped with the setup of solids experiments on the 11.7 T instrument in the University NMR facility. Finally, I would like to thank all the members of the University support staff who helped with various aspects of the research. Joe Lichaa is thanked for all of his assistance with various computer problems and members of the Central Machine Shop are thanked for all of the odds and ends which they built. A special thanks goes to Sinisa Jezdic who helped fix various components of the probes and spectrometer many times over the years. Without Sinisa, the spectrometer would undoubtedly reside in a state of disrepair.
I would also like to acknowledge several collaborators from other universities: Prof. Glen Briand (Mount Allison University), Prof. Paul Deck (Virginia Tech) and Prof. Paul Hazendonk (University of Lethbridge). In addition to our formal collaborators, I would like to thank all of the staff at the Canadian National Ultra-High Field Facility for Solids. In particular I would like to thank Victor Terskikh, Eric Ye and Shane Pawsey for acquiring and/or aiding in the acquisition of high field NMR spectra.

Finally, I would like to thank all of my family and friends for their support. I must thank my wife, Erin, for all of her love and support during the writing of this thesis.
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Scheme 4.1. Titanocene chloride complexes for which $^{47/49}\text{Ti}$ SSNMR spectra have been acquired: Cp$_2$TiCl$_2$ (1), Cp*$_2$TiCl$_2$ (2), CpTiCl$_3$ (3), Cp*TiCl$_3$ (4).

Figure 4.1. Experimental MAS $^{47/49}\text{Ti}$ SSNMR spectra (black traces) of Cp$_2$TiCl$_2$ (1), Cp*$_2$TiCl$_2$ (2), CpTiCl$_3$ (3) and Cp*TiCl$_3$ (4) acquired at 21.1 T [$v_0(49\text{Ti}) = 50.75$ MHz] and spectra of 3 and 4 acquired at 9.4 T [$v_0(49\text{Ti}) = 22.53$ MHz]. Sample spinning speeds are given in the figure. Analytical simulations are overlaid on the experimental spectra (red traces). All spectra at 21.1 T were acquired with a standard rotor synchronized 90°-180° echo pulse sequence. Asterisks denote spinning sidebands. The inset of the spectrum of 4 shows the 49Ti isotropic peak that is obtained when the single high-frequency spinning sideband and the two nearest low-frequency spinning sidebands are added onto the isotropic peak. Spectra at 9.4 T were acquired with the DFS-echo (3) and DFS-QCPMG (4) pulse sequences. The spectrum of 4 was formed by co-adding the QCPMG echoes in the time domain, followed by Fourier transformation of the resultant echo. Additional experimental details are provided in Appendix C.

Figure 4.2. Static $^{47/49}\text{Ti}$ SSNMR spectra of Cp$_2$TiCl$_2$ (1), Cp*$_2$TiCl$_2$ (2), CpTiCl$_3$ (3) and Cp*TiCl$_3$ (4) acquired at 21.1 T and 9.4 T. Analytical simulations (red traces) are overlaid on the experimental spectra (black traces). De-convolutions of the 49Ti (green traces) and 47Ti (blue traces) powder pattern simulations are also shown. Spectra at 21.1 T were acquired with a standard echo sequence. Spectra of 1 and 2 at 9.4 T were acquired with the DFS-QCPMG pulse sequence.

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**Scheme 5.1.** Scandium complexes for which solid-state $^{45}$Sc NMR spectra have been acquired.

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**Figure 5.2.** Solid-state $^{45}$Sc NMR spectra and analytical simulations of Sc(NO$_3$)$_3$·5H$_2$O and Sc(OAc)$_3$. (a) MAS spectrum of Sc(NO$_3$)$_3$·5H$_2$O, $v_{rot} = 8$ kHz. (b) Static spectra of Sc(NO$_3$)$_3$·5H$_2$O at 9.4 T and 11.75 T. (c) MAS spectrum of Sc(OAc)$_3$, $v_{rot} = 8$ kHz. (d) Static spectra of Sc(OAc)$_3$ at 9.4 T and 11.75 T acquired with a 90°-90° echo.

**Figure 5.3.** Solid-state $^{45}$Sc NMR spectra and analytical simulations of ScCl$_3$·6H$_2$O and ScCl$_3$·3THF. (a) MAS spectrum of ScCl$_3$·6H$_2$O, $v_{rot} = 10$ kHz. (b) Static spectra of ScCl$_3$·6H$_2$O at 9.4 T and 11.75 T. (c) MAS spectrum of ScCl$_3$·3THF, $v_{rot} = 12.5$ kHz. (d) Static spectra of recrystallized ScCl$_3$·3THF at 9.4 T and 11.75 T acquired with a 90°-90° echo.

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**Figure 5.7.** Proposed EFG and CS tensor orientations. (a) Sc(acac)$_3$ (b) Sc(TMHD)$_3$ (c) Sc(NO$_3$)$_3$·5H$_2$O (d) Sc(OAc)$_3$ (e) ScCl$_3$·6H$_2$O (f) ScCl$_3$·3THF (g) ScCp$_3$.

**Figure 5.8.** Solid-state $^{45}$Sc NMR spectra and analytical simulations of Sc(OTf)$_3$ and ME Sc(OTf)$_3$. (a) MAS spectrum of Sc(OTf)$_3$, $v_{rot} = 4$ kHz. (b) Static spectra of Sc(OTf)$_3$ at 9.4 T and 11.75 T. (c) MAS spectrum of ME Sc(OTf)$_3$, $v_{rot} = 4$ kHz. (b) Static spectra of
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**Figure 6.5.** MAS $^1$H SSNMR spectra of (a) pure PS (PS), (b) PS recovered from cyclohexane, (c) PS recovered from cyclohexane and hexanes, (d) PS recovered from cyclohexane, hexanes, and acetonitrile, and (e) ME-2. A line-fitting simulation (red trace) is overlaid on the experimental spectrum of ME-2 (black trace). (f) Deconvolution of the individual sites employed in the line-fitting simulation. All spectra were acquired with a Bloch decay pulse sequence (90° pulse-acquire), $\nu_{\text{rot}}$ = 13.5 kHz, 32 scans and a recycle delay of 20 s which is required to obtain full recovery of longitudinal magnetization.

**Figure 6.6.** MAS $^1$H-$^{45}$Sc TRAPDOR SSNMR spectra of ME-2. (a) control experiment with no $^{45}$Sc irradiation, (b) dephasing experiment with irradiation of $^{45}$Sc during the $\tau_1$ period and (c) the difference spectrum resulting from subtraction of the dephasing spectrum from the control spectrum (intensity increased by a factor of 4). Linefitting simulations (red trace) are overlayed on the experimental spectra (black trace). (d) A deconvolution of the three sites employed in the linefitting simulations. $\nu_{\text{rot}}$ = 12.5 kHz and a recycle delay of 20 s were employed. A $\tau_1$ value of 240 s was used, corresponding to 3 rotor cycles, and a $^{45}$Sc rf field ($\nu_1$) of 108 kHz was applied during the $\tau_1$ period of the dephasing experiment.

**Figure 6.7.** Experimental PXRD patterns obtained from (a) anhydrous Sc(OTf)$_3$, (b) Sc(OTf)$_3$•8H$_2$O, (c) Sc(OTf)$_3$•xH$_2$O, (d) ME-1, (e) ME-2, and (f) solvent-treated PS.

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Figure 7.5. A representation of the rotation of vir MOs 139 and 143 of 1. The axes of rotation correspond to the directions of σ₁₁ and σ₂₂ in the molecular frame. Only Pb, S and N atoms are shown.

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Figure 8.4. Integrated intensity of the $^{35}$Cl NQR spectra of 4-chloropyridine as a function of transmitter offset from the resonance frequency for the 90°-180° echo, 90°-90° echo, composite echo and WURST echo. For each transmitter offset the probe was tuned using reflected power measurements available in Spinsight. Spectra with the four pulse sequences were then acquired. For clarity the intensity points have been connected by lines for the 90°-180° echo and WURST echo spectra.

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Figure 8.6. Wideline $^{63/65}$Cu NQR spectrum of the broad resonance of CuCN centered around 37.9 MHz. (a) "Point-by-point" spectrum (see text for details) acquired with the QCPMG pulse sequence and low power pulses (10 $\mu$s 90° pulse). A transmitter increment of 120 kHz was employed and 15 echoes were acquired (1.3 hours total acquisition time). (b) QCPMG spikelet spectrum and echo spectrum formed from time domain co-addition of the echoes. A transmitter increment of 120 kHz and high-power 90° pulses (0.7 $\mu$s) were employed. 12 sub-spectra were required to form the total pattern (1.3 hours total acquisition time). (c) WURST-QCPMG spikelet spectrum and echo spectrum formed from time domain co-addition of the echoes. A transmitter increment of 250 kHz was employed and 6 sub-spectra were required to form the total pattern (0.8 hours total acquisition time).

Scheme 9.1. Preparation of surface supported zirconocenes. Molecular analogs to the surface supported species are also shown.
Figure 9.1. Static $^{91}$Zr SSNMR spectra of (a) Cp$_2$ZrCl-(SiO$_2$) (1-Cl) and (b) Cp$_2$ZrMe-(SiO$_2$) (2-Me) acquired at 18.8 T. Analytical simulations are overlaid on the experimental spectra (solid red traces). Both spectra were acquired with sample temperatures of 10 K, 30 second recycle delays and 512 transients (4.3 hours) per sub-spectrum (50 kHz transmitter offset). 11 sub-spectra and 13 sub-spectra were acquired to form the total spectra of Cp$_2$ZrCl-(SiO$_2$) and Cp$_2$ZrMe-(SiO$_2$), respectively. A simulation with $\Omega = 0$ ppm (dashed blue trace) is shown for Cp$_2$ZrMe-(SiO$_2$). (c) Static $^{91}$Zr SSNMR WURST-QCPMG spectrum of Cp$_2$ZrCl(OSiMe$_3$) at 9.4 T (black trace). The asterisk denotes a small amount of Cp$_2$ZrCl$_2$. Partway through the acquisition of sub-spectra it was necessary to alter the probe configuration, resulting in uneven intensities in the individual sub-spectra, and leading to intensity differentials between the experimental and simulated spectra.

Figure 9.2. (a) Structure of Cp$_2$Zr(OSiMe$_3$) with coordinates based upon the single crystal XRD structure of Cp$_2$Zr(OSiMe$_2$(CH$_2$Cl)). (b) Geometry optimized structure of Cp$_2$Zr(OSiMe$_3$). (c) Geometry optimized model of 1-Cl. The Cp$_2$ZrCl fragment was bonded to a SiO$_2$ cluster based upon the structure of $\beta$-cristoballite. Atomic coordinates for the SiO$_2$ fragment were taken from Blanc et al. Each of the terminal oxygen atoms was capped with a single H atom.
### List of Abbreviations

<table>
<thead>
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>acac</td>
<td>acetylacetonate</td>
</tr>
<tr>
<td>ADF</td>
<td>Amsterdam Density Functional</td>
</tr>
<tr>
<td>AMDFS</td>
<td>amplitude modulated double frequency sweep</td>
</tr>
<tr>
<td>BHP</td>
<td>Bühl, Hopp, von Philipsborn</td>
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<tr>
<td>B3LYP</td>
<td>Becke’s three parameter hybrid functionals using the correlation functional of Lee, Yang and Parr</td>
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<tr>
<td>Cp</td>
<td>cyclopentadienyl</td>
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<td>Cp*</td>
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<td>cross-polarization Carr-Purcell Meiboom-Gill</td>
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<tr>
<td>CPMG</td>
<td>Carr-Purcell Meiboom-Gill</td>
</tr>
<tr>
<td>CS</td>
<td>chemical shift</td>
</tr>
<tr>
<td>CSA</td>
<td>chemical shift anisotropy</td>
</tr>
<tr>
<td>CT</td>
<td>central transition</td>
</tr>
<tr>
<td>DFS</td>
<td>double frequency sweep</td>
</tr>
<tr>
<td>DNP</td>
<td>dynamic nuclear polarization</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive X-ray</td>
</tr>
<tr>
<td>EFG</td>
<td>electric field gradient</td>
</tr>
<tr>
<td>FID</td>
<td>free induction decay</td>
</tr>
<tr>
<td>FWHH</td>
<td>full width at half height</td>
</tr>
<tr>
<td>GIAO</td>
<td>gauge including atomic orbitals</td>
</tr>
<tr>
<td>II</td>
<td>integrated intensity</td>
</tr>
<tr>
<td>Ind</td>
<td>indenyl</td>
</tr>
<tr>
<td>MAO</td>
<td>methyllumoxane</td>
</tr>
<tr>
<td>MAS</td>
<td>magic angle spinning</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>ME</td>
<td>microencapsulated</td>
</tr>
<tr>
<td>MG</td>
<td>Meiboom-Gill</td>
</tr>
<tr>
<td>MOs</td>
<td>molecular orbitals</td>
</tr>
<tr>
<td>MQMAS</td>
<td>multiple-quantum magic angle spinning</td>
</tr>
<tr>
<td>MS</td>
<td>magnetic shielding</td>
</tr>
<tr>
<td>n.a.</td>
<td>natural abundance</td>
</tr>
<tr>
<td>NLMO</td>
<td>natural localized molecular orbital</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NQR</td>
<td>nuclear quadrupole resonance</td>
</tr>
<tr>
<td>NR</td>
<td>non-relativistic</td>
</tr>
<tr>
<td>OAc</td>
<td>acetate</td>
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<tr>
<td>occ</td>
<td>occupied</td>
</tr>
<tr>
<td>OTf</td>
<td>trifluoromethanesulfonate</td>
</tr>
<tr>
<td>PAS</td>
<td>principal axis system</td>
</tr>
<tr>
<td>ppm</td>
<td>part per million</td>
</tr>
<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>PXRD</td>
<td>powder X-ray diffraction</td>
</tr>
<tr>
<td>QCPMG</td>
<td>quadrupolar Carr-Purcell Meiboom-Gill</td>
</tr>
<tr>
<td>QI</td>
<td>quadrupolar interaction</td>
</tr>
<tr>
<td>Q-factor</td>
<td>quality factor</td>
</tr>
<tr>
<td>RF</td>
<td>radiofrequency</td>
</tr>
<tr>
<td>RHF</td>
<td>restricted Hartree-Fock</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>S/N</td>
<td>signal to noise ratio</td>
</tr>
<tr>
<td>SSNMR</td>
<td>solid-state nuclear magnetic resonance</td>
</tr>
<tr>
<td>ST</td>
<td>satellite transitions</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMHD</td>
<td>2,2,6,6-tetramethyl-3,5-heptanedionato</td>
</tr>
<tr>
<td>TPPM</td>
<td>two pulse phase modulated</td>
</tr>
<tr>
<td>TRAPDOR</td>
<td>transfer of populations in double resonance</td>
</tr>
<tr>
<td>VACP</td>
<td>variable amplitude cross-polarization</td>
</tr>
<tr>
<td>vir</td>
<td>virtual</td>
</tr>
<tr>
<td>WURST</td>
<td>wideband uniform rate smooth truncated</td>
</tr>
<tr>
<td>ZORA</td>
<td>zeroth-order regular approximation</td>
</tr>
</tbody>
</table>
List of Symbols

$\alpha, \beta, \gamma$  Euler angles

$B_0$  static applied magnetic field

$B_1$  alternating magnetic field applied in the form of a pulse

$B_{\text{eff}}$  effective magnetic field

$C_Q$  quadrupolar coupling constant

$\Delta E$  energy separation

$\delta_{\text{iso}}$  isotropic chemical shift

$\delta_{11}, \delta_{22}, \delta_{33}$  principal components of the chemical shielding tensor

$e$  the charge of an electron

$\gamma$  gyromagnetic ratio

$h$  Planck’s constant

$\hbar$  Planck’s constant divided by $2\pi$

$\eta_Q$  electric field gradient asymmetry parameter

$I$  nuclear spin quantum number

$I$  nuclear spin angular momentum vector

$I_x, I_y, I_z$  $x, y$ or $z$-component of nuclear spin angular momentum

$k$  Boltzmann’s constant

$M$  macroscopic magnetization

$M_x, M_y, M_z$  components of macroscopic magnetization

$m_1$  nuclear Zeeman spin-state

$\mu$  magnetic dipole moment

$\nu$  frequency of radiation

$\nu_1$  nutation frequency of applied rf fields in Hz

$\nu_0$  Larmor frequency in Hz

$\nu_Q$  quadrupolar frequency in Hz
Chapter 1: Introduction and Theory

1.1 Introduction

The space quantization of electron spin and nuclear spin were first discovered over 80 years ago by Stern and Gerlach in the early 1920's and early 1930's.1-5 Their experiments were conducted with beams of silver atoms and molecular hydrogen in inhomogeneous magnetic fields. From these experiments it was possible to measure the magnetic moments of the electron and proton nuclei. Rabi proposed and conducted further atomic and molecular beam experiments in the late 1930's.6-9 Rabi took the additional step of applying electromagnetic radiation to induce transitions between the nuclear spin states, marking the first demonstrations of nuclear magnetic resonance (NMR). In the late 1940's the research groups of Bloch and Purcell independently undertook experiments which allowed for the detection of ¹H NMR signals by the application of radiofrequency (rf) fields to condensed matter samples in static magnetic fields.10-16 Until the early 1950's, NMR was principally used as tool by physicists to test the predictions of quantum mechanics and to measure the spin angular momentum (I) and magnetic moments (µ) of various nuclei. Underscoring the importance of these early experiments, Nobel prizes in physics were awarded to Stern in 1943, Rabi in 1944, and Purcell and Bloch in 1952.

In the mid-1950's the chemical shift was observed when distinct ¹H resonances were recorded for ethanol.17 Shortly thereafter, the utility of solution NMR for the rapid assessment of molecular structure was realized. With this key discovery in hand and the
implementation of modern pulsed NMR techniques by Ernst in the 1960's and 1970's,\textsuperscript{18, 19} NMR quickly found applications in diverse areas such as magnetic resonance imaging, synthetic chemistry, analytical chemistry, materials science and biochemistry.\textsuperscript{20, 21}

Many of the early (and now routine) NMR experiments employ ubiquitous and/or receptive spin-1/2 nuclei such as $^1$H, $^{13}$C and $^{19}$F. However, many of the elements in the periodic table possess NMR-active nuclei which are classified as “unreceptive” due to their combination of low gyromagnetic ratio ($\gamma$), low natural abundance (n.a.), unfavourable relaxation characteristics, large chemical shielding anisotropies (CSA) and/or large quadrupole moments ($Q$). These unreceptive NMR nuclei can potentially be used to probe the structures of a myriad number of inorganic complexes which have far reaching applications in research areas such as catalysis, energy conversion, and biochemistry. The primary focus of this thesis is upon developing and utilizing solid-state NMR (SSNMR) spectroscopy of unreceptive and/or “exotic” nuclei to characterize the structure of inorganic complexes and materials, many of which find applications in catalysis. The background for the individual systems and the motivation for their study are provided in the introduction sections of the individual chapters.

The contents of this section are derived from a number of excellent texts and reviews which explain the theoretical aspects of NMR spectroscopy, in various levels of detail, to which the reader is referred.\textsuperscript{22-32}

1.2 Background and Theoretical Overview

The NMR phenomenon arises due to the interaction of nuclear magnetic dipole
moments with external magnetic fields. There are additional internal interactions arising from the presence of neighbouring nuclear spins and electrons that affect the energy of the nuclear spin states, and hence the appearance of the NMR spectra that are obtained. A Hamiltonian that describes the principal interactions of NMR, and hence, the energy of the nuclear spin states of a diamagnetic system placed in a magnetic field can be written:

\[ H_{\text{Total}} = H_Z + H_{\text{MS}} + H_Q + H_{\text{DD}} + H_J \]  

(1)

where \( H_Z \) is the Zeeman interaction, \( H_{\text{MS}} \) is the nuclear magnetic shielding interaction, \( H_Q \) is the quadrupolar interaction, \( H_{\text{DD}} \) represents direct dipolar coupling and \( H_J \) represents indirect spin-spin coupling. Each of these interactions are discussed below in detail.

### 1.3 The Zeeman Interaction

Nuclei which possess a nuclear spin quantum number (\( I \)) greater than 0 intrinsically possess nuclear spin angular momentum (\( \mathbf{I} \), the bold face indicates that it is a vector quantity), which is proportional to a nuclear magnetic dipole moment (\( \mu \)):

\[ \mu = \gamma I \]  

(2)

Here, \( \gamma \) is the constant of proportionality known as the gyromagnetic ratio, which relates the magnitude of \( \mu \) to \( I \). The sign of \( \gamma \) can be negative or positive, with a positive \( \gamma \) indicating that \( \mu \) is aligned in the same direction as \( \mathbf{I} \) and a negative \( \gamma \) indicating the
opposite. The magnitude of $I$ is:

$$|I| = \hbar[I(I+1)]^{1/2} \tag{3}$$

Classically, the energy of a magnetic dipole in an external magnetic field ($B$) depends upon its orientation:

$$E = -\mathbf{\mu} \cdot \mathbf{B} = -\mu B \cos(\theta) \tag{4}$$

where $\theta$ is the angle which describes the angle which $\mu$ makes with $B$ (the latter is usually assumed to be directed along the $z$-axis). Therefore, it is energetically favourable for $\mu$ to align with the applied field $B$ ($\theta = 0$), while it is unfavourable for $\mu$ to oppose $B$ ($\theta = \pi$ radians).

Now consider a nuclear magnetic dipole placed in a magnetic field ($B_0$) which is directed along the $z$-axis and possesses no $x$- or $y$- components [$B_0 = (0, 0, B_0)$]. In an analogous manner to the classical expression, there are different energies associated with the possible orientations of $\mu$ with respect to the magnetic field. However, unlike the classical case it is found that for a nucleus the orientations of $\mu$ are quantized, that is, the expectation values of the $z$-component of nuclear spin angular momentum ($I_z$) are restricted to discrete values. For a spin $I$ nucleus, there are $2I+1$ possible values of $I_z$.

The possible values of $I_z$ are termed nuclear spin states and are described by the quantum number $m_I$, where $m_I = I, I - 1, ..., -I$. In a magnetic field the nuclear spin states are non-degenerate (Figure 1.1), and the Hamiltonian describing this interaction and the energy of the respective nuclear spin states are given by:
\[ \mathcal{H}_z = -\hat{I}_z\gamma B_0, \]  

(5)

\[ E_{m_i} = -m_i\hbar\gamma B_0 = -m_i\hbar\omega_0 \]  

(6)

The quantity \( \gamma B_0 \) has units of rad s\(^{-1}\) and is known as the Larmor frequency (\( \omega_0 \)).

Classically, this corresponds to the frequency at which the nuclear spin angular momentum precesses about the magnetic field. This precession occurs over a conical path, which possess a fixed angle between the nuclear spin angular momentum vector and

\[
\begin{align*}
\Delta E &= \hbar\gamma B_0 \\
\omega_0 &= -\hbar\gamma B_0
\end{align*}
\]

\( E_m = -m_i\hbar\omega_0 \)

\textbf{Figure 1.1.} (a) The presence of a magnetic field results in quantization of the z-component of nuclear spin angular momentum (shown for an \( I = 3/2 \) nucleus). This results in distinct nuclear spin states. The energy separation between each of the adjacent nuclear spin states is equivalent, therefore, there is only one transition frequency. (b) The nuclear spin angular momentum precesses about the applied magnetic field.
the applied field for a given $m_i$ (Figure 1b). The Larmor frequency defines the frequency of radiation which is necessary in order to induce transitions between the adjacent nuclear spin states ($\Delta E = h\nu$, *vide infra*). Under the influence of the Zeeman interaction, there is only one transition frequency for a spin $I$ nucleus, as the separation of each nuclear spin state is equivalent and only transitions with $\Delta m_i = 1$ are formally allowed.

Only an isolated spin in a magnetic field has been considered thus far; however, when an NMR experiment is performed one must employ a sample which contains a large number of spins (typically $> 10^{15}$ spins). As a result of the small magnitude of $\mu$, the energy differences between the spin states are very small. For most NMR experiments the magnitude of the thermal energy ($kT$) is much larger than the energy of the Zeeman interaction. For this reason, there is only a slight tendency for the spins to align with the field in the lower energy orientation. The ratio of the populations of the individual spin states in a bulk sample can be determined from the Boltzmann distribution:

$$\frac{N_{\alpha}}{N_{\beta}} = e^{\frac{\Delta E}{kT}} = e^{\frac{h\gamma B_0}{kT}} \quad (7)$$

For an $I = 1/2$ nucleus with positive $\gamma$, $\beta$ corresponds to $m_i = -1/2$ and $\alpha$ to $m_i = +1/2$, $N_{\alpha}$ refers to the number of nuclei populating a lower energy nuclear spin state, and $N_{\beta}$ the number populating a higher energy spin state. For a collection of $^1$H nuclei in an applied magnetic field of 9.4 T ($\nu_0 \approx 400$ MHz) and a temperature of 295 K, the ratio of $N_{\alpha}/N_{\beta}$ is equal to 1.000065102. This illustrates how small the differences in the energies, and subsequently the population differences of the nuclear spin states are. Finally, it is
important to note that the nuclear spins are not restricted to distinct quantum states (i.e., every spin in the sample is aligned or opposed to the field); rather the individual spins exist in superpositions of the allowed quantum states.

While the population differences between the spin states are very small, the slight tendency for the nuclei within the sample to orient such that their magnetic dipole moments are aligned along the magnetic field, gives rise to a bulk macroscopic magnetization \((\mathbf{M})\). The magnitude of the observable NMR signal is directly proportional to the magnitude of the projection of \(\mathbf{M}\) along the z-axis \((M_z)\), necessitating the use of relatively large sample sizes (e.g., samples containing at least \(ca. 10^{15}\) nuclear spins). The signal of the NMR experiment can be increased by working at high magnetic fields, cooling the sample to low temperatures and by utilizing nuclei which possess large gyromagnetic \((\gamma)\) ratios, as all of these factors will also lead to an increase in the magnitude of \(N_u/N_B\), and consequently a larger \(M_z\).

1.4 Interactions of Nuclear Spins with Applied RF Fields

Before further discussing the NMR interactions it is necessary to understand how nuclear spins respond to applied radiofrequency fields. In a typical NMR experiment, a sample is placed into a small coil which is located inside of a large homogeneous static magnetic field. Once in the field, the sample attains an equilibrium value of \(M_z\), after a period of time which is dictated by the relaxation properties of the nuclei. A pulse of alternating current of finite duration \((\tau_p)\), which oscillates at a transmitter frequency \((\omega_{tx})\) equal to, or similar to \(\omega_0\) of the nucleus, is passed through the coil. This generates an
\[ \Delta B = \left( \omega_{tx} - \omega_0 \right) / \gamma \]

Figure 1.2. (a) A component of the \( B_1 \) field appears to be stationary in a frame which rotates at a frequency equal to that of the applied rf field (\( \omega_{tx} \)). If the frequency of \( \omega_{tx} \) and \( \omega_0 \) differ, then an effective magnetic field results, which possesses both \( z \)- and \( x' \)-components. (b) If the frequency \( \omega_{tx} \) is close to \( \omega_0 \), then the bulk magnetization, \( M_Z \) will precess about the applied field \( B_1 \) and be rotated in the \( y' \) \( z \)-plane (the on resonance case of \( \omega_{tx} = \omega_0 \) is shown). The angular displacement (\( \theta_p \)) of \( M_Z \) depends upon the magnitude of the \( B_1 \) field and duration of the applied pulse (\( \tau_p \)). If the pulse duration is such that \( \theta_p = \pi/2 \), then the magnetization ends up along \( -y' \).

oscillating magnetic field (\( B_1 \)). The coil is designed/oriented such that the \( B_1 \) field will possess a component which is perpendicular to the direction of the large static magnetic field (\( B_0 \)). For a solenoidal coil oriented such that its cylindrical axis is perpendicular to \( B_0 \), the \( B_1 \) field will also be perpendicular to \( B_0 \) (in the \( xy \)-plane).

At this point it is convenient to consider a frame which rotates about the \( z \)-axis with angular frequency \( \omega_{tx} \). The \( x \) and \( y \) coordinates of this rotating frame are denoted \( x' \) and \( y' \). In this rotating frame, a component of the \( B_1 \) field appears as a stationary field which is aligned along \( x' \). If the frequency of the applied field (\( \omega_{tx} \)) is equal to that of the Larmor frequency (\( \omega_{tx} = \omega_0 \)), then magnetic dipole moments of the individual nuclei will precess about the applied \( B_1 \) field. A component of \( M_Z \) is rotated into the \( xy \)-plane by the \( B_1 \) field, yielding transverse magnetization (i.e., \( M_X \) and \( M_Y \)). If the frequency of \( \omega_{tx} \) and
\( \omega_0 \) differ, then this reduces the magnitude of the \( x \)'-component of \( B_1 \) field, and results in an effective magnetic field (\( B_{\text{eff}} \)) which has both \( z \)- and \( x \)'-components (or \( y \)'-components depending upon the phase of the pulse). If one defines the quantity \( \Delta B = (\omega_{\text{tx}} - \omega_0)/\gamma \), then the orientation of \( B_{\text{eff}} \) in the rotating frame is found by vector summation of \( B_1 \) and \( \Delta B \) (Figure 2a). If there is a large difference between the frequency of the applied pulse (\( \omega_{\text{tx}} \)) and the Larmor frequency (\( \omega_0 \)), then the pulse will less effective at generating transverse magnetization (\textit{vide infra}).

The magnitude of \( B_1 \) depends upon the amount of current which is passed through the coil; if a large current is passed through the coil then a large \( B_1 \) field will be obtained. The magnitude of the \( B_1 \) field is usually quantified by the nutation frequency, \( \omega_1 = \gamma B_1 \), which describes the rate at which magnetization will precess about \( B_1 \) fields applied on resonance. Large \( B_1 \) fields result in higher nutation frequencies, which are capable of exciting NMR signals with larger frequency offsets. This is a very important consideration for the acquisition of wideline SSNMR spectra, where very large differences between the transmitter and resonance frequencies commonly occur.

Knowledge of the nutation frequency is very important, as it also determines the duration of pulses necessary to obtain optimal signal. If an on-resonance pulse of duration \( \tau_p \) and strength \( \omega_1 \) is applied, \( M_z \) will be rotated through an angle (\( \theta_p \)):

\[
\theta_p = \omega_1 (\tau_p)
\]

\( \theta_p = \pi/2 \) rad, then \( M_z \) is converted into transverse magnetization (in the case of Figure 2b, \(-M_y\)). Power levels of the pulses are
experimentally calibrated by recording a series of spectra with pulses of variable durations at a constant power setting ($B_1$). Maximum signal corresponds to the $\pi/2$- or $90^\circ$-pulse, as this will generate the maximum amount of initial transverse magnetization. It should be noted that many experiments also rely upon $\pi$-pulses, which are double the duration of $\pi/2$ pulses.

In the simplest NMR experiments, a single $\pi/2$ pulse is applied to the sample. After the pulse, transverse magnetization generated remains in the $xy$-plane and precesses about $B_0$. In turn, this induces an alternating current in the sample coil. This induced current is then recorded by a receiver to form a time-domain signal, which is subsequently digitized, and transferred to a computer where it is Fourier transformed to construct a frequency-domain NMR spectrum.

1.5 Relaxation Processes

Relaxation processes will only be briefly addressed here. There are two main types of relaxation commonly encountered in NMR spectroscopy: longitudinal, or spin-lattice relaxation and transverse relaxation. Phenomenological descriptions of both processes are provided by the Bloch equations. The interested reader is referred to other more advanced descriptions of relaxation.

Consider the case of an ensemble of $^1\text{H}$ nuclei; when the sample is initially placed into a magnetic field, the nuclear spins will have no preferred orientation within the sample, and hence there will be no macroscopic magnetization. Due to random molecular motion, the nuclear spins experience an enormous number of small fluctuating local
magnetic fields which cause the nuclear spins to gradually change their orientations such that there is an excess of spins populating the $\alpha$ spin state. Eventually, $M_Z$ reaches the equilibrium value ($M_0$) predicted from the Boltzmann distribution. This buildup of $M_Z$ is known as longitudinal relaxation and is described by the time constant $T_1$. For nuclei in solution, $T_1$ is usually on the order of seconds, although it may range from $\mu$s for paramagnetic complexes, to hours or days for nuclei in some solids. The $T_1$ of the nucleus dictates the amount of time which one must wait in between scans, and hence strongly influences the total time required for NMR experiments. The magnitude of $M_Z$ is related to $T_1$ via an exponential relationship, therefore, in order to obtain complete relaxation ($M_Z = M_0$) one must wait approximately $5 \ T_1$ periods.

In a manner analogous to longitudinal relaxation, the transverse magnetization generated by an applied pulse will also undergo relaxation. After the pulse is applied, the transverse magnetization precesses in the $xy$-plane, however, its magnitude decreases over time and it eventually decays to zero. This occurs due to the individual nuclear spins acquiring random orientations (phases) within the $xy$-plane which leads to a loss of coherence. This process is known as transverse relaxation and is described by the time constant $T_2$. Transverse relaxation results from molecular motion and fluctuating magnetic fields, as for longitudinal relaxation, as well as static time-independent local fields which result in different precession frequencies. $T_2$ is always less than $T_1$ and is typically on the order of ms to s. A long $T_2$ is desirable as this provides sufficient time for the power of the pulse to dissipate in the probe and allows the signal to be recorded without interference. Long $T_2$'s are also beneficial as they allow the magnetization to be
repeatedly refocused, as in the Carr-Purcell Meiboom-Gill pulse sequence,\textsuperscript{36, 37} which is a useful approach for signal enhancement.

1.6 Nuclear Magnetic Shielding and Chemical Shift

The nuclear magnetic shielding (MS) phenomenon was first observed in 1950 in $^{19}$F and $^{14}$N NMR experiments.\textsuperscript{38, 39} In 1951 three distinct $^1$H resonances were observed for the methyl (-CH$_3$), methylene (-CH$_2$) and alcohol (-OH) hydrogen nuclei of ethanol, and their frequency differences were referred to as chemical shifts (CS).\textsuperscript{17} These discoveries spurred the further development of NMR spectroscopy as a tool for the evaluation of molecular structure.

The magnetic shielding (MS) interaction arises due to induced circulation of electrons around the nucleus. Since electrons are charged particles, their circulation about the nucleus induces a magnetic field which alters the local field at the nucleus. The total isotropic magnetic shielding ($\sigma_{iso}$) describes the magnitude of this induced field. The effect of magnetic shielding is to effect the apparent magnitude of $B_0$ and concomitantly alter $\omega_0$:

$$\omega_0 = (1 - \sigma_{iso}) \gamma B_0$$ \hspace{1cm} (9)

$\sigma_{iso}$ is unitless and usually positive, and its magnitude is typically on the order of parts per million (ppm, $10^{-6}$). The “iso” subscript refers to the isotropic (or average) MS, since the MS interaction is usually anisotropic in nature (\textit{vide infra}).

The theoretical basis of the MS interaction was described in the early 1950's
shortly after the observation of the chemical shift. $^{40-42}$ $\sigma_{\text{iso}}$ is usually broken down into diamagnetic ($\sigma_{d, \text{iso}}$) and paramagnetic ($\sigma_{p, \text{iso}}$) contributions:

$$\sigma_{\text{iso}} = \sigma_{d, \text{iso}} + \sigma_{p, \text{iso}}$$ (10)

Diamagnetic contributions ($\sigma_{d, \text{iso}}$) typically shield the nucleus from the external field ($\sigma_d > 0$), and paramagnetic contributions ($\sigma_{p, \text{iso}}$) typically deshield the nucleus ($\sigma_{p, \text{iso}} < 0$). Diamagnetic shielding arises due to circulation of electrons in the ground state orbitals, which is induced by the applied static magnetic field. For a given nucleus, the values of $\sigma_d$ show little variation between different chemical species. Paramagnetic shielding, is also induced by the static magnetic field and arises due to the mixing of low lying excited electronic states (virtual orbitals) with ground electronic states (occupied orbitals). $\sigma_p$ strongly depends upon the oxidation state of the element as well as the symmetry of the nuclear site. Consequently, variations in $\sigma_p$ are responsible for the differences in MS (and CS) observed for different chemical species. The $\sigma_p$ term is usually highly anisotropic in nature and is responsible for the anisotropic nature of total MS. For heavy nuclei relativistic effects lead to a significant spin-orbit contribution ($\sigma_s$) to the total shielding which must also be taken into account. $^{43-46}$ For an in depth discussion of these various shielding terms see Chapter 8 where the contributions of the various shielding terms to the MS of $^{207}\text{Pb}$ in a series of lead(II) thiolate complexes are discussed.

In order to understand how MS affects the appearance of NMR spectra it is necessary to consider the Hamiltonian which describes this interaction:
\[
\mathcal{H}_{\text{MS}} = -\hbar \gamma \mathbf{I} \cdot \mathbf{\sigma} \cdot \mathbf{B}
\] (11)

\(\mathbf{I}\) and \(\mathbf{B}\) are vector quantities describing the nuclear spin angular momentum and the direction of applied field, respectively. From this equation it can be seen that the MS interaction varies with the nuclear spin orientation relative to the external magnetic field. \(\mathbf{\sigma}\) is second-rank tensor that describes the MS of the nucleus in the molecular frame:

\[
\mathbf{\sigma} = \begin{pmatrix}
\sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\
\sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\
\sigma_{zx} & \sigma_{zy} & \sigma_{zz}
\end{pmatrix}
\] (12)

Individual MS tensor components \((\sigma_{ij})\) describe the shielding in the direction \(i\) that results from application of a magnetic field along direction \(j\). The MS tensor can be transformed to its own principal axis system (PAS) by removing the antisymmetric portion of \(\mathbf{\sigma}\) and diagonalizing the symmetric portion. This yields \(\mathbf{\sigma}_{\text{PAS}}\):

\[
\mathbf{\sigma}_{\text{PAS}} = \begin{pmatrix}
\sigma_{11} & 0 & 0 \\
0 & \sigma_{22} & 0 \\
0 & 0 & \sigma_{33}
\end{pmatrix}
\] (13)

The orientation of the PAS within the molecular frame can sometimes be rationalized by considering the symmetry at the nuclear site. The directions corresponding to the principal components of \(\sigma_{\text{PAS}}\) will usually align with molecular symmetry elements (e.g., rotational axes, mirror planes, etc.). The principal components are ordered such that \(\sigma_{11} \leq\)}
\( \sigma_{22} \leq \sigma_{33} \) (i.e., from lowest to highest shielding). The isotropic shielding can be calculated from the principal tensor components:

\[
\sigma_{\text{iso}} = \frac{\sigma_{11} + \sigma_{22} + \sigma_{33}}{3}
\]  

(14)

The zero point of the MS scale is a bare nucleus which does not have any electrons associated with it (e.g., for \(^{13}\)C, \(\sigma_{\text{iso}}(\text{C}^6+) = 0 \text{ ppm}\)). Experimentally, it is usually impossible to measure the resonance frequency of a bare nucleus. Therefore, \(\sigma_{\text{iso}}\) values can not be easily determined for nuclei in atoms and molecules, as the \(\omega_0\) corresponding to \(\sigma = 0.0 \text{ ppm}\) cannot be measured. For this reason, the chemical shift (CS) scale is employed. The CS scale (\(\delta\)) is constructed by assigning a reference material an arbitrary shift (often \(\delta_{\text{iso}} = 0 \text{ ppm}\)) and then measuring the Larmor frequency (\(v_{\text{sample}}\)) of the compound of interest and the standard (\(v_{\text{reference}}\)). If the two resonance frequencies are known, then the isotropic chemical shift (\(\delta_{\text{iso}}\)) can be determined:

\[
\delta_{\text{iso}} = \frac{(v_{\text{sample}} - v_{\text{reference}})}{(v_{\text{reference}} \times 10^6)} - \frac{\sigma_{\text{iso, sample}} - \sigma_{\text{iso, reference}}}{1 - \sigma_{\text{iso, reference}}} = \sigma_{\text{iso, sample}} - \sigma_{\text{iso, reference}}
\]

(15)

\(\delta_{\text{iso}}\) is approximately equal to the difference in the shielding values of the nucleus in the sample (\(\sigma_{\text{iso, sample}}\)) and the shielding values of the nucleus in the reference (\(\sigma_{\text{iso, reference}}\)).

The principal components of the MS tensor (\(\sigma_{kk}\)) can also be converted to the principal components of the CS tensor (\(\delta_{kk}\)) in this manner:
Note that the principal components of the CS tensor are ordered such that \( \delta_{11} \leq \delta_{22} \leq \delta_{33} \), from highest CS (least shielded) to lowest CS (most shielded).

As previously mentioned, the CS tensor is anisotropic in nature. A number of conventions have been developed to describe the magnitude of the chemical shift anisotropy (CSA) as well as the symmetry of the CS tensor. These conventions aim to make it simpler to compare CS tensors measurements between different complexes and nuclei. In this thesis, the Maryland convention is used to specify the CS tensors.\(^{47, 48}\) This convention employs three different parameters which are all derived from the principal components of the CS tensor: \( \delta_{\text{iso}} \), the span (\( \Omega \)) and the skew (\( \kappa \)):

\[
\delta_{\text{iso}} = \frac{\delta_{11} + \delta_{22} + \delta_{33}}{3}
\]

\[
\Omega = \delta_{11} - \delta_{33} \approx \sigma_{11} - \sigma_{33}
\]

\[
\kappa = \frac{3(\delta_{22} - \delta_{\text{iso}})}{\Omega}, \quad -1 \leq \kappa \leq +1
\]

\( \delta_{\text{iso}} \) corresponds to the average value of the principal components of the CS tensor and corresponds to the chemical shift which is measured from solution NMR spectra. \( \Omega \)
describes the magnitude of the CSA and is always a positive number. $\kappa$ ranges from $+1$ to $-1$ and describes the axial symmetry of the CS tensor (e.g., if $\kappa = +1$ then $\delta_{22} = \delta_{11}$ and if $\kappa = -1$ then $\delta_{22} = \delta_{33}$).

Figure 1.3. (a) Simulated $^{13}\text{C}$ ($I=1/2$) static spectra with $\Omega = 20.0$ ppm and $\delta_{\text{iso}} = 0.0$ ppm. $\kappa$ affects the position of $\delta_{22}$. Discontinuities correspond to the principal components of the CS tensor. When $\kappa = +1.0$, $\delta_{11} = \delta_{22}$ and when $\kappa = -1.0$, $\delta_{22} = \delta_{33}$. (b) Different orientations of the CS tensor with respect to the magnetic field give rise to distinct transition frequencies (shown on the left). In a powdered sample the tensor will be present in all orientations with respect to a magnetic field, giving rise to a powder pattern.
The influence of these parameters on the appearance of NMR spectra are now addressed. In solution NMR experiments, the effects of CSA are averaged to zero (although it may broaden the spectrum via relaxation effects) because the molecules containing the nuclei of interest usually experience rapid isotropic tumbling in solution. This leads to the observation of a single relatively narrow resonance with a chemical shift of $\delta_{\text{iso}}$. Conversely, when acquiring SSNMR spectra one normally works with powdered samples in which the molecules are not undergoing rapid isotropic motion. A crystalline powdered sample contains a random array of crystallites, and hence every possible orientation of the molecule (and CS tensors) with respect to the magnetic field exists (Figure 1.3). The anisotropic nature of the CS interaction leads to the broadening of SSNMR spectra of powdered samples, resulting in so-called powder patterns. Examples of static $^{13}$C SSNMR powder patterns which result from CSA are shown in Figure 1.3a. The shape of the powder patterns is controlled by the CS tensor parameters. The breadth of the powder pattern in ppm is equal to $\Omega$, while $\kappa$ determines the location of the central discontinuity (which corresponds to $\delta_{22}$) and $\delta_{\text{iso}}$ is the centre of gravity of the powder pattern.

### 1.7 Quadrupolar Nuclei and the Quadrupolar Interaction

The quadrupolar interaction is observed for nuclei with $I > 1/2$ (e.g., $I = 1, 3/2, 5/2$, etc.). In a quadrupolar nucleus, the nuclear charge is non-spherically distributed, giving rise to a nuclear quadrupole moment ($Q$).$^{22,49}$ The quadrupolar interaction occurs due to the interaction of $Q$ with any surrounding electric field gradients (EFGs). EFGs
arise from the non-spherically symmetric distribution of charges or electron density (i.e., from atoms and bonds) surrounding the nucleus. At any nucleus about which the molecular geometry is non-spherical there will exist a non-zero EFG. \textsuperscript{50, 51} The EFG about a nucleus in the molecular frame is described by a symmetric (e.g., \( V_{xy} = V_{yx} \)) second-rank tensor \( \vec{V} \):

\[
\vec{V} = \begin{pmatrix}
V_{xx} & V_{yx} & V_{zx} \\
V_{xy} & V_{yy} & V_{zy} \\
V_{xz} & V_{yz} & V_{zz}
\end{pmatrix}
\] (20)

Diagonalization of the EFG tensor transforms the EFG to its PAS:

\[
\vec{V}_{\text{PAS}} = \begin{pmatrix}
V_{11} & 0 & 0 \\
0 & V_{22} & 0 \\
0 & 0 & V_{33}
\end{pmatrix}
\] (21)

The EFG tensor is described by three principal components ordered such that \( |V_{11}| \leq |V_{22}| \leq |V_{33}| \). The EFG tensor is also traceless \([V_{11} + V_{22} + V_{33} = 0]\).

The magnitude of the quadrupolar interaction is described by the quadrupolar coupling constant and the quadrupolar frequency (both in units of Hz):

\[
C_Q = \frac{eQV_{33}}{h}, \quad \nu_Q = \frac{3C_Q}{2I(2I - 1)}
\] (22)

For most quadrupolar nuclei residing in non-spherically symmetric environments, \( C_Q \) is
on the order of MHz and in extreme cases may approach the magnitude of the $\nu_0$. The EFG asymmetry parameter, $\eta_Q$, describes the axial symmetry of the EFG tensor:

$$\eta_Q = \frac{V_{11} - V_{22}}{V_{33}}, \quad 0 \leq \eta_Q \leq 1$$  \hspace{1cm} (23)

The cases where $\eta_Q = 0$ ($V_{11} = V_{22}$) and $\eta_Q = 1$ ($V_{11} = 0$, $V_{22} = -V_{33}$) correspond to axially symmetric EFG tensors.

The total Hamiltonian describing the quadrupolar interaction is:

$$\mathcal{H}_Q = \frac{eQ}{2I(2I - 1)\hbar} \mathbf{I} \cdot \mathbf{V} \cdot \mathbf{I} = \frac{eQ}{6I(2I - 1)\hbar} \sum_{a,\beta = X,Y,Z} V_{\alpha \beta} \left[ \frac{3}{2} \left( \hat{I}_{a} \hat{I}_{\beta} + \hat{I}_{\alpha} \hat{I}_{\beta} \right) - \delta_{a \beta} \hat{I}^2 \right]$$  \hspace{1cm} (24)

Expansion of the $\mathbf{I} \cdot \mathbf{V} \cdot \mathbf{I}$ term on the left by matrix multiplication and use of the fact, $V_{\alpha \beta} = V_{\beta \alpha}$, leads to the form of the Hamiltonian on the right. If $\nu_0$ is on the order of 10 times larger than $\nu_Q$, then the quadrupolar interaction may be treated as a perturbation of the Zeeman interaction, allowing for the terms on the right hand side of equation (22) which do not commute with $I_z$ to be discarded. The quadrupolar Hamiltonian is then expanded into a series using perturbation theory:

$$\mathcal{H}_Q = \mathcal{H}_Q^{[1]} + \mathcal{H}_Q^{[2]} + ......$$  \hspace{1cm} (25)

If $\nu_Q$ is relatively small then only the first-order quadrupolar interaction [$\mathcal{H}_Q^{[1]}$] needs to be considered. The main effect of the quadrupolar interaction is to perturb the energies of the Zeeman spin states ($m_I$):
\[ E_m = E_{Z,m} + E_{Q,m}^{[1]} + E_{Q,m}^{[2]} \]  

(26)

where \( E_m \) is the total energy of a given spin state \( m \), \( E_{Z,m} \) is the energy of the Zeeman interaction and \( E_{Q,m}^{[1]} \) and \( E_{Q,m}^{[2]} \) correspond to the energy corrections associated with the first-order and second-order quadrupolar interaction, respectively. The correction of the energy of spin-state \( m \) due to the first order quadrupolar interaction is given by:

\[ E_{Q,m}^{[1]} = \frac{e^2qQ}{4I(2I - 1)}[3m^2 - I(I+1)]F(\theta,\varphi) \]  

(27)

where:

\[ F(\theta,\varphi) = \frac{1}{2}[3\cos^2\theta - 1] + \frac{1}{2}\eta_Q\sin^2\theta\cos2\varphi \]  

(28)

The angles \( \theta \) and \( \varphi \) are polar angles which describe the orientation of the PAS of the EFG tensor with respect to the external magnetic field (\( \theta \) describes the angle \( V_{33} \) forms with \( B_0 \)). If the magnitude of \( \nu_Q \) is relatively large, then the second-order quadrupolar interaction will also significantly effect the energy of the nuclear spin states, and the correction is given by:

\[ E_{Q,m}^{[2]} = \left( \frac{e^2qQ}{4I(2I - 1)} \right)^2 \frac{m}{\omega_0} \times F_2(\theta,\varphi,m,I) \]  

(29)

where \( F_2(\theta, \varphi, m, I) \) is:
\[ F_2(\theta, \phi, m_I) = \left[ -\frac{1}{5}(I(I+1) - 3m^2)(3 + \eta_Q^2) \right. \]
\[ + \frac{1}{10}(8I(I+1) - 12m^2 - 3)[(\eta_Q^2 - 3)(3\cos^2\theta - 1) + 6\eta_Q\sin^2\theta\cos2\phi] \]
\[ + \frac{1}{8}(18I(I+1) - 34m^2 - 5)\left[ \frac{1}{140}(18 + \eta_Q^2)(35\cos^4\theta - 30\cos^2\theta + 3) \right. \]
\[ \times \frac{2}{7}\eta_Q^2\sin^2\theta(7\cos^2\theta - 1)\cos2\phi + \frac{1}{4}\sin^4\theta\cos4\phi \]  

(30)

**Figure 1.4.** The energies of the nuclear spin states under the influence of the first-order quadrupolar interaction and the second-order quadrupolar interaction are shown for a single crystallite orientation. In the presence of the Zeeman interaction there is only a single transition frequency, while the quadrupolar interaction results in multiple transitions. The change in the energy of the nuclear spin states by \( \Delta E_Z \), \( \Delta E_Q^{[1]} \) have been exaggerated with respect to those of \( \Delta E_Q^{[2]} \).

In NMR spectroscopy, the energies that are observed correspond to transitions between adjacent spin states (Figure 1.4). In order to understand the appearance of the
SSNMR spectrum, it is necessary to consider the difference in energy between the adjacent nuclear spin states (e.g., $\Delta m = \pm 1$). Although the energy of the individual spin states are perturbed, the first-order quadrupolar interaction does not perturb the energy of the central transition (CT, $m = +1/2 \rightarrow m = -1/2$). Consequently, the CT remains unaffected by the first-order quadrupolar interaction. However, all satellite transitions (ST, $m \rightarrow m - 1, m \neq +1/2$) are perturbed by the first-order quadrupolar interaction. For large values of $\nu_Q$, the second order quadrupolar interaction becomes significant and perturbs the CT and further perturbs the ST.

From equations (27) and (29) it can be seen that the energy of the nuclear spin states strongly depends upon the magnitude of the quadrupolar interaction and the orientation of the EFG tensor of the nucleus with respect to the magnetic field. For a powdered sample, there will be many crystallites present which will possess EFG tensors in every possible orientation. Therefore, powder patterns which possess characteristic lineshapes are observed in the static SSNMR spectra of quadrupolar nuclei. Usually only the CT powder patterns are observed in SSNMR spectra of quadrupolar nuclei, as the ST powder patterns are normally broadened beyond detection by the first order quadrupolar interaction. Simulations of static CT powder patterns for $^{35}$Cl ($I = 3/2$) are shown in Figure 1.5. Based upon their shapes it is possible to obtain the EFG tensor parameters $C_Q$ and $\eta_Q$. $C_Q$ and $\eta_Q$ provide a measure of the spherical symmetry and the axial symmetry of the EFG tensor at the nuclear site, respectively. Numerous examples of SSNMR spectra of quadrupolar nuclei are found in the subsequent chapters of the thesis.
Figure 1.5. Simulations of static $^{35}$Cl SSNMR spectra at 9.4 T ($\nu_0 = 39.160$ MHz). For all simulated spectra $\delta_{iso} = 0.0$ ppm. (a) Simulated spectra with $\eta_Q = 0.50$ and values of $C_Q$ which range from 0.5 MHz to 7.0 MHz. Vertical scaling factors are indicated to the left of the spectra. (b) Simulated spectra with $C_Q = 5.0$ MHz and $\eta_Q$ values which range from 0.00 to 1.00.

1.8 Euler Angles

Many quadrupolar nuclei possess significant CSA. In these cases, the appearance of the central-transition powder patterns are profoundly affected by the relative orientation of the CS and EFG tensors. The Euler angles, $\alpha$, $\beta$ and $\gamma$, are used to describe the relative orientation of the two tensors, and describe the series of two-dimensional rotations necessary to translate one of the tensors back into its own PAS system. Figure 1.6 shows the rotations necessary to translate the CS tensor to its own
PAS from a frame which is coincident with the PAS of the EFG tensor. Examples of static SSNMR spectra of quadrupolar nuclei influenced by Euler angles are shown in the subsequent chapters of the thesis.

1.9 Direct and Indirect Spin-Spin Coupling

The direct spin-spin coupling and indirect spin-spin coupling interactions are not discussed in great detail here, as these interactions are not heavily involved in the SSNMR experiments conducted in this thesis.

Direct spin-spin coupling, or dipolar coupling, arises from the through space interactions of the magnetic moments of two nuclei. The total dipolar coupling Hamiltonian in Cartesian tensor form is given by:
\[ \mathcal{H}_{DD} = -2 \mathbf{I} \mathbf{D} \cdot \mathbf{S}, \quad \mathbf{D} = \begin{pmatrix} -\frac{d}{2} \\ -\frac{d}{2} \\ +d \end{pmatrix} \] (31)

where \( \mathbf{D} \) is a traceless first-rank tensor and \( d \) is the dipolar coupling constant:

\[ d = -\hbar \left( \frac{\mu_0}{4\pi} \right) \frac{\gamma_I \gamma_S}{r^3} \] (32)

\( d \) is in units of Hz, and \( r \) is the distance between nuclei \( I \) and \( S \). \( d \) describes the magnitude of the dipolar interaction. From (32) it can be seen that \( d \) is proportional to the \( \gamma \) of the two coupled nuclei and is inversely proportional to the cube of the internuclear distance \( (r) \). This means that dipolar couplings are very large for closely spaced high-\( \gamma \) nuclei. For example, \(^1\text{H}\) nuclei contained in organic moieties usually experience dipolar couplings on the order of tens of kHz, and subsequently, \(^1\text{H}\) SSNMR spectra are normally very broad. The influence of the \(^1\text{H}\) dipolar coupling on the SSNMR spectra of heteronuclei is normally removed by the application of heteronuclear decoupling schemes and/or magic-angle spinning (MAS, *vide infra*). Dipolar coupling is also exploited to obtain signal enhancement with the cross-polarization experiment.

Indirect spin-spin coupling (\( J \)-coupling) is similar to the dipolar interaction, however, the coupling of the two nuclei is mediated by chemical bonds rather than through space. The Hamiltonian describing \( J \)-coupling is\(^{24}\):
where $\mathbf{J}$ is a second-rank anti-symmetric tensor that describes the magnitude of the scalar coupling for different orientations of the nucleus, $I$, with respect to the magnetic field.

The magnitude of the coupling is usually described by a coupling constant, $J_{IS}$, which is equal to the average of the principal components of the $\mathbf{J}$. The magnitude of the coupling is proportional to the $\gamma$ values of the two coupled nuclei. In cases where the Fermi contact mechanism is dominant, $J_{IS}$ is proportional to the amount of $s$-orbital overlap between the s-atoms which contain the nuclei. Frequently a reduced coupling constant ($K_{IS}$) is reported:

$$K_{IS} = \frac{4\pi^2 J_{IS}}{h\gamma_I\gamma_S}$$

$K_{IS}$ is independent of the magnitudes of $\gamma$ of the two coupled nuclei and allows for comparisons of coupling constants for different nuclei to be made. Because $J$-coupling is mediated by chemical bonds, comparison of the $K_{IS}$ values can provide insight into the nature of bonding between different atoms.$^56$

$J$-couplings are commonly encountered in solution NMR experiments and are used in order to determine connectivity within molecular systems. Normally, $J$-couplings are only observed in SSNMR spectra when MAS (vide infra) experiments are employed. MAS experiments usually average the anisotropic components of $\mathbf{J}$ so that only the isotropic coupling constant is observed, although it is sometimes possible to observe the
anisotropic portions of $J$-couplings ($\Delta J$).\cite{57} $J$-couplings are usually on the order of several hundred Hz; however if heavy nuclei are involved they may be on the order of kHz.

**NMR Techniques**

**1.10 Magic-Angle Spinning**

MAS is a technique used for the acquisition of high resolution SSNMR spectra. For solution NMR experiments, high resolution is naturally afforded by isotropic molecular motion, which averages many of the anisotropic NMR interactions. In order to obtain “solution-like” SSNMR spectra, MAS is employed. In MAS experiments the sample is rapidly spun ($ca.$ 3-70 kHz) about an axis oriented at 54.74° with respect to the magnetic field (Figure 1.7).\cite{58,59} The magic angle is derived from the term, $3\cos^2\theta - 1$; which is zero when $\theta = 54.74^\circ$. All of the first-order anisotropic NMR interactions have an orientation dependence which is described by this geometric term. Rapid spinning of powdered samples at the magic angle results in partial or complete averaging of these anisotropic interactions. When a powdered sample is spun at the magic angle each crystallite possesses an average orientation of $\langle 3\cos^2\theta - 1 \rangle$ over the course of one full rotation period (where $\theta$ corresponds to the angle between $B_0$ and largest principal component of the interaction tensor). As a rule of thumb, if the

![Figure 1.7. Representation of the sample orientation for a MAS experiment.](image)
sample is spun at a rate in Hz on the order of the anisotropic component of the interaction, then the anisotropic NMR interaction is represented by its isotropic value in the SSNMR spectrum. The specific applications of MAS for the acquisition of SSNMR spectra influenced by the CS and quadrupolar interactions are now discussed.

**Figure 1.8.** (a) Simulations of MAS $^{13}$C SSNMR spectra employing $\nu_0 = 100.15$ MHz, $\delta_{iso} = 50$ ppm, $\Omega = 150$ ppm, $\kappa = 0.50$ and various spinning speeds ($\nu_r$, listed next to spectra). The corresponding static spectrum is also shown (bottom). (b) Simulated MAS (top) and static (bottom) $^{35}$Cl SSNMR spectra with $\nu_0 = 39.16$ MHz, $\delta_{iso} = 0.0$ ppm, $C_Q = 3.0$ MHz and $\eta_Q = 0.50$.

The broadening of SSNMR spectra due to CSA is described by a $3\cos^2 \theta - 1$ term; therefore, MAS can potentially completely average the broadening due to CSA. When MAS is performed on a nucleus solely influenced by CSA, a spectrum containing a sharp
isotropic peak is obtained (Figure 1.8a). Depending upon the sample spinning speed ($v_{\text{rot}}$) employed, there are additional peaks offset from the isotropic peak at integer multiples of the sample spinning speed. These peaks are known as spinning sidebands and their intensities are determined by the CS tensor. It is possible determine the principal components of the CS tensor via Herzfeld-Berger analysis, which takes $v_{\text{rot}}$ and the spinning sideband intensities into account. From a practical standpoint, MAS provides a large degree of signal enhancement in comparison to experiments conducted on static samples, since the signal intensity is concentrated into the relatively sharp isotropic peaks and spinning sidebands.

For quadrupolar nuclei, the broadening due to first-order quadrupolar interaction is also dependent upon $3\cos^2\theta - 1$, where $\theta$ corresponds to the angle between $V_{33}$ and $B_0$. MAS can effectively average the first-order quadrupolar interaction; however, the second-order quadrupolar interaction is only partially averaged, due to its complex angular dependence (29). CT powder patterns are observed for the MAS SSNMR spectra of quadrupolar nuclei, however, their breadths are reduced by a factor of ca. 3 - 4 compared to the static CT powder patterns. Comparisons of static and MAS SSNMR spectra of a half-integer spin quadrupolar nucleus are shown in Figure 1.8b. In most cases, the lineshape of the MAS powder patterns of quadrupolar nuclei only depends upon $C_Q$, $\eta_Q$ and $\delta_{\text{iso}}$. This simplifies the extraction of EFG tensor parameters from these patterns, as the influence of CSA and Euler angles are removed. Consequently only three parameters are necessary to properly fit the MAS spectrum. Although, in certain cases if the CSA is large then intensity from the MAS CT powder pattern may be distributed into the
spinning sidebands. Signal enhancement is also afforded due to narrowing of the MAS quadrupolar powder patterns, with respect to the corresponding static powder patterns.

1.11 Pulsed NMR Techniques

The magnitude of the signal and the information content of NMR spectra are ultimately controlled by the pulse sequence which is used to create the time-domain signal. For example, double-resonance techniques are routinely employed to enhance the signal of NMR spectra by means of polarization transfer from abundant high-γ nuclei. The continued development of new methods and pulse sequences continues to be an area of intense research within NMR spectroscopy. The basic features of several pulse sequences which have been employed to acquire the SSNMR spectra shown in the subsequent chapters are now discussed.

In the most basic NMR experiment, a single \( \pi/2 \) pulse is applied to the sample, and the resultant time domain signal is then recorded. Due to the rapid relaxation behaviour of some nuclei, and the non-ideal characteristics of NMR probe electronics, this experiment is not always viable. For example, when trying to observe an NMR spectrum of a broad resonance the signal will rapidly dephase following the application of the pulse. In such cases it may not be possible to blank the probe (dissipate the power of the pulse) and turn on the receiver quickly enough to record the rapidly decaying NMR signal. One solution to this problem is to use an echo experiment.

*Echo Pulse Sequences.* In 1950 Irwin Hahn introduced the spin-echo experiment (Figure 1.9). In a typical echo experiment a \( \pi/2 \) pulse is applied to create transverse
Figure 1.9. A schematic of the spin echo pulse sequence (top) and the vector model which illustrates the refocusing of the spins (bottom). An explanation of the sequence is given in the main text.

magnetization. The $\pi/2$ pulse is followed by an echo dephasing period ($\tau$). During $t$, vectors representing different offset frequencies are visualized to be precessing about the $z$-axis ($B_0$). The precession of a fast component (F, positive transmitter offset), an on resonance frequency (zero offset), and a slow component (S, negative transmitter offset)
of the transverse magnetization in the rotating frame. The second pulse refocuses the initial transverse magnetization and leads to the formation of a spin echo at time $\tau$ after refocusing pulse is applied. Echo pulse sequences are normally applied whenever broad lines are encountered as they provide enough recovery time for the probe to record the entire signal.

Shortly after Hahn’s description of the spin-echo experiment the Carr-Purcell Meiboom-Gill (CPMG) experiment was introduced as a method to measure $T_2$.\textsuperscript{36,37} Following these initial experiments, the CPMG pulse sequence was frequently employed to measure slow molecular motions and chemical exchange in both solution and liquid-crystal media.\textsuperscript{62-71} Subsequent applications employed the CPMG sequence for signal enhancement.\textsuperscript{71,73} In the late 1990's, the phase cycle of the CPMG pulse sequence was modified and the sequence was employed to acquire high signal to noise SSNMR spectra of quadrupolar nuclei.\textsuperscript{74} This modified form of the sequence is termed quadrupolar CPMG (QCPMG).\textsuperscript{74} The QCPMG pulse sequence is similar to a Hahn echo sequence; however a train of $\pi$-pulses follows the first spin echo (Figure 1.10). This generates a series of spin echoes and allows one to record multiple spin echoes per scan, leading to a large signal enhancement. The resulting CPMG echo trains can be Fourier transformed to provide a “spikelet” spectrum (Figure 1e). Alternatively, all of the echoes can be summed in the time domain to produce a single spin echo, which is then subsequently Fourier transformed to give a standard echo spectrum. The spikelet spectrum is useful as it focuses intensity into the narrow spikelets and gives rise to higher S/N. The QCPMG sequence is very useful for acquiring SSNMR spectra of broad powder patterns which are
characterized by inherently short $T_2^*$ values and relatively long $T_2$ values.

Figure 1.10. (a) Quadrupolar echo pulse sequence. (b) QCPMG pulse sequence. (c) A $^{91}$Zr FID obtained with the QCPMG pulse sequence. (d) Fourier transformation of the first spin echo provides a typical spin echo spectrum. (e) Fourier transformation of the entire CPMG echo train gives a spikelet spectrum. The spacing of the spikelets is equal to, $\tau_{\text{acq}}^{-1}$, where $\tau_{\text{acq}}$ is acquisition time of the individual spin echoes.

Recently a modified version of the QCPMG sequence, known as WURST-QCPMG, has been developed.\textsuperscript{75,76} This pulse sequence is similar to the standard QCPMG sequence, however, the sequence employs frequency swept (wideband uniform rate
smooth truncated, WURST) pulses in the place of conventional rectangular pulses. The WURST pulses are applied at a fixed transmitter frequency, with the frequency sweep achieved via simultaneous modulation of the pulse amplitude and phase of the pulses.\textsuperscript{77-79} The duration of the WURST pulses (\textit{ca.} 50 \(\mu\)s) is typically much longer than conventional rectangular pulses. The WURST-QCPMG sequence is extremely useful for the acquisition of wideline SSNMR spectra as the superior excitation bandwidths affords a large reduction in the number of sub-spectra which must be acquired. Applications of the WURST-QCPMG sequence are demonstrated in the subsequent chapters of the thesis. In particular, Chapter 9 details the application of WURST pulses for the acquisition of nuclear quadrupole resonance (NQR) spectra.

**Figure 1.11.** The typical pulse sequence employed for cross-polarization experiments. I usually corresponds to a highly abundant high \(\gamma\) nucleus, and S corresponds to nucleus of lower \(\gamma\). A description of the experiment is given in the text.

\textit{Cross-Polarization.} Cross-polarization (CP) is routinely employed to enhance the signal to noise of NMR spectra of nuclei which possess low natural abundance and low \(\gamma\) (e.g., \(^{13}\text{C}\), \(^{15}\text{N}\) and \(^{29}\text{Si}\)). The signal enhancement arises by transferring polarization from highly abundant, high \(\gamma\) nuclei such as \(^1\text{H}\) and \(^{19}\text{F}\). The pulse sequence employed for
typical CP experiments is shown in Figure 1.11. A $\pi/2$ pulse is applied to the abundant nucleus (I), which is then followed by a spin-locking pulse on both I and the unreceptive nucleus (S). The duration of the spin-locking pulse is known as the contact time. The strength of the rf fields applied during the contact time are carefully chosen to fulfill the Hartman-Hahn matching condition, which under static conditions is:

$$\omega_{1I} = \omega_{1S}$$

(34)

If this condition is fulfilled, then there will be an efficient transfer of polarization from the I spins to dipolar coupled S spins. The maximum gain in signal is proportional to the ratio of $\gamma_I/\gamma_S$. The Hartman-Hahn matching condition varies for MAS experiments, and is altered when considering spin pairs involving quadrupolar nuclei. Additional time savings are realized with CP experiments because the recycle delays depend upon the $T_1$ of the abundant I spin, which are typically shorter than those of the rare S spin. Recently, CP has been coupled with the CPMG pulse sequence to yield the CP/CPMG sequence. This pulse sequence combines the signal enhancement characteristics of both sequences, and enables the rapid acquisition of both static wideline SSNMR spectra of spin-half and quadrupolar nuclei.

1.12 Quantum Chemical Calculations of NMR Tensor Parameters

Quantum chemical calculations have become an increasingly valuable tool in many areas of chemistry. Many different methods and models have been developed for calculating the energy of atoms and molecules, and from most of these methods it is
possible to obtain NMR parameters such as $J$-couplings, magnetic shielding and electric field gradients. Quantum chemical calculations of NMR properties remains a fertile area of research within the computational chemistry community. With regards to NMR tensor calculations for solids, the continued development of DFT plane-wave methods capable of performing calculations on periodic structures appears to be very promising. Within this thesis, a variety of computational methods have been employed to calculate NMR tensor parameters. These include ab intio methods (Hartree Fock), hybrid density functional (DFT), and pure DFT methods as implemented in the Gaussian 03 and Amsterdam Density Functional Theory (ADF) software packages. The theoretical basis and overviews of these methods are summarized elsewhere.

Calculations of NMR tensor parameters are useful for several reasons: (1) They can be used to generate the orientations of the NMR tensors within molecular frames, providing insight into the origin of the observed anisotropic NMR tensor parameters. (2) They can be used to relate the calculated NMR tensor parameters to the electronic and molecular structures of the complexes. For example, in Chapter 8, the large CSAs that are observed and calculated for a series of lead(II) complexes are related to the presence of stereochemically active electron lone pairs. (3) They can be used to construct models of systems with unknown molecular structures.

SSNMR spectra, in conjunction with calculations of NMR parameters can potentially be used to identify molecular structures. For example, NMR tensor parameters can be calculated for a series of structural models. The experimental NMR tensor parameters can then be compared to the calculated and the most probable
structures can be identified. However, if such an approach is used, it is important to first benchmark the accuracy of computational methods. This can be accomplished by

\[
\begin{align*}
B_0 > 0 & \quad \quad & B_0 = 0, \ \omega_Q > 0 \\
\quad \quad m_i = -3/2 & \quad & \quad \quad \quad \quad m_i = \pm 3/2 \\
\quad \quad m_i = -1/2 & \quad & \quad \quad \quad \quad m_i = \pm 1/2 \\
\quad \quad m_i = +1/2 & \quad & \quad \quad \quad \quad m_i = \pm 1/2 \\
\quad \quad m_i = +3/2 &
\end{align*}
\]

**NMR** \quad **NQR**

*Figure 1.12.* Energy of the nuclear spin states in NMR experiments (Zeeman interaction) and NQR experiments \((B_0 = 0)\). Note that the \(+m\) and \(-m\) spin states are degenerate in the absence of a magnetic field.

performing calculations of NMR tensor parameters on crystalline complexes which have been characterized by SSNMR and single-crystal XRD. This approach is extensively demonstrated throughout the thesis.

1.13 Nuclear Quadrupole Resonance
Nuclear quadrupole resonance (NQR) is a technique which is closely associated with NMR. The NQR phenomenon is observed for quadrupolar nuclei in the absence of a magnetic field, and hence is often referred to as “zero-field” NMR. In NQR, the nuclear spin states are quantized by the quadrupolar interaction rather than by a magnetic field (Figure 1.12). Consequently, there are several differences from NMR spectroscopy. The largest component of the electric field gradient \( V_{33} \) acts as the axis of quantization for the individual nuclear spin-states, resulting in precession of the nuclear spins about \( V_{33} \). Therefore, the NQR frequency is determined entirely by the magnitude of \( \omega_Q \), which is related to the magnitude of \( V_{33} (C_Q) \) and the value of \( \eta_Q \). This can be problematic, because \( C_Q \) is determined by the symmetry at the nuclear site and can take on values which range from zero MHz to thousands of MHz, depending upon the nucleus in question. Therefore, if one does not have some \textit{a priori} knowledge of the NQR frequency, a great deal of time must be devoted to searching for the resonance frequency. NQR experiments on amorphous or disordered systems are also very challenging. This is because atomic/molecular level disorder gives rise to a range of \( C_Q \) values, which in turn gives rise to a range of NQR frequencies and correspondingly broad NQR spectra. Finally, NQR experiments are restricted to solid samples in most cases, because in solution isotropic molecular motion results in an averaging of the quadrupolar interaction.

NQR does have several advantages and complements SSNMR experiments in several ways. For example, if \( \omega_Q \) is large, broad powder patterns are observed for the SSNMR spectra of quadrupolar nuclei; however, the NQR spectrum consists of a single, relatively sharp resonance. This is because the quantization axis is oriented in the same
direction with respect to the molecular/crystalline frame of each crystallite. Therefore, the NQR frequencies of the individual crystallites do not possess any orientation dependence and sharp resonances are observed. Further, for very large values of $C_Q$, the NQR frequency is relatively high. This results in more favourable Boltzmann distributions, and correspondingly larger NQR signals. Additional details on NQR experiments are provided in the introduction to Chapter 8.

1.14 Context of Research

In this thesis SSNMR spectroscopy is employed to characterize an array of inorganic complexes and materials. Emphasis is placed upon characterizing materials with applications in catalysis using SSNMR spectroscopy of exotic and unreceptive nuclei. With the increasing availability of high field NMR spectrometers throughout the world and the continued development of pulsed NMR techniques, SSNMR spectroscopy of nearly any unreceptive nucleus is becoming feasible. SSNMR spectra of these nuclei could potentially provide information that is both unique and complementary to that obtained from other techniques. In particular, this approach can be useful for the characterization of heterogeneous catalysts.

There is a lack of previous SSNMR studies in the literature for many of the unreceptive nuclei which could potentially be useful for characterizing heterogeneous catalysts (e.g., $^{35}$Cl, $^{47/49}$Ti, $^{91}$Zr). Therefore, it is necessary to investigate well-defined crystalline systems in order to make correlations between molecular structure and the anisotropic NMR interactions measured from the SSNMR spectra. In this regard, systems
which have been previously studied by single-crystal X-ray diffraction are useful, as their atomic coordinates are precisely known. These systems are also ideal for testing the accuracy of quantum chemical calculation methods for calculating NMR tensor parameters. The crystalline systems are also suitable for benchmarking new SSNMR methods and observation strategies prior to investigating complex catalyst systems.

Chapters 2 to 4 focus on the characterization of group IV metalloocene complexes, due to their varied applications in homogeneous and heterogeneous catalysis. The acquisition of $^{35}\text{Cl}$ SSNMR spectra of the metalloocene complexes is described in Chapter 2, where it is shown that the $^{35}\text{Cl}$ SSNMR spectra are sensitive to molecular structure. On the basis of the observed $^{35}\text{Cl}$ spectra of $\text{Cp}_2\text{ZrHCl}$, we are able to prove that the complex possesses a dimeric structure in the solid-state. We have also demonstrated that $^{35}\text{Cl}$ SSNMR spectra of metalloccenes can be acquired in a matter of minutes at high magnetic fields (21.1 T).

Chapter 3 focuses on the acquisition of $^{91}\text{Zr}$ SSNMR spectra of zirconocenes. It is demonstrated that the magnitude of $C_Q$ is very sensitive to the local environment of the Zr nucleus and can be utilized to identify the key intermediates involved in the formation of highly active olefin polymerization catalysts. We also demonstrate that wideline $^{91}\text{Zr}$ SSNMR spectra can be acquired in experiment times on the order of minutes at 21.1 T. Methods suitable for the accurate quantum chemical calculations of $^{91}\text{Zr}$ NMR tensor parameters are also identified. Chapter 4 details the acquisition of $^{47/49}\text{Ti}$ SSNMR spectra of titanocenes. This represents the first example of a molecular system which has been studied by $^{47/49}\text{Ti}$ SSNMR. We demonstrate that it is straightforward to acquire $^{47/49}\text{Ti}$
SSNMR spectra at high magnetic fields with standard echo techniques.

Chapters 5 focuses on the application of $^{45}$Sc SSNMR spectroscopy to characterize scandium coordination complexes. Prior to the study presented in Chapter 5, there were very few $^{45}$Sc SSNMR studies conducted on well-defined systems. Correlations between the observed $^{45}$Sc NMR tensor parameters and molecular symmetry and structure are made. Preliminary investigations of some heterogeneous scandium based catalysts are also shown.

The work in Chapter 6 is an extension of that done in Chapter 5 on the characterization of a polymer supported scandium catalyst. $^{45}$Sc SSNMR experiments are employed to investigate the structure of microencapsulated (ME) Sc(OTf)$_3$. Additional $^1$H, $^{19}$F and $^{13}$C SSNMR and PXRD experiments provide information that is complimentary to that obtained from the $^{45}$Sc NMR spectra, allowing for structural models of ME complexes to be proposed.

In Chapter 7, solid-state $^{207}$Pb NMR experiments are applied in combination with density functional theory (DFT) calculations to provide insight into the nature of bonding in a series of lead(II) thiolate complexes. The lead NMR experiments reveal some of the largest chemical shift anisotropies (CSA) observed in lead coordination complexes to date. DFT calculations are utilized to demonstrate that the CS tensor is primarily influenced by mixing of occupied MOs localized on the sulfur and lead atoms with virtual MOs largely comprised of lead 6p-orbitals.

In Chapter 8, the application of WURST pulses for the acquisition of NQR spectra is investigated. $^{75}$As and $^{35}$Cl NQR spectra acquired with the WURST echo sequence are
compared to those acquired with standard echo sequences and echo sequences which employ composite refocusing pulses. The WURST echo sequence is demonstrated to possess superior excitation bandwidths in comparison to the pulse sequences which employ conventional monochromatic rectangular pulses. The utility of WURST pulses for the acquisition of wideline NQR spectra is also demonstrated by acquiring part of the $^{63/65}$Cu NQR spectrum of CuCN.

Finally, Chapter 9 is a preliminary $^{91}$Zr SSNMR study of model heterogeneous catalysts. $^{91}$Zr SSNMR spectra of zirconocenes immobilized on silica surface have been acquired at natural isotopic abundance with the combination of cryogenic temperatures and high magnetic fields. Quantum chemical calculations are used to construct models of the heterogeneous catalysts and calculate $^{91}$Zr NMR tensor parameters.
1.15 Bibliography


36A, (2), 84-126.


Chapter 2: Solid-State Chlorine NMR of Group IV Transition Metal Organometallic Complexes

2.1 Introduction

The “metallocene revolution” has been used to describe the increased use of transition metal metallocene catalysts in industrial olefin polymerization processes over the last fifteen years.\textsuperscript{1-4} Metallocene catalysts have found use as homogeneous catalysts, which are dissolved in solution and reacted with the olefin, or as heterogeneous catalysts, which are immobilized on a support material and applied in gas or slurry phase processes. The single-site nature of the metallocene catalysts allows for the rational improvement and tuning of the polymerization performance by modification of the surface-supported organometallic species; however, this requires that “the interactions and mechanisms at work on the support surface during the immobilization, activation, and polymerization steps must be understood.”\textsuperscript{4}

Solid-state NMR spectroscopy has previously been applied to examine the nature and structure of surface-supported organometallic complexes, as well as their cocatalysts, such as AlMe\textsubscript{3}, methylalumoxane (MAO) and borane complexes.\textsuperscript{5-15} The majority of these studies have utilized solid-state \textsuperscript{1}H, \textsuperscript{13}C and \textsuperscript{29}Si NMR. Solid-state \textsuperscript{13}C NMR studies have clearly demonstrated that cyclopentadienyl ligands remain bound to the metal upon immobilization on surfaces, and that metal-bound alkyl ligands may be transferred to Lewis acid sites on alumina and silica supports.\textsuperscript{6-8,12,14,15} While this information provides much insight into the catalytic processes, there are still many uncertainties regarding the exact nature of the metal-surface bond and cocatalyst-metal-surface interactions. For
example, immobilizing the metallocene pre-catalyst onto the support and subsequent activation with cocatalyst often gives different polymers than contacting the support with cocatalyst, followed by immobilization of the metallocene.3

In light of this, and the fact that the organometallic metal centre is believed to be the active catalytic site in most cases, we have been investigating metallocene structure and dynamics from the perspective of solid-state NMR of quadrupolar metal nuclei. Examples of these previous studies include, 91Zr, 93Nb and 139La SSNMR, of metallocene systems that are similar to or commonly used as polymerization pre-catalysts.16-18 Several solution NMR studies of quadrupolar metal nuclei in transition metal metallocenes have prefaced and inspired our studies.19-24 We have found that the NMR spectra of these half-integer quadrupolar nuclei are responsive to both subtle and dramatic changes in molecular structure, and should serve as excellent probes of metallocene chemistry in homogeneous catalysts and actual heterogeneous catalysts.

Chlorine is frequently found as a ligand in organometallic transition metal complexes, including many of those important in catalytic polymerization processes, and may act as a useful NMR probe. There are two naturally occurring NMR-active nuclei of chlorine, 35Cl and 37Cl, both of which are spin I = 3/2 nuclei, and high natural abundance [n.a.(35Cl) = 75.78 % and n.a.(37Cl) = 24.22 %]. They are considered to be low gyromagnetic ratio (“low γ”) nuclei \( \nu_0^{(35}\text{Cl}) = 39.19 \text{ MHz} \) and \( \nu_0^{(37}\text{Cl}) = 32.62 \text{ MHz} \) at 9.4 T and possess relatively small quadrupole moments \( Q^{(35}\text{Cl}) = -8.165 \text{ fm}^2 \) and \( Q^{(37}\text{Cl}) = -6.435 \text{ fm}^2 \).25 The 35Cl nucleus is preferred for most NMR experiments because of its higher receptivity; however, acquisition of 37Cl NMR spectra is sometimes
useful, since $^{35}\text{Cl}$ and $^{37}\text{Cl}$ powder patterns are affected to different extents by anisotropic quadrupolar and chemical shielding parameters, allowing for the measurement of chlorine chemical shielding anisotropy (CSA).

Bryce and Sward have recently presented a thorough review of solid-state NMR of quadrupolar halogen nuclei.\textsuperscript{26} To date, there are approximately 80 publications featuring solid-state $^{35/37}\text{Cl}$ NMR. Despite the relatively favourable nuclear properties of both chlorine isotopes and the ubiquity of chlorine in many chemical systems, the application of chlorine NMR is usually limited to systems in which chlorine atoms reside in environments of high spherical symmetry. The quadrupolar interaction is greatly reduced in such environments, resulting in small quadrupolar coupling constants ($C_Q = 0.1 - 6.0$ MHz) and correspondingly narrow, easily acquired powder patterns.\textsuperscript{27, 28} There are numerous representative examples of such systems for which $^{35}\text{Cl}$ SSNMR spectra have been acquired, including ionic metal chlorides,\textsuperscript{29-31} perchlorates,\textsuperscript{32} amino acid hydrochlorides,\textsuperscript{33-36} and HCl pharmaceuticals.\textsuperscript{37}

In many systems the chlorine atoms reside in terminal or bridging environments with low spherical symmetry, and the $^{35}\text{Cl}$ nuclei experience correspondingly large quadrupolar interactions. In these cases, second-order quadrupolar broadening can result in powder patterns that are hundreds to thousands of kHz in breadth, complicating spectral acquisition with routine methods. Nuclear quadrupole resonance\textsuperscript{38} (NQR) is predominantly used for the determination of larger values of $C_Q^{(35}\text{Cl})$, e.g., ca. 10 MHz and larger; however, specialized NQR experiments\textsuperscript{39-41} must be performed in order to obtain the EFG asymmetry parameter, $\eta_Q$, and the chemical shift parameters are only
available from $^{35}$Cl NMR experiments. Single-crystal NMR has traditionally been the preferred method for the determination of $^{35}$Cl chemical shift (CS) and electric field gradient (EFG) parameters for systems with large $C_Q(^{35}$Cl) values; however, this method is limited since it relies on the isolation of large single crystals. For example, single-crystal $^{35}$Cl NMR spectra of para-dichlorobenzene reveal that $C_Q = 73.96$ MHz and $\eta_Q = 0.071$, corresponding to a central transition powder pattern of more than 10 MHz in breadth at 21.1 T. Many other systems possess chlorine nuclei with more moderate values of $C_Q$ for which SSNMR spectra of powdered samples may be obtained. To date, the largest value of $C_Q$ measured by solid-state $^{35}$Cl NMR on a powdered sample is that of aluminum trichloride ($C_Q = 9.4$ MHz), which has a $^{35}$Cl powder pattern with a breadth of over 250 kHz at 14.1 T. $^{35}$Cl quadrupolar parameters for halogenated transition metal metallocenes fall in this intermediate regime. For instance, $^{35}$Cl NQR spectra acquired by Bryukhova et al., revealed values of $C_Q$ ranging from ca. 16 MHz in CpTiCl$_3$ to 24 MHz in Cp$_2$TiCl$_2$, corresponding to $^{35}$Cl SSNMR powder patterns between ca. 1 to 3 MHz in breadth at moderate magnetic field strengths (e.g., 9.4 T).

The extreme breadths of such $^{35}$Cl powder patterns necessitates the use of frequency-stepped NMR techniques, where separate spin-echoes are acquired at evenly spaced transmitter frequencies. The total spectrum is then formed either by plotting the echo intensities as a function of transmitter frequency, or by Fourier transforming the spin echoes and co-adding/projecting the sub-spectra. While this methodology is successful for acquiring broad powder patterns, the inherently low signal to noise of broadened NMR spectra leads to lengthy experimental times. Recently,
the Carr-Purcell Meiboom-Gill (CPMG) sequence\textsuperscript{54, 55} has been re-introduced as a method for the signal enhancement of NMR spectra of quadrupolar nuclei (the QCPMG sequence).\textsuperscript{56-60} The combination of the QCPMG pulse sequence and frequency-stepped techniques is especially useful for the rapid acquisition of extremely broad powder patterns.\textsuperscript{16, 18, 50, 61-63}

The current work involves three major facets. First, we demonstrate the application of ultra-wideline QCPMG (UW-QCPMG) for the rapid acquisition of solid-state $^{35}$Cl NMR spectra of early transition metal organometallic compounds (Scheme 2.1) moderate (9.4 T) and high magnetic fields (21.1 T). Second, the origin of the observed $^{35}$Cl NMR parameters are examined with quantum chemical methods, including Hartree-Fock (HF) and density functional theory (DFT). For the first time, the contributions of individual occupied MOs to the EFG tensors are analysed within a natural localized molecular orbital (NLMO) framework. Differences in the metal first-coordination sphere (e.g., Cp$_2$ZrCl$_2$ vs. Cp$_2$ZrMeCl) and the profound impact on the observed $^{35}$Cl NMR parameters are discussed in detail. Finally, application of our methodology (i.e, the combination of wideline $^{35}$Cl SSNMR and quantum chemical calculations) is demonstrated in the characterization of an important organometallic reagent, Cp$_2$ZrHCl (Schwartz’s reagent), whose solid-state structure is hitherto unknown.
Scheme 2.1. Organometallic complexes for which solid-state $^{35}$Cl NMR spectra have been acquired. The complexes are: bis(cyclopentadienyl)titanium dichloride ($\text{Cp}_2\text{TiCl}_2$), cyclopentadienyltitanium trichloride ($\text{CpTiCl}_3$), bis(cyclopentadienyl)zirconium dichloride ($\text{Cp}_2\text{ZrCl}_2$), bis(pentamethylcyclopentadienyl)zirconium dichloride ($\text{Cp}^*\text{ZrCl}_2$), bis(cyclopentadienyl)hafnium dichloride ($\text{Cp}_2\text{HfCl}_2$), methylbis(cyclopentadienyl)zirconium chloride ($\text{Cp}_2\text{ZrMeCl}$), Oxobis[bis(cyclopentadienyl)zirconium chloride] [($\text{Cp}_2\text{ZrCl}_3$)$_2$$\mu$-O], pentamethylcyclopentadienylzirconium trichloride ($\text{Cp}^*\text{ZrCl}_3$), cyclopentadienylzirconium trichloride ($\text{CpZrCl}_3$) and bis(cyclopentadienyl)zirconium chloride hydride ($\text{Cp}_2\text{ZrHCl}$, Schwartz’s reagent).
2.2 Experimental

Sample Preparation. Samples of Cp₂TiCl₂, CpTiCl₃, Cp₂ZrCl₂, Cp₂*ZrCl₂, Cp₂ZrHCl and Cp*ZrCl₃ were obtained from Strem Chemicals Inc. Samples of Cp₂HfCl₂ and CpZrCl₃ were obtained from Sigma-Aldrich. All commercially obtained samples were used without purification. (Cp₂ZrCl)₂μ-O was synthesized according to published procedures.⁶⁴ Cp₂ZrMeCl was obtained from the synthesised sample of (Cp₂ZrCl)₂μ-O by the previously published method.⁶⁵ The bulk purity of (Cp₂ZrCl)₂μ-O and Cp₂ZrMeCl was confirmed by powder X-ray diffraction. All samples were handled in a nitrogen atmosphere glovebox, except for Cp₂HfCl₂, CpZrCl₃ and (Cp₂ZrCl)₂μ-O which were handled in an argon filled glove bag.

Solid-state NMR. Solid-state ³⁵Cl NMR spectra were acquired on a wide-bore Oxford 9.4 T magnet \( v_0(^1\text{H}) = 400 \text{ MHz}, v_0(³⁵\text{Cl}) = 39.16 \text{ MHz} \) with a Varian Infinity Plus console running Spinsight software. High field ³⁵Cl NMR spectra were acquired on a standard-bore 21.15 T magnet \( v_0(^1\text{H}) = 900 \text{ MHz}, v_0(³⁵\text{Cl}) = 88.2 \text{ MHz} \) with a Bruker Avance II console running TopSpin software. ³⁵Cl NMR experiments at 9.4 T were acquired with a Varian/Chemagnetics 5 mm HX static probe. Experiments at 21.1 T were conducted on a home-built single channel 5 mm probe. All samples were finely ground, packed into filed 5 mm glass NMR tubes, capped and sealed with parafilm. ³⁵Cl chemical shifts were reported with respect to an infinitely dilute solution of NaCl(aq) \( (\delta_{\text{iso}} = 0.0 \text{ ppm}) \) by the use of a secondary standard of NaCl(s) for which \( \delta_{\text{iso}} = -45.37 \text{ ppm} \).³³ Pulse calibrations were performed on a saturated solution of NaCl(aq) and central-transition selective \( \pi/2 \) pulse widths were calculated by scaling the solution pulse widths by a factor
of a half, i.e. \((I + \frac{1}{2})\)^{-1}. The QCPMG pulse sequence of the form \(\{\pi/2 - [\tau - \pi - \tau - \text{acquire}]_n\}\) was used for the acquisition of \(^{35}\text{Cl}\) NMR spectra.\(^{56}\) The number of refocusing \(\pi\) pulses varied from 20 to 162 depending upon the sample (Tables A1 and A2). All spectra were processed on a personal computer with the Nuts program from Acorn Software. The FIDs of sub-spectra were left-shifted where necessary, apodized using a Gaussian function of less than 100 Hz, digitally filtered to remove frequencies outside of 200 kHz, Fourier transformed and magnitude calculated. The individual sub-spectra were then co-added to form the total pattern. Curved baselines are visible in some spectra and are apparent when relatively low signal to noise sub-spectra are co-added to generate total NMR spectra. The curved baselines will not affect the positions of discontinuities, and hence, will not affect the NMR parameters extracted from simulations. Analytical simulations of solid-state \(^{35}\text{Cl}\) NMR spectra were performed using the WSolids computer program.\(^{66}\)

Quantum chemical Calculations. Calculations of CS and EFG tensors were performed using Gaussian 03.\(^{67}\) Molecular coordinates were input from structures determined by single-crystal X-ray diffraction experiments and proton positions were geometry-optimized. Calculations were carried out using restricted Hartree-Fock (RHF) and hybrid density functional theory (DFT) employing the hybrid B3LYP functional.\(^{68}\) The Dunning type basis sets indicated in the text were utilized for Cl.\(^{69, 70}\) The 6-311G** basis set was employed for Ti, C, H, and O. The Zr-5F3 basis set of Huzinaga was employed for Zr.\(^{71}\) The LANL2DZ electron core potential (ECP) basis set of Hay and Wadt was employed on Hf for calculations on \(\text{Cp}_2\text{HfCl}_2\).\(^{72, 73}\) CS tensors were calculated
using the gauge-including atomic orbitals (GIAO) method.\textsuperscript{74, 75} HCl was chosen as a chemical shielding standard and calculated chemical shieldings were converted to shifts as described in Table 2.3.\textsuperscript{76} The natural localized molecular orbital (NLMO) EFG analysis were performed with the Amsterdam Density Functional (ADF) program.\textsuperscript{77-79} ADF calculations utilized the B3LYP functional with all-electron doubly-polarized triple-\(\zeta\) basis sets on all atoms.

\textit{X-ray Diffraction Experiments.} Details on single crystal X-ray diffraction experiments are provided in the original publication.\textsuperscript{80} Samples for powder X-ray diffraction were placed into 1.0 mm glass capillary tubes and flame sealed. Powder X-ray diffraction patterns were collected using a Bruker AXS HI-STAR system using a General Area Detector Diffractions System. The X-ray source was Cu K\(\alpha\) radiation (1.540598 Å) and an area detector using a 2\(\theta\) range between 4.0\(^{\circ}\) to 65.0\(^{\circ}\) was employed. Powder X-ray diffraction patterns were simulated with the Powder Cell software package.\textsuperscript{81}

\textbf{2.3 Results and Discussion}

\textbf{Solid-state} \(^{35}\text{Cl} \text{NMR spectroscopy.} \) Before the individual complexes are discussed, there are some common features of the \(^{35}\text{Cl} \text{NMR spectra that should be addressed. First, very broad powder patterns are observed for all of the complexes at 9.4 T (Figures 2.1-2.3) and 21.1 T (Figure 2.4), with minimum breadths of 1 MHz and 500 kHz, respectively. Second, given the breadth of the \(^{35}\text{Cl} \text{powder patterns, chemically similar (e.g., comparable bond lengths, angles, etc.) but crystallographically distinct chlorine sites cannot be resolved in the \(^{35}\text{Cl} \text{NMR spectra, meaning that the spectra}}\)
essentially correspond to those of single chlorine sites, and their simulations represent
average values of the NMR parameters. However, it is possible to resolve chlorine sites
in different bonding environments (e.g., bridging and terminal chlorine sites in CpZrCl₃,
*vide infra*). Third, despite the large breadths of the $^{35}$Cl static powder patterns, which
range from ca. 1.0 to 2.5 MHz at 9.4 T, the spectra can be acquired in a piece-wise
manner with the QCPMG pulse sequence within a reasonable time frame (e.g., 1.6 hours
to 28 hours). This is due to the generally long $^{35}$Cl transverse relaxation time constants
($T_2$) which permit the acquisition of long echo trains. Finally, once the total patterns have
been formed by co-addition of the sub-spectra, analytical simulations provide values of
$C_Q$, $\eta_Q$ and $\delta_{iso}$ (Table 2.1). The effects of chlorine chemical shielding anisotropy (CSA)
are negligible at 9.4 T (Figure A1), but can be detected at 21.1 T, to yield the span, $\Omega$, and
skew, $\kappa$, of the chemical shift tensor. The positions of the discontinuities are crucial for
accurately determining the quadrupolar parameters, which dominate the broad second-
order central transitions, while the chemical shielding parameters are somewhat less
influential. Variations in intensity across these patterns can arise from a variety of
sources, including small CSA contributions, interference from satellite transitions, overlap
of resonances from similar but magnetically distinct chlorine sites, heteronuclear dipolar
interactions, and so forth.

*Cp₂MCl₂ Series.* All of the group IV Cp₂MCl₂ (M = Ti, Zr or Hf) single crystal X-
ray structures contain two distinct molecules in the asymmetric unit, with four
crystallographically and magnetically distinct chlorine sites. The M-Cl bond lengths
and Cl-M-X bond angles are similar for all chlorine sites, which results in powder
patterns that essentially correspond to that of a single site for each complex. Quantum chemical calculations (*vide infra*) and NQR spectra acquired by Bryukhova et al. confirm this for the \( \text{Cp}_2\text{MCl}_2 \) series.\(^{45}\)

The solid-state \(^{35}\text{Cl} \) NMR spectrum of \( \text{Cp}_2\text{TiCl}_2 \) consists of a second-order powder pattern that is ca. 2.5 MHz wide (Figure 2.1). Several distinct discontinuities are visible in the experimental spectrum and all are readily reproduced by the analytical simulation, yielding \( C_Q = 22.1 \) MHz, \( \eta_Q = 0.61 \) and \( \delta_{\text{iso}} = 500 \) ppm (Table 2.1). Given the magnitude of the quadrupolar interaction, the error in the measured value of \( \delta_{\text{iso}} \) is large at 9.4 T.

The \(^{35}\text{Cl} \) NMR spectrum of \( \text{Cp}_2\text{ZrCl}_2 \) is best simulated with \( C_Q = 16.0 \) MHz, \( \eta_Q = 0.72 \) and \( \delta_{\text{iso}} = 300 \) ppm. \(^{35}\text{Cl} \) and \(^{91}\text{Zr} \) satellite transitions are visible at the low frequency end (right side) of the powder pattern. The spectrum of \( \text{Cp}_2\text{HfCl}_2 \) is simulated with \( C_Q = 17.1 \) MHz, \( \eta_Q = 0.65 \) and \( \delta_{\text{iso}} = 400 \) ppm. The breadth of the \(^{35}\text{Cl} \) powder patterns of \( \text{Cp}_2\text{ZrCl}_2 \) and \( \text{Cp}_2\text{HfCl}_2 \) (~1.6 MHz) are drastically reduced in comparison to that of \( \text{Cp}_2\text{TiCl}_2 \). The total spectrum of \( \text{Cp}_2\text{ZrCl}_2 \) was acquired in 1.6 hours at 9.4 T because of the combination of a favourable \( T_2 \) and relatively narrow powder pattern width.

Within the \( \text{Cp}_2\text{MCl}_2 \) series there are several trends evident in the \(^{35}\text{Cl} \) NMR parameters. The values of \( C_Q \) observed for \( \text{Cp}_2\text{ZrCl}_2 \) and \( \text{Cp}_2\text{HfCl}_2 \) are much smaller than that observed for \( \text{Cp}_2\text{TiCl}_2 \). Increases in the average M-Cl bond lengths of \( \text{Cp}_2\text{ZrCl}_2 \) (2.45 Å)\(^{82}\) and \( \text{Cp}_2\text{HfCl}_2 \) (2.42 Å)\(^{83}\) as compared to the average Ti-Cl bond lengths (2.37 Å) of
Figure 2.1. Solid-state $^{35}$Cl QCPMG NMR spectra and analytical simulations (solid trace) of the spectra of Cp$_2$TiCl$_2$, Cp$_2$ZrCl$_2$, Cp$_2$HfCl$_2$, Cp*$_2$ZrCl$_2$ and CpTiCl$_3$. Satellite transitions are visible in the spectra of Cp$_2$ZrCl$_2$, Cp*$_2$ZrCl$_2$ and Cp$_2$HfCl$_2$ and have been included in simulations of the spectra of Cp*$_2$ZrCl$_2$ and Cp$_2$HfCl$_2$ in order to improve the quality of the fits. The asterisk in the spectrum of Cp*$_2$ZrCl$_2$ denotes a discontinuity of a satellite transition.
Cp₂TiCl₂ are expected to lead to reductions in the largest component of the EFG tensor, $V_{33}$, however, the deformation of core and valence atomic orbitals by covalent bonding interactions must also be considered. Relationships between M-Cl bonding and $V_{33}$ are addressed in the theoretical section.

**Table 2.1.** A Summary of Observed $^{35}$Cl EFG Tensor Parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>$C_Q$ (MHz)$^a$</th>
<th>$\eta_Q$$^b$</th>
<th>$\delta_{iso}$ (ppm)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp₂TiCl₂</td>
<td>22.1(5)$^d$</td>
<td>0.61(3)</td>
<td>500(500)</td>
</tr>
<tr>
<td>Cp₂ZrCl₂</td>
<td>16.0(5)</td>
<td>0.72(4)</td>
<td>300(150)</td>
</tr>
<tr>
<td>Cp₂HfCl₂</td>
<td>17.1(4)</td>
<td>0.65(5)</td>
<td>400(500)</td>
</tr>
<tr>
<td>Cp²₂ZrCl₂</td>
<td>16.7(4)</td>
<td>0.73(3)</td>
<td>400(400)</td>
</tr>
<tr>
<td>CpTiCl₃</td>
<td>15.5(4)</td>
<td>0.54(5)</td>
<td>500(150)</td>
</tr>
<tr>
<td>Cp₂ZrMeCl</td>
<td>13.7(4)</td>
<td>0.75(10)</td>
<td>400(400)</td>
</tr>
<tr>
<td>(Cp₂ZrCl)₂µ-O</td>
<td>16.3(4)</td>
<td>0.43(7)</td>
<td>300(400)</td>
</tr>
<tr>
<td>Cp*ZrCl₃ [site 1]</td>
<td>12.8(5)</td>
<td>0.10(10)</td>
<td>400(200)</td>
</tr>
<tr>
<td>Cp*ZrCl₃ [site 2]</td>
<td>13.3(5)</td>
<td>0.12(10)</td>
<td>400(200)</td>
</tr>
<tr>
<td>Cp*ZrCl₃ [site 3]</td>
<td>14.6(5)</td>
<td>0.88(10)</td>
<td>200(200)</td>
</tr>
<tr>
<td>Cp*ZrCl₃ [site 4]</td>
<td>14.0(5)</td>
<td>0.80(10)</td>
<td>200(200)</td>
</tr>
<tr>
<td>CpZrCl₃ [multiple sites]$^e$</td>
<td>14.8 - 18.6</td>
<td>0.7 - 0.8</td>
<td>300</td>
</tr>
<tr>
<td>Cp₂ZrHCl</td>
<td>19.7(3)</td>
<td>0.20(4)</td>
<td>80(50)</td>
</tr>
</tbody>
</table>

$^aC_Q = eQV_{33}/h$, $^b\eta_Q = (V_{11} - V_{22})/V_{33}$, $^c\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$. $^d$The uncertainty in the last digit(s) of each value is denoted in brackets. $^e$Details are given in the text.

The value of $C_Q$ for Cp₂TiCl₂ is the largest observed in this series of complexes, and corresponds to a regime where the quadrupolar interaction is approaching the magnitude of the Zeeman interaction. However, the analytical simulations produced by the WSolids computer program are based on the high-field approximation, where the
Larmor frequency ($\nu_0$) is assumed to be an order of magnitude larger than ($\nu_Q$) quadrupolar frequency, allowing the latter to be treated as a perturbation on the former.

Of course, this raises questions about the validity of the simulations. Fortunately, $\nu_Q$ has been measured for this complex and others via NQR.\textsuperscript{44,45} The value of $\nu_Q$ is related to $C_Q$ for an $I = 3/2$ nucleus by:

$$C_Q = \sqrt{\frac{2\nu_Q}{1 + \frac{\eta_Q^2}{3}}} \quad (1)$$

In all cases the experimentally determined values of $C_Q$ are within experimental error of the values predicted from NQR spectra (Table 2.2).\textsuperscript{85}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Range of $\nu_Q$ values (MHz)$^a$</th>
<th>Average $\nu_Q$ (MHz)$^a$</th>
<th>Average NQR $C_Q$ (MHz)$^b$</th>
<th>NMR $C_Q$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp\textsubscript{2}TiCl\textsubscript{2}</td>
<td>11.787 - 12.090</td>
<td>11.91</td>
<td>22.46</td>
<td>22.1(5)</td>
</tr>
<tr>
<td>CpTiCl\textsubscript{3}</td>
<td>7.970 and 7.984</td>
<td>7.97</td>
<td>15.28</td>
<td>15.5(4)</td>
</tr>
<tr>
<td>Cp\textsubscript{2}ZrCl\textsubscript{2}</td>
<td>8.558 - 8.756</td>
<td>8.68</td>
<td>16.04</td>
<td>16.0(5)</td>
</tr>
<tr>
<td>Cp\textsubscript{2}MoCl\textsubscript{2}</td>
<td>16.875 - 17.273</td>
<td>17.13</td>
<td>32.92</td>
<td>-</td>
</tr>
<tr>
<td>Cp\textsubscript{2}WCl\textsubscript{2}</td>
<td>17.723 - 18.063</td>
<td>17.84</td>
<td>34.28</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Taken from refs 44 and 45. NQR measurements for Cp\textsubscript{2}TiCl\textsubscript{2}, Cp\textsubscript{2}ZrCl\textsubscript{2} and CpTiCl\textsubscript{3} were conducted at 293.5 K. An average of the values of $\nu_Q$ for crystallographically distinct sites has been used to calculate the NQR $C_Q$. $^b$ Calculated using equation 1 with values of $\nu_Q$ taken from NQR experiments and values of $\eta_Q$ from NMR experiments.

$Cp^*\textsubscript{2}ZrCl\textsubscript{2}$. Analytical simulation of the $^{35}\text{Cl}$ NMR spectrum of $Cp^*\textsubscript{2}ZrCl\textsubscript{2}$ yields $C_Q = 16.7$ MHz, $\eta_Q = 0.73$ and $\delta_{iso} = 400$ ppm. The fit of the spectrum was aided by the detection of a discontinuity in the satellite transition on the low frequency side of the
powder pattern. The single crystal X-ray structure reveals Zr-Cl bond lengths (2.46 Å) similar to those of Cp₂ZrCl₂, and correspondingly similar ³⁵Cl NMR parameters are observed.⁸⁶ There is a slight difference in the values of $C_Q$, suggesting that ³⁵Cl NMR may be able to detect differences in the Cp ligand framework.

*CpTiCl₃*. Simulation of the ³⁵Cl NMR spectra of CpTiCl₃ (Figure 2.1) yields $C_Q = 15.5$ MHz, $\eta_Q = 0.54$ and $\delta_{iso} = 500$ ppm. The values of $C_Q$ and $\eta_Q$ are significantly different than those obtained for Cp₂TiCl₂, demonstrating the sensitivity of ³⁵Cl NMR parameters to differences in the first coordination sphere of the metal. It should also be recognized that the signal to noise ratio of the ³⁵Cl NMR spectrum of CpTiCl₃ is much lower than that of Cp₂TiCl₂ due to a much shorter $T_2$ in the former, which results in a shorter echo train and acquisition of fewer echoes.

The previously reported ³⁵Cl NQR spectra of CpTiCl₃ display two distinct quadrupolar frequencies,⁴⁴ inconsistent with the single crystal X-ray structure reported by Engelhardt et al.,⁸⁷ which identifies three magnetically and crystallographically distinct chlorine sites. We have reported a newly refined structure which possesses two distinct Cl sites, in agreement with the NQR data.⁸⁰ The new single-crystal X-ray structure reveals Ti-Cl bond lengths (2.22 Å) that are 0.15 Å shorter (on average) than those observed for Cp₂TiCl₂ (2.37 Å).

In a purely electrostatic (ionic) model, shorter Ti-Cl bond lengths would lead to larger $C_Q$ values; $V_{33}$ is proportional to the cube of the interatomic distance(s) $(1/r^3)$ under the point charge approximation.³⁸ However, the value of $C_Q$ observed for CpTiCl₃ is significantly smaller than that of Cp₂TiCl₂. The difference between values of $C_Q$ in these
two species must therefore arise from differences in Ti-Cl covalent bonding. In this light, Bryukhova has previously ascribed the lower $C_Q$ in CpTiCl$_3$ to increased Ti-Cl $\pi$-bonding in comparison to Cp$_2$TiCl$_2$.\textsuperscript{44,45} This hypothesis is further discussed in the quantum chemical calculations section.

**Figure 2.2.** Solid-state $^{35}$Cl QCPMG NMR spectra and analytical simulations (solid trace) of the spectra of Cp$_2$ZrMeCl and (Cp$_2$ZrCl)$_2\mu$-O. The simulation of the spectrum of (Cp$_2$ZrCl)$_2\mu$-O includes the satellite transitions. A minor impurity (marked with an asterisk), which is most likely aniline hydrochloride, is visible in the central region of both spectra.

*Cp$_2$ZrMeCl.* It has been proposed that the alkylation of an organometallic complex by an activator or cocatalyst increases the activity of surface-supported
organometallic species.\textsuperscript{3,4} Solid-state \textsuperscript{35}Cl NMR may be useful to monitor the abstraction of chloride ligands by cocatalysts and quantify the amounts of chlorinated metallocene centres remaining after activation. Analytical simulations reveal \( C_Q = 13.7 \text{ MHz} \), \( \eta_Q = 0.75 \) and \( \delta \text{iso} = 400 \text{ ppm} \) (Figure 2.2). This complex possesses the smallest value of \( C_Q \) observed in this series of complexes. \( \text{Cp}_2\text{ZrMeCl} \) has a lower \( C_Q \) than \( \text{Cp}_2\text{ZrCl}_2 \), likely due to changes in the Zr-Cl bond lengths induced by the presence of the methyl ligand (i.e., 2.49 Å and 2.45 Å, respectively).\textsuperscript{88} It should be noted that a minor impurity is visible, resulting in a relatively poor fit of the central part of the pattern. This impurity signal is most likely due to a small amount of aniline hydrochloride which was formed in the synthesis of the compound.

\((\text{Cp}_2\text{ZrCl})_2\mu\text{-O}\). The oxo-bridged complex \((\text{Cp}_2\text{ZrCl})_2\mu\text{-O}\) is a synthetic precursor to \( \text{Cp}_2\text{ZrMeCl} \) and is the product of the hydrolysis of \( \text{Cp}_2\text{ZrMeCl} \).\textsuperscript{65} The \textsuperscript{35}Cl NMR parameters obtained from the spectrum are \( C_Q = 16.3 \text{ MHz} \), \( \eta_Q = 0.43 \) and \( \delta \text{iso} = 300 \text{ ppm} \). The observed value of \( \eta_Q \) is significantly lower than those observed for the other zirconium complexes. A minor amount of impurity is visible in the spectrum (\textit{vide supra}).

\textit{Cp}^*\text{ZrCl}_3. \textit{Cp}^*\text{ZrCl}_3 is a dimer with three magnetically distinct chlorine sites in its crystal structure.\textsuperscript{89} Two of the chlorine atoms are terminally bound to Zr and the third site bridges adjacent Zr centres. The spectrum of \( \text{Cp}^*\text{ZrCl}_3 \) is distinct from those of the previous complexes (Figure 2.3). Specifically, the central discontinuities of the powder pattern are not readily observable and ‘shoulders’ are apparent at the edges of the
Figure 2.3. Solid-state $^{35}$Cl QCPMG NMR spectra and analytical simulations (solid trace) of the spectra of Cp*ZrCl₃, CpZrCl₃. Satellite transitions are visible in the spectra of both complexes. The simulation of the Cp*ZrCl₃ spectrum utilizes four sites (two bridging and two terminal); representative simulations of bridging and terminal sites are shown (see Figure A2 for all simulations).
spectrum. An accurate simulation of the experimental spectrum is more difficult to obtain and larger uncertainties are associated with the NMR parameters, because the observed powder pattern corresponds to both bridging and terminal chlorine sites. The general features of the spectrum can be reproduced by a simple simulation which employs high- and low-\(\eta_Q\) powder patterns in a 1:2 intensity ratio, both of which possess similar values of \(C_Q\) (Figure A2), however, in order to properly account for the shoulders a four site simulation must be used (two bridging and two terminal sites with 1:2 intensity ratios). The inclusion of an additional bridging site (with an \(\eta_Q\) value near 1) disagrees with the current crystal structure, but it is required to reproduce the shoulder features of the spectrum. The ratio of intensities suggests that the low \(\eta_Q\) pattern corresponds to the terminal chloride ligands and quantum chemical calculations confirm this (\textit{vide infra}).

The NMR parameters obtained for both \(\text{Cp}^*\text{ZrCl}_3\) and \((\text{Cp}_2\text{ZrCl})_2\mu\text{-O}\) suggests that the observation of lower values of \(\eta_Q\) may be used to identify the terminal chloride ligands of dimers (this information is absent from standard NQR experiments). It is also interesting to note the extremely high values of \(\eta_Q\) observed for the bridging ligands of the complex.

\(\text{CpZrCl}_3\). \(\text{CpZrCl}_3\) is a coordination polymer in the solid-state.\(^{87}\) The crystal structure reveals three magnetically distinct chlorine sites, with bridging and terminal chloride ligands present in a 2:1 ratio. The \(^{35}\text{Cl}\) NMR spectrum is relatively broad and lacks central discontinuities; however, several shoulders are visible at the sides of the spectrum (Figure 2.3). The number of magnetically distinct sites and lack of features make it difficult, if not impossible, to determine the NMR parameters of the individual sites. However, the appearance of the spectrum is clearly distinct from those of the
complexes which possess only terminal chlorine ligands, and despite its complexity, can be utilized to differentiate between monomeric and oligomeric metallocene species. Quantum chemical calculations of $^{35}$Cl EFG tensors (vide infra) can be used to provide parameters which adequately reproduce the experimental spectrum, though there is some disagreement in the positions of the discontinuities of the experimental and simulated spectra.

Solid-State $^{35}$Cl NMR spectra acquired at 21.1 T. It is expected that the use of high magnetic fields will be very beneficial for $^{35}$Cl NMR for two reasons: first, the signal to noise of an NMR experiment is proportional to the square of the magnetic field ($B_0^2$), greatly reducing the time required to acquire each sub-spectrum; and second, the breadths of the $^{35}$Cl powder patterns will be inversely proportional to $B_0$, greatly reducing the number of sub-spectra which must be acquired. The $^{35}$Cl NMR spectra of CpTiCl$_3$, Cp$_2$ZrCl$_2$ and Cp*ZrCl$_3$ at 21.1 T are shown in Figure 2.4. The QCPMG spectra of CpTiCl$_3$ and Cp$_2$ZrCl$_2$ were acquired in 13 and 7 minutes, respectively, at 21.1 T, as compared to 11 and 1.6 hours at 9.4 T.

The breadths of the $^{35}$Cl powder patterns acquired at 21.1 T are reduced to approximately half of the breadths of the corresponding spectra acquired at 9.4 T, consistent with powder patterns dominated by the second-order quadrupolar interaction; however, if spectra are simulated without accounting for chlorine CSA, a relatively poor fit is obtained (dashed trace, Figure 2.4). Simulations of the $^{35}$Cl SSNMR spectra from 21.1 T which include the CS tensor parameters, $\Omega$ and $\kappa$, and the Euler angles, $\alpha$, $\beta$ and $\gamma$, which describe the relative orientations of the CS and EFG tensors$^{90}$ (Table 2.3) result in
Figure 2.4. Solid-state $^{35}$Cl NMR spectra of CpTiCl$_3$, Cp$_2$ZrCl$_2$ and Cp*ZrCl$_3$ acquired at 21.1 T and analytical simulations of the spectra. Piece-wise QCPMG spectra have been acquired for CpTiCl$_3$ and Cp$_2$ZrCl$_2$. A piece-wise Hahn-echo spectrum was acquired for Cp*ZrCl$_3$. Representative simulations of the bridging and terminal sites are shown for Cp*ZrCl$_3$. 

CpTiCl$_3$

Cp$_2$ZrCl$_2$

Cp*ZrCl$_3$

Figure 2.4. Solid-state $^{35}$Cl NMR spectra of CpTiCl$_3$, Cp$_2$ZrCl$_2$ and Cp*ZrCl$_3$ acquired at 21.1 T and analytical simulations of the spectra. Piece-wise QCPMG spectra have been acquired for CpTiCl$_3$ and Cp$_2$ZrCl$_2$. A piece-wise Hahn-echo spectrum was acquired for Cp*ZrCl$_3$. Representative simulations of the bridging and terminal sites are shown for Cp*ZrCl$_3$. 

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improved fits of the experimental spectra of CpTiCl$_3$ and Cp$_2$ZrCl$_2$ and Cp*ZrCl$_3$ (solid trace, Figure 2.4). However, the reader is cautioned that the errors associated with $\Omega$, $\kappa$ and the Euler angles are large in all cases due to the relative magnitude of the quadrupolar and chemical shielding interactions. Due to the overlap of multiple distinct chlorine sites in Cp*ZrCl$_3$, the uncertainties associated with the CS tensors parameters and Euler angles are especially large. In general the observed values of $\Omega$ are several times larger than those observed for amino acid hydrochlorides ($\Omega < 150$ ppm) and alkaline earth chlorides ($\Omega < 75$ ppm),$^{29,35,36}$ however, given the low local symmetry about the chlorine nuclei in the organometallic complexes, the large values of $\Omega$ are expected and are predicted by quantum chemical calculations. Finally, simulations of the spectra at 9.4 T are seen to be largely unaffected by the inclusion of CSA (Figure A1).

**Table 2.3.** Observed $^{35}$Cl CS Tensor Parameters and Euler Angles

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta_{\text{iso}}$ (ppm)$^a$</th>
<th>$\Omega$ (ppm)$^b$</th>
<th>$\kappa$</th>
<th>$\alpha$ (°)$^d$</th>
<th>$\beta$ (°)</th>
<th>$\gamma$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpTiCl$_3$</td>
<td>500(150)</td>
<td>750(400)</td>
<td>-0.4(5)</td>
<td>80(30)</td>
<td>5(15)</td>
<td>5(30)</td>
</tr>
<tr>
<td>Cp$_2$ZrCl$_2$</td>
<td>300(150)</td>
<td>800(500)</td>
<td>0.0(5)</td>
<td>2(10)</td>
<td>72(20)</td>
<td>-70(20)</td>
</tr>
<tr>
<td>Cp*ZrCl$_3$ [site 1, 2]</td>
<td>400(200)</td>
<td>500(400)</td>
<td>0.4(8)</td>
<td>10(90)</td>
<td>15(30)</td>
<td>0(90)</td>
</tr>
<tr>
<td>Cp*ZrCl$_3$ [site 3, 4]</td>
<td>200(200)</td>
<td>200(200)</td>
<td>-$^e$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Defined in Table 2.1. $^b\Omega = \delta_{11} - \delta_{33}$. $^c\kappa = 3(\delta_{22} - \delta_{33})/\Omega$. $^d$The Rose convention is used for the Euler angles.$^{91,92}$ $^e$The overlap of sites and small CSA make it difficult to estimate $\kappa$ and the Euler angles for the bridging sites.

**Quantum Chemical Calculations.** First principles calculations of $^{35}$Cl NMR parameters are extremely useful as they may provide insight into the origin of the observed NMR parameters and/or aid in the interpretation of $^{35}$Cl NMR data from systems which are not amenable to X-ray diffraction techniques. The origin of the observed $^{35}$Cl
$C_Q$ values are further investigated within the framework of a NLMO analysis. Computations were performed with the Gaussian 03\textsuperscript{67} and ADF codes.\textsuperscript{77-79}

*Gaussian 03 Calculations of Chlorine NMR Parameters.* Chlorine basis sets for the accurate calculation of $^{35/37}$Cl EFG and CS tensor parameters have previously been suggested by Bryce et al.\textsuperscript{36} Both B3LYP and RHF calculations, which employ the cc-pVDZ, cc-pVDZ DK or aug-cc-pVDZ chlorine basis sets, yield EFG tensor parameters that are in excellent agreement with the experimental values (Tables 2.4). There are several notable trends in the calculated values that should be discussed. Calculations employing the RHF method and aug-cc-pVDZ basis set on chlorine consistently yield values of $C_Q$ that are within ±5% of the experimental values for all of the monomeric complexes, with the exception of Cp$_2$ZrMeCl; however, the theoretical values of $\eta_Q$ and $\delta_{iso}$ are typically lower than the experimental values. On the other hand, B3LYP calculations generally produce more accurate values of $\delta_{iso}$, while overestimating the values of $C_Q$, $\eta_Q$, and $\Omega$.

Theoretically calculated $^{35}$Cl EFG tensors are distinct for terminal and bridging chlorine sites, helping to account for their disparate EFG parameters. For instance, in the dimeric Cp*ZrCl$_3$ species, theoretical values of $C_Q$ are similar in magnitude for both the bridging and terminal chlorine sites; however, for the terminal chlorine, the sign of $C_Q$ is negative and $\eta_Q$ is predicted to be near 0 (i.e., $V_{33}$ is the unique component of the EFG tensor), whereas for the bridging chlorine, the sign of $C_Q$ is positive and the $\eta_Q$ is near 1 ($V_{11}$ is the unique component).
Table 2.4. $^{35}\text{Cl}$ NMR Parameters Calculated with the RHF Method and aug-cc-PVDZ Basis Set$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method/Cl basis set$^b$</th>
<th>Site</th>
<th>$C_{\alpha}$ (MHz)$^c$</th>
<th>$\eta_{\alpha}$</th>
<th>$\delta_{\text{iso}}$ (ppm)$^d$</th>
<th>$\Omega$ (ppm)$^e, f$</th>
<th>$\kappa$ $^e, f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cp}_2\text{TiCl}_2$</td>
<td>experimental</td>
<td>-</td>
<td>22.1</td>
<td>0.62</td>
<td>500</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>RHF/aug-cc-pVDZ 1</td>
<td>1</td>
<td>-23.0</td>
<td>0.46</td>
<td>216</td>
<td>958</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>RHF/aug-cc-pVDZ 2</td>
<td>2</td>
<td>-23.3</td>
<td>0.46</td>
<td>210</td>
<td>958</td>
<td>0.1</td>
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<tr>
<td>$\text{CpTiCl}_3$</td>
<td>experimental</td>
<td>-</td>
<td>15.5</td>
<td>0.54</td>
<td>500</td>
<td>750</td>
<td>-0.4</td>
</tr>
<tr>
<td></td>
<td>RHF/aug-cc-pVDZ 1</td>
<td>1</td>
<td>-15.6</td>
<td>0.45</td>
<td>470</td>
<td>909</td>
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</tr>
<tr>
<td></td>
<td>RHF/aug-cc-pVDZ 2</td>
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<td>902</td>
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<td></td>
<td>RHF/aug-cc-pVDZ 3</td>
<td>3</td>
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<td>0.45</td>
<td>474</td>
<td>901</td>
<td>-0.3</td>
</tr>
<tr>
<td>$\text{Cp}_2\text{ZrCl}_2$</td>
<td>experimental</td>
<td>-</td>
<td>16.0</td>
<td>0.72</td>
<td>300</td>
<td>800</td>
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<tr>
<td></td>
<td>RHF/aug-cc-pVDZ 1</td>
<td>1</td>
<td>-16.1</td>
<td>0.46</td>
<td>204</td>
<td>571</td>
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<tr>
<td>$\text{Cp}^*_2\text{ZrCl}_2$</td>
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<td>-</td>
<td>16.7</td>
<td>0.73</td>
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<td>RHF/aug-cc-pVDZ 1</td>
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<td>-16.1</td>
<td>0.46</td>
<td>204</td>
<td>571</td>
<td>-0.5</td>
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<tr>
<td>$\text{Cp}_2\text{HfCl}_2$</td>
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<td>0.65</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>RHF/aug-cc-pVDZ 1</td>
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<td>608</td>
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<tr>
<td>$(\text{Cp}_2\text{ZrCl})_2(\mu-\text{O})$</td>
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<td>65</td>
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<tr>
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<td>0.12</td>
<td>400</td>
<td>500</td>
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<td>experimental 3</td>
<td>3</td>
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<td>200</td>
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<tr>
<td></td>
<td>experimental 4</td>
<td>4</td>
<td>14.0</td>
<td>0.80</td>
<td>200</td>
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<td>472</td>
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<td>RHF/aug-cc-pVDZ 2</td>
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<td>335</td>
<td>478</td>
<td>-0.1</td>
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<td></td>
<td>RHF/aug-cc-pVDZ 3, 4</td>
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<td>12.1</td>
<td>0.95</td>
<td>131</td>
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<td>-0.4</td>
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<td>RHF/aug-cc-pVDZ 5</td>
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<td>-17.4</td>
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<td>341</td>
<td>688</td>
<td>-0.8</td>
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</tbody>
</table>

$^a$ Additional computational results can be found in the original publication. $^b$ See the experimental section for details on the basis sets used on other atoms. $^c$ Only the magnitude of $C_{\alpha}$ can be measured experimentally. For definitions of all NMR parameters refer to Table 2.1. $^d$ The theoretical values of $\delta_{\text{iso}}$ were determined by comparison to the shielding values of HCl calculated with the corresponding method and basis sets. The equation used was, $\delta_{\text{iso}} = \sigma_{\text{iso}}(\text{HCl}) - \sigma_{\text{iso}} + 28$ ppm. $^e$ Experimental CSA parameters are available only for compounds for which a spectrum at 21.1 T was recorded. $^f$ Defined in Table 2.3.
Calculations on CpZrCl₃ are complicated because it exists as a coordination polymer in the solid-state. A cluster with a charge of \(-2\), containing 3 zirconium centres, 3 Cp rings and 9 chlorine atoms was used for calculations on CpZrCl₃ (Figure 2.5). The five chlorine atoms bound to the central Zr unit provide an adequate model of the chlorine atoms in the full coordination polymer structure. However, there is one key difference between the cluster model and crystal structure: the cluster contains five magnetically distinct chlorine sites, while the crystal structure contains only three distinct chlorine sites. For this reason, the NMR parameters calculated for the pairs of bridging sites have been averaged to obtain values used for the analytical simulation. The resulting analytical

![Figure 2.5. The cluster model used for Gaussian 03 calculations on CpZrCl₃. The chlorine sites in Table 2.4 of the manuscript are labelled. Selected bond lengths are also shown. Sites 1 and 2 are symmetry related and magnetically distinct in this model, but not in the crystal structure. Sites 3 and 4 are also magnetically distinct in the cluster model, but not in the crystal structure. Therefore, averages of the calculated NMR parameters from the pairs of sites have been used in the analytical simulation of the spectrum.](image)

\[
\begin{align*}
A &= 2.61 \, \text{Å} \\
B &= 2.66 \, \text{Å} \\
C &= 2.52 \, \text{Å} \\
D &= 2.73 \, \text{Å}
\end{align*}
\]
simulation adequately reproduces the features of the experimental spectrum (Figure 2.3 and Table 2.4), particularly the ‘shoulders’ that are visible at the sides of the spectrum.

There are also some interesting features of the calculated NMR parameters for this complex. The two pairs of bridging chloride ligands possess significantly different calculated EFG and CS tensor parameters (see Table 2.4). Most notably, for one pair (sites 1 and 2) the values of $C_Q$ are negative ($-15.7$ MHz and $-14.7$ MHz), and for the other pair (sites 3 and 4) the values of $C_Q$ are positive and slightly larger in magnitude ($19.8$ MHz and $18.7$ MHz). The EFG and CS tensor parameters of sites 1 and 2 are similar to those of the terminal chlorine sites observed in other complexes. The single-crystal X-ray structure reveals that the site 1 and 2 chloride ligands are opposite to Cp rings, and each makes a short (2.52 Å) and a long (2.73 Å) contact with the zirconium centres that they bridge. It would appear that the presence of a distant second zirconium centre has little effect on the $^{35}$Cl NMR parameters, making the NMR parameters of sites 1 and 2 more similar to those observed for terminal chloride ligands. Conversely, the geometry of sites 3 and 4 is similar to that of the bridging site observed in Cp*ZrCl$_3$ with two relatively equal contacts to each zirconium centre (2.66 Å and 2.61 Å). This explains the similarity of the NMR parameters of sites 3 and 4 of CpZrCl$_3$ to those for the bridging site of Cp*ZrCl$_3$.

The visualization of calculated orientations of EFG tensors within molecular frames can provide insight into the origin of the observed EFG tensor parameters. Several chlorine EFG tensor orientations are shown in Figure 2.6. The EFG tensor orientation of Cp$_2$TiCl$_2$ is representative of terminal chlorine sites. The largest component of the EFG,
$V_{33}$, nearly parallel to the Ti-Cl bond ($V_{33}$-Cl-Ti angle of 4.3°). Since $V_{33}$ is directed near the metal-Cl bond in Cp$_2$TiCl$_2$, the observation that longer M-Cl bond lengths lead to smaller $C_Q$ values in the Cp$_2$MCl$_2$ series is to be expected. The chlorine EFG tensor orientations for Cp*ZrCl$_3$, which possesses both bridging and terminal chloride ligands, are also pictured in Figure 2.6. The EFG orientation of the terminal site is similar to that of Cp$_2$TiCl$_2$ ($V_{33}$-Cl-Zr angle of 6.1°). Conversely, for the bridging site, $V_{33}$ is directed perpendicular to Zr-Cl-Zr plane (angle of 86° with respect to the Zr-Cl-Zr plane). Similar $V_{33}$ orientations have been calculated for aluminum EFGs where $V_{33}$ is oriented perpendicular to the horizontal mirror plane of trigonal planar systems.$^{61}$ Cartesian coordinates for EFG tensor orientations are provided in the original publication.

**Figure 2.6.** EFG tensor orientations in Cp$_2$TiCl$_2$ and Cp*ZrCl$_3$. The tensor orientations are shown for the terminal and bridging Cl sites of Cp*ZrCl$_3$. The orientations are taken from the calculations listed in Table 2.4.
**ADF NLMO Analysis of EFG Tensors.** In order to further probe the origins of the observed $^{35}$Cl EFG tensor parameters we have undertaken an NLMO analysis\(^{93,94}\), i.e. we have determined the contributions of individual NLMOs to the observed $^{35}$Cl EFGs.

Computations were performed with a developer’s version of the ADF code, version 2007.\(^{77-79}\) For the present work, a new module has been developed for a molecular orbital (MO) based analysis of EFG tensors, using either delocalized or localized MOs.\(^{95}\) A similar approach for the analysis of NMR spin-spin coupling constants and chemical shifts has been demonstrated and thoroughly discussed by Autschbach.\(^{96-99}\)

For the NLMO analysis quadrupole coupling constants are obtained from $C_Q = eQ \cdot V_{33}/h$, such that the NLMO contributions for $V_{33}$ are directly related to $C_Q$. In the analysis, contributions smaller than an arbitrary threshold of 5% of $V_{33}$ are omitted to keep the amount of data at a manageable level. The information available from the NLMO analysis is similar to that from NBO analysis, and includes classification of the NLMOs (e.g. bonding, core and lone pair orbitals), the composition of the NLMOs in terms of atomic orbitals (AOs), and a measure of how well the molecular wavefunction is described by a given Lewis structure (as indicated by the occupancy numbers). NLMO EFG analyses for $\text{Cp}_2\text{TiCl}_2$, $\text{CpTiCl}_3$ and $\text{Cp}_2\text{ZrCl}_2$ are examined and compared in order to understand the origins of the chlorine EFG tensors in terms of localized MOs for which individual intuitive bonding, lone pair, and core contributions to the EFG can be obtained.

The generally delocalized, canonical MOs available from standard HF and DFT calculations are not as convenient for such an analysis since many of these MOs may
### Table 2.5. Analysis of NLMO Contributions to EFG Tensors for Cp₂TiCl₂, CpTiCl₃ and Cp₂ZrCl₂

<table>
<thead>
<tr>
<th>Compound</th>
<th>Exp. $V_{33}$ (a.u.)</th>
<th>Calc. $V_{33}$ (a.u.)</th>
<th>NLMO Number</th>
<th>Electron Pair Type</th>
<th>Occ.</th>
<th>NLMO Composition</th>
<th>$V_{33}$ Lewis (a.u.)</th>
<th>$V_{33}$ non-Le (a.u.)</th>
<th>$V_{33}$ Total (a.u.)</th>
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<td>Cp₂TiCl₂</td>
<td>1.152</td>
<td>1.386</td>
<td>36</td>
<td>core</td>
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<td>100 Cl (100 2p)</td>
<td>79.634</td>
<td>0.020</td>
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<td>52.777</td>
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Sum of Cl lone pair/bonding orbital contributions

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<td>100 Cl (100 2p)</td>
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Sum of Cl core orbital contributions

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<td>lone pair, σ</td>
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Sum of Cl lone pair/bonding orbital contributions

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<th>Sum of all NLMO contributions</th>
<th>0.796</th>
<th>0.092</th>
<th>0.888</th>
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</table>

The experimental values of $C_Q$ have been converted to $V_{33}$ values. The sign of $V_{33}$ cannot be determined experimentally. This is the index number assigned by the NBO program. This is the label assigned by the NBO program. Bond refers to a bonding pair of electrons, core to a non-bonding pair of electrons in the sub-shell below the valence shell, and lone pair to an electron lone pair localized on Cl. The chlorine electron lone pairs have also been qualitatively described as non-bonding (nb) or participating in Ti-Cl $\pi$- or $\sigma$-bonding. $\delta$Occ refers to the occupancy of the parent NBO of the NLMO, the analysis data is for the NLMO. Occupancies less than 2 indicate deviation away from an ideal Lewis structure. This is the number before the atom symbol indicates the percentage composition of each NLMO in terms of atomic orbitals from the given atom(s). The contribution of each atom is then broken down by percentage orbital type (eg. $s$, $p$, $d$). The $V_{33}$ summed from all printed NLMO contributions differs from the calculated $V_{33}$ due to the exclusion of many small contributions which are not printed.
contribute to a local bonding environment with large contributions of opposite signs.

The output from the NLMO EFG analysis of Cp₂TiCl₂ is discussed in detail below in order to clarify the contents of Table 2.5. The experimentally determined and calculated values of $V_{33}$ are shown in columns 2 and 3 of the table. The chlorine site with the calculated value of $V_{33}$ closest to experimental value of $V_{33}$ has been chosen for analysis. There are 8 NLMOs shown in column 4 (54-57 are shown in Figure 2.7), since they make contributions to $V_{33}$ larger than $|5|\%$ of the total value of $V_{33}$. Columns 5 and 6 indicate the electron pair type and occupancy, respectively. The ‘NLMO Composition’ in column 7 provides a percentage composition of the NLMOs in terms of atomic orbitals from individual atoms as printed by the NBO program. The contributions of each atom are further decomposed into percentage contributions from specific atomic orbitals (e.g., $2s$, $3d$). The Lewis, non-Lewis and total contributions to $V_{33}$ made by each NLMO are given in the columns 8, 9 and 10.

NLMOs 36-38 are completely comprised of core Cl $2p$ orbitals. The individual Lewis contributions of NLMOs 36-38 to $V_{33}$ are very large; however, because they correspond to a closed $2p$ shell, their combined contribution to $V_{33}$ amounts to only 0.193 a.u. A filled sub-shell of AOs should make no net contribution to the EFG tensor due to its spherical symmetry; however, in this case, the non-zero contribution of orbitals 36-38 to $V_{33}$ arises from the deformation of these orbitals by nearby atoms and bonds. The small combined contributions of the core Cl NLMOs is seen for both of the other systems. NLMOs 54-57, primarily composed of Cl $3s$ and $3p$ AOs, contribute 1.362 a.u. to $V_{33}$, representing a large portion of the total of 1.470 a.u. NLMOs 54 and 57 make large
negative contributions to $V_{33}$, and represent a non-bonding electron lone pair and Ti-Cl $\sigma$-bond, respectively. NLMOs 55 and 56 make large positive contributions to $V_{33}$, and represent lone pairs which participate in Ti-Cl $\pi$-bonding. It is evident that NLMO 56 represents a greater degree of Ti-Cl $\pi$-bonding than NLMO 55 as indicated by the lower occupancy (1.833 vs. 1.924) of its parent NBO and its larger fraction of Ti character (8.7 % vs. 2.7%). It also makes a smaller contribution to $V_{33}$ than NLMO 55 (3.895 a.u. vs. 4.377 a.u.).

Bryukhova has previously hypothesized that increased Ti-Cl $\pi$-bonding leads to a
decrease in the observed $^{35/37}$Cl EFGs. This hypothesis was used to explain the large decrease in $C_0$ observed when comparing the $^{35}$Cl NQR data from CpTiCl$_3$ and Cp$_2$TiCl$_2$. It is interesting to see if this hypothesis can be confirmed by comparing the NLMO-EFG analyses of Cp$_2$TiCl$_2$ and CpTiCl$_3$. The NLMO-EFG analysis of CpTiCl$_3$ is shown in Table 2.5 and NLMOs 47-49 and 1 are shown in Figure 2.7.

Minor negative contributions to $V_{33}$ from core Ti AOs are observed for CpTiCl$_3$, which likely arise because of much shorter Ti-Cl bond lengths compared to Cp$_2$TiCl$_2$. The majority of $V_{33}$ is seen to once again arise from contributions from the valence Cl AOs and Ti-Cl bonding orbitals which are described by NLMOs 47-49 and 1. The non-bonding Cl lone pair orbital, NLMO 47, and one of the $\pi$-bonding electron lone pairs, NLMO 48, make contributions to $V_{33}$ similar in sign and magnitude to their counterparts in Cp$_2$TiCl$_2$ (NLMOs 54 and 55, respectively). However, the remaining two Cl electron lone pairs of CpTiCl$_3$ are quite different from those of Cp$_2$TiCl$_2$. NLMO 49 is classified as a “lone pair” by the NBO program, however, it is evident that NLMO 49 represents a significant degree of Ti-Cl bonding based upon its appearance and low occupancy (1.693). The contribution to $V_{33}$ from NLMO 49 is $-2.923$ a.u., which is of the same sign and lower in magnitude than that from the $\sigma$-bonding lone pair of Cp$_2$TiCl$_2$ (NLMO 57, $-4.743$ a.u.). NLMO 1 is classified as a bonding orbital and possesses a high occupancy (1.986). The $V_{33}$ contribution of NLMO 1 (1.692 a.u.) is of the same sign as that of the $\pi$-bonding lone pair of Cp$_2$TiCl$_2$ (NLMO 56); however, the magnitude of the contribution is significantly lower. The $V_{33}$ contributions of NLMOs 1 and 49 of CpTiCl$_3$ total $-1.231$ a.u. as compared to the total of $-0.848$ a.u. of NLMOs 56 and 57 of Cp$_2$TiCl$_2$. In
summary, it is clear from the visualization of NLMOs 48, 49 and 1 of CpTiCl₃ and the much lower parent NBO occupancies for NLMOs 48 and 49 that there is much more π-bonding in CpTiCl₃ than in Cp₂TiCl₂. By comparing the NLMOs and EFG tensors in CpTiCl₃ and Cp₂TiCl₂, it is clear that the decreased $V_{33}$ contributions from the CpTiCl₃ NLMOs arise from increased Ti-Cl π-bonding character, in agreement with Bryukhova’s hypothesis,⁴⁴,⁴⁵ which is based upon the semi-empirical Townes-Daily theory.¹⁰⁰

\[ \text{Cp}_2\text{ZrCl}_2 \]

**Figure 2.8.** Images of NLMOs which are the main contributors to the observed $^{35}\text{Cl}$ EFGs in Cp₂ZrCl₂. The contributions of the individual NLMOs to the observed $^{35}\text{Cl}$ EFGs are described in Table 2.5.

Finally, the NLMO analysis of Cp₂ZrCl₂ is compared to that of Cp₂TiCl₂, in order to explain the large differences in their $C_Q$ values. The reduced $C_Q$ in Cp₂ZrCl₂ occurs for the following reasons: minor negative contributions to $V_{33}$ are seen to arise from NLMO 28 and 37, which are comprised of core Zr 4$s$ and 4$p$ AOs. The major reduction in $C_Q$ seems to arise from the valence Cl 3$s$ and 3$p$ orbitals, NLMOs 67-70 (Figure 2.8), where the contributions to $V_{33}$ are reduced by 0.514 a.u. This is mainly due to a large increase in the magnitude of the negative contribution (−2.663 a.u.) from the non-bonding Cl electron
lone pair, NLMO 67. The non-bonding lone pair is of much higher $p$-character in 
Cp$_2$ZrCl$_2$ (36.6%) than in Cp$_2$TiCl$_2$ (29.5%), resulting in a more asymmetric distribution 
of charge, and a larger negative contribution to $V_{33}$.

Solid-state $^{35}$Cl NMR Spectroscopy and Quantum Chemical Modelling of 
Cp$_2$ZrHCl. Cp$_2$ZrHCl was first synthesized in 1970's$^{64,101,102}$ and the utility of the 
compound as a reagent for hydrogenation, halogenation and carbon-carbon bond forming 
reactions was quickly realized.$^{103,104}$ Development of new reactions which utilize the 
complex continues today.$^{105-107}$ There is currently no known single-crystal or powder X-
ray diffraction structure of Schwartz's reagent (Cp$_2$ZrHCl). In order to probe the solid-
state structure of this important reagent, the solid-state $^{35}$Cl NMR spectrum has been 
acquired and quantum chemical calculations on several models have been performed, 
following the methodologies discussed above.

The solid-state $^{35}$Cl NMR spectra and analytical simulations of Cp$_2$ZrHCl are 
shown in Figure 2.9. The spectra very closely conform to that of a standard quadrupolar 
powder pattern, indicating that the powdered sample is crystalline (powder X-ray 
diffraction also confirms this, Figure A3) and contains one type of chlorine ligand. The $^{35}$Cl 
NMR spectrum at 9.4 T is best simulated with $C_Q = 19.7$ MHz, $\eta_Q = 0.20$ and $\delta_{iso} = 
80$ ppm (Table 2.1). Simulations of the spectra at 21.1 T utilize $\Omega = 400$ ppm, $\kappa = 0.5$ 
(Table 2.6), and non-zero Euler angles [$\alpha = \gamma = 0(30)^\circ$, $\beta = 85(30)^\circ$]. The chlorine CSA 
is much smaller than that observed for Cp$_2$ZrCl$_2$ and CpTiCl$_3$.

Previously acquired IR spectra of Cp$_2$ZrHCl and Cp$_2$ZrDCl suggest the hydride 
ligands bind in a bridging manner, implying that the complex exists as an oligomer in the
Figure 2.9. Solid-state $^{35}$Cl NMR spectra of Cp$_2$ZrHCl acquired at 9.4 T and 21.1 T and analytical simulations of the spectra. Simulations with (solid red trace) and without (dashed blue trace) the effects of CSA are shown. The effects of $^1$H decoupling on an individual sub-spectrum from 9.4 T are shown in the inset. The application of $^1$H decoupling greatly increases the number of echoes that may be acquired and leads to a dramatic increase in signal to noise.
The observed $^{35}\text{Cl}$ NMR parameters unequivocally confirm this hypothesis. The value of $C_Q$ is significantly larger than that observed for Cp$_2$ZrCl$_2$. The observed value of $\eta_Q$ is similar to the low values of $\eta_Q$ observed for the terminal chloride ligands of Cp*ZrCl$_3$ and (Cp$_2$ZrCl)$_2$µ-O, and distinct from the intermediate to high $\eta_Q$ values observed in all of the monomeric complexes which possess terminal chloride ligands. This indicates that the complex is a dimer which contains bridging hydride ligands and terminal chloride ligands. The application of $^1\text{H}$ decoupling during the acquisition of the sub-spectra greatly lengthens the time for which echoes can be acquired with the QCPMG sequence. This subsequently improves the signal to noise of the spectrum (inset of Figure 2.9 and Figure A4) and indicates the proximity of the hydride and chlorine atoms.

In order to confirm the model derived from experiment, quantum chemical calculations of $^{35}\text{Cl}$ EFG and CS tensors were performed on a series of model structures. As a starting point for developing our structural models, a search of the Cambridge Structural Database (CSD) for other bis(cyclopentadienyl)zirconium hydride complexes was performed. A single crystal X-ray structure was found for methyl-bis(cyclopentadienyl)zirconium hydride (Cp$_2$ZrHMe), which exists as a dimer in the solid-state. Given the similarity of the molecular structures of Cp$_2$ZrCl$_2$ and Cp$_2$ZrMeCl, Cp$_2$ZrHMe is a reasonable starting point for modelling the solid-state structure of Cp$_2$ZrHCl. Monomeric bis(cyclopentadienyl)zirconium chloride hydride and dihydride structures were also located, however all of these complexes contained bulky, substituted Cp' ligands, which have a strong influence on the structure and chemistry in general.
Two models were constructed from the crystal structure of Cp$_2$ZrHMe (Figure 2.10). The positions of the Zr, hydride and Cp carbon atoms are not altered in both models. In Model 1, the methyl ligand is replaced with a chloride ligand. The positions of Cl and Cp H atoms were geometry optimized. Optimized Cl-Zr bond lengths of 2.61 Å (RHF) and 2.56 Å (B3LYP) were obtained and calculations with both methods result in an angular displacement of the Cl ligand by ca. 2° from the position of the methyl carbon. Calculations of $^{35}$Cl NMR parameters from Model 1 yield reasonable agreement with the experimental parameters (Table 2.6). Model 2 is identical to Model 1, except the Zr-Cl bond lengths are set to a more reasonable distance of 2.46 Å, based upon the terminal Zr-Cl bond lengths observed in other zirconium complexes. The calculated EFG tensor parameters of Model 2 are in better agreement with the experimental values than those of Model 1. The success of the calculations on Models 1 and 2 at reproducing the experimental NMR parameters suggest that they are accurate representations of the
molecular structure.

Powder X-ray diffraction results also support the proposed structure model of Cp₂ZrHCl. The observed powder X-ray diffraction pattern of Cp₂ZrHCl bears a striking resemblance to that which is predicted from the single crystal X-ray structure of Cp₂ZrHMe (Figure A3). If the methyl group in the crystal structure of Cp₂ZrHMe is removed and a Cl atom is placed at the methyl carbon position, the powder X-ray diffraction pattern predicted from this ‘rough crystal structure’ of Cp₂ZrHCl is seen to provide an extremely close match with the experimental diffraction pattern. While a full Rietveld refinement of Cp₂ZrHCl is beyond the scope of this study, the diffraction results suggests that the proposed dimer structure of Cp₂ZrHCl is correct and that it crystallizes in the same space group as Cp₂ZrHMe with very similar unit cell parameters.

Table 2.6. Observed and Calculated ³⁵Cl NMR Parameters of Cp₂ZrHCl

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method/basis set</th>
<th>C_0 (MHz) ¹</th>
<th>η</th>
<th>δ_iso (ppm)</th>
<th>Ω (ppm)</th>
<th>κ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp₂ZrHCl</td>
<td>Experimental</td>
<td>19.7</td>
<td>0.20</td>
<td></td>
<td>400(250)</td>
<td>0.5(5)</td>
</tr>
<tr>
<td>Model 1</td>
<td>RHF/aug-cc-pVDZ</td>
<td>-20.9</td>
<td>0.08</td>
<td>-40</td>
<td>318</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>B3LYP/aug-cc-pVDZ</td>
<td>-23.1</td>
<td>0.15</td>
<td>124</td>
<td>485</td>
<td>0.7</td>
</tr>
<tr>
<td>Model 2</td>
<td>RHF/aug-cc-pVDZ</td>
<td>-18.9</td>
<td>0.12</td>
<td></td>
<td>6</td>
<td>351</td>
</tr>
<tr>
<td></td>
<td>B3LYP/aug-cc-pVDZ</td>
<td>-21.1</td>
<td>0.18</td>
<td>154</td>
<td>476</td>
<td>0.8</td>
</tr>
<tr>
<td>Model 3</td>
<td>RHF/aug-cc-pVDZ</td>
<td>11.5</td>
<td>0.94</td>
<td>224</td>
<td>793</td>
<td>-0.3</td>
</tr>
<tr>
<td></td>
<td>B3LYP/aug-cc-pVDZ</td>
<td>13.4</td>
<td>0.55</td>
<td>482</td>
<td>1074</td>
<td>-0.2</td>
</tr>
</tbody>
</table>

¹See Table 2.1 for definitions of parameters.

Finally, to demonstrate that the ³⁵Cl NMR parameters are distinct for monomeric and dimeric species, a third model was constructed from the crystal structure of the monomeric complex, Cp₂ZrMeCl (Figure 2.10). The methyl ligand was replaced with a
hydride, and the hydride and chloride positions were optimized. Calculations on Model 3 result in values of $C_Q$ and $\eta_Q$ that show very poor agreement with experimental values. Further, the B3LYP values of $\delta_{iso}$ for Models 1 and 2 are in good agreement with the experimental parameters, while calculated values for Model 3 are not. The calculated values of $\Omega$ and $\kappa$ from Models 1 and 2 are quite distinct from those of Model 3 as well, demonstrating the potential of CS tensor parameters for distinguishing between monomeric and dimeric structures.

2.4 Conclusions

Extremely broad $^{35}\text{Cl}$ NMR spectra of early transition organometallic complexes can be acquired using the QCPMG sequence in 2 and 28 hours of experimental times at a moderate magnetic field of 9.4 T. The acquisition of $^{35}\text{Cl}$ spectra at 21.1 T results in an order of magnitude reduction of experimental times as compared to those of 9.4 T. It is possible to acquire a high quality $^{35}\text{Cl}$ spectra of $\text{Cp}_2\text{ZrCl}_2$ and $\text{CpTiCl}_3$ in less than 13 minutes at 21.1 T due to the increase in signal to noise and the reduction in the breadth of the $^{35}\text{Cl}$ powder patterns. This suggests that it is possible to utilize $^{35}\text{Cl}$ NMR spectroscopy to probe surface supported organometallic complexes, despite the low loading levels (approximately 5 weight % catalyst or less). The $^{35}\text{Cl}$ NMR parameters act as sensitive probes of molecular structure because of their dependence upon the number and types of ligands coordinated to the metal centre(s) to which they are bound. Chlorine CSA is quite large and may be observed in high field NMR spectra. Quantum chemical
calculations can accurately reproduce the experimentally observed NMR parameters. In particular, the NLMO-EFG analyses should shed much light on the relationships between EFG tensors and molecular symmetry and bonding. NMR spectra, powder X-ray diffraction data and theoretical methods demonstrate that \( \text{Cp}_2\text{ZrHCl} \) exists as a dimer in the solid-state and possesses a structure similar to that of \( \text{Cp}_2\text{ZrHMe} \). The tandem of \(^{35}\text{Cl} \) NMR spectroscopy and quantum chemical calculations will ultimately allow one to examine the molecular structure of surface supported organometallics.

While this work has focussed on the \(^{35}\text{Cl} \) NMR spectroscopy of early transition metal metallocenes it is clear that the methods describe herein can easily be extended to characterization of countless chlorine-containing main group and transition metal coordination compounds. Lucken has summarized the values of \( \nu_Q^{(35}\text{Cl}) \) obtained from NQR spectra of chloride complexes of B, Al, Ga, Si, Sn, Sb, and Bi and the corresponding values of \( C_Q^{(35}\text{Cl}) \) for these complexes range from approximately 9 MHz (Al complexes) to 40 MHz (Si, Sn, and Sb complexes).\(^{38} \) The values of \( \nu_Q^{(35}\text{Cl}) \) observed for late transition metal complexes (e.g. Re, Os, Pt) indicate that rapid acquisition of \(^{35}\text{Cl} \) SSNMR spectra of these complexes is also feasible. The combination of high magnetic fields (e.g., 21.1 T) and new NMR techniques designed to increase excitation bandwidths\(^{111,112} \) should permit comprehensive structural characterization of inorganic species in a variety of solid phases by \(^{35}\text{Cl} \) SSNMR, especially those for which single crystal data is unavailable.
2.5 Bibliography


(34) Gervais, C.; Dupree, R.; Pike, K. J.; Bonhomme, C.; Profeta, M.; Pickard, C. J.;


Chapter 3: Solid-State $^{91}\text{Zr}$ NMR Spectroscopy Studies of Zirconocene Olefin Polymerization Catalyst Precursors

3.1 Introduction

Cyclopentadienyl (Cp) transition metal complexes (metallocenes) have found increasing use as both homogeneous and heterogeneous olefin polymerization catalysts in industrial processes over the last 15 to 20 years.$^{1-5}$ Metallocene catalysts offer several advantages over the traditional heterogeneous Ziegler-Natta$^{6-9}$ (i.e., TiCl$_4$ supported on MgCl$_2$) and Philips$^7,10,11$ (i.e., CrO supported on SiO$_2$) catalysts, such as generally higher polymerization activities and resultant polymers with narrow molecular weight distributions and potentially higher molecular weights. The tacticity of the resulting polymers can also be easily controlled via judicious alteration of the Cp ligand framework.$^2,5,12,13$ All of these advantages can be attributed to the “single site” nature of the metallocene catalysts, standing in stark contrast to the heterogeneous Ziegler-Natta and Philips catalysts, which possess several different active surface sites that give rise to correspondingly non-uniform polymers. In particular, zirconium metallocene derivatives (zirconocenes) have probably attracted the most research interest due to their practical properties, which include stability at conventional polymerization temperatures, low relative cost of materials and high catalytic activities.$^5$

For most industrial processes heterogeneous catalysts are preferred. For this reason, metallocenes and other organometallic catalysts are frequently immobilized onto inorganic support materials (e.g., SiO$_2$, MgCl$_2$, Al$_2$O$_3$). A cocatalyst, usually methylaluminoxane (MAO), may be contacted with the support before or after
immobilization of the metallocene.\textsuperscript{3, 4} However, the insolubility and disordered nature of the surface-supported metallocene pre-catalysts and cocatalysts prevent their characterization by standard techniques, such as X-ray diffraction (XRD) and solution NMR spectroscopy. Classical surface chemistry characterization techniques such as IR,\textsuperscript{14-18} XPS,\textsuperscript{16, 19-21} and MAS \textsuperscript{1}H, \textsuperscript{13}C and \textsuperscript{29}Si SSNMR\textsuperscript{15, 16, 18, 22-28} spectroscopy have frequently been employed to study supported organometallic complexes and cocatalysts. Data obtained from these techniques have revealed that the peripheral Cp ligands remain coordinated to the metal centre upon immobilization and that alkyl groups bound to the metal center may be transferred to Lewis acid sites on the support. However, there are several ambiguities regarding the interactions between the metallocene pre-catalyst and cocatalyst in both homogeneous and heterogeneous systems. For example, (MAO) is the preferred cocatalyst for zirconocenes in industrial olefin polymerization; however, its molecular structure remains poorly understood.\textsuperscript{3, 4, 29-32} Studies by Jordan, Marks and Rausch on dimethyl zirconocene and tris- and tetra(pentafluorophenyl)boron adducts have demonstrated that the generation of a zirconocene-cocatalyst ion pair of the form [Cp\textsubscript{2}ZrMe\textsuperscript{+}][\textit{A}^-] is required to generate an active olefin polymerization catalyst.\textsuperscript{33-38} Solution \textsuperscript{13}C and \textsuperscript{91}Zr NMR\textsuperscript{39, 40} and solid-state \textsuperscript{13}C NMR experiments\textsuperscript{41} conducted on MAO-zirconocene adducts with low Al:\textit{M} (\textit{M} = Zr, Ti) ratios (\textit{ca.} 5-20) have demonstrated that the reaction between metallocene dichlorides and MAO results in the formation of similar cationic zirconocenes. However, in order to obtain highly active catalysts very large MAO:zirconocene ratios are required (typically $10^2$ to $10^4$:1).\textsuperscript{38, 42} The catalyst structure at high MAO:zirconocene ratios also remains poorly understood.\textsuperscript{38}
Similarly, intermediate species of the type Cp₂Zr(R)(olefin)⁺ are generally assumed to form during the polymerization process.⁵,⁴³ For all of these reasons, the development of additional tools capable of probing the structure of zirconocenes would be invaluable.

Our group has been investigating the possibility of utilizing solid-state NMR (SSNMR) spectra of quadrupolar (nuclear spin, \( I > \frac{1}{2} \)) metal nuclei in metallocenes to probe the structures and identities of a variety of metallocene species, including some which are utilized in olefin polymerization. Our previous studies on model crystalline metallocene systems include \(^{139}\text{La SSNMR of tris(cyclopentadienyl)lanthanides, }^{93}\text{Nb SSNMR of a variety of half-sandwich niobocenes, and }^{91}\text{Zr SSNMR of bis(cyclopentadienyl)zirconium dichloride (Cp₂ZrCl₂).}^{44-46} The SSNMR spectra of metal nuclei that lie at the “heart” of these metallocenes have allowed us to examine the electronic environment and molecular symmetry from the perspective of the central metal atom. Additionally, we have also recently presented a \(^{35}\text{Cl SSNMR study of crystalline group IV metallocene chloride complexes.}^{47} Because of our success with these bulk crystalline systems, and the importance of zirconocenes in heterogeneous catalytic production of polyolefins, it seems that \(^{91}\text{Zr SSNMR is a logical choice for the characterization of immobilized metallocene catalysts.}

Owing to advances in hardware and pulse sequence programming, as well as the increased availability of high field NMR spectrometers, there has been a recent flurry of activity in the acquisition of SSNMR spectra of unreceptive quadrupolar nuclei⁴⁸-⁵⁶ such as \(^{91}\text{Zr (vide infra).} Notably, the significant signal to noise (S/N) enhancement brought about by the quadrupolar Carr-Purcell Meiboom-Gill (QCPMG) pulse sequence⁵⁷ has
encouraged much of this work. Recently, Bhattacharyya and Frydman demonstrated the use of adiabatic frequency swept pulses (WURST pulses)\(^5\) for the acquisition of wideline SSNMR spectra of quadrupolar nuclei.\(^6\) Our research group has combined this approach with the QCPMG protocol and developed the WURST-QCPMG experiment.\(^6\) We have found that WURST-QCPMG, in combination with frequency stepped acquisition, is the most efficient method to date for the acquisition of ultra-wideline SSNMR powder patterns of quadrupolar nuclei (which we define as patterns > 250 kHz in breadth, which require frequency-stepped experiments, specialized pulse sequences and/or hardware, high magnetic fields, etc. for their acquisition). These techniques are vital for \(^{91}\)Zr SSNMR studies because many zirconium compounds exhibit large quadrupolar interactions (\(^{91}\)Zr quadrupole coupling constants, \(C_Q\), typically range from 10 to 30 MHz) which result in extremely broad central transition (CT) patterns.

There are relatively few NMR studies of zirconium compounds in the condensed phase owing to the relatively low sensitivity of \(^{91}\)Zr (\(I = 5/2\)), which has a moderate quadrupole moment (\(Q^{(91}\)Zr) = \(-1.76(3) \times 10^{-29}\) m\(^2\)),\(^6\) a low natural abundance (11.23\%) and a relatively low magnetogyric ratio (\(-2.49750 \times 10^7\) rad T\(^{-1}\) s\(^{-1}\)). Previous studies have been limited to extended systems such as zirconium oxides, phosphates, silicates and halides.\(^6\)-\(^7\) Our previous work on \(\text{Cp}_2\text{ZrCl}_2\) remains the only example of a molecular system studied by \(^{91}\)Zr SSNMR.\(^4\) Therefore, it is of importance to initially characterize model zirconocene compounds in order to correlate the structural features of metallocenes with the NMR interaction tensor parameters obtained from experimental NMR spectra. These model systems will also aid in determining the most suitable quantum chemical
methods for the accurate calculation of $^{91}\text{Zr}$ NMR parameters, which should permit future theoretical predictions of unknown metallocene structures.

Herein, we report a comprehensive $^{91}\text{Zr}$ SSNMR study of a series of zirconocenes, which serve as precursors for the preparation of heterogeneous and homogeneous catalysts (compounds 1-8, Scheme 3.1). We have also acquired the $^{91}\text{Zr}$ SSNMR spectrum of an active polymerization catalyst $[\text{Cp}_2\text{ZrMe}][\text{MeB(}\text{C}_6\text{F}_5)_3]$ (9). These samples were examined in order to obtain the $^{91}\text{Zr}$ electric field gradient (EFG) and chemical shift (CS) tensor parameters for a diverse range of zirconocene structural motifs. Extensive quantum chemical calculations of $^{91}\text{Zr}$ EFG and CS tensor parameters are presented herein, and are used to rationalize the origin of the observed NMR parameters and related to the molecular and electronic structures of the complexes. Quantum chemical calculations conducted with variable Zr-X (X = Cl, Me) bond lengths were performed in order to understand the large differences observed in the EFG tensors parameters of several complexes. Previous solution $^{91}\text{Zr}$ NMR studies have prefaced and inspired this current work. In particular, Bühl, Hopp, von Philipsborn (BHP) and co-workers have studied compounds 1, 2, 3, 7, 8 and other compounds analogous to 4 and 5 using solution $^{91}\text{Zr}$ NMR and quantum mechanical calculations; therefore, we will often refer to their work for comparison with the results presented here.
1. Schematic representation of compounds which have been studied by solid-state $^{91}$Zr NMR: bis(cyclopentadienyl)zirconium dichloride [$\text{Cp}_2\text{ZrCl}_2$], bis(pentamethylcyclopentadienyl)zirconium dichloride [$\text{Cp}^*_2\text{ZrCl}_2$ (1)], bis(cyclopentadienyl)zirconium dibromide [$\text{Cp}_2\text{ZrBr}_2$ (2)], bis(trimethylsilylcyclopentadienyl)zirconium dibromide [($\text{Me}_3\text{SiC}_5\text{H}_4$)$_2\text{ZrBr}_2$ (3)], [O($\text{Me}_2\text{SiC}_5\text{H}_4$)$_2\text{ZrBr}_2$ (4)], [(1,3-$\text{C}_5\text{H}_3$)$_2\text{OsMe}_2\text{SiMe}_2$](1,3-$\text{C}_5\text{H}_3$)$_2\text{ZrBr}_2$ (5)], bis(indenyl)zirconium dichloride [$\text{Ind}_2\text{ZrCl}_2$ (6)], bis(cyclopentadienyl)methylzirconium chloride [$\text{Cp}_2\text{ZrMeCl}$ (7)], bis(cyclopentadienyl)dimethylzirconium [Cp$_2$ZrMe$_2$ (8)], and the active polymerization catalyst [Cp$_2$ZrMe][MeB(C$_6$F$_5$)$_3$] (9).
3.2 Experimental

_Samples._ Samples of Cp₂ZrCl₂, Cp⁺₂ZrCl₂ (1) and Ind₂ZrCl₂ (6) were purchased from Strem Chemicals, Inc. and used without purification. Samples of Cp₂ZrBr₂ (2), (Me₃SiC₅H₄)₂ZrBr₂ (3), O(Me₂SiC₅H₄)₂ZrBr₂ (4), (O(Me₂Si)₂C₅H₃)₂ZrBr₂ (5), Cp₂ZrMeCl (7), Cp₂ZrMe₂ (8), and [Cp₂ZrMe][MeB(C₆F₅)₃] (9) were synthesized according to previously published literature procedures and characterized by ¹H, ¹³C and ¹⁹F solution NMR.

_Solid-State NMR Spectroscopy._ NMR experiments were performed on a Varian Infinityplus NMR console with an Oxford 9.4 T wide bore magnet for which the ⁹¹Zr resonance frequency (ν₀) is 37.16 MHz. Typical central transition selective 90° pulse widths of ca. 2.0 µs (corresponding to radio frequency fields of ~ 40 kHz) were employed along with pulse delays between 0.7 s and 2.0 s. Between 6500 and 150000 transients were acquired. Continuous wave ¹H decoupling was applied for most MAS and static experiments. For the acquisition of static and MAS spectra a Hahn echo sequence with a 16-step phase cycle was employed. Double frequency sweep (DFS) or fast radio-frequency amplitude modulated (FAM) schemes were employed for some of the ⁹¹Zr static and MAS spectra in order to provide signal enhancement and reduce experimental times at 9.4 T. For the acquisition of broad static ⁹¹Zr NMR spectra the QCPMG pulse sequence and WURST-QCPMG pulse sequences were employed. MAS ⁹¹Zr NMR spectra were typically acquired at spinning frequencies (ν_rot) between 10000 and 15000 Hz. 5.0 mm outer diameter (o.d.) ZrO₂ rotors were employed for acquisition of MAS spectra. Teflon or Delrin 5.0 mm o.d. sample tubes and shortened glass NMR tubes were
used for non-spinning experiments. Zirconium chemical shifts were referenced to a concentrated dichloromethane (CH$_2$Cl$_2$) solution of Cp$_2$ZrCl$_2$ ($\delta_{iso} = 0.0$ ppm). A complete list of experimental details can be found in Appendix B (Tables B1 - B5).

High-field static NMR experiments were performed on a 21.1 T Bruker Avance II NMR spectrometer for which $\nu_0(^{91}\text{Zr}) = 83.7$ MHz. Samples were placed in sealed shortened 5.0 mm or 4.0 mm o.d. glass NMR tubes or a 10 o.d. mm teflon sample tube. Spectra were acquired on home built 5 mm or 10 mm single channel probes or a Bruker 4 mm MAS HX probe. The Hahn echo, QCPMG or WURST-QCPMG pulse sequences were employed.

**Spectral Simulations.** Analytical simulations of NMR spectra were performed with the WSOLIDS software package.$^{89}$ The convention used for the specification of the chemical shift (CS) tensors is: $\delta_{11} \geq \delta_{22} \geq \delta_{33}$; $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$; $\Omega = \delta_{11} - \delta_{33}$; $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$. The convention used for specification of electric field gradient (EFG) tensors is: $|V_{33}| \geq |V_{22}| \geq |V_{11}|$; $C_Q = eQV_{33}/\hbar$; $\eta_Q = (V_{11} - V_{22})/V_{33}$. The Rose convention is used to describe the order and direction of Euler angle rotations, which describe the relative orientation of the EFG and CS tensors.$^{90,91}$

**Theoretical Calculations.** Calculations of EFG tensors were performed using Gaussian 03$^{92}$ employing molecular coordinates for isolated molecules resolved by X-ray diffraction.$^{79,93,94}$ Atomic coordinates for 5 were obtained from a preliminary single crystal XRD structure. In all cases idealized hydrogen atom positions were employed. For some calculations, “idealized” Cp ring coordinates were employed (see discussion section for details). Computations were carried out using the restricted Hartree-Fock
(RHF), and hybrid density functional theory methods (B3LYP).\textsuperscript{95-97} Several all-electron basis sets on zirconium were employed (see Appendix B), including (17s13p9d)\textsuperscript{98,99} contracted to [12s9p5d], with two sets of diffuse \textit{p} functions\textsuperscript{100} ($\alpha_{p} = 0.11323$ and 0.04108) and one diffuse \textit{d} function ($\alpha_{d} = 0.0382$),\textsuperscript{79} and (17s11p8d) contracted to [6s3p3d] or [12s7p4d].\textsuperscript{98} The double-zeta basis set of Dunning was employed for Cl.\textsuperscript{101} Additional Cl basis sets were also tested. The 6-311G** basis sets included with Gaussian 03 were used for all other atoms. Calculations with all electron basis sets on Br were also attempted (see Appendix B). These Br basis sets include (13s10p1d) contracted to [4s3p1d],\textsuperscript{102} the triple-zeta basis set of Dunning\textsuperscript{103} and the quadruple-zeta [11s7p4d]\textsuperscript{104} and triple-zeta [8s6p2d]\textsuperscript{99} basis sets of Ahlrich. Most basis sets were obtained from the EMSL Basis Set Exchange.\textsuperscript{105} Quadrupolar coupling constants were converted from atomic units (a.u.) to Hz by multiplying the largest component of the EFG tensor, $V_{33}$, by $eQ/h \times 9.71736 \times 10^{21}$ V m$^{-2}$, where $Q(\text{Zr}) = 1.76(3) \times 10^{-29}$ m$^2$,\textsuperscript{63} and $e = 1.602188 \times 10^{-19}$ C. The EFGShield program was used to extract Euler angles and generate EFG and CS tensor orientations from the Gaussian 03 output.\textsuperscript{106}

\textit{X-ray Diffraction Experiments.} Results from single crystal X-ray diffraction experiments are provided in Appendix B (Figures B1-B3 and Tables B6 - B8). Samples for powder X-ray diffraction (PXRD) experiments were placed into 0.7 mm glass capillary tubes and flame sealed. PXRD patterns were collected using a Bruker AXS HI-STAR system using a General Area Detector Diffractions System. The X-ray source was Cu K\textalpha\ radiation (1.540598 Å) and an area detector using a 2θ range between 4.0° to 65.0° was employed. PXRD patterns were simulated with the PowderCell software package.\textsuperscript{107}
3.3 Results and Discussion

**MAS $^{91}\text{Zr}$ Solid-State NMR Spectra.** MAS $^{91}\text{Zr}$ SSNMR spectra of $\text{Cp}_2\text{ZrCl}_2$ and complexes 1 - 5 are pictured in Figure 3.1. Before the spectra of individual complexes are discussed, there are several general observations to be made. Those complexes which feature coordination by unsubstituted or substituted Cp ligands (denoted as $\text{Cp}'$) and halogens possess relatively small $^{91}\text{Zr}$ quadrupolar coupling constants resulting in relatively narrow static and MAS $^{91}\text{Zr}$ powder patterns (6 being the exception, *vide infra*). This allows for central-transition (CT) MAS $^{91}\text{Zr}$ SSNMR spectra of complexes 1 - 5 to be acquired at a moderate magnetic field strength (9.4 T) and at sample spinning speeds below 15 kHz. All of the MAS $^{91}\text{Zr}$ SSNMR spectra are clearly influenced by second-order quadrupolar broadening. The $^{91}\text{Zr}$ EFG parameters ($C_Q$ and $\eta_Q$) and isotropic chemical shift values ($\delta_{\text{iso}}$) derived from simulation of these spectra are compiled in Table 3.1. The isotropic chemical shifts for 1 - 5 are in good agreement with values measured by BHP using solution $^{91}\text{Zr}$ NMR. It is apparent that MAS $^{91}\text{Zr}$ SSNMR spectra can serve as a powerful tool for identification of zirconocenes, as variations in the ring substitution, type of halide, and overall symmetry of the molecule have an obvious influence on the lineshape of the spectra, with observed $C_Q$ values ranging from 2.4 MHz to 6.35 MHz and $\eta_Q$ values ranging from near 0 to near 1. In order to relate the molecular structures to the observed $^{91}\text{Zr}$ NMR parameters, we have compiled the average bond lengths and inter-ligand angles from the single crystal XRD structures in Table 3.2.
### Table 3.1. Experimentally Determined $^{91}$Zr EFG and CS Tensor NMR Parameters

| Compound | $\delta_{\text{iso}}$ (ppm) | $|C_Q|$ (MHz)$^a$ | $\eta_Q$$^b$ | $\Omega$ (ppm)$^c$ | $\kappa$$^d$ | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) |
|----------|-----------------|-----------------|--------------|---------------|-------------|-----------|-----------|-----------|
| Cp$_2$ZrCl$_2$ (site 1) | 21(5) | 6.2(3) | 0.18(10) | 340(40) | -0.6(3) | 90(35) | 86(10) | 2(10) |
| Cp$_2$ZrCl$_2$ (site 2) | 21(5) | 6.5(3) | 0.30(10) | 350(40) | -0.7(3) | 90(35) | 86(10) | 3(10) |
| Cp$_2$ZrBr$_2$ 1 | 208(2) | 2.6(1) | 0.22(10) | 235(25) | -0.75(20) | 20(40) | 90(25) | 90(10) |
| Cp$_2$ZrBr$_2$ 2$^f$ | 128(10) | 2.4(3) | 0.40(20) | 550(50) | -0.55(20) | 40(90) | 0(90) | 0(90) |
| (Me$_3$Si–C$_5$H$_4$)$_2$ZrBr$_2$ 3 | 154(5) | 4.7(1) | 0.88(4) | - | - | - | - | - |
| O(Me$_2$SiC$_5$H$_4$)$_2$ZrBr$_2$ 4 | 143(3) | 2.5(1) | 0.68(7) | 620(70) | -0.8(2) | 40(20) | 90(15) | 35(40) |
| (1,3-C$_5$H$_3$)(SiMe$_2$OSiMe$_2$)$_2$(1,3-C$_5$H$_3$)ZrBr$_2$ 5 | 163(7) | 3.9(2) | 0.25(9) | 530(60) | -0.55(20) | 40(20) | 30(15) | 85(10) |
| Ind$_2$ZrCl$_2$ 6 (single site fit)$^g$ | 20(50) | 31.5(15) | 0.33(20) | 700(300) | 0.6(9) | 20(10) | 75(15) | -40(40) |
| 6 (two site fit, site 1) | 60(50) | 32.0(10) | 0.25(20) | 200(400) | -0.3(8) | 80(60) | 60(40) | 4(60) |
| 6 (two site fit, site 2) | 60(50) | 30.7(10) | 0.38(20) | 200(400) | -0.3(8) | 80(60) | 60(40) | 4(60) |
| Cp$_2$ZrMeCl 7 (site 1) | 230(100) | 23.3(10) | 0.35(10) | 900(500) | -0.6(8) | 5(70) | 15(45) | 85(70) |
| Cp$_2$ZrMeCl 7 (site 2) | 230(100) | 20.0(30) | 0.75(15) | 1000(500) | 0.8(9) | 80(40) | 20(20) | 5(40) |
| Cp$_2$ZrMe$_2$ 8 | 475(40) | 28.0(3) | 0.40(4) | 1750(300) | -0.9(3) | 80(40) | 90(5) | 0(5) |
| [Cp$_2$ZrMe][MeB(C$_6$F$_5$)$_3$] 9 | 350(100) | 39.0(8) | 0.76(6) | 1000(400) | 0.2(5) | 90(10) | 80(15) | 86(40) |

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$^aC_Q = eQV_{33}/h$.  $^b\eta_Q = (V_{11} - V_{22})/V_{33}$.  $^c\Omega = \delta_{33} - \delta_{11}$.  $^d\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$.  $^e$We have previously studied this compound by $^{91}$Zr SSNMR, see reference 45.  $^f$Estimated parameters from overlapping sites (see text for details).  $^g$See text for details regarding single site and two site fits.
Table 3.2. Average Metrical Parameters of Single Crystal X-ray Diffraction Structures of Zirconocene Complexes\(^a\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(r(\text{Zr-Hal})) (Å)</th>
<th>(r(\text{Zr-Me})) (Å)</th>
<th>(\angle \text{X-Zr-X}) (°)</th>
<th>(r(\text{Zr-Cp'_{Cent}})) (Å)</th>
<th>(\angle \text{Cp'<em>{Cent}-Zr-Cp'</em>{Cent}}) (°)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cp}_2\text{ZrCl}_2)</td>
<td>2.45</td>
<td>-</td>
<td>97.0</td>
<td>2.20</td>
<td>129.3</td>
<td>[93]</td>
</tr>
<tr>
<td>(\text{Cp}^*_2\text{ZrCl}_2) (^1)</td>
<td>2.46</td>
<td>-</td>
<td>95.4</td>
<td>2.26</td>
<td>130.9</td>
<td>[107]</td>
</tr>
<tr>
<td>((\text{Me}_4\text{EtCp}))_2\text{ZrCl}_2 (^b)</td>
<td>2.44</td>
<td>-</td>
<td>94.6</td>
<td>2.25</td>
<td>137.0</td>
<td>[122]</td>
</tr>
<tr>
<td>(\text{Cp}_2\text{ZrBr}_2) (^2) (^c)</td>
<td>2.61</td>
<td>-</td>
<td>96.7</td>
<td>2.19</td>
<td>129.0</td>
<td>[79]</td>
</tr>
<tr>
<td>((\text{Me}_3\text{SiC}_5\text{H}_4))_2\text{ZrBr}_2 (^3)</td>
<td>2.61</td>
<td>-</td>
<td>94.2</td>
<td>2.20</td>
<td>128.1</td>
<td>[112]</td>
</tr>
<tr>
<td>O((\text{Me}_3\text{SiC}_5\text{H}_4))_2\text{ZrBr}_2 (^4)</td>
<td>2.61</td>
<td>-</td>
<td>98.0</td>
<td>2.20</td>
<td>131.2</td>
<td>This work</td>
</tr>
<tr>
<td>(1,3-(\text{C}_5\text{H}_3))((\text{SiMe}_2\text{OSiMe}_2))_2(1,3-(\text{C}_3\text{H}_3)) (\text{ZrBr}_2) (^5) (^e)</td>
<td>2.60</td>
<td>-</td>
<td>96.7</td>
<td>2.19</td>
<td>130.4</td>
<td>This work</td>
</tr>
<tr>
<td>(1,3-(\text{C}_5\text{H}_3))((\text{SiMe}_2\text{OSiMe}_2))_2(1,3-(\text{C}_3\text{H}_3)) (\text{ZrBr}_2) (^5) (123 K)</td>
<td>2.60</td>
<td>-</td>
<td>99.0</td>
<td>2.20</td>
<td>130.6</td>
<td>This work</td>
</tr>
<tr>
<td>(\text{Ind}_2\text{ZrCl}_2) (^6)</td>
<td>2.44</td>
<td>-</td>
<td>94.7</td>
<td>2.23</td>
<td>128.3</td>
<td>[93]</td>
</tr>
<tr>
<td>(\text{Cp}_2\text{ZrMeCl}) (^7) (^d)</td>
<td>2.51</td>
<td>2.23</td>
<td>94.5</td>
<td>2.21</td>
<td>131.4</td>
<td>This work</td>
</tr>
<tr>
<td>(\text{Cp}_2\text{ZrMeCl}) (^7)</td>
<td>2.49</td>
<td>2.36</td>
<td>95.1</td>
<td>2.21</td>
<td>131.1</td>
<td>[94]</td>
</tr>
<tr>
<td>(\text{Cp}_2\text{ZrMe}_2) (^8)</td>
<td>-</td>
<td>2.28</td>
<td>95.5</td>
<td>2.26</td>
<td>132.5</td>
<td>[94]</td>
</tr>
<tr>
<td>([\text{Cp}_2\text{ZrMe}]\text{[MeB(C}_6\text{F}_5)_3]) (^9) (^e)</td>
<td>-</td>
<td>2.25, 2.56</td>
<td>87.7</td>
<td>2.20</td>
<td>131.1</td>
<td>[119]</td>
</tr>
</tbody>
</table>

\(^a\) Parameters have been taken from previously reported single crystal X-ray diffraction structures. The parameters for 4, 5 and 7 are taken from the structures reported in this work. \(^b\) Quantum chemical calculations utilizing coordinates from the published crystal structure of 1 gave poor agreement with experimental NMR tensor parameters. Calculations employing atomic coordinates from (Me\(_4\)EtCp\(_2\))ZrCl\(_2\) gave much better results, therefore, we have listed the metrical parameters of this complex. \(^c\) Conformation 2 of the second site in the asymmetric unit has been disregarded because the Cp\(_{\text{cent}}\)-Zr bond distance is significantly longer (2.21 Å) than the other distances in the structure. \(^d\) The second methyl position in the asymmetric unit has been disregarded because the Zr-Me distance is abnormally short (2.176 Å). \(^e\) The second Zr-Me distance reported corresponds to the methyl group which is bridging between the Zr and B atoms.
Figure 3.1. MAS $^{91}$Zr SSNMR spectra (black traces) of (a) Cp$_2$ZrCl$_2$ at $\nu_{\text{rot}} = 15000$ Hz, (b) 1 [Cp*$_2$ZrCl$_2$] at $\nu_{\text{rot}} = 10000$ Hz, (c) 2 [Cp$_2$ZrBr$_2$] at $\nu_{\text{rot}} = 10000$ Hz, (d) 3 [(Me$_3$SiC$_5$H$_4$)$_2$ZrBr$_2$] at $\nu_{\text{rot}} = 15500$ Hz, (e) 4 [O(Me$_2$SiC$_5$H$_4$)$_2$ZrBr$_2$] at $\nu_{\text{rot}} = 11000$ Hz and (f) 5 [(1,3-C$_5$H$_3$)(SiMe$_2$OSiMe$_2$)$_2$(1,3-C$_5$H$_3$)ZrBr$_2$] at $\nu_{\text{rot}} = 10000$ Hz. Corresponding analytical simulations (red traces) are shown beneath all experimental spectra. All spectra were acquired at 9.4 T. Asterisks denote spinning sidebands.
We previously acquired the MAS $^{91}$Zr SSNMR spectrum of Cp$_2$ZrCl$_2$ at 9.4 T.\cite{45} For the present work, a MAS spectrum was acquired at 21.1 T in an attempt to resolve two separate signals corresponding to the two distinct sites observed in the single crystal X-ray diffraction structure.\cite{93} Multiple magnetic fields are useful for resolving overlapping sites, because broadening of the CT powder pattern due to the second order quadrupolar interaction and chemical shift dispersion are inversely and directly proportional to $B_0$, respectively. The spectrum acquired at 21.1 T possesses a distinct “splitting” of the high frequency discontinuity of the CT powder pattern, indicative of the presence of two sites (Figure B4). A simulation employing two sites yielded similar values of $C_Q$ (6.2 MHz and 6.5 MHz) and $\eta_Q$ (0.18 and 0.30), and identical values of $\delta_{iso} = 21$ ppm, which is unsurprising given the similarity of the two Zr environments. The parameters obtained from the MAS spectra are similar to those previously reported by our research group.

The spectrum of 1 (Figure 3.1b) is characterized by a $^{91}$Zr quadrupole coupling constant that is smaller than that of Cp$_2$ZrCl$_2$ by a factor of 2.4. The value of $\eta_Q$ for 1 is similar to that observed for Cp$_2$ZrCl$_2$, and $\delta_{iso}$ is approximately 180 ppm more positive. Examination of the crystal structures\cite{93,108} of Cp$_2$ZrCl$_2$ and 1 reveals a slight lengthening in the average Zr-Cp’ centroid and Zr-Cl distances in 1 compared to Cp$_2$ZrCl$_2$, which is likely due to the steric bulk of the Cp* rings in 1. A decrease in $C_Q$ with lengthening of the metal-Cp’ centroid distance is consistent with observations made from variable-temperature experiments on linear sodocenes\cite{109} and CpK.\cite{110} BHP have also used ab initio calculations to demonstrate that the decrease in $C_Q$ of 1 compared to Cp$_2$ZrCl$_2$ is caused
largely by the electronic effects of the highly basic Cp* ligand.\textsuperscript{79}

The MAS \(^{91}\)Zr SSNMR spectrum of 2 (Figure 3.1c) appears to show the overlap of narrow patterns from two distinct zirconium species. The observation of more than one zirconium site is in agreement with the existence of two distinct molecules in the asymmetric unit of 2.\textsuperscript{79} Unfortunately, the chemical shift dispersion at \(B_0 = 9.4\) T is insufficient to resolve the nonequivalent sites of 2, even with a high-resolution solid-state NMR technique such as triple-quantum (3Q) multiple-quantum (MQ) MAS\textsuperscript{111,112} (Figure B5). Nevertheless, by considering the approximate width of the pattern, it is possible to make rough estimates of the maximum \(C_Q\), as well as \(\delta_{iso}\) and \(\eta_Q\). The simulation of the MAS \(^{91}\)Zr SSNMR spectrum employs two sites which possess identical EFG tensor parameters and distinct \(\delta_{iso}\) values of 125 ppm and 132 ppm. A MAS \(^{91}\)Zr SSNMR spectrum of 2 was also acquired at 21.1 T (Figure B6); however, even at this field, there is still insufficient resolution of the two sites. Nonetheless, acquisition of MAS and static \(^{91}\)Zr SSNMR spectra at two magnetic fields still allows for the accurate determination of the EFG tensor parameters (\textit{vide infra}).

The average \(\delta_{iso}\) of 2 is 128.5 ppm, which is \textit{ca.} 100 ppm higher than that observed for \(\text{Cp}_2\text{ZrCl}_2\). The \(\eta_Q\) value of 2 is similar to \(\text{Cp}_2\text{ZrCl}_2\), while the \(C_Q\) value is approximately 2.5 times smaller, in accordance with the narrower \(^{91}\)Zr solution NMR line-widths observed by BHP for 2. The Cp-Zr bond lengths and Cp-Zr-Cp angles are similar in both \(\text{Cp}_2\text{ZrCl}_2\) and 2, suggesting that the reduction in \(C_Q\) can be attributed to the increased lengths of Zr-Br bonds in comparison to Zr-Cl bonds (averages of 2.61 Å and 2.45 Å, respectively). This is further addressed in the quantum chemical calculation.
The MAS $^{91}$Zr SSNMR spectra of the zirconocene dibromides, 3, 4 and 5 are shown in Figures 3.1d, 3.1e, and 3.1f, respectively. Complex 3 has a silane moiety on the Cp rings, while 4 and 5 have *ansa*-bridging siloxane moieties on the Cp ring. The observed values of $\delta_{\text{iso}}$ are between 143 and 163 ppm, which are near the value observed for 2 (128.5 ppm). The $C_Q$ values are larger than those observed for 2, but smaller than that observed for Cp$_2$ZrCl$_2$. The values of $\eta_Q$ are observed to be near 0 (5, $\eta_Q = 0.25$), intermediate (4, $\eta_Q = 0.68$) and near 1 (3, $\eta_Q = 0.88$), despite the superficial similarities in molecular structure for the three complexes, which have similar Zr-Cp’ and Zr-Br bond lengths and Cp’-Zr-Cp’ and Br-Zr-Br angles$^{113}$ (Table 3.2), suggesting that the differences in the EFG tensor parameters may be due to inductive effects of the various silane substituents. In this regard, Bercaw and co-workers have performed a comprehensive spectroscopic and theoretical study of *ansa*-bridged zirconocene complexes and found that the electronic structure of the Cp’-zirconium bonds can be significantly affected by *ansa* bridges.$^{114}$

Compounds 3, 4 and 5 comprise a set of structures which model zirconocenes that have been tethered to a surface via reactive ancillary moieties. The conformation of 3 reflects zirconocene molecules prior to adsorption, while 4 and 5 serve as models of surface-tethered species. These results show great promise for using $^{91}$Zr SSNMR for the characterization of surface-tethered zirconocenes, since (i) large changes in the substitution and conformation of the Cp’ rings, such as for 3, 4 and 5, do not appear to cause large increases in $C_Q$, which would render simple MAS NMR experiments
untenable due to broadening of the MAS powder patterns, and (ii) MAS $^{91}$Zr NMR spectra show sensitivity to slight changes in coordination and molecular geometry.

*Static $^{91}$Zr SSNMR Spectra.* We have previously demonstrated that Cp$_2$ZrCl$_2$ possesses a significant $^{91}$Zr chemical shift anisotropy (CSA); hence, CSA and associated Euler angles$^{115-118}$ must be considered in simulations of static $^{91}$Zr SSNMR spectra.$^{45}$ The broadening of CT powder patterns of half integer quadrupolar nuclei by the second-order quadrupolar interaction is inversely proportional to $B_0$, while the broadening due to CSA is directly proportional to $B_0$. Static spectra of all complexes have been acquired at two magnetic fields, in order to confirm the values of CS tensor parameters, the span ($\Omega$) and skew ($\kappa$), and the Euler angles, which describe the relative orientations of the CS and EFG tensors. When the CSA and quadrupolar interaction are similar in magnitude, the Euler angles can influence the position and intensity of the discontinuities of the static powder patterns. The CS tensor parameters and Euler angles determined from the simulations are reported in Table 3.1.

The static $^{91}$Zr SSNMR spectra of Cp$_2$ZrCl$_2$, 1 and 2 acquired at 9.4 T and 21.1 T, and their analytical simulations are shown in Figure 3.2. The CS tensor parameters presented herein for Cp$_2$ZrCl$_2$ are $\Omega = 340$ and 350 ppm and $\kappa = -0.60$ and $-0.70$, for sites 1 and 2, respectively. These parameters are slightly different from our previous values ($\Omega = 430$ ppm and $\kappa = -0.55$), due to the increased sensitivity of the spectrum acquired at 21.1 T to changes in the CS tensor parameters. The observation of a $\kappa$ values near $-1$ indicates that the distinct component of the CS tensor is $\delta_{31}$ (and that $\delta_{22}$ and $\delta_{33}$ are similar in value). $\kappa$ values near $-1$ are observed for most of these complexes,
suggesting that this is a general feature of zirconocenes.

Figure 3.2. Static $^{91}\text{Zr}$ SSNMR spectra acquired at 9.4 T (bottom) and 21.1 T (top) of (a) Cp$_2$ZrCl$_2$, (b) 1 [Cp*$_2$ZrCl$_2$] and (c) 2 [Cp$_2$ZrBr$_2$]. Analytical simulations (red traces) which include the effects of CSA and Euler angles are overlayed on the experimental spectra.

The static spectra of 1 reveal that $\Omega = 235$ ppm and $\kappa = -0.75$. The symmetry of the CS tensor of 1 is similar to that of Cp$_2$ZrCl$_2$, as indicated by $\kappa$, however, the value of $\Omega$ is reduced. The value of $\delta_{iso}$ for 1 indicates that the Zr nucleus is significantly deshielded with respect to Cp$_2$ZrCl$_2$. The Zr-Cl distances of 1 are similar to those of Cp$_2$ZrCl$_2$, suggesting that the differences in $\delta_{iso}$ and $\Omega$ arise from the increased basicity of the Cp* ligand in comparison to the Cp ligands. The Euler angle $\beta$ is near 90° for both 1 and Cp$_2$ZrCl$_2$. $\beta$ describes the angle separating the largest principal component of the EFG tensor ($V_{33}$) and the most shielded component of the CS tensor ($\delta_{33}$) (meaning in this case they are perpendicular to one another). Calculated tensor orientations are discussed in the quantum chemical calculations section.
The static spectra of complex 2 reveals $\kappa = -0.6$, which is similar to Cp$_2$ZrCl$_2$ and 1, but $\Omega = 550$ ppm, which is significantly larger than those of the chlorinated complexes. It is worth noting that the simulations of Cp$_2$ZrBr$_2$ provide a relatively poor match with the low frequency discontinuity of the static spectrum acquired at 21.1 T. Simulation of this spectrum is more difficult because of the presence of the two crystallographic sites with distinct NMR parameters, and the small quadrupolar interaction. For this reason, the uncertainties in Euler angles are large however, the breadths of the static spectra at both fields allows accurate measurements of $\Omega$ and $\kappa$ to be obtained. With respect to the large zirconium CSA and small $C_Q$, the MAS $^{91}$Zr SSNMR spectrum acquired at 21.1 T is of particular interest, possessing an extensive spinning sideband manifold not commonly observed for $^{91}$Zr (Figure B6).

The static spectra of 4 and 5 are shown in Figure 3.3. The values of $\Omega$ obtained from these spectra are 530 ppm and 620 ppm, respectively. These CS tensor parameters are similar to those obtained from the other brominated species, 2; however, the Euler angles of 4 and 5 are substantially different: $\beta$ is near 90° and $\gamma$ is 35° for 4, while $\beta$ is 30° and $\gamma$ is near 90° for 5. The similarity of their CS tensor parameters and their distinct $n_Q$ values suggest that the EFG tensor is oriented differently within the molecular frames of these complexes (this is further addressed in the quantum chemical calculation section). Unfortunately, static spectra of 3 could not be obtained due to limited sample quantity and sample degradation. In summary, the MAS and static $^{91}$Zr spectra of Cp$_2$ZrCl$_2$ and compounds 1 through 5 suggest that the solid-state $^{91}$Zr NMR spectra of brominated zirconocenes are generally characterized by more positive $\delta_{iso}$ values and
larger $\Omega$ values than those of chlorinated zirconocenes, while the $C_Q$ values are generally similar in magnitude.

![Static $^{91}$Zr SSNMR spectra](image)

**Figure 3.3.** Static $^{91}$Zr SSNMR spectra acquired at fields of 9.4 T (bottom) and 21.1 T (top) of (a) $4 \{\text{O(Me}_2\text{SiC}_5\text{H}_4\}_2\text{ZrBr}_2\}$ and (b) $5 \{(1,3\text{-C}_5\text{H}_3)(\text{SiMe}_2\text{OSiMe}_2)_2(1,3\text{-C}_5\text{H}_3)\text{ZrBr}_2\}$. The 21.1 T spectrum of $4$ was acquired with the QCPMG sequence due to limited sample quantity. Both a spikelet spectrum and an echo spectrum resulting from co-addition of the echoes in the time domain are shown for $4$. Analytical simulations (red traces) which include the effects of CSA and Euler angles are overlayed on the experimental spectra.

In order to control the tacticity of the polymers produced by metallocene catalysts, it is necessary to alter the structure and symmetry of the coordinating Cp ligands.$^{1,2,119}$ This is often accomplished by preparing metallocenes with modified Cp ligands such as the indenyl (Ind) and fluorenyl ligands. The static $^{91}$Zr NMR spectra of the bis(indenyl)
complex, 6, acquired at 9.4 T and 21.1 T are shown in Figure 3.4. Spectra acquired at 9.4 T display significant overlap with the $^{35/37}\text{Cl}$ satellite transitions, making it difficult to resolve the static $^{91}\text{Zr}$ powder pattern at this field. This problem is lessened at 21.1 T due to a greater separation between the Larmor frequencies of $^{35/37}\text{Cl}$ and $^{91}\text{Zr}$. When a simulation with only a single site is employed, poor agreement with the intensities of the experimental spectrum is observed (Figure 3.4a). The single site simulation also requires the use of a large value of $\Omega$ (700 ppm), in order to obtain the “splitting” of the two high-frequency discontinuities, which is much larger than the other chloride complexes (single site fit listed in Table 3.1). A simulation employing two sites (Figure 3.4b and 3.4c) results in an improved fit of the experimental spectrum and employs more realistic $\Omega$ values (200 ppm for each site). However, the previously published single crystal XRD structure shows the presence of only one magnetically distinct Zr site. Solution $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy confirm the sample is pure, and that the second pattern does not arise from an impurity (Figure B7). The single crystal X-ray data was acquired at 153 K while the $^{91}\text{Zr}$ NMR spectra presented herein were acquired at room temperature, so it is possible that the second site is a result of temperature-dependent polymorphism. In fact, a powder XRD pattern measured at room temperature (Figure B8) reveals the sample is highly crystalline; however, the experimental pattern does not match that predicted from the low temperature crystal structure, confirming the possible existence of a different phase at room temperature.
Figure 3.4. Static $^{91}$Zr SSNMR spectra and analytical simulations of 6 [Ind$_2$ZrCl$_2$] acquired at fields of 21.1 T (top) and 9.4 T (bottom). (a) Analytical simulation employing a single site overlayed on the experimental WURST-QCPMG spectrum. (b) Deconvolution of the individual sites of the two site simulation. (c) Analytical simulation employing two-sites overlayed on the experimental WURST-QCPMG spectrum. (d) Simulation of the experimental pattern employing a single site. (e) Analytical simulation employing two sites overlayed on experimental piece-wise QCPMG spectrum. The satellite transitions of nearby $^{35/37}$Cl resonances are much more intense in the 9.4 T spectrum and obscure the $^{91}$Zr signal.
Regardless of whether a one- or two-site fit is employed for 6, a value of $C_Q (>30$ MHz) much larger than those observed for the other halogen complexes is obtained. Quantum chemical calculations employing atomic coordinates from the single-crystal XRD structure predict a large $C_Q$ (*vide infra*) of ca. 30 MHz suggesting that our simulations are valid (this assumes, of course, that the local structure of 6 is similar in both polymorphs). This provides confidence that the two-site fit is correct and that the CS tensor parameters and Euler angles are similar to those determined for the other chloride complexes. However, these parameters are associated with large uncertainties due to overlap of the two sites and the large magnitude of $C_Q$. 6 possesses Zr-Cl distances and Cl-Zr-Cl angles similar to those observed for Cp$_2$ZrCl$_2$ and 1, suggesting that the large difference in $C_Q$ must then be due to the asymmetry of the indenyl ligands. It has been noted that the two carbon atoms common to the five- and six-membered rings within the indenyl ligands possess much longer C-Zr bond lengths [average $r$(Zr-C) of 2.599 Å] than the Zr-C bond lengths of the three carbon atoms [average $r$(Zr-C) of 2.486 Å] exclusive to the five-membered ring. The large asymmetry in Zr-Cp carbon atom bond lengths is not observed for the other complexes, suggesting that this is the most likely source of the large increase in $C_Q$ for 6.

Complexes 7 to 9 were investigated because of their roles in the olefin polymerization process (Scheme 3.2). In industrial olefin polymerization processes, a chlorinated form of the metallocene precatalyst, such as Cp$_2$ZrCl$_2$, is reacted with an excess of the cocatalyst, MAO (10$^2$ to 10$^4$ equivalents) in order to generate an active catalyst. The role of MAO is to abstract the chloride ligands and transfer methyl
ligands to the zirconium centers, resulting in the monomethyl and dimethyl complexes, 7 and 8. MAO also serves as an activator by further abstracting a coordinated methyl group from the zirconium center, leading to a cationic complex, which is the active polymerization catalyst. In this case, complex 9 will serve as a mimic of the active catalyst site that is generated by MAO (i.e., a cationic zirconocene).

**Scheme 3.2.** The reaction of excess amounts of methylalumoxane (MAO) with a catalyst precursor (Cp₂ZrCl₂) results in the abstraction of the chloride ligands and methylation of the zirconium center leading to the formation of 7 and 8. Further abstraction of a methyl group by MAO results in a cationic zirconocene with a vacant coordination site (the active polymerization catalyst) and generation of an anionic methyl-MAO adduct.

The static $^{91}$Zr NMR spectra of 7 acquired at magnetic fields of 9.4 T and 21.1 T seem to indicate the presence of two distinct Zr sites (Figure 3.5); however, a previously published single crystal XRD structure contains only one magnetically distinct Zr site. An abnormally long Zr-methyl carbon distance [$r$(Zr-Me) = 2.36 Å] was observed in this structure, suggesting that the methyl and chlorine positions may be disordered. We obtained a new single crystal XRD structure of 7, which has been modelled with disordered methyl carbon and chlorine positions, resulting in two magnetically distinct Zr sites with uneven occupancies. The new structure possesses a $r$(Zr-Me) of 2.227 Å (occupancy of 0.616) and a $r$(Zr-Me) of 2.176 Å (occupancy of 0.384) for the two distinct
Zr sites. The latter distance seems unrealistically short and is probably a by-product of limited resolution in the XRD experiments. Extensive characterization with both powder XRD, solution $^{13}$C, $^1$H and $^{91}$Zr NMR and $^{13}$C SSNMR experiments confirms the sample of 7 was of high purity (see Figures B9-B14), and that the presence of a second powder pattern in the static $^{91}$Zr SSNMR spectrum is not due to an impurity phase.

Simulations of the experimental spectra of 7 employing two sites of equal integrated intensity are shown in Figure 3.5. For both sites, $\delta_{\text{iso}} = 230$ ppm while values of $\Omega$ (900 and 1000 ppm) and $C_Q$ (23.3 and 20.0 MHz) are similar in magnitude; however, the two sites have very distinct $\eta_Q$ values (for site 1, $\eta_Q = 0.35$ and for site 2, $\eta_Q = 0.75$) and Euler angles, perhaps reflecting the uneven occupancies and slightly differing Zr environments indicated by the single-crystal structure. Simulated spectra at both fields possess low frequency discontinuities which are slightly more intense than those of the experimental spectra; even if the Euler angles and CS tensor parameters are freely varied, it is not possible to produce a fit of the 9.4 T spectrum which possesses a low frequency discontinuity of the appropriate intensity. We are uncertain of the origin of the broadening of the discontinuities and non-ideal intensities at 9.4 T; however, this spectrum is still useful for determining $C_Q$ and $\eta_Q$. Hence, though there are large uncertainties associated with the experimental EFG and CS tensor parameters of 7, the static $^{91}$Zr SSNMR spectra are distinct from those of the other complexes, and still provide a useful “fingerprint” of this complex.
Figure 3.5. Static solid-state $^{91}$Zr NMR spectra of 7 [Cp$_2$ZrMeCl] acquired with the WURST-QCPMG sequence at fields of 21.1 T (top) and 9.4 T (bottom). (a) Deconvolution of the individual sites employed in the two site simulation. (b) Two site analytical simulation (red trace) overlayed on the experimental spectrum formed by time domain co-addition of the echoes in the WURST-QCPMG echo train. (c) Two site analytical simulation overlayed on the experimental WURST-QCPMG spikelet spectrum. (d) Deconvolution of the individual sites employed in the two site simulation. (e) Two site analytical simulation (red trace) overlayed on the experimental piece-wise WURST-QCPMG spikelet spectrum.
The static $^{91}$Zr wideline QCPMG NMR spectrum of 8 exhibits a powder pattern with a breadth of 850 kHz at 9.4 T (Figure 3.6b), which yields a large $C_Q$ of 27.9 MHz, and an $\eta_Q$ value of 0.41, similar to that of Cp$_2$ZrCl$_2$. The Euler angles of 8 are found to be nearly identical to those of Cp$_2$ZrCl$_2$. A very large span of $\Omega = 1750$ ppm is obtained from simulations of the static spectra at both fields. The large $C_Q$ value of 8 is consistent with the broad signal (FWHH of 2530 Hz at 300 K) observed in the solution $^{91}$Zr NMR spectrum of 8 by BHP, and agrees qualitatively with their theoretical calculations; specifically, that 8 should have a $C_Q$ larger than Cp$_2$ZrCl$_2$ by a factor of $ca. 3$. The difference of $ca. 450$ ppm in the $\delta_{iso}$ values of 8 and Cp$_2$ZrCl$_2$ in the solid-state is similar to the difference of approximately 500 ppm that is observed in solution $^{91}$Zr NMR spectra (Figure B13). Comparison of the crystal structures of Cp$_2$ZrCl$_2$ and 8 reveal that the Zr-Cp centroid (Zr-Cp$_{cent}$) distances and Cp-Zr-Cp angles are similar; however, the Zr-Me bond is much shorter than the Zr-Cl bond [$r$(Zr–Me) = 2.28 Å and $r$(Zr-Cl) = 2.47 Å]. The larger $C_Q$ observed in 8 compared to that of Cp$_2$ZrCl$_2$ is likely due to the shorter bond lengths; however, the differences in the electronic structure of the two ligands also play an important role (this is further investigated in the theoretical section). It should be noted that the spectrum at 21.1 T was acquired with a single transmitter offset with the WURST-QCPMG technique (with $^1$H decoupling) in a total time of 1.1 hours, suggesting that the study of samples with dilute zirconium contents and broad resonances is feasible at natural abundance.
Figure 3.6. Static $^{91}$Zr SSNMR spectra of 8 \([\text{Cp}_2\text{ZrMe}_2]\) and 9 \([\text{Cp}_2\text{ZrMe}]\text{[MeB(C}_6\text{F}_5)_3]\). Analytical simulations (red traces) overlayed on the experimental WURST-QCPMG spectra of 8 acquired at fields of (a) 21.1 T and (b) 9.4 T. (c) Analytical simulation (red trace) overlayed on the experimental WURST-QCPMG spectrum of 9 acquired at a field of 21.1 T. Experiments on 9 were attempted at 9.4 T, however no signal could be observed. This is due to the large breadth of the central transition powder pattern at this field.
The static \(^{91}\text{Zr}\) SSNMR spectrum of \(9\) at 21.1 T is shown in Figure 3.6c. The spectrum reveals an extremely large \(C_Q\) value of 39.0 MHz and an \(\eta_Q\) value of 0.76. This \(C_Q\) is significantly larger than those observed for \(7\) and \(8\) and slightly smaller than the value of 44.7 MHz measured for \(\text{K}_2\text{ZrF}_6\), which is the largest \(C_Q^{(91\text{Zr})}\) measured by NMR to date.\(^{76}\) The Zr-methyl carbon bond lengths are highly asymmetric for this complex; the methyl group which is bound solely to Zr possesses \(r(\text{Zr–Me}) = 2.25 \text{ Å}\), while the methyl group which bridges the adjacent Zr and B atoms possesses \(r(\text{Zr–Me}) = 2.56 \text{ Å}\).\(^{120}\)

Presumably, the large increase in \(C_Q\) for \(9\) arises due to the reduction in spherical symmetry about the zirconium centre as compared to complex \(8\). A sizable value of \(\Omega = 1000 \text{ ppm}\) is also observed, although this is reduced in comparison to \(8\). The Euler angles are similar to those observed for \(\text{Cp}_2\text{ZrCl}_2\) and \(8\), with the exception of \(\gamma\) which is found to be near 90° for \(9\). The observation of large \(C_Q\) and \(\eta_Q\) values distinct from those of the catalyst precursors, \(\text{Cp}_2\text{ZrCl}_2\), \(7\) and \(8\), suggests that \(^{91}\text{Zr}\) solid-state NMR can readily distinguish the polymerization active cationic zirconocenes, although samples containing a mixture of the species would give rise to complicated \(^{91}\text{Zr}\) NMR spectra. The spectrum of \(9\) was acquired with the WURST-CPMG pulse sequence (with \(^1\text{H}\) decoupling) and required 8 sub-spectra at 21.1 T to form the total pattern giving a total acquisition time of slightly over 9 hours. Acquisition of spectra at 9.4 T was attempted, however, no signal was observed. This is unsurprising given that the static \(^{91}\text{Zr}\) spectrum of \(9\) at a field of 9.4 T would exceed 2 MHz in breadth and the long experiment times required at 21.1 T. This suggests that \(^{91}\text{Zr}\) SSNMR studies of catalytically active zirconocenes in heterogeneous catalysts systems with dilute zirconium contents would be extremely challenging (though
not impossible) and require high fields and cryogenic temperatures, and possibly isotopic enrichment, to be feasible.

**Theoretical Calculations.** BHP have presented extensive quantum chemical calculations of $^{91}$Zr EFG and CS tensors for a large series of zirconocenes. They obtained the best results by using DFT methods, and basis sets similar to those employed herein. BHP estimated the magnitude of the largest component of the EFG tensor ($V_{33}$) based upon the observed linewidths of solution $^{91}$Zr NMR spectra and were able to successfully reproduce the relative magnitudes of $V_{33}$ with quantum chemical calculations. However, the $V_{33}$ values calculated by BHP are ca. two to three times greater in magnitude than those determined from the $C_Q$ values obtained from our $^{91}$Zr SSNMR spectra (Table 3.3). The $^{91}$Zr EFG tensor parameters obtained from SSNMR spectra are much more accurate than those obtained from solution $^{91}$Zr NMR spectra, where under the assumptions of the extreme-narrowing limit, it is necessary to estimate the correlation time ($\tau_c$) and $\eta_Q$. A summary of results obtained from B3LYP calculations performed on atomic coordinates obtained from single crystal XRD structures is presented in Table 3.3. Extensive tests of Zr, Cl and Br basis sets were performed on Cp$_2$ZrCl$_2$ and 2 (Tables B9 and B10). Regardless of the basis sets and methods employed, relatively poor agreement between the experimentally determined and calculated EFG tensor parameters, $C_Q$ and $\eta_Q$, is generally observed when coordinates from single crystal X-ray structures are employed in the calculations for Cp$_2$ZrCl$_2$ and complexes 1 to 5 (Table 3.3). Examination of the individual crystal structures of the complexes reveals that there is a substantial variation.
Table 3.3. Experimental and Calculated $^{91}$Zr CS and EFG Tensor Parameters Determined with the B3LYP method and [6s3p3d] Basis Set on Zr

<table>
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<th>Compound</th>
<th>Site/Structure</th>
<th>$V_{13}$</th>
<th>$C_\eta$</th>
<th>$\eta_0$</th>
<th>$\delta_{iso}$</th>
<th>$\Omega$</th>
<th>$\kappa^\prime$</th>
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<td>0.18</td>
<td>21</td>
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<tr>
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<td>21</td>
<td>454</td>
<td>-0.6</td>
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<tr>
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<td>-6.1</td>
<td>0.30</td>
<td>21</td>
<td>456</td>
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<td>335</td>
<td>0.7</td>
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<td>-0.7</td>
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<td>-2.0</td>
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<td>(Me₅SiC₅H₅)₂ZrBr₂ 3</td>
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<td>-</td>
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<tr>
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<td>-4.3</td>
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<td>692</td>
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<td>(1,3-C₅H₅)(SiMe₂OSiMe₂)₂ 5</td>
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<tr>
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<tr>
<td>Ind₂ZrCl₂ 6</td>
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<td>1/X-ray ($^o$)</td>
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<tr>
<td>Cp₂ZrMeCl 7</td>
<td>experimental site 1</td>
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<td>23.3</td>
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<tr>
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<td>1000</td>
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<td>1/X-ray ($^p$)</td>
<td>0.535</td>
<td>22.1</td>
<td>0.23</td>
<td>325</td>
<td>1205</td>
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</tr>
<tr>
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<td>19.7</td>
<td>0.07</td>
<td>334</td>
<td>1194</td>
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<tr>
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<td>1/new X-ray ($^q$)</td>
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<tr>
<td>Cp₂ZrMe₂ 8</td>
<td>experimental site 1</td>
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<td>27.9</td>
<td>0.41</td>
<td>475</td>
<td>1750</td>
<td>-0.9</td>
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</table>

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in the interatomic carbon-carbon distances; for example, in $\text{Cp}_2\text{ZrCl}_2$ the C-C distances range from 1.364 Å to 1.414 Å. There are also deviations of the Cp rings from planarity, as indicated by torsional angles of four carbons in the Cp rings. Distortions of up to 2.19° are observed in the crystal structure of $\text{Cp}_2\text{ZrCl}_2$ (this is typical of torsional angles observed in the other complexes). For this reason calculations with “idealized” Cp rings were attempted. In these calculations, the crystallographically refined Cp ring structures have been replaced with perfectly flat Cp rings (0° torsional angles) with all C-C distances set to 1.40 Å and C-C-C internal angles of 108°. The crystallographically determined Zr-CpCent distances have been retained.

Calculations which employ such idealized Cp rings lead to significantly reduced $V_{33}$ and $C_Q$ values for $\text{Cp}_2\text{ZrCl}_2$, 1, 2, and 3, and yield much better agreement with experimental values of $C_Q$ (Table 3.3 and Tables B11 and B12). All of these complexes possess small $V_{33}$ values, and minor deviations in the Cp’ carbon atom positions would be expected to reduce the symmetry around the Zr atom and give rise to larger EFGs.

<table>
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<th>$\delta_1$</th>
<th>$\beta_1$</th>
<th>$\gamma_1$</th>
<th>$\delta_2$</th>
<th>$\beta_2$</th>
<th>$\gamma_2$</th>
<th>$\delta_3$</th>
<th>$\beta_3$</th>
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<tr>
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<td>-0.615</td>
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<td>0.29</td>
<td>624</td>
<td>1842</td>
<td>-1.0</td>
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</tbody>
</table>

$[^9]$ Additional computational results can be found in Tables B9 to B13. See text for details on basis sets used in the calculations. The 6s3p3d basis set was used for Zr, cc-pVDZ for Cl and 6-311G** on Br. $[^6]$ See the experimental section for details on the basis sets used on other atoms. $[^b]$ Only the magnitude of $C_Q$ can be measured experimentally. For definitions of all NMR parameters refer to Table 3.1. $[^d]$ The theoretical values of $\delta_{iso}$ were determined by comparison to the magnetic shielding values calculated from calculations on $\text{Cp}_2\text{ZrCl}_2$ which utilized ideal Cp rings and the corresponding method and basis sets (Table B2). The equation used was, $\delta_{iso} = \sigma_{iso}(\text{Cp}_2\text{ZrCl}_2,\text{ideal Cp}) - \sigma_{iso}(x) + 21$ ppm. $[^c]$ Defined in Table 3.1. $[^7]$ X-ray refers to calculations with Cp carbon atom coordinates determined from single crystal XRD structures. “ideal Cp” refers to calculations where idealized Cp carbon atom coordinates have been used. See text for details. $[^f]$ These calculations employ coordinates from the single crystal XRD structure of (Me$_4$EtCp)$_2\text{ZrCl}_2$, where the Et groups have been replaced with Me groups. $[^g]$ These calculations employ coordinates from the single crystal XRD structure of $\text{Cp}_2\text{ZrMeCl}$ presented in this work.
however, it is somewhat surprising to observe that minor deviations in the positions of the carbons within the Cp rings can lead to two- to four-fold differences in the magnitude of $V_{33}$. For complexes 4 and 5, calculations on structures with ideal Cp rings lead to only slight differences in the calculated EFG and CS tensor parameters. Complexes 7, 8 and 9 feature coordination by methyl ligands and possess values of $C_Q$ greater than 20 MHz. The use of ideal Cp rings leads to changes in calculated values of $C_Q$ by 3 to 4 MHz compared to calculations utilizing X-ray coordinates for Cp carbon atoms. This suggests that the large values of $V_{33}$ observed for 7, 8 and 9 relative to those of the halogenated zirconocenes mainly arise from the presence of the methyl ligands coordinated to Zr rather than from differences in the Cp carbon positions (vide infra). Calculations utilizing X-ray coordinates for Cp’ carbon atoms and the idealized Cp’ rings yield very similar CS tensor parameters for all complexes. In summary, calculations utilizing idealized Cp’ rings with Zr-Cp’Cent distances determined from X-ray structures should be used for quantum chemical calculations of $^{91}$Zr EFG tensor parameters of zirconocenes.

Discrepancies and observations about the quantum chemical calculations of NMR tensor parameters for some of the individual complexes are now briefly discussed. Our initial quantum chemical calculations on 1 employed atomic coordinates from the previously published single-crystal X-ray structure. These calculations resulted in $^{91}$Zr NMR tensor parameters showing poor agreement with experimental values, regardless of whether X-ray or idealized Cp* rings were utilized. An X-ray crystal structure of 1 was unavailable at the time of BHP’s study, so the authors used atomic coordinates from the previously published crystal structure of bis(tetramethylethylcyclopentadienyl)zirconium.
dichloride\textsuperscript{123} [(Me\textsubscript{4}EtCp)\textsubscript{2}ZrCl\textsubscript{2}] to construct a model of 1, by replacing the ethyl groups on both Cp ligands with methyl groups. With this approach, they observed good agreement between the calculated and experimental values of $\delta$\textsubscript{iso} for 1.\textsuperscript{79} We have taken a similar approach, and our calculations yield \textsuperscript{91}Zr NMR tensor parameters in excellent agreement with experimental values (Table 3.3). The largest differences evident in the crystal structures of 1 and (Me\textsubscript{4}EtCp)\textsubscript{2}ZrCl\textsubscript{2} are the Cp'\textsubscript{Cent}-Zr-Cp'\textsubscript{Cent} angles (130.9° and 137.0°, respectively, Table 3.2). The success of these calculations suggest to us that there may be an error in the previously determined crystal structure of 1.

The crystal structure of 2 has two crystallographically distinct Zr atoms (sites 1 and 2); in addition, site 2 has two Cp ring conformations which differ by rotation of one of the Cp rings about its five-fold axis by an angle of 30°, as well as different Zr-Cp\textsubscript{Cent} distances (2.185 Å and 2.213 Å for conformations 1 and 2 respectively). Calculations of EFG tensor parameters for 2 reveal $C_Q$ and $\eta_Q$ values which differ by greater than 20% for sites 1 and 2. There is a significant variation in calculated $C_Q$ and $\eta_Q$ values for the two distinct Cp ring conformations of site 2; however, the Zr-Cp\textsubscript{Cent} distance of conformation 2 is significantly longer than the other distances within the structure, and casts doubt on the accuracy of the crystal structure. This suggests that the two resonances observed in the MAS \textsuperscript{91}Zr NMR spectrum arise from the two crystallographically distinct Zr sites, rather than from distinct conformations of the Cp rings.

Calculations on 7 employing coordinates from the previously published single crystal XRD structure yield much smaller $C_Q$ values than those obtained from the crystal structure presented herein. The major difference between the two structures is a
significantly shorter $r(Zr–Me)$ in the new structure (2.23 Å versus 2.36 Å). Simulations of the static $^{91}\text{Zr}$ SSNMR spectra of 7 required two sites with disparate $^{91}\text{Zr}$ NMR tensor parameters in order to produce reasonable fits of the experimental spectra. The calculations on our new crystal structure suggests that the only parameter which should vary significantly between the two sites is $C_Q$, with both sites possessing similar $\eta_Q$ and CS tensor parameters, suggesting that the latter parameters are not highly dependent upon $r(Zr–Me)$.

Our new single-crystal XRD structure of 7 indicates that the Me and Cl positions are disordered. Calculations on twelve-molecule clusters of 7 were performed to see how the presence of neighbouring molecular units affects the calculated EFG tensor parameters. Calculations were performed on two clusters (Figure B15). In both cases the central molecule of the cluster corresponds to site 2 (i.e., $r(Zr-Me)$ = 2.23 Å and $r(Zr-Cl)$ = 2.51 Å) and X-ray coordinates of the Cp carbon atoms were used. In cluster 1, all neighbouring units correspond to site 2 of the single crystal XRD structure (i.e., all neighbouring units possess $r(Zr-Me)$ = 2.23 Å and $r(Zr-Cl)$ = 2.51 Å). In cluster 2, four of the neighbouring units correspond to site 1 (i.e., $r(Zr-Me)$ = 2.18 Å and $r(Zr-Cl)$ = 2.51 Å). The four neighbouring units that were changed in cluster 2 were chosen because their Me or Cl ligands were directed toward the central molecule of the cluster. Calculations on both cluster 1 and 2 result in calculated values of $C_Q$ for the central molecule which are similar in magnitude to that calculated for an isolated molecule, however, the $\eta_Q$ value calculated for cluster 1 is 0.66 (Table B14). The $\eta_Q$ values calculated for cluster 2 and the isolated molecule are near 0. This suggests that the orientation of the neighbouring
molecules can effect the EFG tensor, and that the high \( \eta_q \) site observed in the experimental spectra of 7 may originate from the disorder in the orientation of the neighbouring molecules within the crystal lattice.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method/Structure</th>
<th>( \alpha ) (°)</th>
<th>( \beta ) (°)</th>
<th>( \gamma ) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mathrm{Cp}_2\mathrm{ZrCl}_2 )</td>
<td>experiment site 1</td>
<td>90(35)</td>
<td>86(10)</td>
<td>2(10)</td>
</tr>
<tr>
<td></td>
<td>experiment site 2</td>
<td>90(35)</td>
<td>86(10)</td>
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</tr>
<tr>
<td></td>
<td>site 1 ideal Cp</td>
<td>103</td>
<td>89</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>site 2 ideal Cp</td>
<td>108</td>
<td>88</td>
<td>-1</td>
</tr>
<tr>
<td>( \mathrm{Cp}^#_2\mathrm{ZrCl}_2 ) ( \text{1} )</td>
<td>experiment</td>
<td>20(40)</td>
<td>90(25)</td>
<td>90(10)</td>
</tr>
<tr>
<td></td>
<td>ideal (( \mathrm{Me}_4\mathrm{EtCp} ))</td>
<td>-20</td>
<td>82</td>
<td>90</td>
</tr>
<tr>
<td>( \mathrm{Cp}_2\mathrm{ZrBr}_2 ) ( \text{2} )</td>
<td>experiment site 1 ideal Cp</td>
<td>40(90)</td>
<td>0(90)</td>
<td>0(90)</td>
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<tr>
<td></td>
<td>experiment</td>
<td>98</td>
<td>56</td>
<td>-91</td>
</tr>
<tr>
<td>( \mathrm{O}(\mathrm{Me}_2\mathrm{SiC}_5\mathrm{H}_4)\mathrm{ZrBr}_2 ) ( \text{4} )</td>
<td>experiment ideal Cp</td>
<td>40(20)</td>
<td>90(15)</td>
<td>35(40)</td>
</tr>
<tr>
<td></td>
<td>site 1 ideal Cp</td>
<td>98</td>
<td>56</td>
<td>-91</td>
</tr>
<tr>
<td>( \text{(1,3-C}_5\mathrm{H}_3)(\mathrm{SiMe}_2\mathrm{OSiMe}_2)\text{ZrBr}_2 ) ( \text{5} )</td>
<td>experiment ideal Cp</td>
<td>40(20)</td>
<td>30(15)</td>
<td>85(10)</td>
</tr>
<tr>
<td>( \text{Ind}_2\mathrm{ZrCl}_2 ) ( \text{6} ) (two site fit, site 1)</td>
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<td>80(60)</td>
<td>60(40)</td>
<td>4(60)</td>
</tr>
<tr>
<td></td>
<td>experiment site 1 ideal Cp</td>
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<td>60</td>
<td>0</td>
</tr>
<tr>
<td>( \text{Ind}_2\mathrm{ZrCl}_2 ) ( \text{6} ) (two site fit, site 2)</td>
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<td>60(40)</td>
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<td></td>
<td>experiment ideal Cp</td>
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<td>0</td>
</tr>
<tr>
<td>( \mathrm{Cp}_2\mathrm{ZrMeCl} ) ( \text{7} ) (site 1)</td>
<td>experiment site 2 ideal Cp</td>
<td>5(70)</td>
<td>15(45)</td>
<td>85(70)</td>
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<td>60</td>
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<tr>
<td>( \mathrm{Cp}_2\mathrm{ZrMeCl} ) ( \text{7} ) (site 2)</td>
<td>experiment site 2 ideal Cp</td>
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<td>20(20)</td>
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<td>97</td>
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<td>( \mathrm{Cp}_2\mathrm{ZrMe}_2 ) ( \text{8} )</td>
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<td>90(5)</td>
<td>0(5)</td>
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<td>ideal Cp</td>
<td>93</td>
<td>89</td>
<td>1</td>
</tr>
<tr>
<td>( \text{[Cp}_2\text{ZrMe}][\text{MeB(C}_6\text{F}_5)_3] ) ( \text{9} )</td>
<td>experiment ideal Cp</td>
<td>90(10)</td>
<td>80(15)</td>
<td>86(40)</td>
</tr>
</tbody>
</table>

\(^a\)Euler angle conventions are specified in the experimental section.
Figure 3.7. Theoretical $^{91}$Zr EFG and MS tensor orientations in the molecular frames of (a) Cp$_2$ZrCl$_2$, (b) 7 [Cp$_2$ZrMeCl] and (c) 8 [Cp$_2$ZrMe$_2$]. All tensor orientations are taken from the calculations which employ idealized Cp rings. The tensor orientation for Cp$_2$ZrCl$_2$ has been taken from site 1. The tensor orientation for 7 has been taken from calculations on site 2 of the new structure (see text for full explanation).

The theoretically obtained $^{91}$Zr EFG and magnetic shielding (MS) tensor orientations within the molecular frames are now discussed (Figures 3.7 and 3.8). Euler angles extracted from the quantum chemical calculations are shown in Table 3.4. For all complexes, the least shielded component of the MS tensor ($\sigma_{11}$) is oriented in a direction approximately perpendicular to the X-Zr-X plane (X = Me, Cl, Br). Nuclear deshielding in this direction arises from magnetic dipole induced mixing of occupied and virtual
molecular orbitals (MOs) within the X-Zr-X plane (i.e., virtual MOs of high Zr d atomic orbital character and occupied Zr-X σ- (X = CH₃, Cl, Br) and π-bonding (X = Cl, Br) MOs). This is consistent with previous Hückel MO calculations on bent metallocene complexes by Lauher and Hoffman, which show that Zr-X σ and π MOs are the highest occupied MOs in these complexes, and that their electron densities are largely concentrated within or about the X-Zr-X plane. The only exception we note is 6, where a significant deviation away from normality is observed (σ₁₁ forms a torsional angle of ca. 78° with the Cl-Zr-Cl plane); this may arise from the positioning of the indenyl rings.

The tensor orientations for the series of complexes found in Scheme 3.2 (Cp₂ZrCl₂ and 7 - 9) are discussed first. Quantum chemical calculations predict similar orientations of EFG tensors for Cp₂ZrCl₂ (Figure 3.7a) and 8 (Figure 3.7c): V₁₁ and V₂₂ lie approximately within the X-Zr-X (X = Me, Cl) plane and V₃₃ is directed towards the Cp rings forming torsional angles with the X-Zr-X plane of 88.4° and 90.3° for X = Me and X = Cl, respectively. The tensor orientations presented for Cp₂ZrCl₂ are similar to those previously reported by our research group. The EFG orientations in Cp₂ZrCl₂ and 8 are consistent with experimental values of η₁ being closer to 0 than 1, which indicate that V₃₃ is the distinct component, oriented in an electronic environment different from those of V₁₁ and V₂₂. For both complexes, the least shielded component of the MS tensor (σ₁₁) is approximately co-linear with the largest component of the EFG tensor (V₃₃), and the most shielded component (σ₃₃) is predicted to lie in the X-Zr-X plane near V₂₂; this is consistent with the Euler angles of α ≈ β ≈ 90° obtained from simulations of the static ^{91}Zr NMR spectra.
Complex 7 possesses a similar MS tensor orientation to the other compounds where \( \sigma_{11} \) is oriented normal to the Me-Zr-Cl plane, while \( \sigma_{22} \) and \( \sigma_{33} \) are approximately contained within the Me-Zr-Cl plane, near the Zr-Cl and Zr-Me bonds, respectively (Figure 3.7b, bottom). However, the EFG tensor orientation in 7 is distinct from that of the other complexes; \( V_{33} \) is oriented such that it is coincident with the Zr-Me bond, while \( V_{11} \) and \( V_{22} \) make angles of approximately 45 \(^\circ\) with respect to the Me-Zr-Cl plane (Figure 3.7b, top). The orientation of \( V_{33} \) along the Zr-Me bond suggests that the increase in \( C_Q \) observed for 7 compared to that of \( \text{Cp}_2\text{ZrCl}_2 \) can be attributed to the asymmetry of the Zr-Me and Zr-Cl bonds. Unfortunately, given the uncertainty regarding the simulations of the static NMR spectra of 7, it is difficult to compare experimental and calculated Euler angles, although a calculated value of \( \beta \) near zero is distinct from the other complexes.

The EFG and MS tensor orientation for 9 are shown in Figure 3.8a. The \( \eta_Q \) value near 1 is consistent with the orientation of \( V_{11} \) towards the Cp rings, with \( V_{33} \) and \( V_{22} \) oriented near the Zr-Me carbon bonds (\( V_{33} \) is directed towards the bridging methyl group). This suggests that the large \( C_Q \) observed for this complex results in part from the asymmetry of the Zr-Me carbon bond lengths (\textit{vide infra}).

Complexes 1 - 5 are all characterized by small \( C_Q \) values (less than that of \( \text{Cp}_2\text{ZrCl}_2 \)) and \( \eta_Q \) values which vary from near 0 to near 1. For all of these complexes, \( V_{33} \) is oriented such that it is contained within or near the X-Zr-X plane (Figure 3.8b - e, orientations for 3 not shown), although the direction of \( V_{33} \) within this plane is variable and seems to be uncorrelated to the predicted sign of \( C_Q \) or value of \( \eta_Q \). We posit that this is because when \( V_{33} \) is small, subtle differences in ligand positions can result in completely
different EFG tensor orientations. In complex 6, $V_{33}$ is directed towards the carbon atoms which are common to the five and six-membered rings of the indenyl ligands (Figure 3.8f). The average Zr-C bond lengths of 2.599 Å of the two carbon atoms, are much longer than the average Zr-C bond length 2.489 Å of the three carbon atoms exclusive to the five-membered ring. This supports the notion that the large increase in $C_Q$ for 6 as compared to Cp$_2$ZrCl$_2$ can be attributed to the asymmetric binding of the indenyl ligands.

![Diagram](image_url)

**Figure 3.8.** Theoretical $^{91}$Zr EFG and MS tensor orientations in the molecular frames of (a) 9, (b) 1 [Cp*$_2$ZrCl$_2$], (c) 2 [Cp$_2$ZrBr$_2$], (d) 4 [O(Me$_2$SiC$_5$H$_4$)$_2$ZrBr$_2$], (e) 5 [(1,3-C$_5$H$_3$)(SiMe$_2$OSiMe$_2$)$_2$(1,3-C$_5$H$_3$)ZrBr$_2$] and (f) 6 [Ind$_2$ZrCl$_2$]. All tensor orientations are taken from the calculations which employ idealized Cp rings. The tensor orientation for complex 2 has been taken from site 1.
Finally, due to the importance of Cp₂ZrCl₂ and complexes 7 - 9 in olefin polymerization catalysis, it is important to further probe the origin of the large differences observed and predicted in the values of $C_Q$ and $\eta_Q$ in this series. We have calculated the EFG tensor parameters for structures with variable Zr-X (X = Cl, Me) bond lengths, since all of these complexes possess similar CpCent-Zr bond lengths, CpCent-Zr-CpCent angles and X-Zr-X angles (Table 3.2). A plot of calculated $C_Q$ values as a function of Zr-X bond lengths is shown in Figure 3.9a for Cp₂ZrCl₂ and 8. Cp₂ZrCl₂ and 8 possess crystallographically determined average Zr-X bond lengths of $r$(Zr–Cl) = 2.45 Å and $r$(Zr–Me) = 2.28 Å, respectively. As the Zr-X bonds are symmetrically shortened (e.g., both Zr-Cl bond lengths are decreased in length by the same amount for Cp₂ZrCl₂) from their crystallographic distances, $C_Q$ remains negative and is observed to steadily increase in magnitude for both complexes (Figure 3.9a). As both bond lengths are symmetrically increased from their crystallographic distances, $C_Q$ is observed to approach zero, then become positive and steadily increase in magnitude. $\eta_Q$ remains relatively constant for Cp₂ZrCl₂ over the full range of Zr-Cl bond lengths employed in calculations, while for 8, a steady increase in $\eta_Q$ is observed as the average Zr-Me bond lengths are symmetrically increased from 1.98 Å to 2.58 Å (Figure 3.9b).

It is interesting to note that when the Zr-Me distances in 8 are set approximately equal to the crystallographic Zr-Cl distances of Cp₂ZrCl₂, the calculated values of $C_Q$ for 8 are nearly double those of Cp₂ZrCl₂ (Figure 3.9a). This suggests that the electronic nature of the Zr-X bonding, and not only the bond lengths, has an major effect on the magnitude of $C_Q$. This is not surprising considering that Cl ligands possess electron lone pairs.
capable of ligand-to-metal π-donation, whereas Me ligands do not. In summary, the increase in $C_Q$ observed for 8 compared to that of Cp$_2$ZrCl$_2$ is primarily due to both the relatively short Zr-Me bond lengths and the differing electronic structures of these bonds.

Figure 3.9. Values of $^{91}\text{Zr}$ EFG tensor parameters obtained from B3LYP calculations on structures with variable Zr-Cl and Zr-Me carbon bond lengths. The bond lengths were varied in increments of 0.05 Å. Calculated (a) $C_Q$ and (b) $\eta_Q$ values when both of the Zr-X (X = Cl, Me) bond lengths in Cp$_2$ZrCl$_2$ and 8 [Cp$_2$ZrMe$_2$] are varied. Calculated (c) $C_Q$ and (d) $\eta_Q$ values when the Zr-Me bond length of 7 [Cp$_2$ZrMeCl] is varied and when the bridging Zr-Me bond length of [Cp$_2$ZrMe][BMe$_4$] is varied. The model complex, [Cp$_2$ZrMe][BMe$_4$], was created by replacing the three pentafluorophenyl groups of 9 with Me groups. Crystallographic bond lengths are marked with open circles and squares. Atomic coordinates with idealized Cp rings were employed for all calculations. Coordinates from site 1 of Cp$_2$ZrCl$_2$ and site 2 of 7 of the respective crystal structures were employed.
Calculations of $^{91}\text{Zr}$ EFG tensors are also helpful in understanding the significant differences in the values of $\eta_Q$ for the two structurally similar (but magnetically distinct) Zr sites in 7. Since there is some uncertainty associated with the crystallographically determined values of $r(\text{Zr–Me})$ for 7 (vide supra), EFG tensor parameter calculations were performed on a model structure of 7 in which $r(\text{Zr–Me})$ was altered, while $r(\text{Zr–Cl})$ was held constant at its crystallographically determined value (Figure 3.9c and 3.9d). These calculations reveal that $C_Q$ is positive and steadily decreases in magnitude as $r(\text{Zr–Me})$ is increased in length from 1.83 Å to 2.63 Å. Calculations predict $C_Q$ values near the experimentally determined values of 20.0 and 23.3 MHz when $r(\text{Zr–Me})$ is ca. 2.33 Å (0.1 Å longer than the crystallographic bond length). The value of $\eta_Q$ is relatively constant and near 0 when $r(\text{Zr–Me})$ is less than 2.48 Å, but at longer $r(\text{Zr–Me})$, the value of $\eta_Q$ rapidly approaches 1. This suggests that the high $\eta_Q$ site observed in the static $^{91}\text{Zr}$ SSNMR spectra is not arising from disorder in the position of the methyl group. Calculations on twelve-molecule clusters of 7 (vide supra) suggest that this variation in $\eta_Q$ arises from longer range electrostatic interactions which depend upon the orientation of the Me and Cl ligands in neighbouring molecules.

In order to probe the origins of the large $C_Q$ and high $\eta_Q$ observed for 9, EFG tensor parameters were calculated for a model complex which is analogous to 9, [Cp$_2$ZrMe][BMe$_4$]. The $r(\text{Zr–Me})$ of the bridging Me group was then varied (the BMe$_3$ group was also moved by the same amount), while the terminal $r(\text{Zr–Me})$ was fixed at the crystallographic distance observed for 9 (2.25 Å). As the bridging $r(\text{Zr–Me})$ is increased from 2.16 Å to 2.51 Å, $C_Q$ (which is positive) steadily increases in magnitude (Figure
At \( r(\text{Zr–Me}) = 2.56 \, \text{Å} \), \( C_Q \) becomes negative, and steadily increases in magnitude as the bond length is increased. The change in the sign of \( C_Q \) occurs because \( V_{22} \) and \( V_{33} \) are similar in magnitude and opposite in sign (corresponding to \( \eta_Q \) values near 1) for \( r(\text{Zr-\text{Me}}) \) near 2.56 Å, and further increases in \( r(\text{Zr-\text{Me}}) \) causes the \( V_{22} \) and \( V_{33} \) principal components to switch directions and leads to a sign change for \( C_Q \). \( \eta_Q \) is observed to fluctuate between 0 and 1 over the range of \( r(\text{Zr–Me}) \) (Figure 3.9d), with \( \eta_Q \) values greater than 0.70 observed at \( r(\text{Zr–Me}) \) greater than 2.41 Å. When \( r(\text{Zr–Me}) = 2.56 \, \text{Å} \), \( C_Q = -35 \, \text{MHz} \) and \( \eta_Q = 1.0 \) are predicted, similar to the experimentally obtained EFG tensor parameters for 9. Therefore, the large value of \( C_Q \) observed for 9 and the \( \eta_Q \) values close to 1 arise from unequal Zr-Me bond lengths for the bridging and terminal methyl groups. When the bridging \( r(\text{Zr-\text{Me}}) \) is equal to 2.26 Å, both the bridging and terminal \( r(\text{Zr-\text{Me}}) \) are approximately equal and are similar to those of 8. In this case, \( C_Q \) is calculated to be 30.9 MHz for \([\text{Cp}_2\text{ZrMe}][\text{BMe}_4]\), while \( C_Q \) is calculated to be \(-25.6 \, \text{MHz} \) for 8. This suggests that when the hydrogen atoms of the bridging Me group are directed towards the Zr centre, an increase in \( |C_Q| \) will also occur.

### 3.4 Conclusions

The use of \(^{91}\text{Zr}\) SSNMR and quantum mechanical calculations has allowed for the examination of the \(^{91}\text{Zr}\) quadrupolar and chemical shift interactions in zirconocenes possessing Cp ligands of varying substitution patterns and different heteroligands (i.e., Cl, Br, Me). The combination of QCPMG and/or WURST-QCPMG pulse sequences with
frequency-stepped techniques facilitates the acquisition of broad static patterns that span hundreds of kilohertz (i.e., spectra of 6, 7, 8 and 9). In general, halide complexes are characterized by small $C_Q$ values, while the coordination of methyl ligands leads to larger $C_Q$ values. The increase in $C_Q$ by a factor of *ca.* 4.4 for 8 as compared to $\text{Cp}_2\text{ZrCl}_2$ is explained on the basis of shortened bond lengths Zr-X bond lengths. Isotropic $^{91}\text{Zr}$ chemical shifts are seen to closely parallel those previously observed in solution $^{91}\text{Zr}$ NMR spectra, and allow for variations in the Cp ring substitution patterns as well as the types of heteroligands coordinated to the metal to be differentiated. Consistent with our previous $^{91}\text{Zr}$ SSNMR study of $\text{Cp}_2\text{ZrCl}_2$, simulations of static spectra at both high (9.4 T) and ultrahigh fields (21.1 T) require that CSA and Euler angles be accounted for. CSA is observed to be very sensitive to the nature of the heteroligand; $\Omega$ is seen to increase for the ligand series Cl, Br, and Me, affording another parameter which allows for insight into zirconocene structure and bonding. Methods for the accurate calculation of $^{91}\text{Zr}$ EFG and CS tensor parameters have been identified and show excellent agreement with experimental values. Visualization of EFG and MS tensor orientations within the molecular frames obtained from quantum chemical calculations allows for the origin of the NMR interactions to be rationalized.

The purpose of studying compounds 3 - 5 was to mimic the structures of zirconocene species before (3) and after (4 and 5) chemisorption to surface materials via the ancillary functional groups of the Cp ligands. $\text{Cp}_2\text{ZrCl}_2$ and complexes 7 - 9 were studied in order to demonstrate that solid-state $^{91}\text{Zr}$ NMR can differentiate the key intermediates that result from the reaction of MAO with a pre-catalyst ($\text{Cp}_2\text{ZrCl}_2$). This
may also allow for the interactions between MAO and zirconocenes to be probed in the future, for both homogeneous and heterogeneous catalysts. The ability of solid-state $^{91}$Zr NMR to distinguish Cp$_2$ZrCl$_2$ and complexes 7, 8 and 9 is of importance if industrial heterogeneous olefin polymerization catalysts are to be examined in the future. We have also recently demonstrated that the acquisition of solid-state $^{35}$Cl NMR spectra of zirconocenes is feasible and can provide complimentary insight into zirconocene structure.\textsuperscript{47} The combination of quantum chemical calculations and $^{91}$Zr and $^{35}$Cl SSNMR should allow for the structure of immobilized zirconocenes with ambiguous structures to be probed.

The acquisition of $^{91}$Zr NMR spectra of heterogeneous catalyst systems will prove challenging due to the dilution of the $^{91}$Zr nuclei (typical heterogeneous catalysts are 0.5 - 5\% Zr by mass). For samples which possess narrow central-transition powder patterns (e.g., Cp$_2$ZrCl$_2$) it is possible to acquire static spectra in a matter of minutes at 21.1 T with standard echo sequences, suggesting that the acquisition of solid-state $^{91}$Zr spectra of heterogeneous catalysts featuring narrow resonances is feasible with standard techniques. However, if the halide ligands are replaced during immobilization and/or the metallocene structure is significantly altered, a large increase in the breadth of the NMR pattern is expected (compare spectra of Cp$_2$ZrCl$_2$ and 8). The combination of WURST-QCPMG and ultrahigh magnetic fields allows for the acquisition of ultra-wideline solid-state $^{91}$Zr NMR spectra of 7, 8, and 9 in total experimental times of 4.6, 1.1 and 9.1 hours, respectively. Therefore, the acquisition of solid-state $^{91}$Zr NMR spectra of heterogeneous catalysts possessing broad $^{91}$Zr resonances would be a considerable challenge. In these cases $^{91}$Zr
isotopic enrichment and/or cryogenic temperatures in combination with $^1$H cross-polarization QCPMG (CP/QCPMG) pulse sequences would be necessary in order to enhance the signal of NMR experiments.$^{51, 52, 125}$ This approach has been pioneered and extensively demonstrated by Ellis and Lipton for SSNMR studies of quadrupolar metal nuclei present in extremely low concentrations in the active sites of metallo-proteins.$^{126-128}$
3.5 Bibliography


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Chapter 4: Solid-State $^{47/49}$Ti NMR of Titanocene Chlorides

4.1 Introduction

Early transition metal metallocene complexes are highly active catalysts for olefin polymerization, affording better control over the stereospecificity and molecular weight distributions of resulting polymers than the traditional heterogeneous TiCl$_4$/MgCl$_2$ Ziegler-Natta system.$^{1-4}$ While certain metallocenes can be dissolved in polymerization media and used as homogeneous catalysts, they are also employed as heterogeneous catalysts on support materials such as alumina and silica.$^{1,3}$ The solubilized homogeneous catalysts are amenable to traditional structural, kinetic and mechanistic studies; however, the active sites of supported catalysts are often difficult to characterize.$^{1,3}$ We have demonstrated that solid-state NMR (SSNMR) spectra of metal quadrupolar nuclei that lie at the “hearts” of metallocenes can act as sensitive probes of molecular structure and dynamics,$^{5-9}$ and could therefore find use for characterizing heterogeneous catalysts. In this regard,$^{47/49}$Ti SSNMR could potentially serve as a powerful probe of molecular structure for titanocene-based heterogeneous catalysts.

Titanium possesses two NMR-active nuclei, $^{47}$Ti ($I = 5/2$) and $^{49}$Ti ($I = 7/2$),$^{10}$ both of which are unreceptive owing to their low natural abundances [n.a.$^{(47}$Ti) = 7.44%, n.a.$^{(49}$Ti) = 5.41%], moderate quadrupole moments [$Q^{(47}$Ti) = 29.0 fm$^2$, $Q^{(49}$Ti) = 24.0 fm$^2$] and low gyromagnetic ratios [$\gamma^{(47}$Ti) = $-1.5105 \times 10^7$ rad s$^{-1}$ T$^{-1}$, $\gamma^{(49}$Ti) = $-1.51095 \times 10^7$ rad s$^{-1}$ T$^{-1}$].$^{10}$ $^{49}$Ti is preferred for SSNMR experiments, as the central-transition (CT) powder patterns are significantly narrower due to its slightly smaller quadrupole moment and higher nuclear spin. However, the similarity of the gyromagnetic ratios of $^{47}$Ti and $^{49}$Ti complicates the acquisition and analysis of SSNMR spectra: the difference
of the Larmor frequencies is so small that the $^{49}$Ti and $^{47}$Ti resonances are located ca. 267 ppm apart, which often results in overlapping CT powder patterns. Despite these difficulties there are numerous examples of $^{47/49}$Ti solution\textsuperscript{11-25} and solid-state\textsuperscript{26-48} NMR found in the literature, reflecting the myriad number of important systems containing titanium.

To date, most $^{47/49}$Ti SSNMR studies have been restricted to oxides and other extended solids. In this work, we report the first application of $^{47/49}$Ti SSNMR for the structural characterization of molecular titanium-containing complexes. Before complex solid catalysts can be investigated by SSNMR of quadrupolar nuclei such as $^{47/49}$Ti, fundamental studies on well-characterized crystalline species are required. To this end, MAS and static $^{47/49}$Ti SSNMR spectra of the titanocenes, Cp$_2$TiCl$_2$ (1), Cp*$_2$TiCl$_2$ (2), CpTiCl$_3$ (3), and Cp*TiCl$_3$ (4) have been acquired (Scheme 4.1). Quantum chemical calculations of NMR tensor parameters are also presented.

\begin{scheme}
\centering
\includegraphics[width=\textwidth]{titanocene_chloride_complexes.png}
\caption{Titanocene chloride complexes for which $^{47/49}$Ti SSNMR spectra have been acquired: Cp$_2$TiCl$_2$ (1), Cp*$_2$TiCl$_2$ (2), CpTiCl$_3$ (3) and Cp*TiCl$_3$ (4).}
\end{scheme}
4.2 Experimental Methods

Samples of 1 to 4 were purchased from Strem Chemicals Inc. and used without purification. All samples were finely ground into powders and packed into zirconia rotors or shortened glass NMR tubes under an inert N\textsubscript{2} atmosphere. \textsuperscript{47/49}Ti SSNMR spectra were acquired on a 21.1 T Bruker Avance II NMR spectrometer at the Canadian National Ultrahigh-Field Facility and a 9.4 T Varian InfinityPlus. A complete listing of experimental details is given in Appendix C (Tables C1-C4). Experiments at 9.4 T were conducted with Chemagnetics 5 mm HXY MAS, 4 mm HXY and 5 mm static probes equipped with a Chemagnetics low-γ tuning box. Experiments at 21.1 T were acquired with a Bruker 4 mm HX MAS probe and home-built single-channel static 5 mm and 7 mm probes. Pulse width calibrations were performed on saturated solutions of 1 dissolved in CH\textsubscript{2}Cl\textsubscript{2}. Chemical shifts were referenced to neat TiCl\textsubscript{4}(l) \([\delta_{\text{iso}}^{(49}\text{Ti}) = 0.0 \text{ ppm}\)] via an external standard of powdered SrTiO\textsubscript{3} \([\delta_{\text{iso}}^{(49}\text{Ti}) = -843 \text{ ppm}]\). Experiments at 21.1 T employed standard echo sequences for acquisition. Experiments at 9.4 T employed DFS-echo\textsuperscript{49,50} or DFS-QCPMG\textsuperscript{51,52} pulse sequences for signal enhancement. Analytical simulations of MAS and static \textsuperscript{47/49}Ti SSNMR spectra were performed with the WSolids program.\textsuperscript{53} The Rose convention is used to describe the direction and order of the Euler angles which describe the CS and EFG tensor orientation.\textsuperscript{54,55} The SIMPSON program was employed for numerical simulations of the MAS \textsuperscript{49}Ti SSNMR spectrum of 4 (Figure C2).\textsuperscript{56}

Quantum chemical calculations of NMR tensor parameters were performed with the Gaussian 03\textsuperscript{57} software package and employed molecular coordinates for isolated molecules resolved from single-crystal X-ray diffraction structures.\textsuperscript{58-61} In all cases, the
hydrogen atoms were fixed to idealized positions prior to calculations. Both restricted
Hartree-Fock (RHF) and hybrid density functional theory (B3LYP) calculations were
performed. Several Ti basis sets were tested and results from these calculations are
given in Appendix C. The double-\( \zeta \) basis set of Dunning was employed for Cl and the
6-311G* basis set was employed for C and H. Additional ab initio plane-wave density
functional calculations were performed using the CASTEP NMR program
(Table C5).

4.3 Results and Discussion

*Solid-state* \(^{47/49}\)Ti NMR Spectroscopy. Magic angle spinning (MAS) \(^{47/49}\)Ti SSNMR
spectra of compounds 1 to 4 acquired at 21.1 T are shown in Figure 4.1. At 21.1 T, spectra
of 1, 3 and 4 could be acquired in relatively short experimental times (< 1.5 hours). The
spectrum of 2 required \(ca.\) 32000 scans (1 day) due to the increased breadth of its MAS
powder pattern and the reduced Ti content. The \(^{49}\)Ti MAS spectra of 1 and 2 display
characteristic second-order quadrupolar CT powder patterns, indicative of sizable
quadrupolar interactions. From the simulations of these patterns, it is possible to obtain \(C_Q,\)
\(\eta_Q\) and \(\delta_{iso}\) (Table 4.1). For both 1 and 2, the \(^{47}\)Ti powder patterns are obscured due to their
comparably larger breadths and subsequently lower signal-to-noise ratios. Simulations of
the \(^{47}\)Ti powder patterns which utilize a \(C_Q(^{47}\)Ti) that has been scaled by the ratio of \(^{47}\)Ti
and \(^{49}\)Ti quadrupole moments, indicate that much faster sample spinning speeds are
necessary to prevent sideband overlap. For this reason the reported \(^{47/49}\)Ti NMR tensor
parameters are based upon simulations of the MAS \(^{49}\)Ti CT powder patterns, with the MAS
\(^{47}\)Ti CT patterns providing additional constraints on these parameters. It should be noted
that the crystal structure of 1 contains two crystallographically distinct titanium sites with similar local environments.\textsuperscript{58} As a result, the $^{47/49}$Ti NMR spectrum of 1 is composed of two very similar powder patterns which can be simulated with a single set of quadrupolar and chemical shift parameters. Quantum chemical calculations also confirm the similarities between the sites (\textit{vide infra}).

In comparison to 1 and 2, the MAS $^{47/49}$Ti CT powder patterns of the trichloride species, 3 and 4, are relatively narrow, and at 21.1 T, it is difficult to accurately extract values of $C_Q$ and $\eta_Q$. The $^{47}$Ti powder patterns of 3 and 4 are slightly broader and can be used to estimate $C_Q$ and $\eta_Q$, although with large uncertainties. In order to obtain accurate measurements of $C_Q$ and $\eta_Q$ for 3 and 4, additional MAS spectra were recorded at 9.4 T (Figure 4.1, bottom). The CT powder patterns are considerably broader than those obtained at 21.1 T, and exhibit features typical of a strong second-order quadrupolar interaction. From these spectra, EFG tensor parameters of $C_Q = 1.6$ MHz and $\eta_Q = 0.95$ and $C_Q = 3.0$ MHz and $\eta_Q = 0.35$ were obtained for 3 and 4, respectively, comparable to the small $C_Q(^{95}$Mo) values observed for a similar “piano-stool” complex, (Me$_3$C$_6$H$_3$)Mo(CO)$_3$.\textsuperscript{69} Experimental times at 9.4 T were significantly greater than those at 21.1 T. The MAS $^{47/49}$Ti SSNMR spectrum of 3 was acquired in 2 hours (3680 scans, 2 s pulse delay) with a DFS-echo pulse sequence, while the spectrum of 4 was acquired in ca. 21 hours (25000 scans, 3 s pulse delay) with a DFS-QCPMG sequence.
Figure 4.1. Experimental MAS $^{47/49}$Ti SSNMR spectra (black traces) of Cp$_2$TiCl$_2$ (1), Cp*$_2$TiCl$_2$ (2), CpTiCl$_3$ (3) and Cp*TiCl$_3$ (4) acquired at 21.1 T [$\nu_0$($^{49}$Ti) = 50.75 MHz] and spectra of 3 and 4 acquired at 9.4 T [$\nu_0$($^{49}$Ti) = 22.53 MHz]. Sample spinning speeds are given in the figure. Analytical simulations are overlaid on the experimental spectra (red traces). All spectra at 21.1 T were acquired with a standard rotor synchronized 90°-180° echo pulse sequence. Asterisks denote spinning sidebands. The inset of spectrum 4 shows the $^{49}$Ti isotropic peak that is obtained when the single high-frequency spinning sideband and the two nearest low-frequency spinning sidebands are added onto the isotropic peak. Spectra at 9.4 T were acquired with the DFS-echo (3) and DFS-QCPMG (4) pulse sequences. The spectrum of 4 was formed by co-adding the QCPMG echoes in the time domain, followed by Fourier transformation of the resultant echo. Additional experimental details are provided in Appendix C.
Table 4.1. Experimental and Calculated $^{47/49}$Ti EFG and CS Tensor Parameters

<table>
<thead>
<tr>
<th>Complex/Method/Structure</th>
<th>$\delta_{\text{iso}}^{(49)}$(Ti) (ppm)$^a$</th>
<th>$C_Q^{(49)}$(Ti) (MHz)$^b$</th>
<th>$\eta^b$</th>
<th>$\Omega$ (ppm)$^c$</th>
<th>$\kappa^c$</th>
<th>$\alpha^d$ (°)</th>
<th>$\beta^d$ (°)</th>
<th>$\gamma^d$ (°)</th>
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<tr>
<td>Cp$_2$TiCl$_2$ (1)/Experiment</td>
<td>$-732(5)$</td>
<td>$4.2(4)$</td>
<td>$0.45(30)$</td>
<td>$275(50)$</td>
<td>$0.65(30)$</td>
<td>$20(70)$</td>
<td>$20(20)$</td>
<td>$-10(90)$</td>
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<tr>
<td>1/RHF/Site 1 Ideal Cp$^e$</td>
<td>$-689$</td>
<td>$-6.1$</td>
<td>$0.21$</td>
<td>$166$</td>
<td>$0.7$</td>
<td>$63$</td>
<td>$82$</td>
<td>$9$</td>
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<td>1/RHF/Site 1 X-ray$^e$</td>
<td>$-737$</td>
<td>$-2.0$</td>
<td>$0.55$</td>
<td>$252$</td>
<td>$0.2$</td>
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<td>-</td>
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<td>1/RHF/Site 2 Ideal Cp</td>
<td>$-692$</td>
<td>$-6.0$</td>
<td>$0.16$</td>
<td>$168$</td>
<td>$0.7$</td>
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<td>-</td>
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<td>1/RHF/Site 2 X-ray</td>
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<td>$4.2$</td>
<td>$0.95$</td>
<td>$230$</td>
<td>$0.3$</td>
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<td>1/B3LYP/Site 1 Ideal Cp</td>
<td>$-678$</td>
<td>$3.8$</td>
<td>$0.16$</td>
<td>$526$</td>
<td>$-0.3$</td>
<td>-</td>
<td>-</td>
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<td>1/B3LYP/Site 1 X-ray</td>
<td>$-729$</td>
<td>$7.8$</td>
<td>$0.07$</td>
<td>$588$</td>
<td>$-0.4$</td>
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<td>1/B3LYP/Site 2 Ideal Cp</td>
<td>$-680$</td>
<td>$3.8$</td>
<td>$0.12$</td>
<td>$530$</td>
<td>$-0.3$</td>
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<td>-</td>
<td>-</td>
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<td>1/B3LYP/Site 2 X-ray</td>
<td>$-708$</td>
<td>$8.3$</td>
<td>$0.04$</td>
<td>$576$</td>
<td>$-0.3$</td>
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<td>-</td>
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<td>Cp$_{2*}$TiCl$_2$ (2)/Experiment</td>
<td>$-449(4)$</td>
<td>$5.5(3)$</td>
<td>$0.72(10)$</td>
<td>$165(60)$</td>
<td>$-0.1(8)$</td>
<td>$80(40)$</td>
<td>$90(30)$</td>
<td>$-5(60)$</td>
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<tr>
<td>2/RHF/Ideal Cp</td>
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<td>$-5.9$</td>
<td>$0.40$</td>
<td>$101$</td>
<td>$-0.1$</td>
<td>$154$</td>
<td>$19$</td>
<td>$37$</td>
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<td>2/RHF/X-ray</td>
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<td>$-6.5$</td>
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<td>$-0.4$</td>
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<td>-</td>
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<td>2/B3LYP/Ideal Cp</td>
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<td>$-0.1$</td>
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<td>2/B3LYP/X-ray</td>
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<td>$6.4$</td>
<td>$0.83$</td>
<td>$317$</td>
<td>$0.1$</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>CpTiCl$_3$ (3)/Experiment</td>
<td>$-341(2)$</td>
<td>$1.6(2)$</td>
<td>$0.95(10)$</td>
<td>$85(10)$</td>
<td>$0.8(2)$</td>
<td>$50(30)$</td>
<td>$12(12)$</td>
<td>$10(40)$</td>
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<tr>
<td>3/RHF/Ideal Cp</td>
<td>$-200$</td>
<td>$3.8$</td>
<td>$0.46$</td>
<td>$44$</td>
<td>$-0.5$</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>3/RHF/X-ray</td>
<td>$-214$</td>
<td>$3.8$</td>
<td>$0.60$</td>
<td>$43$</td>
<td>$-0.2$</td>
<td>$71$</td>
<td>$86$</td>
<td>$171$</td>
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<tr>
<td>3/B3LYP/Ideal Cp</td>
<td>$-239$</td>
<td>$8.5$</td>
<td>$0.19$</td>
<td>$375$</td>
<td>$-0.8$</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>3/B3LYP/X-ray</td>
<td>$-253$</td>
<td>$8.5$</td>
<td>$0.24$</td>
<td>$369$</td>
<td>$-0.8$</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Cp$_{2*}$TiCl$_3$ (4)/Experiment</td>
<td>$-33(3)$</td>
<td>$3.0(3)$</td>
<td>$0.35(10)$</td>
<td>$650(75)$</td>
<td>$0.9(3)$</td>
<td>$30(90)$</td>
<td>$0(10)$</td>
<td>$0(90)$</td>
</tr>
<tr>
<td>4/RHF/Ideal Cp</td>
<td>$-33$</td>
<td>$1.2$</td>
<td>$0.62$</td>
<td>$394$</td>
<td>$0.9$</td>
<td>$43$</td>
<td>$63$</td>
<td>$26$</td>
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<tr>
<td>4/RHF/X-ray</td>
<td>$-33$</td>
<td>$1.4$</td>
<td>$0.57$</td>
<td>$414$</td>
<td>$1.0$</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>4/B3LYP/Ideal Cp</td>
<td>$-33$</td>
<td>$2.6$</td>
<td>$0.77$</td>
<td>$102$</td>
<td>$0.7$</td>
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</tr>
<tr>
<td>4/B3LYP/X-ray</td>
<td>$-33$</td>
<td>$2.1$</td>
<td>$0.62$</td>
<td>$138$</td>
<td>$0.7$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cp$_2$TiMe$_2$/Experiment</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cp$_2$TiMe$_2$/RHF/Ideal Cp</td>
<td>$-218$</td>
<td>$22.5$</td>
<td>$0.79$</td>
<td>$1809$</td>
<td>$-1.0$</td>
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<td>-</td>
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<tr>
<td>Cp$_2$TiMe$_2$/RHF/X-ray</td>
<td>$-234$</td>
<td>$25.5$</td>
<td>$0.84$</td>
<td>$1811$</td>
<td>$-1.0$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$The shifts are referenced to neat TiCl$_4(l)$ [$\delta_{\text{iso}}^{(49)}$(Ti) = 0.0 ppm] via a secondary external standard of solid SrTiO$_3$ for which $\delta_{\text{iso}}^{(49)}$(Ti) = -843 ppm. The value of $\delta_{\text{iso}}^{(47)}$(Ti) = $\delta_{\text{iso}}^{(49)}$(Ti) - 267 ppm. Calculated isotropic magnetic shielding (MS) values ($\sigma_{\text{iso}}$) were converted to $\delta_{\text{iso}}$ values by subtracting the calculated MS values from those calculated for $^4$, $\delta_{\text{iso}} = \sigma_{\text{iso}}(^4) - \sigma_{\text{iso}}$(complex) - 33 pm. $^b$The EFG tensor is defined by three principal components ordered such that $|V_1| \leq |V_2| \leq |V_3|$ where, $C_Q = eQV_3/h$ and $0.0 \leq \eta_Q = (V_11 - V_{22})/V_{33} \leq 1.0$. The value of $C_Q(^{49}Ti) = 1.21C_Q(^{47}Ti)$. $^c$The CS tensor is described by three principal components ordered such that $\delta_{11} \geq \delta_{22} \geq \delta_{33}$ where, $\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, $\Omega = \delta_{11} - \delta_{33}$ and $\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$. $^d$The Rose convention is used to describe the Euler angles. Uncertainties associated with the last digit of the experimental NMR parameters are given in parentheses. $^e$Quantum chemical calculations employed atomic coordinates obtained from single crystal X-ray diffractions structures. The “X-ray” and “Ideal Cp” labels indicate whether XRD coordinates of the Cp carbon atoms were employed or whether idealized Cp rings were employed (see main text).

Complex 4 possesses a relatively large $^{47/49}$Ti chemical shift anisotropy (CSA, vide infra), which further disperses spectral intensity into the spinning sidebands and affects the shape of the isotropic CT pattern; therefore, it is necessary to sum the sideband intensity into the isotropic position to obtain an undistorted CT pattern (inset, Figure 4.1). $^70$ The spectrum of 4 at 9.4 T does not require the addition of spinning sidebands into the isotropic pattern.
pattern due to an increase in the relative magnitude of the quadrupolar interaction with respect to the CSA.

The trends in the titanium isotropic chemical shifts mirror those observed in previous solution NMR studies. An increase in $\delta_{\text{iso}}$ is observed for the Cp* complexes in comparison to the analogous Cp complexes, and the mono-Cp' species possess higher chemical shifts than the bis-Cp' species (Cp' refers to a Cp ligand of any substitution pattern). The differences in $\delta_{\text{iso}}$ of 3 and 4 have previously been correlated to the absorption maxima ($\lambda_{\text{max}}$) of UV-visible spectra, which are 380 and 437 nm for 3 and 4, respectively. It is well known that smaller energy separations between occupied and virtual orbitals give rise to larger paramagnetic shielding interactions, and hence more positive chemical shifts (increased deshielding). Thus, correlations between $\delta_{\text{iso}}$ and $\lambda_{\text{max}}$ are observed when the MOs that make large contributions to the nuclear magnetic shielding are the same MOs involved in optical transitions.

A comparison of the $^{47/49}$Ti EFG tensor parameters obtained from solid-state and solution $^{47/49}$Ti NMR experiments is not as straightforward. In solution, the values of $C_Q$ are estimated from the full widths at half height (FWHH) of the $^{47/49}$Ti peaks, under the approximation of the extreme narrowing limit. Furthermore, the values of $\eta_Q$ cannot be accurately determined from solution NMR spectra (many instances of predicting $C_Q$ values from FWHHs rely on the assumption is that $\eta_Q = 0$, which is most often not the case). Nonetheless, the previously measured FWHH values from solution $^{47/49}$Ti NMR spectra of 1 to 3 correlate well with the relative magnitudes of $C_Q$ obtained from the corresponding solid-state NMR spectra, and the values of $C_Q(^{49}$Ti) are slightly larger for the bis-Cp' species in comparison to those of the mono-Cp' species. However, FWHH values
obtained from solution NMR spectra of 4 suggest that it possesses a smaller $C_Q$ than that of 3,\textsuperscript{22,25} which is not the case in the solid state. Both 3 and 4 possess very small quadrupolar coupling constants; therefore, the differences in the magnitude of $C_Q$ may be a result of subtle structure deviations and/or long range intermolecular electrostatic interactions. However, given the limitations of the approximations described above, it is more likely that the solid-state measurement of $C_Q$ is simply more accurate. For complexes 1, 2 and 4, $\eta_Q$ values are not close to either 0 or 1, indicating that all of the components of the EFG tensor are distinct from one another. For 3, $\eta_Q$ is close to 1, indicating that $V_{11}$ is the distinct component of the EFG tensor and $V_{22} \approx -V_{33}$).

The values of $C_Q^{(49}\text{Ti})$ obtained for 1 to 4 are on the smaller end of the range previously measured from SSNMR spectra of non-cubic oxides and other extended solids, where $C_Q^{(49}\text{Ti})$ is found to range from 2.6 to 24.0 MHz.\textsuperscript{36} Similarly, in our $^{91}\text{Zr}$ SSNMR study of bis-Cp zirconocene dihalide complexes, we found that $C_Q^{(91}\text{Zr})$ was relatively small compared to those of oxides and related systems.\textsuperscript{9} This indicates that the ground state electronic environment at the metal atoms in $d^0$ metallocene halide complexes are of comparatively higher spherical symmetry than those of the metal oxides.

Titanium CSA has previously been observed for several titanates ($\Omega = 22 - 180$ ppm)\textsuperscript{36} and the rutile phase of TiO$_2$ ($\Omega = 30$ ppm).\textsuperscript{43} Furthermore, our previous $^{91}\text{Zr}$ SSNMR studies of zirconocenes,\textsuperscript{5,9,45} Sc SSNMR study of coordination complexes\textsuperscript{78} and extensive $^{51}\text{V}$ SSNMR studies of Polenova et al.\textsuperscript{79-83} have indicated that CSAs are substantial for the nuclei of the elements directly adjacent to Ti in the periodic table. In order to measure the CS tensor parameters, the span ($\Omega$) and skew ($\kappa$), static $^{47/49}\text{Ti}$ SSNMR spectra of 1 to 4 were acquired at 21.1 T and 9.4 T (Figure 4.2). The static spectra also
Figure 4.2. Static $^{47/49}$Ti SSNMR spectra of Cp$_2$TiCl$_2$ (1), Cp$^*$$_2$TiCl$_2$ (2), CpTiCl$_3$ (3) and Cp$^*$TiCl$_3$ (4) acquired at 21.1 T and 9.4 T. Analytical simulations (red traces) are overlaid on the experimental spectra (black traces). De-convolutions of the $^{49}$Ti (green traces) and $^{47}$Ti (blue traces) powder pattern simulations are also shown. Spectra at 21.1 T were acquired with a standard echo sequence. Spectra of 1 and 2 at 9.4 T were acquired with the DFS-QCPMG pulse sequence.
serve to confirm EFG tensor parameters isolated from MAS spectra, and allow for the
determination of the Euler angles which describe the relative orientation of the EFG and CS
tensors in each complex.

The appearance of the static spectra are indicative of the presence of substantial
titanium CSA (Figure 4.2); it is not possible to simulate the static powder patterns using
only the quadrupolar interaction (Figure C1). For all static spectra, $^{47}\text{Ti}$ and $^{49}\text{Ti}$ powder
patterns are observed to overlap, except for the spectrum of 3 acquired at 21.1 T. Overlap
of the patterns can complicate simulations of the static spectra; however, with spectra from
two magnetic fields it is possible to obtain reasonably accurate measurements of the CS
tensors. If more accurate measurements of the CS tensors and Euler angles are desired,
QCPMG experiments which employ pulses with nutation angles designed to give a
spectrum with only one of the $^{47/49}\text{Ti}$ nuclei may be employed.\(^{43}\) However, acquisition
times for the static spectra were significantly longer than those for the MAS spectra, due to
much wider dispersion of the signal intensity in the former. At 21.1 T, static echo spectra
were acquired in 3 to 20 hours, while at 9.4 T, DFS-echo and DFS/QCPMG pulse
sequences were used, with experiment times on the order of days.

From the static spectra, $\Omega$ is found to range from 85 ppm (3) to 650 ppm (4). The $\Omega$
of 1 is greater than 2 (Cp vs. Cp*), while for 3 and 4 the opposite is observed. The value of
$\Omega$ for 4 is substantially larger than those of the other complexes, as well as those previously
reported for other systems ($\Omega \leq 180$ ppm).\(^{36}\) As mentioned above, the MAS spectrum of 4
possesses a number of intense spinning sidebands not observed in any of the other MAS
spectra, consistent with this large CSA. SIMPSON simulations of the $^{47/49}\text{Ti}$ MAS spectra
with variable values of $\Omega$, confirm the unusually large value of $\Omega = 650$ ppm (Figure C2).
The values of $\kappa$ are close to +1 for 1, 3 and 4, indicating that the CS tensors are all nearly axially symmetric (i.e., $\delta_{11} \approx \delta_{22}$, and $\delta_{33}$ is the distinct component of each CS tensor). Axial symmetry of the CS tensor is expected for 3 and 4, given that these complexes possess pseudo-$C_3$ rotational axes. This is similar to the $\kappa$ values near +1 measured for the $^{55}$Mn and $^{95}$Mo SSNMR spectra of piano-stool, arene-metal complexes. However, it is interesting to note that for a series of bis-Cp zirconocene dihalide complexes analogous to 1 and 2, we have found that $\kappa$ is always close to −1 (a full discussion of this is beyond the scope of this paper). For 2, $\kappa = -0.1$, which indicates that the three principal components of the CS tensor are unequal and approximately evenly spaced, although there is large uncertainty associated with the experimental value of $\kappa$. In summary, titanium CSA is found to be relatively large for 1 to 4, and distinct values of $\Omega$ are observed for each complex, suggesting that this parameter can act as a useful secondary probe of molecular structure.

**Quantum chemical calculations.** Results from the quantum chemical calculations of titanium EFG and magnetic shielding (MS) tensors are shown in Table 4.1. We note that quantum chemical calculations provide the principal components of the MS tensor ($\sigma_{ii}$), which can then be converted to CS tensor parameters for comparison to experimental results (see footnote of Table 4.1). A number of methods and basis set combinations were tested, and summarized in Appendix C (Tables C5-C8). In addition, we have performed calculations with atomic coordinates which employ “idealized” Cp rings. In these calculations, the crystallographically determined Cp centroid distances have been retained; however, perfectly planar Cp rings with ideal C-C bond lengths (1.40 Å) and C-C-C angles (108°) have been employed. We have found this approach necessary to obtain accurate
quantum chemical calculations of $^{91}$Zr EFG tensor parameters of zirconocenes. In general, RHF and B3LYP calculations which employ Ahlrichs valence double-$\zeta$ polarized (pVDZ) basis set on Ti give the best agreement between experiment and theory, although calculations of some EFG and CS tensor parameters are not satisfactory. In particular, calculated values of $C_Q$, $\eta_Q$ and $\Omega$ are poor for many of the complexes. Given the small size of the data set, it is also not clear whether the use of ideal Cp ring coordinates gives superior results to those which employ Cp ring coordinates determined by X-ray crystallography.

The RHF calculations are clearly superior for the calculation of the CS tensor parameters, yielding nearly quantitative values of $\delta_{iso}$ and correctly predicting the symmetry of the CS tensor ($\kappa$) for 1, 2 and 4. While the calculations do not accurately predict the values of $\Omega$, they do correctly predict the relative values for complexes 1 to 4 (i.e., $\Omega$ for $4 > 1 > 2 > 3$). B3LYP calculations yield accurate values of $\delta_{iso}$; however, calculated values of $\Omega$ and $\kappa$ show poor agreement with experimental values.

Both RHF and B3LYP calculations yield $C_Q$ and $\eta_Q$ values which show relatively poor agreement with the experimental data. The calculations are able to correctly predict that $C_Q$ is relatively small for 1–4; however, they are unable to predict the relative magnitudes of $C_Q$ within the series. Accurate calculations of $^{45}$Sc and $^{51}$V EFG tensor parameters have previously been demonstrated, and Ti is a relatively light element for which relativistic effects should be minimal. This suggests that calculations of titanium EFG tensors should be straightforward. It may be that because $C_Q$ is relatively small for 1 to 4, minor errors in the calculated EFG tensor principal components ($V_{ii}$) lead to substantial errors in both $C_Q$ and $\eta_Q$. Periodic plane-wave DFT calculations were also attempted for 1
to 4 (Table C9); however, the calculated NMR tensor parameters also show poor agreement with experiment. All of this data suggests that more quantum chemical methods and functionals should be tested in the future in order to identify suitable methods for calculations of $^{47/49}$Ti NMR tensor parameters.

Finally, we present calculated EFG and MS tensor orientations for 1 to 4 (Figure 4.3). The tensor orientations provide insight into the origin of the observed anisotropic NMR interactions and allow for correlations between the NMR interaction tensors and molecular symmetry and structure. The orientation of the calculated EFG tensors in 1 and 2 are similar. The orientation of $V_{33}$ perpendicular to the Cl-Ti-Cl plane arises because the electric field is large in the direction of the chloride ligands, but small along the direction of the Cp ligands, giving rise to the large gradient. We have previously calculated that the magnitude of $V_{33}$ significantly increases as the Zr-Cl bond lengths of Cp$_2$ZrCl$_2$ are shortened. In fact, the EFG and MS tensor orientations calculated for 1 are similar to those previously calculated for Cp$_2$ZrCl$_2$. At this time, we do not comment on the orientation of the EFG tensors for 3 and 4, as the calculated values of $C_Q$ and $\eta_Q$ show relatively poor agreement with experiment, though they are shown for reference in Figure 4.3.

For the Cp complexes, 1 and 3, $\sigma_{11}$, the least shielded components of the MS tensors, are oriented towards the Cp ring carbon atom which lies above the Ti atom. For 1, $\sigma_{11}$, is oriented such that it is approximately perpendicular to the Cl-Ti-Cl plane. Deshielding along this direction likely arises from mixing of high energy occupied Ti-Cl bonding molecular orbitals with low-lying unoccupied $d$-orbitals, both of which are located in the Cl-Ti-Cl plane. It is known that paramagnetic deshielding arises due to magnetic
Figure 4.3. EFG and CS tensor orientations for 1 to 4 obtained from quantum chemical calculations. The Euler angles associated with these tensor orientations are listed in Table 4.1. Methyl groups and hydrogen atoms bound to the Cp rings have been omitted for clarity.
field induced mixing of occupied and virtual molecular orbitals,\textsuperscript{71-77} and deshielding contributions are largest in the direction perpendicular to the plane of mixing. In this regard, Hoffman has previously presented Hückel calculations which demonstrate that the valence molecular orbitals in titanocenes correspond to Cl-Ti $\sigma$- and $\pi$-bonding orbitals.\textsuperscript{86}

In 2, the most shielded component of the MS tensor, $\sigma_{33}$ is directed towards a Cp* carbon atom which lies above the Ti atom, while in 4, $\sigma_{33}$ is directed towards the centroid of the Cp* ligand. The distinct orientations of the MS tensors for 2 and 4 compared to 1 and 3 suggest that the energies and symmetries of the molecular orbitals are undoubtedly influenced by the increased basicity of the Cp* ligand in comparison to the Cp ligands. The orientations of $\sigma_{11}$ and $\sigma_{22}$ for both 2 and 4 suggests deshielding primarily arises due to mixing of high energy occupied or low-lying virtual orbitals of Ti-Cp* bonding character, which is also consistent with the observations of more positive $\delta_{\text{iso}}$ values for the Cp* complexes. As noted above, previous UV-Vis measurements on 3 and 4 have found that $\lambda_{\text{max}}$ occurs at longer wavelengths in the latter. If the MOs that make large anisotropic contributions to the nuclear magnetic shielding are the same MOs involved in optical transitions, then it is anticipated that decreased energy separations between these MOs will lead to a larger titanium CSA in 4 than 3.

Finally, EFG and CS tensor calculations were also performed for Cp\textsubscript{2}TiMe\textsubscript{2} (5), which is a species important to catalytic processes involving titanocenes. In order to obtain active metalloocene olefin polymerization catalysts, it is necessary to treat them with an activator or co-catalyst, such as methylaluminoxane (MAO).\textsuperscript{1,3} MAO abstracts the chloride ligands, replaces them with methyl ligands, and subsequently abstracts a methyl group to generate a catalytically active, coordinatively unsaturated, cationic metalloocene. We have
previously observed that Cp₂ZrMe₂ possesses relatively large values of $C_Q^{(91Zr)} = 28.0$ MHz and $\Omega^{(91Zr)} = 1750$ ppm.⁹ Consistent with these findings, quantum chemical calculations indicate that 5 has a very large $C_Q$ (ca. 22-25 MHz) and CSA ($\Omega > 1800$ ppm). From these calculations it is clear that $^{47/49}$Ti SSNMR spectra very distinct from those of 1 and 2 would be observed for methyl titanocenes. However, due to the large $C_Q$ and $\Omega$ values, Cp₂TiMe₂ would be expected to possess a wideline $^{47/49}$Ti SSNMR spectrum of ca. 300-400 kHz in breadth at 21.1 T, the acquisition of which would be difficult, and beyond the scope of the current work.

4.4 Conclusions

MAS and static $^{47/49}$Ti SSNMR spectra were acquired for complexes 1 to 4, each yielding unique sets of EFG and CS tensor parameters. $C_Q$ values for these complexes are small with respect to the known range of $C_Q$ values. All of the complexes possess significant titanium CSAs, affording another set of NMR parameters which can be used to provide insight into their molecular and electronic structures. Quantum chemical calculations can accurately predict $\delta_{iso}$ for 1 – 4; however, further computational methods and basis sets must be evaluated in order to obtain better agreement between experimental and theoretical $^{47/49}$Ti NMR parameters.

At an ultrahigh magnetic field of 21.1 T, it is possible to acquire MAS and static $^{47/49}$Ti SSNMR spectra in several hours with standard echo techniques. However, at a moderate magnetic field of 9.4 T, signal-enhancement techniques are required for the acquisition of $^{47/49}$Ti SSNMR spectra, and acquisition times remain on the order of days. The lengthy experiment times required to obtain adequate signal-to-noise ratios suggest that
\(^{47/49}\text{Ti}\) SSNMR experiments on systems with low Ti contents, such as heterogeneous catalysts, would be very challenging. However, isotopic labeling in conjunction with cross-polarization (CP)-CPMG experiments at cryogenic temperatures could enable the acquisition of \(^{47/49}\text{Ti}\) spectra of heterogeneous catalysts. Ellis and Lipton have extensively utilized this approach to acquire SSNMR spectra of metalloproteins, which contain dilute concentrations of low-\(\gamma\) nuclei such as \(^{25}\text{Mg}\) and \(^{67}\text{Zn}\).\(^87-91\) CP from \(^1\text{H}\) could be especially beneficial for \(^{47/49}\text{Ti}\) given that the maximum theoretical signal enhancement is \(\gamma_{1\text{H}}/\gamma_{49\text{Ti}} = -17.7\). In addition, the differences in CP Hartmann-Hahn matching conditions which arise from the different spins of \(^{47}\text{Ti}\) and \(^{49}\text{Ti}\) could be useful for selectively exciting only one of the isotopes.\(^92, 93\) In an analogous manner to CP experiments, the development of dynamic nuclear polarization (DNP) experiments may also be very beneficial for SSNMR studies of unreceptive nuclei such as \(^{47/49}\text{Ti}\), as the maximum signal enhancement is, \(\gamma_e/\gamma_{49\text{Ti}} = 11654\).\(^94, 95\) These signal-enhancing methods and the sensitivity of \(^{47/49}\text{Ti}\) NMR parameters to differences in molecular structure make \(^{47/49}\text{Ti}\) SSNMR very appealing for continued study of such systems.
4.5 Bibliography


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Chapter 5: Experimental and Theoretical Studies of $^{45}$Sc NMR Interactions in Solids

5.1 Introduction

The chemistry of scandium has not been explored to the extent of other transition metals due to the relatively high costs of materials and its limited reactivity arising from restriction to the +3 oxidation state. The use of scandium in both inorganic and organometallic chemistry has recently received more attention, as observed by the increasing number of compounds that have been synthesized and characterized by single-crystal X-ray diffraction and other methods.\textsuperscript{1, 2} Scandium is found in an assortment of materials, such as alloys,\textsuperscript{3} inorganic materials,\textsuperscript{4-9} ferroelectric relaxors and ceramics.\textsuperscript{10-15} Scandium complexes are also used in a number of organic syntheses and polymerization reactions. Certain Sc(III) complexes, due to the extreme electron deficiency at the Sc atom, act as some of the strongest Lewis acids among transition metal complexes. For instance, scandium triflate is extensively used in organic synthesis to catalyse a wide variety of reactions.\textsuperscript{16, 17} There is also increasing interest in the organometallic chemistry of scandium, since Sc-C bonds are especially susceptible to insertion reactions involving unsaturated molecules. Active scandium catalysts for the copolymerisation of ethylene with styrene or norbornene have been synthesized.\textsuperscript{18, 19} Further advances have also been made with the incorporation of non-cyclopentadieny1 ligand systems.\textsuperscript{20, 21} Given the increased interest in scandium chemistry, development of solid-state $^{45}$Sc NMR spectroscopy for characterization of molecular structure and dynamics in both crystalline
and disordered materials is of great importance.

Scandium has one naturally occurring NMR active isotope, $^{45}\text{Sc}$, which is 100% naturally abundant, possesses a gyromagnetic ratio of $6.50880 \times 10^7$ rad T$^{-1}$ s$^{-1}$ (close to $^{13}\text{C}$), a nuclear spin of $I = 7/2$, and a moderate nuclear quadrupole moment ($Q$) of $0.22 \times 10^{-28}$ m$^2$. These factors result in a relative receptivity of 1780 in comparison to $^{13}\text{C}$, making $^{45}\text{Sc}$ an excellent nucleus for NMR experimentation. Solid-state $^{45}\text{Sc}$ NMR spectra are normally comprised of relatively broad powder patterns which result from anisotropic NMR interactions. The quadrupolar interaction (QI) normally determines the appearance of such spectra, though the effects of chemical shift anisotropy (CSA) also significantly influence the appearance of the spectra. $^1\text{H}$-$^{45}\text{Sc}$ dipolar coupling can be observed in some instances. While the presence of these interactions generally complicate solid-state NMR spectra and increase acquisition times, they also act as a rich source of information on molecular structure and dynamics.

Several solution $^{45}\text{Sc}$ NMR studies have established a chemical shift range of approximately 250 ppm.$^{22-35}$ By contrast, there are few reported examples of solid-state $^{45}\text{Sc}$ NMR, and even fewer in which chemical shift (CS) and electric field gradient (EFG) tensor parameters have been measured. In a preliminary study by Thompson and Oldfield, the isotropic scandium chemical shift ($\delta_{\text{iso}}$), $^{45}\text{Sc}$ quadrupolar coupling constant ($C_Q$) and the electric field gradient asymmetry parameter ($\eta_Q$) of $\text{Sc(OAc)}_3$ (OAc = acetate) and $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$ were measured.$^{36}$ Solid-state $^{45}\text{Sc}$ NMR was also utilized by Han et al. to observe hydrogen diffusion in hexagonally close packed scandium metal,$^{37}$ by Kataoka et al. to observe temperature-induced phase transitions in $\text{Sc(OAc)}_3$,$^{38}$ and by Koyama et al.,
who examined a ternary superconductor, Sc$_2$Co$_4$Si$_{10}$. Several NMR studies on ferroelectric relaxors$^{40-43}$ and a variety of Sc-containing alloys and materials of mixed compositions$^4$, $^9$, $^{44}$, $^{45}$ have also been reported. In addition, due to the favourable NMR characteristics, $^{45}$Sc NMR has been employed for the design and optimization of pulse sequences for spin ($I$) $7/2$ nuclei.$^{46-48}$

In this paper we report a comprehensive solid-state $^{45}$Sc NMR study of scandium coordination complexes, in an effort to gain an understanding of the relationship between scandium coordination environments and the observed NMR parameters. The complexes under study are pictured in Scheme 1 (hydrogen atoms and molecules not bound to scandium are omitted for clarity). These complexes are Sc(acac)$_3$, Sc(TMHD)$_3$, Sc(OAc)$_3$, Sc(NO$_3$)$_3$•5H$_2$O, ScCl$_3$•6H$_2$O, ScCl$_3$•3THF, and ScCp$_3$ (acac = acetylacetonate, TMHD = 2,2,6,6-tetramethyl-3,5-heptanedionato, THF = tetrahydrofuran and Cp = cyclopentadienyl). All of these complexes have crystal structures which were previously reported or are reported for the first time herein. These complexes were chosen because they afford a range of coordination environments about the scandium nucleus leading to the observation of an assortment of distinct CS and EFG tensor parameters. Quantum mechanical calculations of NMR interaction tensors are utilized to examine the orientation of NMR tensors within molecular frames, and to help rationalize the origin of scandium NMR interactions. We also demonstrate the application of solid-state $^{45}$Sc NMR for probing unknown molecular structures, including the Lewis acid catalyst Sc(OTf)$_3$ and a polystyrene microencapsulated (ME) form of Sc(OTf)$_3$ (OTf = SO$_3$CF$_3$). Application of solid-state NMR to the ME-Sc(OTf)$_3$ is of particular interest, since
structural changes imparted by microencapsulation increase the catalytic activity of Sc(OTf)₃ in carbon-carbon bond-forming reactions.

Scheme 5.1. Scandium complexes for which solid-state ⁴⁵Sc NMR spectra have been acquired.

5.2 Experimental

**Sample Preparation.** Samples of tris(cyclopentadienyl) scandium (ScCp₃) and scandium chloride hexahydrate (ScCl₃·6H₂O) were purchased from Sigma-Aldrich Canada, Ltd. and used without purification. A sample of scandium acetate hydrate (Sc(OAc)₃·xH₂O) was acquired from Sigma-Aldrich Canada, Ltd. and was recrystallized from a 5.0 M aqueous solution of acetic acid and dried in vacuo to produce anhydrous
scandium acetate (Sc(OAc)₃). Samples of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)
scandium (Sc(TMHD)₃), scandium nitrate pentahydrate (Sc(NO₃)₃·5H₂O), scandium
trifluoromethanesulfonate (Sc(OTf)₃) and scandium trifluoromethanesulfonate
microencapsulated in a styrene polymer (ME Sc(OTf)₃) were purchased from Strem
Chemicals, Inc., and used without further purification. Samples of scandium
tris(acetylacetonate) (Sc(acac)₃) and scandium chloride tris(tetrahydrofuran)
(ScCl₃·3THF) were synthesized in the research laboratories of Prof. Warren Piers at the
University of Calgary using standard procedures. A second sample of ScCl₃·3THF
was prepared by adding anhydrous ScCl₃ to an excess of THF. The sample was then dried
in vacuo and used without further purification. All samples were finely ground, packed
into 4 mm outer diameter zirconia rotors and sealed with airtight caps under a nitrogen or
argon atmosphere. The Sc(acac)₃ and Sc(TMHD)₃ samples were prepared in a similar
manner outside of the glovebox.

Solid-state NMR Spectroscopy. Solid-state Sc, C and F NMR spectra were
acquired on a Varian Infinity Plus spectrometer with an Oxford 9.4 T (ν₀(1H) = 400 MHz)
wide-bore magnet. Additional static spectra were acquired on a Bruker Avance 500
spectrometer with an 11.75 T (ν₀(1H) = 500 MHz) magnet. Sc chemical shifts were
reported with respect to an external standard solution of 0.11 molal (moles of solute/kg of
solvent) ScCl₃ in 0.05 M HCl (δiso = 0.0 ppm). As there is currently no universally
applied scandium NMR standard, this sample was chosen due to the sharp peak observed
in its solution NMR spectrum, and the insensitivity of the scandium chemical shift to
changes in hydrogen chloride concentrations from 0.05 M to 1.0 M. C chemical shifts
were referenced to tetramethylsilane ($\delta_{iso} = 0.0$ ppm) by using the high-frequency peak of adamantane as a secondary reference ($\delta_{iso} = 38.57$ ppm). $^{19}$F chemical shifts were referenced to fluorotrichloromethane ($\delta_{iso} = 0.0$ ppm) by setting the $^{19}$F resonance of Teflon ($\delta_{iso} = -122.0$ ppm) as a secondary reference.

Central-transition selective $\pi/2$ pulse widths were calculated by scaling the non-selective pulses by a factor of a quarter, i.e., $(I + \frac{1}{2})^\frac{1}{2}$. Unless otherwise noted, a quadrupolar echo pulse sequence of the form \{\(\pi/2_x - \tau_1 - \pi_{2y} - \tau_2 - \text{acquire}\)\} was used for the acquisition of $^{45}$Sc NMR spectra. Static $^{45}$Sc NMR spectra of Sc(acac)$_3$, Sc(OAc)$_3$ and ScCl$_3$·3THF were also acquired with a echo pulse sequence of the form \{\(\pi/2_x - \tau_1 - \pi/2_{2y} - \tau_2 - \text{acquire}\) \} (90°-90° echo). Rotary-assisted polarization transfer (RAPT)$^{51}$ and amplitude-modulated double frequency sweep (AM-DFS)$^{52}$ pulse sequences were employed for the acquisition of selected spectra. $^{45}$Sc NMR experiments were conducted at $\nu_0(^{45}$Sc) = 97.4 MHz (9.4 T) and 122.0 MHz (11.75 T). The rf fields used for acquisition of the static $^{45}$Sc NMR spectra were generally set to one half of the pattern width in order to avoid lineshape distortions.$^{53}$ All experimental parameters can be found in Table D1. Analytical simulations of $^{45}$Sc solid-state NMR spectra were performed using WSolids$^{54}$ and numerical simulations were performed using SIMPSON.$^{55}$

$^{13}$C NMR spectra were acquired using Hahn-echo and variable-amplitude cross-polarization MAS (VACP/MAS) pulse sequences. $^1$H→$^{13}$C CP was performed on all samples for the acquisition of $^{13}$C spectra, except for the Sc(OTf)$_3$ samples, for which $^{19}$F→$^{13}$C CP was applied. The TPPM$^{56}$ decoupling sequence was employed in all cases. Solid-state $^{19}$F NMR spectra were acquired with a rotor-synchronized Hahn-echo pulse
Quantum Chemical Calculations. Calculations of CS and EFG tensors were performed using Gaussian 03 running on two Dell Precision workstations running Red Hat Linux 9.0. Molecular coordinates were input from structures determined by single-crystal X-ray diffraction experiments and proton positions were geometry-optimized for most structures. Calculations were carried out using restricted Hartree-Fock (RHF) and hybrid density functional theory (DFT) employing the B3LYP functional. The basis sets 6-31G**, 6-31+G**, 6-311G** and 6-311+G** were used for all calculations. All-electron basis sets on scandium were also employed for calculations on Sc(acac)₃. CS tensors were calculated using the gauge-including atomic orbitals (GIAO) method. [Sc(H₂O)₆]³⁺ was chosen to model the magnetic shielding (MS) of the solution standard, and absolute shieldings were converted to shifts as described in Tables 5.1 and 5.2.

X-ray Diffraction Experiments. Powdered ScCl₃•3THF, Sc(OAc)₃ and Sc(OTf)₃ were packed into 1.0 mm glass capillary tubes under nitrogen and flame sealed. Powder X-ray diffraction patterns were collected using a Bruker AXS HI-STAR system using a General Area Detector Difractons System. The X-ray source employed was a Cu Kα radiation (1.540598 Å) with an area detector using a 2θ range between 4.0° to 65.0°. Powder X-ray diffraction patterns were simulated with the Powder Cell software package.

5.3 Results and Discussion

In the first part of this section, a detailed discussion of ⁴⁵Sc NMR spectroscopy of
scandium coordination compounds is presented. In all of the cases discussed herein, it is possible to utilize MAS to almost completely average the scandium CSA, while partially averaging the second-order QI. Therefore, the values of $C_Q$, $\eta_Q$, and $\delta_{iso}$ can be readily obtained by analytical simulations of the $^{45}$Sc MAS NMR central transition spectra (Table 5.1). Static $^{45}$Sc NMR spectra allow for the measurement of both quadrupolar ($C_Q$ and $\eta_Q$) and CS tensor parameters ($\delta_{iso}$, as well as the span, $\Omega$, and the skew, $\kappa$), as well as the Euler angles ($\alpha$, $\beta$, and $\gamma$) which describe the relative orientation of EFG and CS tensors (see Table 5.1 for definitions of these parameters). Static spectra acquired at a second field are used to confirm the observed CS tensor parameters and Euler angles. The shapes of the static powder patterns are sensitive to the pulse sequences and rf fields used in their acquisition (Figure D1); fortunately, the locations of discontinuities, which are paramount for determination of spectral parameters, are largely unaffected by these factors. To the best of our knowledge, there are no previous reports of scandium CSA in the literature. Spectral simulations presented throughout the paper account for scandium CSA; for comparison, spectral simulations that neglect the presence of CSA are found in the Appendix D (Figure D2). In the second part of this section, theoretically calculated CS and EFG tensors, and their orientations and origins, are investigated in depth. In the final part of this section, we examine the application of $^{45}$Sc NMR to structurally characterize systems for which crystallographic and/or other structural data are unavailable. Details of crystal structure determinations are given in the original publication.
## Table 5.1. A Summary of Observed $^{45}$Sc EFG and CS Tensor Parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\alpha$ (°)</th>
<th>$\beta$ (°)</th>
<th>$\gamma$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(acac)$_3$</td>
<td>13.0(3)$^f$</td>
<td>0.22(3)</td>
<td>82(1)</td>
<td>70(10)</td>
<td>-0.7(2)</td>
<td>90(15)</td>
<td>83(4)</td>
</tr>
<tr>
<td>Sc(TMHD)$_3$</td>
<td>13.1(2)</td>
<td>0.93(2)</td>
<td>89.5(10)</td>
<td>110(20)</td>
<td>-0.7(3)</td>
<td>0(10)</td>
<td>15(15)</td>
</tr>
<tr>
<td>Sc(NO$_3$)$_3$·5H$_2$O</td>
<td>6.2(2)</td>
<td>0.75(5)</td>
<td>-18.5(10)</td>
<td>60(10)</td>
<td>-0.8(1)</td>
<td>80(15)</td>
<td>10(15)</td>
</tr>
<tr>
<td>Sc(OAc)$_3$</td>
<td>4.6(2)</td>
<td>0.18(6)</td>
<td>6.2(8)</td>
<td>73(5)</td>
<td>0.65(10)</td>
<td>0(45)</td>
<td>7(3)</td>
</tr>
<tr>
<td>ScCl$_3$·6H$_2$O</td>
<td>3.9(2)</td>
<td>0.77(9)</td>
<td>125.4(5)</td>
<td>180(10)</td>
<td>0.9(1)</td>
<td>45(10)</td>
<td>30(5)</td>
</tr>
<tr>
<td>ScCl$_3$·3THF</td>
<td>8.4(2)</td>
<td>0.30(5)</td>
<td>202(1)</td>
<td>200(20)</td>
<td>-0.1(3)</td>
<td>85(35)</td>
<td>4(4)</td>
</tr>
<tr>
<td>Cp$_3$Sc</td>
<td>8.3(2)</td>
<td>0.88(4)</td>
<td>62.8(8)</td>
<td>135(15)</td>
<td>0.0(3)</td>
<td>-24(10)</td>
<td>73(8)</td>
</tr>
</tbody>
</table>

The CS tensor is described by three principal components ordered such that $\delta_{11} \leq \delta_{22} \leq \delta_{33}$. The EFG tensor is described by three principal components ordered such that $|V_{11}| \leq |V_{22}| \leq |V_{33}|$. $^a C_Q = eQV_{33}/h$, $^b \eta_Q = (V_{11} - V_{22})/V_{33}$, $^c \delta_{jj} = (\sigma_{iso, ref} - \sigma_{jj})(10^6)/(1 - \sigma_{iso, ref}) \approx \sigma_{iso, ref} - \sigma_{jj}$ where $jj = 11, 22$ or $33$, $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, $^d \Omega = \delta_{11} - \delta_{33}$, $^e \kappa = 3(\delta_{22} - \delta_{iso})/\Omega$, $^f$ The uncertainty in the last digit of each value is denoted in brackets.

**Solid-State $^{45}$Sc NMR Experiments.** Sc(acac)$_3$. The solid-state $^{45}$Sc MAS NMR spectrum of the central transition (Figure 5.1a) is simulated with $C_Q = 13.0$ MHz, $\eta_Q = 0.22$, and $\delta_{iso} = 82$ ppm. Experimental and simulated static $^{45}$Sc NMR spectra of Sc(acac)$_3$ acquired at two different magnetic field strengths (Figure 5.1b) reveal that $\Omega = 70$ ppm and $\kappa = -0.7$ (all Euler angles are tabulated in Table 5.1). The "shoulder" on the low-frequency side of the MAS spectrum is not predicted by the analytical simulation; however, a numerical simulation using SIMPSON reveals that this shoulder is due to the presence of an underlying satellite transition (Figure 5.1a, inset).
Figure 5.1. Solid-state $^{45}\text{Sc}$ NMR spectra and analytical simulations of Sc(acac)$_3$ and Sc(TMHD)$_3$. (a) MAS spectrum of Sc(acac)$_3$, $\nu_{\text{rot}} = 15$ kHz. Inset, a SIMPSON simulation utilizing ideal pulses and processed with 100 Hz of exponential line broadening. (b) Static spectra of Sc(acac)$_3$ at 9.4 T and 11.75 T. The static spectrum at 9.4 T was acquired with a 90°-90° echo. (c) MAS RAPT-Echo spectrum of Sc(TMHD)$_3$, $\nu_{\text{rot}} = 15$kHz. (d) Static spectra of Sc(TMHD)$_3$ at 9.4 T and 11.75 T.

The nature of the EFG and CS tensors and their relation to one another as well as the molecular frame can be rationalized by considering the molecular structure. The scandium atom is coordinated by six oxygen atoms from the three bidentate acetylacetonato ligands.$^{67}$ Inspection of the crystal structure reveals that the coordination sphere formed by the oxygen atoms more closely resembles a trigonal anti-prism, and deviates considerably from octahedral geometry (and therefore spherical symmetry).$^2$

There are only minor variations in the Sc-O bond lengths (~0.02 Å); however, deviations
of up to 10° from ideal octahedral angles are observed in the O-Sc-O bond angles. In this respect, the observation of a relatively large $C_Q$ is not surprising (this is the second largest value of $C_Q$ observed in this series of complexes). The value of $\eta_Q$ is closer to zero than one, indicating that $V_{33}$ is the pseudo-unique component of the EFG tensor. The appreciable span indicates that the scandium magnetic shielding is anisotropic, and the skew indicates that $\sigma_{11}$ is the pseudo-unique component (i.e., the values of $\sigma_{22}$ and $\sigma_{33}$ are closer to one another than $\sigma_{11}$ and $\sigma_{22}$). The Euler angles indicate that the largest component of the EFG tensor which defines the magnitude of the quadrupolar interaction, $V_{33}$, is nearly coincident with $\sigma_{11}$, the principal component of the MS tensor which describes the direction of least magnetic shielding. Given the near-axial symmetry of each tensor, one would expect that $V_{33}$ and $\sigma_{11}$ are aligned near the pseudo three-fold axis of the molecule. Proposed tensor orientations are investigated further in the discussion of ab initio calculations for this molecule and all remaining systems.

**Sc(TMHD)$_3$.** Simulation of the $^{45}$Sc MAS NMR spectrum of Sc(TMHD)$_3$ (Figure 5.1c), reveals $C_Q = 13.1$ MHz and $\delta_{\text{iso}} = 89.5$ ppm. Simulation of the static $^{45}$Sc NMR spectra (Figure 5.1d) yield parameters similar to those observed in Sc(acac)$_3$, with $\Omega = 110$ ppm and $\kappa = -0.7$; however, the Euler angles are different. The ligands and their coordination to Sc in Sc(acac)$_3$ and Sc(TMHD)$_3$ are analogous, so that the observation of similar values of $\delta_{\text{iso}}$ and $C_Q$ are not surprising. However, $\eta_Q = 0.93$, which indicates that $V_{11}$ is the most distinct component of the EFG tensor and is oriented along or near the two-fold molecular axis, in contrast to Sc(acac)$_3$. The difference in relative tensor orientations between the two complexes can be explained by comparison of the crystal
structures. In Sc(acac)_3, each of the ligands forms an approximately planar six-membered ring with the scandium centre; however, in Sc(TMHD)_3, there is a 22° deviation away from planarity in two of the three six-membered rings. The molecule is now more properly described as possessing \( C_2 \) symmetry, and this difference in symmetry is the major cause of the distinct EFG tensor orientation. The low value of \( \beta \) also means that \( V_{33} \) and \( \sigma_{33} \) are closely oriented, unlike in Sc(acac)_3. Thus, changes in the geometry of the ligand at a distance from the scandium centre have dramatically affected the relative orientation of the EFG and CS tensors.

**Sc(NO_3)_3\cdot5H_2O.** The \(^{45}\text{Sc}\) MAS NMR spectrum of Sc(NO_3)_3\cdot5H_2O (Figure 5.2a) reveals a much narrower powder pattern than those observed for the diketonato compounds. From the MAS and static spectra (Figure 5.2b) the measured parameters are, \( C_Q = 6.2 \text{ MHz}, \eta_Q = 0.75, \delta_{\text{iso}} = -18.5 \text{ ppm}, \Omega = 60 \text{ ppm} \) and \( \kappa = -0.8 \). The \(^{45}\text{Sc}\) nucleus is highly shielded in comparison to the distorted octahedral environments discussed above, and a relatively small scandium CSA is also observed. The observation of a relatively small \( C_Q \) is unexpected, given the considerably non-spherical coordination environment about scandium that is revealed in the single crystal X-ray structure.\(^{66}\) However, inspection of the Sc-O bond lengths reveals that they are longer than those observed in Sc(acac)_3 and Sc(OAc)_3 (the Sc-O bonds of water and the nitrate ligands are on average 0.14 Å and 0.21 Å longer, respectively). The decreased EFG must therefore result from the increased Sc-O bond distances. Similar observations have been made in numerous systems where increased bond lengths and augmented ionic character tend to result in lowering of \( C_Q \), since the magnitude of \( V_{33} \) is proportional to \( 1/r^3 \) in a simple point charge.
Figure 5.2. Solid-state $^{45}$Sc NMR spectra and analytical simulations of Sc(NO$_3$)$_3$$\cdot$5H$_2$O and Sc(OAc)$_3$. (a) MAS spectrum of Sc(NO$_3$)$_3$$\cdot$5H$_2$O, $\nu_{\text{rot}} = 8$ kHz. (b) Static spectra of Sc(NO$_3$)$_3$$\cdot$5H$_2$O at 9.4 T and 11.75 T. (c) MAS spectrum of Sc(OAc)$_3$, $\nu_{\text{rot}} = 8$ kHz. (d) Static spectra of Sc(OAc)$_3$ at 9.4 T and 11.75 T acquired with a 90°-90° echo.

Sc(OAc)$_3$. MAS and static $^{45}$Sc NMR spectra of Sc(OAc)$_3$ reveal a relatively narrow central transition (Figure 5.2c and 5.2d), and simulations yield $C_Q = 4.6$ MHz, $\eta_Q = 0.18$, $\delta_{\text{iso}} = -6.2$ ppm, $\Omega = 73$ ppm, $\kappa = 0.65$. Solid-state $^{45}$Sc NMR spectra of Sc(OAc)$_3$ have been reported previously by Thompson and Oldfield, as well as Kataoka et al. Both groups reported $C_Q = 5$ MHz and $\eta_Q = 0$ from simulations of static central transition spectra.$^{36,38}$ Kataoka reported a refined $C_Q = 4.45$ MHz based upon a simulation of satellite transitions, which is closer to our result. In both papers, the effects of CSA were
neglected in the simulations, and $\eta_Q$ was assumed to be zero. From the appearance of our static spectra, it is apparent that scandium CSA is present and the EFG tensor is non-axial. These factors must be accounted for to properly simulate the static spectra.

The previously determined X-ray crystal structure\textsuperscript{70} reveals a coordination polymer structure, with a unique Sc atom in a six-coordinate environment that results from bridging acetate ligands (powder XRD patterns (Figure D3) confirms that recrystallization successfully produced anhydrous Sc(OAc)$_3$). The Sc-O bond lengths are similar to those in Sc(acac)$_3$; however, the Sc(acac)$_3$ metal environment is nearly octahedral, with all $trans$-O-Sc-O bond angles equal to 180° and $cis$-O-Sc-O bond angles deviating only slightly from 90° (±3.5°). The relatively small $C_Q$ can be accounted for by the nearly spherically symmetric arrangement of oxygen atoms about the scandium. The $\delta_{iso}$ and $\Omega$ are similar to that of Sc(NO$_3$)$_3$$\cdot$5H$_2$O, but the $^{45}$Sc nucleus is relatively shielded from the external magnetic field compared to those in Sc(acac)$_3$ and Sc(TMHD)$_3$, which have distorted octahedral oxygen coordination environments. The symmetry of both the CS and EFG tensors is quite distinct from that of Sc(NO$_3$)$_3$$\cdot$5H$_2$O, which is to be expected given their structural differences. The value of $\eta_Q$ for Sc(OAc)$_3$ indicates that $V_{33}$ is the distinct component of the EFG tensor, and $\kappa$ indicates that $\sigma_{33}$ is the unique component of the CS tensor. The low value of $\beta$ indicates that $V_{33}$ and $\sigma_{33}$ are nearly co-linear and are likely directed along the $C_3$ axis of the molecule, in the direction of propagation of the
polymer structure.

Figure 5.3. Solid-state $^{45}$Sc NMR spectra and analytical simulations of ScCl$_3$•6H$_2$O and ScCl$_3$•3THF. (a) MAS spectrum of ScCl$_3$•6H$_2$O, $\nu_{\text{rot}}$ = 10 kHz. (b) Static spectra of ScCl$_3$•6H$_2$O at 9.4 T and 11.75 T. (c) MAS spectrum of re-crystallized ScCl$_3$•3THF, $\nu_{\text{rot}}$ = 12.5 kHz. (d) Static spectra of recrystallized ScCl$_3$•3THF at 9.4 T and 11.75 T acquired with a 90°-90° echo.

ScCl$_3$•6H$_2$O. The $^{45}$Sc MAS NMR spectrum of ScCl$_3$•6H$_2$O (Figure 5.3a) reveals a very narrow powder pattern with a breadth of ca. 1 kHz, with $C_Q = 3.9$ MHz, $\eta_Q = 0.77$ and $\delta_{\text{iso}} = 125.4$ ppm. Static spectra (Figure 5.3b) reveal a large span, $\Omega = 180$ ppm, and a nearly axial CS tensor, $\kappa = 0.9$. The static spectra contain a distortion that is unaccounted for in the lineshape of the static simulations at both fields, which likely arises from a small amount of impurity, as opposed to incomplete excitation or intramolecular
dynamics. The EFG parameters for ScCl$_3$•6H$_2$O are different than those reported by Thompson and Oldfield, who found that $C_Q = 14$ MHz and $\eta_Q = 0.60$, based upon the acquisition and simulation of a static $^{45}$Sc NMR spectrum. The differences in their parameters from ours could arise from their neglect of scandium CSA and the absence of $^{45}$Sc MAS NMR data. It is also unclear whether proton decoupling was applied in their NMR experiments, which has adverse effects on the appearance of the $^{45}$Sc static NMR powder pattern in this case (Figure D4).

This complex possesses the smallest observed $C_Q$ and largest $\Omega$ in the series of compounds studied herein. These two observations can be rationalized in terms of molecular structure. The crystal structure for ScCl$_3$•6H$_2$O was not previously reported and our initial assumption was that the scandium atom would be coordinated by six oxygen atoms. While this structural model is consistent with the quadrupolar data, it is inconsistent with the high isotropic shift and large span. Refinement of the crystal structure of ScCl$_3$•6H$_2$O reveals a highly symmetrical coordination environment about scandium, involving two Cl and four O atoms which form a [ScCl$_2$(H$_2$O)$_4$]$^+$ unit of approximately $D_{4h}$ symmetry. The two Sc-Cl distances are equivalent and the angle separating them is 180.0°, while there is less than 1.0° deviation from ideal octahedral O-Sc-O angles. In this respect, the observations of a relatively small $C_Q$ and large scandium CSA is not surprising. The large span and axially symmetric skew indicate that $\sigma_{33}$ is likely oriented near the Sc-Cl bond axis, and that there are large paramagnetic deshielding contributions perpendicular to this axis.

**ScCl$_3$•3THF.** $^{45}$Sc NMR spectra were acquired from two different samples of
ScCl$_3$•3THF (Figures 5.3 and 5.4). Initial $^{45}$Sc MAS NMR spectra acquired from this compound revealed the presence of two distinct scandium sites. A $^{45}$Sc multiple-quantum MAS (MQMAS) NMR experiment$^{71}$ was performed in order to resolve the overlapping sites observed in the first sample (Figure 5.4a), with simulations (Figure 5.4b) yielding $C_Q = 8.5$ MHz, $\eta_Q = 0.32$ and $\delta_{\text{iso}} = 201.5$ ppm (site 1) and $C_Q = 8.5$ MHz, $\eta_Q = 0.50$ and $\delta_{\text{iso}} = 211$ ppm (site 2). Simulated spectra are co-added to simulate the observed MAS spectra (Figure 5.4c). The overlapping static powder patterns render determination of the CS tensor parameters and Euler angles difficult (Figure 5.4d).

Figure 5.4. Solid-state $^{45}$Sc NMR spectra of ScCl$_3$•3THF (first sample). (a) MQMAS contour plot, $\nu_{\text{rot}} = 8$ kHz. (b) The two resolved sites from cross-sections of the indirect dimension and analytical simulations. (c) MAS spectrum ($\nu_{\text{rot}} = 15$ kHz) and the simulated pattern that results from addition of the individually simulated patterns. (d) Static spectra.
The observation of two scandium sites in the NMR spectra was surprising because the previously reported crystal structure indicates that only one crystallographically and magnetically distinct Sc site should be present.\textsuperscript{49} The powder XRD pattern (Figure D3) indicates that this sample is highly crystalline, though additional high intensity peaks indicate that there is a second crystalline phase present. The presence of impurities in this sample is unlikely, given the roughly equal NMR signal intensities and the similar NMR parameters of the two scandium sites. Re-crystallization of anhydrous ScCl\textsubscript{3} in an excess of THF was performed. NMR spectra acquired from this second sample yielded one scandium resonance as expected (Figures 5.3c and 5.3d), and spectra are simulated with $C_Q = 8.4$ MHz, $\eta_Q = 0.30$, $\delta_{iso} = 202$ ppm, $\Omega = 200$ ppm and $\kappa = -0.1$. The powder XRD pattern of the re-crystallized sample closely matches the predicted pattern. Clearly, the combination of $^{45}$Sc MQMAS NMR and powder XRD is extremely useful for differentiating Sc sites in similar coordination environments.

ScCl\textsubscript{3}•3THF consists of a scandium atom coordinated by three chlorine atoms and three THF molecules in a meridional fashion. The large positive chemical shift (the highest in this series) and large span are consistent with the notion that replacement of an oxygen with chlorine in the first coordination sphere results in magnetic deshielding of the scandium nucleus. The Sc-Cl bonds are considerably more covalent than Sc-O bonds; as such, there are increased paramagnetic shielding contributions perpendicular to the Sc-Cl bond axes. Given the meridional arrangement of Cl and O atoms, $\sigma_{11}$ should be oriented in a direction perpendicular to all three Sc-Cl bonds. The non-axial $\kappa$ indicates that the CS tensor does not have a pseudo-unique component. The skew, the moderate
value of $C_Q$ and the non-axial $\eta_Q$ are all consistent with the meridional arrangement of Cl and O atoms in the in the first coordination sphere.

**ScCp$_3$.** This compound represents a departure from all other systems studied herein, and is mentioned as an aside. Given current interest in organometallic scandium compounds,$^{18-21}$ solid-state $^{45}$Sc NMR could be a useful method to gain insight into their molecular structure and dynamics. In this regard, ScCp$_3$ is a good entry point for studies upon $\pi$-coordinated systems. Herein we present some preliminary room-temperature NMR data. Analytical simulation of $^{45}$Sc MAS (Figure 5.5a) and static (Figure 5.5b) NMR spectra of ScCp$_3$ yield $\delta_{iso} = 62.8$ ppm, $C_Q = 8.3$ MHz, $\eta_Q = 0.88$ and $\Omega = 135$ ppm, $\kappa = 0.0$. The discontinuities in static spectra are difficult to resolve at both 9.4 T and 11.75 T, increasing the errors in the CS tensor parameters and Euler angles. The appearance of the spectra are suggestive of some intramolecular dynamics, though this is beyond the scope of the current paper (see $^{13}$C NMR data in Figure D5).

**Figure 5.5.** Solid-state $^{45}$Sc NMR spectra of ScCp$_3$ and simulations. (a) MAS spectrum, $\nu_{rot} = 12$ kHz. (b) Static spectra at 9.4 T and 11.75 T.

The structure of ScCp$_3$ consists of two $\eta^5$-Cp rings and two $\eta^1$-Cp rings. The $\eta^1$-
Cp rings bridge two adjacent scandium atoms leading to the formation of polymeric chains. In the majority of NMR studies of metal nuclei in metallocene systems\textsuperscript{72-76} the values of $\delta_{iso}$ typically occur far to the low-frequency end of the chemical shift range, consistent with nuclei which are highly shielded from the magnetic field. In this respect, the “mid-range” $\delta_{iso}$ for this metallocene system is unusual. The \eta$^5$-Cp rings are likely responsible for significant magnetic shielding of the $^{45}$Sc nucleus, while the \eta$^1$-Cp must result in some degree of deshielding. With the absence of other organometallic species for comparison, it is difficult to assess the origin of the moderate value of $C_Q$.

Figure 5.6. $^{45}$Sc chemical shift and magnetic shielding scales. The magnetic shielding scale was generated from the RHF/6-311G** on Sc series of calculations. The theoretical result for ScCp$_3$ has been omitted.
Summary of Observed $^{45}$Sc NMR Parameters. To aid in illustrating the observed trends, a chemical shift scale has been constructed from all of the complexes studied herein (Figure 5.6). Magnetic deshielding is observed upon replacement of oxygen with chlorine; for instance, the isotropic chemical shift of scandium in ScCl$_3$•6H$_2$O is 125 ppm (coordination by two chlorine atoms), while the observed shift of ScCl$_3$•3THF is 202 ppm (coordination by three chlorine atoms). Sc-Cl bonding must play a significant role in making paramagnetic shielding contributions and increasing the span of the scandium CS tensors. A trend in the observed values of $\Omega$ is also observed: coordination of scandium by more than one type of atom or by ligands engaging in multiple binding modes (e.g. ScCp$_3$) is seen to result in sizable $\Omega$ values.

A correlation between molecular symmetry and size of $C_Q$ is also observed. A $C_Q$ of 2.02 MHz in hexagonally closed packed Sc metal has been previously observed,$^{37}$ which is reflective of the spherically symmetric scandium environment. Compounds that possess coordination environments with bond-angles close to ideal octahedral angles, such as Sc(OAc)$_3$ and ScCl$_3$•6H$_2$O, are seen to possess relatively small values of $C_Q$. Distortions away from octahedral symmetry result in an increase in $C_Q$ as observed in Sc(acac)$_3$ and Sc(TMHD)$_3$. Values of $\eta_Q$ near zero or one are observed when symmetry elements such as rotational axes are present.

The aforementioned trends illustrate the utility of solid-state $^{45}$Sc NMR for the analysis of molecular structure. Values of $C_Q$ can be used to gauge the spherical symmetry of the ground state electronic structure about a scandium nucleus, while the values of $\delta_{iso}$ and $\Omega$ can be used to provide information about the nature of the ligands that are bound to
scandium and their modes of bonding. The presence of symmetry elements, such as rotational axes and mirror planes, are reflected in the values of \( \eta_Q \) and \( \kappa \), as well as in the Euler angles.

**Table 5.2.** Calculated \(^{45}\)Sc NMR Parameters Showing Best Agreement With Experiment

<table>
<thead>
<tr>
<th>Compound/Method</th>
<th>( C_Q ) (MHz)(^a)</th>
<th>( \eta_Q )</th>
<th>( \delta_{iso} ) (ppm)(^b)</th>
<th>( \Omega ) (ppm)</th>
<th>( \alpha (^\circ) )</th>
<th>( \beta (^\circ) )</th>
<th>( \gamma (^\circ) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(acac)(_3)</td>
<td>13.0(3)</td>
<td>0.22(3)</td>
<td>82(1)</td>
<td>70(10)</td>
<td>-0.7(2)</td>
<td>90(15)</td>
<td>83(4)</td>
</tr>
<tr>
<td>RHF/6-311G** on Sc</td>
<td>-11.6</td>
<td>0.44</td>
<td>77</td>
<td>61.3</td>
<td>-0.69</td>
<td>89</td>
<td>85</td>
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<tr>
<td>B3LYP/6-311G**</td>
<td>-12.3</td>
<td>0.40</td>
<td>101.8</td>
<td>95.1</td>
<td>-0.67</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>Sc(TMHD)(_3)</td>
<td>13.1(2)</td>
<td>0.93(2)</td>
<td>89.5(10)</td>
<td>110(20)</td>
<td>-0.7(3)</td>
<td>90(15)</td>
<td>90(15)</td>
</tr>
<tr>
<td>RHF/6-311+G** on Sc</td>
<td>14.4</td>
<td>0.67</td>
<td>76.1</td>
<td>82.5</td>
<td>0.57</td>
<td>90</td>
<td>68</td>
</tr>
<tr>
<td>B3LYP/6-311G** on Sc</td>
<td>15.3</td>
<td>0.71</td>
<td>98.4</td>
<td>118.8</td>
<td>0.36</td>
<td>90</td>
<td>5</td>
</tr>
<tr>
<td>Sc(NO(_3))(_3)(_2)(_5)H(_2)O</td>
<td>6.2(2)</td>
<td>0.75(5)</td>
<td>-18.5(10)</td>
<td>60(10)</td>
<td>-0.8(1)</td>
<td>80(15)</td>
<td>10(10)</td>
</tr>
<tr>
<td>B3LYP/6-311+G** on Sc</td>
<td>-5.6</td>
<td>0.72</td>
<td>7.3</td>
<td>58.9</td>
<td>-0.74</td>
<td>51</td>
<td>39</td>
</tr>
<tr>
<td>Sc(OAc)(_3)</td>
<td>4.6(2)</td>
<td>0.18(6)</td>
<td>-6.2(8)</td>
<td>73(5)</td>
<td>0.65</td>
<td>10(45)</td>
<td>7(3)</td>
</tr>
<tr>
<td>RHF/6-311G**</td>
<td>3.3</td>
<td>0.18</td>
<td>15.8</td>
<td>24.9</td>
<td>0.86</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>B3LYP/6-311G**</td>
<td>4.6</td>
<td>0.00</td>
<td>-19.4</td>
<td>102.6</td>
<td>0.99</td>
<td>0</td>
<td>0</td>
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<tr>
<td>ScCl(_3)(_6)H(_2)O</td>
<td>3.9(2)</td>
<td>0.77(9)</td>
<td>125.4(5)</td>
<td>180(10)</td>
<td>0.91</td>
<td>145(10)</td>
<td>30(5)</td>
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<tr>
<td>RHF/6-311G** on Sc</td>
<td>5.3</td>
<td>0.78</td>
<td>154.4</td>
<td>228.9</td>
<td>0.96</td>
<td>51</td>
<td>26</td>
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<tr>
<td>B3LYP/6-311+G** on Sc</td>
<td>5.3</td>
<td>0.74</td>
<td>231.3</td>
<td>486.2</td>
<td>0.98</td>
<td>52</td>
<td>25</td>
</tr>
<tr>
<td>ScCl(_3)(_3)THF</td>
<td>8.4(2)</td>
<td>0.30(5)</td>
<td>202(1)</td>
<td>200(20)</td>
<td>-0.1(3)</td>
<td>85(35)</td>
<td>4(4)</td>
</tr>
<tr>
<td>RHF/6-311G** on Sc</td>
<td>9.7</td>
<td>0.26</td>
<td>176.8</td>
<td>157.8</td>
<td>-0.11</td>
<td>80</td>
<td>5</td>
</tr>
<tr>
<td>B3LYP/6-311G**</td>
<td>10.0</td>
<td>0.35</td>
<td>303.0</td>
<td>316.7</td>
<td>-0.26</td>
<td>73</td>
<td>4</td>
</tr>
<tr>
<td>ScCp(_3)</td>
<td>8.3(2)</td>
<td>0.88(4)</td>
<td>62.8(8)</td>
<td>135(15)</td>
<td>0.0(3)</td>
<td>24(10)</td>
<td>73(8)</td>
</tr>
<tr>
<td>RHF/6-311G** on Sc</td>
<td>-8.5</td>
<td>0.90</td>
<td>-74.6</td>
<td>86.1</td>
<td>-0.02</td>
<td>60</td>
<td>43</td>
</tr>
<tr>
<td>B3LYP/6-311+G** on Sc</td>
<td>-7.9</td>
<td>0.74</td>
<td>115.1</td>
<td>300.5</td>
<td>-0.34</td>
<td>-47</td>
<td>36</td>
</tr>
</tbody>
</table>

\(^a\) Only the magnitude of \( C_Q \) can be measured experimentally. For definitions of all NMR parameters refer to Table 5.1.

\(^b\) The theoretical isotropic shifts were calculated by comparison of the calculated shielding to that calculated from a geometry optimized model of [Sc(H\(_2\)O)\(_6\)]\(^{3+}\) at the appropriate level of theory.

\(^c\) In cases where the basis set used for scandium is explicitly stated the 6-31G** basis set was employed on all other atoms.
Quantum Chemical Calculations of $^{45}$Sc Interaction Tensors. Ab initio calculations are performed to predict the orientations of the CS and EFG tensors in the molecular frames (Figure 5.7). This allows for relationships between the observed $^{45}$Sc NMR parameters and molecular structure and symmetry to be confirmed and/or established. Calculated EFG and CS tensor parameters showing the best agreement with experimental values are presented for Sc(acac)$_3$, Sc(TMHD)$_3$, Sc(NO$_3$)$_3$·5H$_2$O, Sc(OAc)$_3$, ScCl$_3$·6H$_2$O, ScCl$_3$·3THF and ScCp$_3$ in Table 5.2. Calculations on Sc(acac)$_3$ employing the basis sets of Huzinaga$^{59}$ and the results of all other calculations are given in the original publication.$^{66}$ Cartesian coordinate files containing the orientation of the EFG and CS tensors for each compound are provided with the original publication.$^{66}$

Sc(acac)$_3$ and Sc(TMHD)$_3$. Calculations performed upon Sc(acac)$_3$ generally produce results which are in good agreement with the experimentally observed parameters. The B3LYP/6-311G** calculation on Sc(acac)$_3$ orients the largest component of the EFG tensor, $V_{33}$, and least shielded component of the CS tensor, $\sigma_{11}$, coincident with the pseudo-$C_3$ axis, in agreement with our proposed orientation based on the experimental values of $\kappa$ and $\eta_Q$. The theoretical Euler angles are found to be in excellent agreement with experimentally determined angles. Similar tensor orientations have been observed in Co(acac)$_3$ and Al(acac)$_3$, both of which have analogous molecular geometries.$^{77,78}$

All calculations performed upon Sc(TMHD)$_3$ predict intermediate positive values of $\kappa$, distinct from the experimentally determined value of -0.7. $V_{11}$ is the pseudo-unique component of the EFG tensor (Figure 5.7b) and is oriented near the pseudo-$C_2$ axis of the
molecule and $\sigma_{22}$, while $V_{33}$ and $\sigma_{33}$ are nearly coincident and directed toward the bent ligands. The theoretical Euler angles are close to the observed angles (if $\beta$ is near zero, $\alpha$ and $\gamma$ are approximately interchangeable). The calculations are correctly predicting the orientation of the EFG and CS tensors within the molecular frame, but consistently underestimate $\sigma_{22}$ and overestimate $\sigma_{33}$.

![Figure 5.7](image)

**Figure 5.7.** Proposed EFG and CS tensor orientations. (a) Sc(acac)$_3$ (b) Sc(TMHD)$_3$ (c) Sc(NO$_3$)$_3$•5H$_2$O (d) Sc(OAc)$_3$ (e) ScCl$_5$•6H$_2$O (f) ScCl$_5$•3THF (g) ScCp$_3$.

**Sc(NO$_3$)$_3$•5H$_2$O and Sc(OAc)$_3$.** Calculations performed upon Sc(NO$_3$)$_3$•5H$_2$O yield several results which are close to the experimental values. There are no discernable symmetry elements present, with the exception of a pseudo-mirror plane, that could account for the observation of such a small value of $C_Q$. As mentioned earlier, the most
reasonable explanations for the small $C_Q$, despite the lack of spherical symmetry, are the increased Sc-O distances. It is notable that $V_{33}$ is oriented in the direction of one of the nitrogen atoms in a nitrate group (Figure 5.7c), though it is uncertain why this is the case. The calculated orientation of the CS tensor conforms to the symmetry of the atomic arrangement and is oriented such that the $\sigma_{11}$ and $\sigma_{33}$ are contained in the pseudo-mirror plane formed by the nitrate ligands.

In Sc(OAc)$_3$, calculations successfully predict that $V_{33}$ and $\sigma_{33}$ are the pseudo-distinct components (Figure 5.7d), and reveals that they are nearly co-linear with the $C_3$ axis of the molecule. Thus, the tensors are aligned in the direction of chain propagation of this coordination polymer and are clearly constrained by the symmetry of the molecule. The predicted Euler angles are in excellent agreement with the experimental values.

**ScCl$_3$$\cdot$6H$_2$O and ScCl$_3$$\cdot$3THF.** The experimental and theoretical parameters obtained for ScCl$_3$$\cdot$6H$_2$O indicate that $V_{11}$ and $\sigma_{33}$ are the pseudo-unique components, and the value of $\alpha$ indicates they are not closely aligned (Figure 5.7e). The values of $\eta_Q$ indicate that $V_{11}$ is the pseudo-unique component, and should be aligned along or near the $C_4$ axis of the molecule; however, this is not the case. The theoretical prediction aligns $V_{33}$ at ca. 27° from the $C_4$ axis, with $V_{11}$ and $V_{22}$ oriented approximately 27° and 18° away from Sc-O bonds ($C_2$ axes), respectively. The theoretical CS tensor places $\sigma_{33}$ along the Sc-Cl bond, approximately 26° from from $V_{33}$, which is consistent with $\sigma_{33}$ being the unique component of the CS tensor, while $\sigma_{11}$ and $\sigma_{22}$ are in the ScO$_4$ plane, oriented near the Sc-O bonds. Close agreement is observed between the experimental and predicted NMR tensor parameters and tensor orientations.
The orientation of the CS tensor in ScCl₃•6H₂O which gives rise to high magnetic shielding along the Cl-Sc-Cl axis and deshielding in the ScO₄ plane can be explained using Ramsey’s description of contributions to paramagnetic shielding. The paramagnetic shielding tensor at a nucleus, A, is given as:

$$\sigma_{\text{Pa}}^A = -\frac{\mu_0}{4\pi} \frac{e^2}{2m^2} \sum_{k \neq 0} (E_k - E_0)^{-1} \times \left[ \langle 0 | \sum_i L_{ia} | k \rangle \langle k | \sum_j L_{\text{A}j}^A r_{ij}^3 | 0 \rangle + \langle 0 | \sum_i L_{\text{A}i}^A r_{ij}^3 | k \rangle \langle k | \sum_j L_{ij}^0 | 0 \rangle \right]$$

where $E_k - E_0$ is the energy difference between occupied ($|0\rangle$) and virtual ($|k\rangle$) MOs, and $L_i$ and $L_{ia}^A$ are the orbital angular momentum operators of the $i$th electron with respect to the gauge origin and nucleus, respectively. The angular momentum operators describe the mixing of occupied and virtual MOs via rotation about an axis perpendicular to a plane containing the MOs, which can be visualized as physical rotation of charge about an applied magnetic field.

Magnetic shielding along the Cl-Sc-Cl axis is high since the occupied and virtual MOs in the ScO₄ plane are far apart in energy and do not have the appropriate symmetry for magnetic-dipole allowed mixing; as a result, the paramagnetic contribution to deshielding perpendicular to the ScO₄ plane is minimal. Conversely, deshielding arising from paramagnetic contributions in the plane are high, since there are energetically similar MOs of appropriate symmetry in the ScO₂Cl₂ planes which are available for mixing. The large $\Omega$ and high $\delta_{iso}$ are consistent with this qualitative model, and are not observed in any of the complexes which do not have Sc-Cl bonds.
For ScCl$_3$•3THF, the calculated value of $\eta_0$ is in good agreement with the observed value and indicates that $V_{33}$ is the pseudo-unique component of the tensor. $V_{33}$ is nearly coincident with the Cl-Sc-Cl pseudo-axis ($\angle 174.5^\circ$), whereas $V_{11}$ coincides with the $C_2$ axis of the molecule formed by O-Sc-Cl axis ($\angle 179.4^\circ$) (Figure 5.7f). It is important to note that $\sigma_{33}$ is oriented near the Cl-Sc-Cl axis (⊥ to the ClScO$_3$ plane), $\sigma_{22}$ near the Cl-Sc-O axis (⊥ to the Cl$_2$ScO$_2$ plane), and $\sigma_{11}$ near the O-Sc-O axis (⊥ to the Cl$_3$ScO plane). This is consistent with arguments above, where the large paramagnetic deshielding contributions are generated perpendicular to the plane with the most coordinated Cl atoms. A detailed MO analysis is beyond the scope of the current study.

**ScCp$_3$**. Calculated and observed EFG parameters of ScCp$_3$ are in good agreement. Calculations were carried out using a [ScCp$_4$] cluster (Figure 5.7g), and reveal that $V_{11}$ is nearly coincident with one of the $\eta_1$-Cp-Sc bonds, and that $V_{33}$ is oriented in the direction of propagation of the metallocene polymer. The observation of a high value of $\eta_0$, which indicates that $V_{11}$ is the unique component of the EFG tensor, is not surprising in this context. It is difficult to comment on the observed CS tensor orientation; nonetheless, it is of interest to note that the calculations do predict a relatively large span. The predicted isotropic shifts fluctuate widely between the B3LYP and RHF calculations, perhaps suggesting that use of an isolated cluster in this instance is insufficient to properly model the CS tensor.

**Summary of Ab Initio Calculations.** Inspection of all the calculations reveals that the RHF method is generally superior to the B3LYP method. The former typically result in both CS and EFG tensor parameters that are close to the experimentally observed
values, while the latter do not correctly predict CS tensor parameters in most cases. In the case of extended systems (i.e., coordination polymers like Sc(OAc)$_3$ and ScCl$_3$$\cdot$6H$_2$O) calculations upon isolated small charged clusters are sufficient to accurately calculate the observed $^{45}$Sc EFG and CS tensor parameters, indicating that the interactions are mainly intramolecular in origin. Examination of the calculated isotropic shifts reveals that the RHF calculations typically result in errors of less than ±25 ppm with larger basis sets (with the exception of ScCp$_3$), while the B3LYP calculations generally produce poorer agreement and greatly overestimate the effects of coordination by chlorine on chemical shifts.

Solid-State $^{45}$Sc NMR Experiments on Sc(OTf)$_3$ and ME Sc(OTf)$_3$. The following section represents a preliminary study of Sc(OTf)$_3$ and ME Sc(OTf)$_3$. The interested reader is directed to Chapter 6 where a more thorough study of Sc(OTf)$_3$ and ME Sc(OTf)$_3$ is described. With our new data in Chapter 6 it is clear that some of our original hypotheses regarding the structure of ME Sc(OTf)$_3$ are incorrect. These portions of the original publication have been removed.

$^{45}$Sc NMR spectra of Sc(OTf)$_3$ and corresponding analytical simulations are shown in Figure 5.8. Simulations of MAS (Figure 5.8a) and static (Figure 5.8b) patterns yield $C_Q = 4.7$ MHz, $\eta_Q = 0.15$, and $\delta_{iso} = -28.0$ ppm, $\Omega = 32.0$ ppm and $\kappa = 0.3$. The static spectra possess rounded edges and do not terminate sharply into the baseline. This is most likely due to minor long-range disorder in the sample.
Figure 5.8. Solid-state $^{45}$Sc NMR spectra and analytical simulations of Sc(OTf)$_3$ and ME Sc(OTf)$_3$. (a) MAS spectrum of Sc(OTf)$_3$, $\nu_{\text{rot}} = 4$ kHz. (b) Static spectra of Sc(OTf)$_3$ at 9.4 T and 11.75 T. (c) MAS spectrum of ME Sc(OTf)$_3$, $\nu_{\text{rot}} = 4$ kHz. (b) Static spectra of Sc(OTf)$_3$ at 9.4 T (AMDFS-Hahn Echo) and 11.75 T.

There is currently no crystal structure of Sc(OTf)$_3$; however, the $^{45}$Sc NMR data can be used to make structural inferences. The small $C_Q$ suggests that the coordination environment of scandium must be of high symmetry, while the low $\Omega$ and negative isotropic chemical shift suggest that there is symmetric coordination by oxygen atoms from one type of ligand. The oxygen atoms should form a nearly idealized octahedron about the scandium centre. Given the similarity of these parameters with those of Sc(OAc)$_3$ (Table 5.3), Sc(OTf)$_3$ should have a coordination polymer structure akin to that of Sc(OAc)$_3$. This is reasonable because triflate and acetate anions are similar in
structure, and can therefore coordinate to Sc in an equivalent manner. This is in accordance with the previously reported IR studies which suggests that the triflate ligands are bridging.\textsuperscript{80} The structure of Sc(OAc)\textsubscript{3} is shown in Figure 5.9 along with a proposed model of a [Sc\textsubscript{3}(OTf)\textsubscript{6}]\textsuperscript{3+} unit. In addition, the \textsuperscript{13}C and \textsuperscript{19}F NMR spectra only contain one signal apiece (Figure D6), which is also consistent with the proposed structure (one type of carbon and fluorine atom). Thus, \textsuperscript{45}Sc NMR spectroscopy can be applied as a rapid probe of structure and bonding in the context of the other systems examined within this work.

Table 5.3. Observed \textsuperscript{45}Sc NMR Parameters of Sc(OTf)\textsubscript{3}, ME Sc(OTf)\textsubscript{3}, and Sc(OAc)\textsubscript{3}.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(C_Q) (MHz)\textsuperscript{a}(\eta_Q)</th>
<th>(\delta_{iso}) (ppm)</th>
<th>(\Omega) (ppm)</th>
<th>(\kappa)</th>
<th>(\alpha^\circ)</th>
<th>(\beta^\circ)</th>
<th>(\gamma^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(OTf)\textsubscript{3}</td>
<td>4.7(2)</td>
<td>0.15(5)</td>
<td>-28(1)</td>
<td>32(3)</td>
<td>0.3(1)</td>
<td>75(30)</td>
<td>18(4)</td>
</tr>
<tr>
<td>ME Sc(OTf)\textsubscript{3}</td>
<td>4.2(2)</td>
<td>0.1(1)</td>
<td>1.8(3)</td>
<td>26(8)</td>
<td>-0.1(2)</td>
<td>90(30)</td>
<td>15(5)</td>
</tr>
<tr>
<td>Sc(OAc)\textsubscript{3}</td>
<td>4.6(2)</td>
<td>0.18(6)</td>
<td>-6.2(8)</td>
<td>73(5)</td>
<td>0.65(10)</td>
<td>0(45)</td>
<td>7(3)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}See Table 5.1 for definitions of parameters.

Figure 5.9. Proposed model of Sc(OTf)\textsubscript{3} (left) and the known structure of Sc(OAc)\textsubscript{3} (right). Fluorine and hydrogen atoms have been omitted for clarity.
**Solid-state NMR of microencapsulated (ME) Sc(OTf)₃.** The $^{45}$Sc NMR spectra of ME Sc(OTf)₃ reveal spectra similar to those observed from the microcrystalline sample (Figure 5.8c and 5.8d), with $\delta_{iso} = 1.8$ ppm, $C_Q = 4.2$ MHz, $\eta_Q = 0.1$, $\Omega = 26.0$ ppm and $\kappa = -0.1$. Acquisition of static solid-state $^{45}$Sc NMR spectra of ME Sc(OTf)₃ without $^1$H decoupling results in significant broadening (Figure D7). This strong $^1$H-$^{45}$Sc dipolar interaction could not be completely decoupled in the static experiments at 11.75 T (Figure 5.8d), as evidenced by the lack of definition in the pattern. However, the visible discontinuities in the pattern are useful for the confirmation of the parameters obtained from the simulation of the spectrum acquired at 9.4 T. In comparing the $^{45}$Sc NMR parameters of Sc(OTf)₃ and ME Sc(OTf)₃ (Table 5.3), the latter has a significantly higher chemical shift (scandium is less shielded) and a slightly smaller $C_Q$. Preliminary $^{13}$C and $^{19}$F SSNMR spectra have also been acquired (Figure D6). For interpretations of the SSNMR data regarding the structure of ME Sc(OTf)₃, the reader is referred to Chapter 6.

### 5.4 Conclusions

The $^{45}$Sc NMR interaction tensor parameters have been measured for a number of well-characterized scandium compounds possessing a broad range of metal coordination environments. For the first time, clear relationships are drawn between the scandium coordination environments and the nature of the $^{45}$Sc NMR interaction tensors. EFG tensor parameters are primarily affected by the geometry of the scandium coordination environment, while CS tensor parameters are affected by both the symmetry of the coordination environment and nature of bonding in the first coordination sphere.
Anisotropic chemical shielding of the scandium nucleus is observed in all of the systems, and plays a significant role in defining the scandium chemical shift range. Ab initio calculations of the CS and EFG tensor parameters are in very good agreement with experimental data. In addition, the predicted tensor orientations within the molecular frames aids in rationalizing the origin of the observed CS and EFG tensor parameters. Solid-state $^{45}$Sc NMR spectroscopy has also been successfully applied to structurally characterize two systems for which single-crystal X-ray diffraction data is unavailable and/or unobtainable. It has been demonstrated that Sc(OTf)$_3$ is a coordination polymer that possesses a structure similar to Sc(OAc)$_3$. A distinct chemical shift and significant $^1$H-$^{45}$Sc dipolar coupling was observed in the $^{45}$Sc NMR spectra of ME Sc(OTf)$_3$. 
5.5. Bibliography

2326-2330.


Chapter 6: Multinuclear Solid-State NMR Studies of Polymer Supported Scandium Triflate Catalysts

6.1 Introduction

Green chemistry is a term used to describe the creation of products or processes in chemistry that will reduce or eliminate hazardous by-products or solvents used in a chemical process or reaction.\(^1\), \(^2\), \(^3\) One of the simplest ways to attain more environmentally friendly chemical processes is to eliminate potentially toxic and expensive organic solvents and stoichiometric reagents, and replace them with aqueous media and/or catalytic reagents.\(^4\)-\(^6\) For these reasons, there has been intense research in both academic and industrial sectors towards developing water-tolerant reagents and catalysts.\(^6\)

Kobayashi and co-workers have introduced scandium(III) trifluoromethanesulfonate (triflate) [Sc(OTf)\(_3\)] as an effective carbon-carbon bond forming Lewis acid catalyst capable of catalyzing a variety of synthetic organic reactions in aqueous media.\(^7\)-\(^18\) This work is part of a larger field of research into water-tolerant Lewis acid catalysts.\(^6\), \(^19\)-\(^21\) In 1998, Kobayashi and co-workers introduced microencapsulation as a method of immobilizing Sc(OTf)\(_3\) in polystyrene (PS).\(^22\) These microencapsulated (ME) catalysts are recoverable, reusable, often reduce metal leaching and have similar activity to their microcrystalline counterparts; however, they are most often employed with organic solvents.\(^21\) ME Sc(OTf)\(_3\) has been shown to catalyze many of the same synthetic reactions as microcrystalline Sc(OTf)\(_3\), while imparting the aforementioned beneficial characteristics of ME catalysts.\(^21\), \(^23\), \(^24\) In some cases, ME Sc(OTf)\(_3\) exhibits superior catalytic activity to Sc(OTf)\(_3\); for example, Lewis acids can be
decomposed by basic aldimines; however, it was shown that ME Sc(OTf)₃ is able to tolerate and activate such aldimines.²¹ In addition, ME Sc(OTf)₃ is able to catalyze Friedel-Crafts alkylation and acylation reactions,²⁵ which are important in large scale reactions that exhibit characteristics desirable for green chemistry.²⁶-²⁸

Despite the importance of ME Sc(OTf)₃, the interactions between the microencapsulating polymer and Sc(OTf)₃ is not well understood. Kobayashi and co-workers have characterized ME Sc(OTf)₃ by ⁴⁵Sc solution NMR spectroscopy²⁹ and energy dispersive X-ray (EDX) and scanning electron microscopy (SEM) imaging (in addition to reactivity studies).²² EDX and SEM images showed that the Sc is well dispersed on the surface of the polymer in sub-µm size particles, which suggests the presence of nanocrystalline or molecular-level Sc(OTf)₃ domains in ME Sc(OTf)₃.²² Solution ⁴⁵Sc NMR studies of ME Sc(OTf)₃ revealed a positive chemical shift of ca. 18 ppm compared to that of Sc(OTf)₃.²⁹ Furthermore, ⁴⁵Sc NMR of solutions of Sc(OTf)₃ with a “PS analogue” (1,3,5-triphenylpentane) also display a positive chemical shift of ca. 14 ppm.²⁹ It was also found that loading levels corresponding to 43% and 0% of the amount of Sc loaded onto PS were obtained with polybutadiene and polyethylene as the support materials, respectively. The positive chemical shift of ca. 18 ppm observed in solution ⁴⁵Sc NMR spectra and the higher loading levels observed for PS ME Sc(OTf)₃ and were attributed by Kobayashi to an interaction between the π-electrons of the PS phenyl groups and vacant Sc d-orbitals.²¹,²⁹ It was posited that this electronic interaction is responsible for immobilizing Sc(OTf)₃ in the polymer, although it was also suggested the steric bulk of the polymer may be important as well, i.e., physical envelopment of Sc(OTf)₃ by bulky phenyl groups may play a role in microencapsulation.²²
Solid-state NMR (SSNMR) is an ideal technique for probing the structures of non-crystalline materials, such as polymers, and by extension, polymer based ME catalysts. In addition to SSNMR experiments which employ ubiquitous nuclei, such as $^1$H, $^{13}$C and $^{19}$F, it is also possible to utilize $^{45}$Sc ($I = 7/2$, N.A. = 100%) SSNMR to probe the structure of ME Sc(OTf)$_3$. $^{45}$Sc SSNMR has recently been employed to probe the structure of a variety of scandium-containing materials, and the $^{45}$Sc quadrupolar interactions and chemical shifts have been found to be very sensitive to the structural differences in local Sc environments.

In our preliminary study of Sc(OTf)$_3$ and ME Sc(OTf)$_3$, we observed a single $^{45}$Sc powder pattern in the $^{45}$Sc SSNMR spectra of both ME Sc(OTf)$_3$ and Sc(OTf)$_3$. The $\delta_{iso}$ of ME Sc(OTf)$_3$ was observed to be ca. +30 ppm higher than that of microcrystalline Sc(OTf)$_3$ (similar to the positive chemical shifts observed in Kobayashi’s solution $^{45}$Sc NMR studies). Similar electric field gradient (EFG) tensor and chemical shift (CS) tensor parameters were observed in both cases (excepting the difference in isotropic chemical shifts). These preliminary results were consistent with Kobayashi’s hypothesis that electronic interactions between the $\pi$-electrons of the PS phenyl groups and Sc are partly responsible for microencapsulation.

Questions still remain regarding the local Sc environments in ME Sc(OTf)$_3$. This is further exacerbated by the absence of any known single crystal X-ray diffraction structure for Sc(OTf)$_3$. Hence, further intensive study of Sc(OTf)$_3$ and ME Sc(OTf)$_3$ is necessary to understand the mode (and perhaps mechanism) of microencapsulation, as well as the local catalyst structure. To this end, we have acquired $^{45}$Sc SSNMR NMR spectra of a series of ME Sc(OTf)$_3$ samples, freshly prepared under a variety of different conditions.
conditions, as well as crystalline and ME Sc(OTf)$_3$•8H$_2$O (the former features hydrated Sc$^{3+}$ ions). $^1$H-$^{45}$Sc TRAPDOR NMR experiments were employed in order to probe for possible interactions between the polymer and Sc atoms. In addition, solid-state $^{13}$C, $^{19}$F, and $^1$H NMR experiments, as well as powder X-ray diffraction (PXRD) experiments, were also performed in order to obtain complementary information on the bulk structures of the ME catalysts.

6.2 Experimental

*Sample Preparation.* Samples of scandium trifluoromethanesulfonate [Sc(OTf)$_3$] were purchased from Strem Chemicals, Inc. and Sigma-Aldrich Chemicals, Inc. Some of the commercial samples of anhydrous Sc(OTf)$_3$ were found to be partially hydrated when received, as indicated by solid-state $^{45}$Sc NMR and PXRD. Completely anhydrous Sc(OTf)$_3$ was obtained by drying the powdered sample under vacuum at 160 °C for four hours. Sc(OTf)$_3$•8H$_2$O and Sc(OTf)$_3$•8D$_2$O were synthesized by dissolving anhydrous Sc(OTf)$_3$ in H$_2$O and D$_2$O, respectively, followed by drying under vacuum at elevated temperatures (80 °C). PS (PS) (M$_w$ = 60500 and 22400) and Deuterated PS ($d_8$, M$_w$ = 66000, approximately 98% deuterated) were purchased from Polymer Source Inc. and used without purification.

Scandium acetate (Sc(OAc)$_3$) was purchased from Strem Chemicals, Inc. and purified following a literature procedure to remove water of hydration.$^{43}$ Sc(OAc)$_3$ was added to a 5.0 M glacial acetic acid solution and stirred until dissolution. The solvent was then removed by vacuum and the resulting solid was collected and isolated under inert atmosphere. The identity of the purified sample was confirmed by PXRD.
Synthesis of Microencapsulated (ME) Sc(OTf)₃. The synthesis of ME Sc(OTf)₃ was based upon a modified literature procedure.²² All reagents were handled under an inert N₂ atmosphere (except where noted) and all reactions were carried out using Schlenk lines. All solvents were dried by overnight reactions with calcium hydride, followed by distillations, with the exception of acetonitrile, which was obtained from a solvent system. 0.250 g of PS was combined with approximately 6 mL of cyclohexane in a Schlenk flask. The mixture was heated to 40 °C, while stirring, to dissolve the PS. 0.050 g of Sc(OTf)₃ (or Sc(OTf)₃•8H₂O, where indicated) was weighed into a first Schlenk flask. The hot PS/cyclohexane mixture was then cannulated into a second Schlenk flask containing Sc(OTf)₃ and stirred for one hour at 40 °C. The mixture was slowly cooled to 0 °C in an ice bath, during which time PS was observed to precipitate. 8 mL of hexanes were then added in a drop-wise manner to precipitate the remaining PS. After this, the solution was stirred at room temperature for one hour. The solvent was pumped off and the PS was washed several times with dry acetonitrile to remove excess Sc(OTf)₃. After the final washing, the resulting ME Sc(OTf)₃ was dried at 50 °C under vacuum.

Some refinements of the literature procedure are as follows: cooling of the PS/cyclohexane/Sc(OTf)₃ solution to room temperature was done at a slow rate (over ca. 1.5 hours) by allowing the solution to remain in the oil bath used for heating with the hot plate turned off. When the solution reached room temperature it was then placed in a water bath to which ice was slowly added over the span of 0.5 hours until 0 °C was reached. The addition of hexanes to the solution was performed in a drop-wise manner over the course of ca. 20 min.
Solid-state NMR Spectroscopy. Solid-state NMR spectra were obtained on a Varian Infinity Plus NMR Spectrometer with an Oxford 9.4 T ($\nu_0^{(1\text{H})} = 399.73$ MHz) wide-bore magnet with $\nu_0^{(45\text{Sc})} = 97.10$ MHz, $\nu_0^{(13\text{C})} = 100.52$ MHz and $\nu_0^{(19\text{F})} = 376.09$ MHz. All samples were ground into powders, packed into 4 mm outer diameter (o.d.) zirconium oxide rotors under an inert atmosphere and sealed with airtight caps. Chemagnetics 4 mm triple-resonance (HXY) or double-resonance (HX) MAS probes were used for all experiments. A detailed list of $^{45}\text{Sc}$ SSNMR acquisition parameters can be found in Tables E1-E6. Scandium chemical shifts were referenced to an aqueous solution of dilute (less than 0.05 M) ScCl$_3$ ($\delta_{\text{iso}} = 0.0$ ppm). An echo pulse sequence $[\pi/2 - \tau_1 - \theta_{\text{ref}} - \tau_2 - \text{acquire}, \theta_{\text{ref}} = \pi/2 \text{ or } \pi]$ was utilized to acquire all $^{45}\text{Sc}$ NMR spectra, and the radiofrequency field of the pulses, $\nu_1^{(45\text{Sc})}$, was set to ca. one-half of the static central-transition powder pattern width. A double frequency sweep (DFS) sequence was applied to enhance the signal of some $^{45}\text{Sc}$ echo spectra of the ME samples. $^{1}\text{H}$ decoupling was applied with $\nu_1^{(1\text{H})}$ between 22 and 30 kHz, where indicated. Magic-angle spinning (MAS) spectra were acquired with a 90°-90° echo sequence $[\pi/2 - \tau_1 - \pi/2 - \tau_2 - \text{acquire}]$ using high power pulses and large spectral widths. MAS spinning frequencies ($\nu_{\text{rot}}$) ranged from 4 kHz to 12 kHz, with inter-pulse delays equal to $1/\nu_{\text{rot}}$. Non-selective pulse widths were adjusted by a factor of $(I + \frac{1}{2})^{-1}$ (where $I = 7/2$) in order to achieve central-transition (CT) selective $^{45}\text{Sc}$ pulses for all experiments. A large number of scans were acquired for ME spectra when compared to spectra of the crystalline complexes.

Hydrogen chemical shifts were referenced to tetramethylsilane ($\delta_{\text{iso}} = 0.00$ ppm) via a secondary standard of adamantane ($\delta_{\text{iso}} = 1.85$ ppm). $\pi/2$ pulse widths between 2.30
and 2.40 µs were used corresponding to ν₁(¹H) = 105 to 109 kHz. A recycle delay of 20 s was applied for all MAS ¹H SSNMR experiments. 32 to 128 scans were obtained for ¹H MAS SSNMR spectra and ν_rot ranged from 10 kHz to 13.5 kHz. ¹H TRAPDOR MAS SSNMR experiments were acquired at ν_rot = 12.5 kHz and the first echo dephasing period (τ₁) was set to 240 µs. ν₁(⁴⁵Sc) of ca. 108 kHz was applied during the echo dephasing period. The control and dephasing spectra were acquired in an inter-leaved manner, in order to eliminate any variability in spectrometer performance, which could give rise to false reductions in ¹H signal intensity. Deconvolutions of MAS ¹H SSNMR spectra were performed with the line-fitting routine in the Nuts NMR processing software.

Carbon chemical shifts were referenced to tetramethylsilane (δ_iso = 0.00 ppm) by setting the high-field shift of adamantane (δ_iso = 38.57 ppm) as a secondary reference. ¹H → ¹³C variable amplitude cross-polarization MAS (VACP/MAS) SSNMR experiments utilized a contact time between 1 to 5 ms, a pulse delay of 12 s, and ν_rot ranged from 6.5 to 13.5 kHz. ¹⁹F chemical shifts were referenced to fluorotrichloromethane (δ_iso = 0.00 ppm) by setting the shift of teflon (δ_iso = −122.00 ppm) as a secondary reference. ¹⁹F → ¹³C VACP/MAS NMR experiments utilized a contact time of 2 ms, a pulse delay of 5 s, and a spectral width of 100 kHz.

**Powder X-ray Diffraction.** PXRD patterns were acquired using a Bruker AXS Hi-STAR system utilizing a General Area Detector Diffractions System (GADDS). A Copper Kα radiation source (1.540598 Å) with area detector 2θ range of ca. 3° – 70° was utilized. Powdered samples were packed in 1.0 mm glass capillaries under an inert atmosphere and flame sealed to prevent atmospheric exposure. In order to expose some
of the samples to air, the capillary was broken with a pair of tweezers at the flame sealed (top) side. PXRD patterns were simulated using the Powdercell computer program. 

6.3 Results and Discussion

Solid-state $^{45}$Sc NMR Spectra of Sc(OTf)$_3$, Sc(OAc)$_3$, Sc(OTf)$_3$$\cdot$8H$_2$O. Anhydrous crystalline scandium(III) trifluoromethanesulfonate [herein referred to as Sc(OTf)$_3$] does not have a known crystal structure. For this reason, our research group previously performed $^{45}$Sc SSNMR and PXRD experiments on Sc(OTf)$_3$, in order to characterize the scandium coordination environment. The major findings of this previous study are reviewed at this point in order to clarify some of the structural features of Sc(OAc)$_3$ and Sc(OTf)$_3$, and to compare these data to that of Sc(OTf)$_3$$\cdot$8H$_2$O, prior to discussion of the increasingly complex microencapsulated (ME) systems.

Magic angle spinning (MAS) and static (i.e., stationary sample) $^{45}$Sc SSNMR spectra reveal that the $^{45}$Sc quadrupolar parameters of Sc(OTf)$_3$ are similar to those of Sc(OAc)$_3$ (Figure 6.1, Table 6.1). We have acquired new static NMR spectra of Sc(OTf)$_3$ at 9.4 T and 11.7 T with a 90°-90° echo sequence (Figure E1). This was done because our previous spectra were acquired with 90°-180° echo sequences and DFS for signal enhancement, which can introduce non-ideal intensities into static $^{45}$Sc SSNMR spectra. The CS tensor parameters and Euler angles reported herein are slightly different than those previously reported by our research group (Chapter 5). 

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Figure 6.1. MAS (left) and static (right) $^{45}$Sc SSNMR spectra acquired at 9.4 T. Analytical simulations of the spectra (red traces) are overlayed on top of the experimental spectra (black traces). (a) MAS spectrum of Sc(OTf)$_3$ at a sample spinning speed of $\nu_{\text{rot}} = 4.0$ kHz and (b) static spectrum of Sc(OTf)$_3$. (c) MAS spectrum of Sc(OAc)$_3$ at $\nu_{\text{rot}} = 8.0$ kHz and (d) static spectrum with $^1$H decoupling. (e) MAS spectrum of Sc(OTf)$_3$•8H$_2$O at $\nu_{\text{rot}} = 8.0$ kHz and (f) static spectrum with $^1$H decoupling. Spinning sidebands are indicated with asterisks. $^{45}$Sc EFG and CS tensor parameters extracted from simulations are listed in Table 6.1. All static spectra were acquired with a 90°-90° echo sequence. 90°-90° echo static spectra of Sc(OTf)$_3$ and Sc(OTf)$_3$•8H$_2$O at 11.7 T were acquired in order to confirm the $^{45}$Sc CS tensor parameters and Euler angles (Figure E1).

Table 6.1. Experimental $^{45}$Sc EFG and CS Tensor Parameters of Crystalline Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$C_Q$ (MHz)$^a$</th>
<th>$\eta_Q$$^b$</th>
<th>$\delta_{\text{iso}}$ (ppm)$^d$</th>
<th>$\Omega$ (ppm)$^d$</th>
<th>$\kappa$$^e$</th>
<th>$\alpha$ (°)$^f$</th>
<th>$\beta$ (°)</th>
<th>$\gamma$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(OAc)$_3$</td>
<td>4.6(2)</td>
<td>0.18(6)</td>
<td>-6.2(8)</td>
<td>73(5)</td>
<td>0.65(10)</td>
<td>0(45)</td>
<td>7(3)</td>
<td>90(45)</td>
</tr>
<tr>
<td>Sc(OTf)$_3$</td>
<td>4.7(2)</td>
<td>0.15(10)</td>
<td>-28(1)</td>
<td>26(5)</td>
<td>0.5(2)</td>
<td>35(20)</td>
<td>20(4)</td>
<td>-5(30)</td>
</tr>
<tr>
<td>Sc(OTf)$_3$•8H$_2$O</td>
<td>4.2(2)</td>
<td>0.10(10)</td>
<td>1.8(8)</td>
<td>22(5)</td>
<td>0.1(3)</td>
<td>60(90)</td>
<td>22(20)</td>
<td>-75(30)</td>
</tr>
<tr>
<td>ME</td>
<td>4.2(2)</td>
<td>0.10(10)</td>
<td>1.8(8)</td>
<td>22(5)</td>
<td>0.1(3)</td>
<td>60(90)</td>
<td>22(20)</td>
<td>-75(30)</td>
</tr>
</tbody>
</table>

$^aC_Q = eQV_{33}/h$.  $^b\eta_Q = (V_{11} - V_{22})/V_{33}$.  $^d\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$.  $^e\Omega = \delta_{33} - \delta_{11}$.  $^f\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$.  $^f$The Rose convention is used to describe the Euler angles.$^{48,49}$
Both Sc(OTf)$_3$ and Sc(OAc)$_3$ possess similar $^{45}$Sc EFG tensor parameters ($\eta_Q$ and $C_Q$) and $\kappa$ values. Their similarity suggests that the Sc coordination environments are comparable for both complexes. A single-crystal X-ray diffraction structure of Sc(OAc)$_3$ has been previously reported,$^{43}$ which describes a coordination polymer with bridging acetate groups linking adjacent scandium atoms which reside in pseudo-octahedral coordination environments (Figure 6.2a). The PXRD patterns of Sc(OTf)$_3$ and Sc(OAc)$_3$ (Figure 6.2d and 6.2e) have peaks of similar intensity (though peaks are shifted to slightly lower $2\theta$ values for Sc(OTf)$_3$). Since $2\theta$ is inversely proportional to the $d$-spacings, this difference in $2\theta$ values suggests that the Sc(OTf)$_3$ crystal structure has increased spacings between the diffraction planes of the unit cell compared to Sc(OAc)$_3$, consistent with the triflate ligands being larger in size than the acetate ligands. The combination of the NMR and PXRD data suggest that Sc(OTf)$_3$ is isomorphous with Sc(OAc)$_3$ in the solid-state, and that Sc(OTf)$_3$ has pseudo-octahedral Sc coordination environments which are formed by six oxygen atoms from six separate triflate ligands. The triflate ligands bridge to neighboring Sc sites to form polymeric chains (i.e., a classic coordination polymer structure, Figure 6.2b).

Characterization of the hydrated forms of Sc(III) complexes is important, as many of these complexes are hygroscopic and readily form hydrates. For example, several of the commercially purchased samples of anhydrous Sc(OTf)$_3$ were delivered as the hydrated form [Sc(OTf)$_3$•8H$_2$O]. The solid-state structure of Sc(OTf)$_3$•8H$_2$O has been extensively investigated by Sandstrom et al.$^{50}$ who found that nine water molecules are coordinated to the Sc atom; however, the oxygen atoms of the water molecules which cap the rectangular faces of the trigonal prism possess fractional occupancies of 0.67 (labeled
Figure 6.2. Structures of (a) Sc(OAc)$_3$, (b) Sc(OTf)$_3$ and (c) Sc(OTf)$_3$•8H$_2$O. Hydrogen and fluorine atoms have been omitted for clarity from the structures of Sc(OAc)$_3$ and Sc(OTf)$_3$. Experimental (black trace) powder X-ray diffraction patterns of (d) Sc(OAc)$_3$, (e) Sc(OTf)$_3$ and (f) Sc(OTf)$_3$•8H$_2$O. Powder X-ray diffraction patterns calculated (red trace) from the corresponding single crystal X-ray diffraction structures are shown for Sc(OAc)$_3$ and Sc(OTf)$_3$•8H$_2$O. Single crystal XRD structures of Sc(OAc)$_3$ and Sc(OTf)$_3$•8H$_2$O have been previously published [references 43 and 50]. The oxygen atoms labelled OC possess fractionaly occupancies of 0.67 in the single crystal XRD structure of Sc(OTf)$_3$•8H$_2$O, leading to eight-coordinate Sc. There is no crystal structure of Sc(OTf)$_3$ available. The model of Sc(OTf)$_3$ presented herein, is based upon our $^{45}$Sc SSNMR spectra and the powder X-ray diffraction patterns.

$^{45}$Sc SSNMR spectra of the crystalline complex Sc(OTf)$_3$•8H$_2$O (Figure 6.1e and 6.1f). The $^{45}$Sc SSNMR spectra of Sc(OTf)$_3$•8H$_2$O reveal that the $^{45}$Sc EFG and CS tensor parameters are similar to those of Sc(OTf)$_3$ and Sc(OAc)$_3$, with the exception of $\delta_{\text{iso}}$, which is +30 ppm more than that observed for Sc(OTf)$_3$. Of greater import, the $^{45}$Sc
SSNMR spectra of Sc(OTf)$_3$•$8\text{H}_2\text{O}$ are almost identical in appearance to those of ME Sc(OTf)$_3$ (vide infra). The CS and EFG tensor parameters of Sc(OTf)$_3$•$8\text{H}_2\text{O}$ were confirmed by acquiring static 90°-90° echo $^{45}\text{Sc}$ SSNMR spectra at 9.4 T and 11.7 T (Figure E1).

During the course of this work, we also identified a new hydrated phase of Sc(OTf)$_3$, which we refer to as Sc(OTf)$_3$•$x\text{H}_2\text{O}$. Sc(OTf)$_3$•$x\text{H}_2\text{O}$ possesses a PXRD pattern which is distinct from that of Sc(OTf)$_3$•$8\text{H}_2\text{O}$ (Figure E2). Further PXRD experiments were performed to identify the order in which the hydrated phases of Sc(OTf)$_3$ are formed. A sample of anhydrous Sc(OTf)$_3$ was packed into a sealed glass capillary and a PXRD pattern was acquired. The top of the capillary was then broken open so that the sample would be exposed to atmospheric moisture. A PXRD pattern was then periodically acquired. After ca. 19 hours, the PXRD patterns show complete conversion of Sc(OTf)$_3$ to the Sc(OTf)$_3$•$x\text{H}_2\text{O}$ phase, and after ca. 29 hours, the PXRD pattern is identical to that of the Sc(OTf)$_3$•$8\text{H}_2\text{O}$ phase (Figure E2). From these PXRD experiments it is clear that the anhydrous Sc(OTf)$_3$ readily absorbs water and is first converted into the Sc(OTf)$_3$•$x\text{H}_2\text{O}$ phase, followed by adsorption of additional water to form the previously characterized Sc(OTf)$_3$•$8\text{H}_2\text{O}$ phase. The Sc(OTf)$_3$•$x\text{H}_2\text{O}$ and Sc(OTf)$_3$•$8\text{H}_2\text{O}$ phases possess identical MAS and static $^{45}\text{Sc}$ SSNMR spectra (Figure E2b), suggesting that both phases possess very similar eight-coordinate scandium environments. MAS $^1\text{H}$ SSNMR spectra of the two phases are distinct (Figure E2c). The MAS $^1\text{H}$ SSNMR spectra of Sc(OTf)$_3$•$x\text{H}_2\text{O}$ are much broader than those of Sc(OTf)$_3$•$8\text{H}_2\text{O}$, suggesting that the $^1\text{H}$ nuclei of the water molecules are less mobile in the former. Further investigation of the Sc(OTf)$_3$•$x\text{H}_2\text{O}$ phase is beyond the scope and aim of the current study; however, given the interest in characterizing the hydration state
of Sc(III) ions in aqueous solution and the solid-state,\textsuperscript{51-55} and the role hydrated Sc(III) ions play in aqueous phase catalysis, it merits future study.

![Figure 6.3](image-url)

**Figure 6.3.** MAS and static \textsuperscript{45}Sc SSNMR spectra of Sc(OTf)\textsubscript{3}•8H\textsubscript{2}O and the commercial sample of ME Sc(OTf)\textsubscript{3} acquired at 9.4 T. (a) MAS spectrum of Sc(OTf)\textsubscript{3}•8H\textsubscript{2}O at a sample spinning speed of \(\nu_{\text{rot}} = 8.0\) kHz and (b) static spectra with and (c) without \textsuperscript{1}H decoupling. (d) MAS spectrum of ME Sc(OTf)\textsubscript{3} at \(\nu_{\text{rot}} = 12.0\) kHz and (e) static spectra with and (f) without \textsuperscript{1}H decoupling. All static spectra were acquired with a DFS 90°-180° echo pulse sequence.

\textsuperscript{45}Sc SSNMR Spectra of Microencapsulated (ME) Sc(OTf)\textsubscript{3}. We previously acquired \textsuperscript{45}Sc SSNMR spectra of ME Sc(OTf)\textsubscript{3} which revealed a distinct \textsuperscript{45}Sc isotropic chemical shift of \(\delta_{\text{iso}} = 1.8\) ppm and a moderate decrease in \(C_Q\) in comparison to that of Sc(OTf)\textsubscript{3}.\textsuperscript{42} Our new data reveal that the MAS and static \textsuperscript{45}Sc SSNMR spectra of ME Sc(OTf)\textsubscript{3} are identical to those of Sc(OTf)\textsubscript{3}•8H\textsubscript{2}O (Figure 6.3), as mentioned above.

There is a large reduction in the signal to noise of \textsuperscript{45}Sc SSNMR spectra of ME Sc(OTf)\textsubscript{3} in comparison to Sc(OTf)\textsubscript{3}•8H\textsubscript{2}O, consistent with the reduced Sc content of the former (ca. 1 \% Sc by mass, \textit{vide infra}). When \textsuperscript{1}H decoupling is not applied during the
acquisition of the static $^{45}$Sc SSNMR spectra, significant broadening of the static $^{45}$Sc
central transition powder patterns is observed for both Sc(OTf)$_3$$\cdot$8H$_2$O and ME Sc(OTf)$_3$
(Figure 6.3c, 6.3f). In the case of crystalline Sc(OTf)$_3$$\cdot$8H$_2$O, this indicates the presence
of relatively large $^1$H-$^{45}$Sc dipolar couplings, which arise from the close spatial proximity
of the $^{45}$Sc nucleus and the $^1$H nuclei of the coordinated water molecules (Sc-H distances
of ca. 2.5 to 3.0 Å). All of this data suggests that Sc(OTf)$_3$ is hydrated during the
microencapsulation process and exists as domains of Sc(OTf)$_3$$\cdot$8H$_2$O within the polymer,
and not as Sc(OTf)$_3$ as previously suggested (though it is possible that the broadening
under conditions of no $^1$H decoupling also arises from $^1$H nuclei in the surrounding PS,
for more discussion vide infra).

One initially puzzling aspect of these data was the origin of the hydrating water
molecules in the ME Sc(OTf)$_3$ samples. The commercial sample of ME Sc(OTf)$_3$ arrived
packed under an argon atmosphere, suggesting that it was prepared under inert
conditions; however, we are not absolutely certain of this (the manufacturer would not
comment) and cannot comment on the origin of the water of hydration for this sample.
Further, Kobayashi’s synthetic procedures for ME Sc(OTf)$_3$ do not call for inert
atmosphere synthetic techniques, suggesting that water may be absorbed during
preparation of the ME systems.$^{22}$ For all of these reasons, we undertook synthesis of our
own samples of ME Sc(OTf)$_3$, and characterized them with further SSNMR and PXRD
experiments, in order to confirm the nature of the hydrated Sc$^{3+}$ environments and posit a
source for the hydrating water molecules.

MAS and static $^{45}$Sc SSNMR spectra for samples of ME Sc(OTf)$_3$ prepared under
a variety of conditions are shown in Figure 6.4 (all syntheses employed dried solvents).
The variations in the synthetic procedure include microencapsulating Sc(OTf)$_3$$\cdot$8H$_2$O
under an inert atmosphere (ME-1), and microencapsulation of Sc(OTf)₃ under an ambient atmosphere (ME-2) and an inert atmosphere (ME-3). It is clear that regardless of the conditions employed for the synthesis of the ME samples, ⁴⁵Sc SSNMR spectra similar in appearance to those of Sc(OTf)₃•8H₂O and the commercial sample of ME Sc(OTf)₃ are obtained, excepting the spectra of ME-3 (*vide infra*).

**Figure 6.4.** MAS (left) and static (right) ⁴⁵Sc SSNMR spectra of Sc(OTf)₃•8H₂O and samples of ME Sc(OTf)₃ prepared with various synthetic procedures. All spectra were acquired at 9.4 T. Spectra of (a) Sc(OTf)₃•8H₂O, (b) ME Sc(OTf)₃ prepared by microencapsulating Sc(OTf)₃•8H₂O in PS under an inert atmosphere (ME-1), (c) ME Sc(OTf)₃ prepared under ambient atmosphere (ME-2), (d) ME Sc(OTf)₃ prepared under inert conditions (ME-3), and (e) ME Sc(OTf)₃ prepared with fully deuterated PS (ME ScOTf₃-d₈) under ambient conditions. All static spectra were acquired with a DFS 90°-90° echo sequence and ¹H decoupling (except where noted) and all MAS spectra were acquired with a DFS 90°-180° echo sequence. Static ⁴⁵Sc SSNMR spectra of Sc(OTf)₃•8H₂O and ME Sc(OTf)₃-d₈ acquired without ¹H decoupling are also shown.
Table 6.2. Estimates of Sc Loading Levels of ME Sc(OTf)₃ Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number of Scans [NS]</th>
<th>Integrated Intensity [II]</th>
<th>II/NS</th>
<th>mₜot (mg)</th>
<th>mₜot (mg)</th>
<th>Sc Mass %d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(OTf)₃•8H₂O</td>
<td>64</td>
<td>271</td>
<td>4.234</td>
<td>83</td>
<td>5.87e</td>
<td>7.07e</td>
</tr>
<tr>
<td>ME-1</td>
<td>3264</td>
<td>516</td>
<td>0.161</td>
<td>46</td>
<td>0.22</td>
<td>0.49</td>
</tr>
<tr>
<td>ME-2</td>
<td>752</td>
<td>265</td>
<td>0.352</td>
<td>54</td>
<td>0.49</td>
<td>0.90</td>
</tr>
<tr>
<td>ME-3</td>
<td>3200</td>
<td>719</td>
<td>0.229f</td>
<td>42</td>
<td>0.32</td>
<td>0.27, 0.48f</td>
</tr>
<tr>
<td>ME Sc(OTf)₃-d₈</td>
<td>1376</td>
<td>99</td>
<td>0.072</td>
<td>46</td>
<td>0.10</td>
<td>0.22</td>
</tr>
</tbody>
</table>

a The integral was taken over the central transition of a MAS DFS 90°-180° echo spectrum recorded at νrot = 8.0 kHz for all samples. Identical pulse sequence parameters (e.g., recycle delays, pulse widths, receiver gain) were employed for all samples. All MAS experiments were acquired over the course of two days. b mₜot corresponds to the measured total mass of sample in the rotor. Uncertainties are ±2 mg. c mₜot corresponds to the mass of scandium in the rotor. This was found by the following formula: mₜot = 5.87 × [(II/NS) of Sample]/[(II/NS) of Sc(OTf)₃•8H₂O]. d Sc Mass % = 100 × [mSc]/[mₜot].

We estimate uncertainties levels of ca. ±10% for the experimentally determined Sc Mass %. e mₜot and the Sc mass % of the sample of crystalline Sc(OTf)₃•8H₂O were calculated from the molecular formula and the measured mass of Sc(OTf)₃•8H₂O in the rotor. f This includes integration of the impurity resonance. The first Sc mass % listed corresponds to the resonance attributed to Sc(OTf)₃•8H₂O, while the second Sc mass % listed corresponds to the resonance attributed to anhydrous Sc(OTf)₃. These were determined from the relative integrated intensities of the two resonances in the MAS spectrum.

While the lineshapes of the static and MAS spectra of the ME complexes are similar, the S/N ratios of the spectra are variable. For this reason, we have determined the Sc loading levels of the synthesized samples. The integrated intensity (II) and number of scans (NS) for the MAS ⁴⁵Sc SSNMR spectra of individual samples, acquired under the exact same conditions, are listed in Table 6.2. From these parameters, and knowledge of the total sample mass within the rotor, it is possible to estimate the Sc loading level (Sc mass %) by comparison to the II of MAS ⁴⁵Sc SSNMR spectra of crystalline Sc(OTf)₃•8H₂O. The Sc mass % of the ME Sc(OTf)₃ samples obtained under different synthetic conditions ranges from 0.22 % (ME Sc(OTf)₃-d₈) to 0.90 % (ambient ME Sc(OTf)₃). Unfortunately, we do not have any of the commercial sample of ME Sc(OTf)₃ left over from our previous study in order to determine the Sc mass % by ⁴⁵Sc SSNMR;
however, the manufacturer claims the sample is ca. 13% Sc(OTf)₃ by mass. This corresponds to a Sc mass % of ca. 1.2 %, which is similar to the loading levels determined herein for ME-2.

The $^{45}$Sc SSNMR spectra indicate the presence of domains of Sc(OTf)₃•8H₂O within the polymer; therefore, it is expected that the Sc loading levels will be low if water of hydration is not supplied during the synthesis. This is clearly the case for ME-3, the sample of ME Sc(OTf)₃ prepared under inert conditions with anhydrous Sc(OTf)₃ (Figure 6.4d), which has a loading level much lower than the other samples (ca. 0.27 Sc mass %). In addition, there is a second broad powder pattern visible in the MAS $^{45}$Sc SSNMR spectrum of ME-3, which corresponds closely to the spectral region of anhydrous Sc(OTf)₃. This is consistent with a lack of water which is required to form significant amounts of a hydrate phase. The small amount of Sc(OTf)₃•8H₂O visible in $^{45}$Sc SSNMR spectrum of ME-3 likely results from residual water in the solvents, a minor amount of hydrated Sc(OTf)₃ mixed in with the anhydrous Sc(OTf)₃ and/or from water that entered the reaction flask during the synthetic procedure.

Kobayashi hypothesized that there are bonding interactions between the phenyl groups of PS and the vacant $d$-orbitals of Sc in ME Sc(OTf)₃. In our previous $^{45}$Sc SSNMR study of ME Sc(OTf)₃, we incorrectly attributed the origin of the $^{1}$H-$^{45}$Sc dipolar couplings to spatially proximate $^{1}$H nuclei of PS, and proposed that there were domains of crystalline Sc(OTf)₃ encapsulated in the polymer. In order to further confirm the presence of Sc(OTf)₃•8H₂O, and that the $^{1}$H-$^{45}$Sc dipolar couplings arise from H₂O coordinated to the Sc³⁺ ions, we have prepared a sample of ME Sc(OTf)₃ with a fully deuterated sample of PS (ca. 98 % $^2$H, we refer to this sample as “ME Sc(OTf)₃-$d_8$”). The static $^{45}$Sc SSNMR spectrum of ME Sc(OTf)₃-$d_8$ acquired without $^{1}$H decoupling are
significantly broadened, indicating that there is still a substantial $^1\text{H}$-$^{45}\text{Sc}$ dipolar coupling (Figure 6.4e). This confirms that the $^1\text{H}$-$^{45}\text{Sc}$ dipolar coupling does not arise from proximate $^1\text{H}$ nuclei of PS, but rather, from coupling to the $^1\text{H}$ nuclei of coordinated water molecules. This new data and structural interpretation raise questions about the nature of the interaction between Sc$^{3+}$ and PS in ME samples. It is unlikely that there will be any interactions between the $\pi$-systems of the phenyl groups of PS and Sc $d$-orbitals, as the eight-coordinate hydrated Sc ions are coordinatively saturated. In order to probe for such interactions, we have acquired MAS $^1\text{H}$ and $^1\text{H}$-$^{45}\text{Sc}$ TRAPDOR SSNMR spectra.

**MAS $^1\text{H}$ SSNMR Spectra of ME Sc(OTf)$_3$.** In order to aid in properly assigning the resonances observed in the MAS $^1\text{H}$ SSNMR spectra of ME Sc(OTf)$_3$, spectra were obtained from pristine PS, and PS samples which were treated with the organic solvents that are utilized in the synthesis of ME Sc(OTf)$_3$. The solvent-treated PS samples were obtained by following the procedure for the synthesis of ME Sc(OTf)$_3$, without the addition of any Sc(OTf)$_3$ to the polymer-solvent mixtures. All samples were dried under vacuum at 50°C.

The MAS $^1\text{H}$ SSNMR spectrum of PS at a sample spinning speed ($\nu_{\text{rot}}$) of 13.5 kHz possesses two broad overlapping resonances (Figure 6.5a) attributable to the phenyl protons [$\delta_{\text{iso}}(^1\text{H}) = 6.9$ ppm, FWHH = 2192 Hz] and aliphatic protons [$\delta_{\text{iso}}(^1\text{H}) = 1.4$ ppm, FWHH = 2616 Hz]. It is not possible to fully resolve the aliphatic and aromatic proton resonances in this sample due to the strong $^1\text{H}$-$^1\text{H}$ homonuclear dipolar couplings and the absence of long-range order. The MAS $^1\text{H}$ SSNMR spectrum of PS treated with cyclohexane (Figure 6.5b) contains an additional, comparatively sharp resonance [$\delta_{\text{iso}}(^1\text{H}) = 1.2$ ppm, FWHH = 582 Hz], which obscures the aliphatic proton resonance of PS.
Figure 6.5. MAS $^1$H SSNMR spectra of (a) pure PS (PS), (b) PS recovered from cyclohexane, (c) PS recovered from cyclohexane and hexanes, (d) PS recovered from cyclohexane, hexanes, and acetonitrile, and (e) ME-2. A line-fitting simulation (red trace) is overlaid on the experimental spectrum of ME-2 (black trace). (f) Deconvolution of the individual sites employed in the line-fitting simulation. All spectra were acquired with a Bloch decay pulse sequence (90° pulse-acquire), $v_{\text{rot}} = 13.5$ kHz, 32 scans and a recycle delay of 20 s which is required to obtain full recovery of longitudinal magnetization.

The chemical shift of this resonance correlates well with that of cyclohexane in solution, and is attributed to cyclohexane absorbed within the polymer. The MAS $^1$H SSNMR spectra
of all subsequent solvent treated PS samples and ME Sc(OTf)₃ are similar to that of PS treated with cyclohexane only (compare Figure 6.5b to Figures 6.5c-e). There are no ¹H resonances clearly visible in the methyl region (ca. 0.9 ppm) of the MAS ¹H NMR spectra, suggesting that acetonitrile and hexanes are not substantially adsorbed within the polymer. ¹³C SSNMR spectra of the polymer samples and a ¹H-¹³C dipolar correlation spectrum⁵⁷ of ME-2 confirm this (Figures E3 and E4). The spectrum of PS treated with cyclohexane, hexanes and acetonitrile shows an additional sharp peak at δiso(¹H) = 0.1 ppm (Figure 6.5d), which is attributed to the silicone grease used to seal the joints of the Schlenk flask, which occasionally contaminates some of the samples.⁵⁶

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<th>Line</th>
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<td>582</td>
<td>8</td>
</tr>
<tr>
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<td>2616</td>
<td>33</td>
</tr>
<tr>
<td>Line 3</td>
<td>6.86</td>
<td>2192</td>
<td>100</td>
</tr>
</tbody>
</table>

The MAS ¹H SSNMR spectrum of ME-2 (Figure 6.5e) is similar in appearance to that of the solvent treated PS samples. We have fit the MAS ¹H SSNMR spectra of ME-2 with a line-fitting routine (Figure 6.5). The relative integrated intensities are reported with respect to the aromatic peak which was set to 100 (Table 6.3). From this deconvolution, the ratio of PS ¹H nuclei to cyclohexane ¹H nuclei is ca. 94 : 6, this yields an approximate molar ratio of ca. 96 : 4 (PS monomer unit : cyclohexane). It is not necessary to account for signal from the ¹H nuclei of the Sc(OTf)₃·8H₂O domains, due to the breadth of these resonances and their low loading levels (Figure E5). We note that the deconvolutions do not account for intensity dispersed into the spinning sidebands, which may lead to overestimates of the amount of cyclohexane adsorbed in the polymer. In
summary, the MAS \(^1\)H NMR spectra indicate that a substantial amount of cyclohexane is adsorbed within the polymer during the microencapsulation process.

\(^1\)H-\(^{45}\)Sc TRAPDOR SSNMR Spectra. In order to determine if there is any interaction between PS/cyclohexane and the domains of Sc(OTf)\(_3\)•8H\(_2\)O within ME Sc(OTf)\(_3\), we have performed \(^1\)H-\(^{45}\)Sc TRAPDOR SSNMR experiments. TRAPDOR is a double resonance pulse sequence which has been extensively used to deduce the spatial proximity of spin-1/2 and quadrupolar nuclei (e.g., \(^1\)H and \(^{27}\)Al).\(^{58-60}\) In the course of a TRAPDOR experiment, two Hahn-echo spectra of the spin-1/2 nucleus (\(^1\)H) are acquired.\(^{60}\) The first is acquired in the usual manner (90°-\(\tau_1\)-180°-\(\tau_2\)-acquire) and serves as the control experiment, while the second is acquired with irradiation of the quadrupolar nucleus (\(^{45}\)Sc) during the first dephasing period (\(\tau_1\)). If the quadrupolar and spin-1/2 nuclei are dipolar coupled (spatially proximate), then a reduction in signal is observed in the second echo spectrum. The attenuation of the \(^1\)H NMR signal will increase with larger dipolar couplings, smaller quadrupolar coupling constants, longer echo dephasing periods (\(\tau_1\)), slower spinning speeds (\(\nu_{\text{rot}}\)) and higher power irradiation of the quadrupolar nucleus.\(^{59,60}\)
Figure 6.6. MAS $^1$H-$^{45}$Sc TRAPDOR SSNMR spectra of ME-2. (a) control experiment with no $^{45}$Sc irradiation, (b) dephasing experiment with irradiation of $^{45}$Sc during the $\tau_1$ period and (c) the difference spectrum resulting from subtraction of the dephasing spectrum from the control spectrum (intensity increased by a factor of 4). Linefitting simulations (red trace) are overlayed on the experimental spectra (black trace). (d) A deconvolution of the three sites employed in the linefitting simulations. $\nu_{rot} = 12.5$ kHz and a recycle delay of 20 s were employed. A $\tau_1$ value of 240 $\mu$s was used, corresponding to 3 rotor cycles, and a $^{45}$Sc rf field ($\nu_1$) of 108 kHz was applied during the $\tau_1$ period of the dephasing experiment.
MAS $^1$H-$^{45}$Sc TRAPDOR SSNMR spectra of ME-2 are shown in Figure 6.6. Spectra were acquired with sample spinning speed of 12.5 kHz because this afforded a nice compromise between resolution of the $^1$H spectrum and the amount of dephasing induced by $^{45}$Sc irradiation. In addition, with a $\nu_1$ field of ca. 105 kHz, the experiment is well in the adiabatic regime at this spinning speed (adiabaticity parameter, $\alpha \approx 2.4$), where the dephasing efficiencies are high.\textsuperscript{59} The intensity of the broad patterns in the aromatic region of the $^1$H-$^{45}$Sc TRAPDOR spectra of ME-2 is significantly reduced in comparison to that observed in the Bloch decay spectra of ME-2 (Figure 6.5e). This is because $^1$H nuclei which possess short transverse relaxation time constants [$T_2(^1\text{H})$], such as the PS $^1$H nuclei, will possess low intensity in the TRAPDOR spectrum due to the relatively long $\tau_1$ value employed (240 $\mu$s).

The II of the difference spectrum, obtained by subtracting the $^1$H-$^{45}$Sc TRAPDOR dephasing spectrum from the control spectrum, is equal to approximately 12\% of the II of the control spectrum. This suggests that a substantial fraction of the PS and cyclohexane $^1$H nuclei are dipolar coupled to $^{45}$Sc nuclei, meaning that a substantial fraction of the cyclohexane and PS $^1$H nuclei are spatially proximate to the Sc(OTf)$_3$$^{8}$H$_2$O domains. The relatively low loading level of Sc within the sample (0.90 Sc mass \%) and the amount of dephasing observed in the TRAPDOR experiments suggest that the Sc(OTf)$_3$$^{8}$H$_2$O is uniformly dispersed throughout the polymer. At these low Sc loading levels, the Sc(OTf)$_3$$^{8}$H$_2$O must be present as nm scale domains to create a substantial number of dipolar contacts between $^1$H and $^{45}$Sc nuclei, which lead to significant dephasing in $^1$H-$^{45}$Sc TRAPDOR experiments. These findings are entirely consistent with Kobayashi’s SEM-EDX images of ME Sc(OTf)$_3$, which show that Sc is
homogeneously dispersed over the polymer surface in sub-µm size domains.\(^{22}\) ¹H-⁴⁵Sc TRAPDOR NMR spectra of ME Sc(OTf)₃-\(d₈\) were also acquired since this sample possesses relatively narrow \(^1\)H spectra due to isotopic dilution of the \(^1\)H nuclei (Figure E6). These spectra show a signal decrease in \(\eta\) of ca. 9.7 % when \(^{45}\)Sc irradiation is applied, consistent with the decreased Sc content of this sample. In the difference spectrum, it appears as if the degree of dephasing is unequal for the aromatic resonances; however, the spectra have low S/N because of the low \(^1\)H content and lengthy pulse delays required to obtain complete longitudinal relaxation (20 s).

<table>
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<tr>
<td>(\Delta\eta^a)</td>
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\(\Delta\eta = (\eta_{\text{Control}} - \eta_{\text{Dephasing}})/\eta_{\text{Control}}\)

Deconvolutions of the \(^1\)H-⁴⁵Sc TRAPDOR spectra of ME-2 were performed to see if the individual \(^1\)H resonances experience differing degrees of dephasing. The \(^1\)H spectra could be effectively fit with three individual resonances, for which the \(\delta_{\text{iso}}\), FWHH and \(\eta\) of the individual resonances are listed in Table 6.4. Due to \(T_2\) relaxation, the \(\delta_{\text{iso}}\) and \(\eta\) values obtained from deconvolution of the TRAPDOR spectra are significantly different from those obtained from the Bloch decay spectra. From examination of the \(\eta\) values for the control and dephasing experiments, it appears that the signal intensity of the \(^1\)H resonances which correspond to cyclohexane and the PS phenyl groups undergo the greatest degree of dephasing (signal reduction of ca. 13%), while, the resonance which
corresponds to the aliphatic PS backbone undergoes a lesser degree of dephasing (signal reduction of ca. 9%). This would suggest that the cyclohexane molecules and the phenyl groups of PS make the closest contacts with the Sc(OTf)₃•8H₂O domains; however, given the poor resolution of these experiments and the error inherent to the line fitting routines, these results are not conclusive.

Additional ¹⁹F and ¹³C SSNMR Experiments. Several ²H, ¹³C and ¹⁹F SSNMR experiments were performed on ME Sc(OTf)₃; however, these experiments provided little new information on the molecular structure of the complex (Figures E7 and E8), but are consistent with our hypotheses regarding the molecular structure of ME Sc(OTf)₃. We present a brief discussion of these results in the appendix for the interested reader.

Powder X-ray Diffraction. The static and MAS ⁴⁵Sc SSNMR spectra of ME Sc(OTf)₃ possess sharp spectral features, which are indicative of ordered, crystalline domains of Sc(OTf)₃•8H₂O. PXRD experiments were conducted on ME-1 and ME-2 in order to confirm the presence of crystalline domains within the polymer (Figure 6.7). The PXRD pattern of the two different ME Sc(OTf)₃ samples possess sharp peaks overlaid on a broad underlying peak. The intensity and position of the peaks sharp peaks observed in the PXRD pattern of ME-1 and ME-2 closely match those of the crystalline hydrate phases, Sc(OTf)₃•8H₂O and Sc(OTf)₃•xH₂O, respectively. The shape and position of the broad underlying peak observed in the PXRD pattern of both ME Sc(OTf)₃ samples is similar to that observed in the PXRD pattern of solvent-treated PS (Figure 6.7f). The PXRD patterns of both ME Sc(OTf)₃ samples also indicates the absence of any anhydrous Sc(OTf)₃. In summary, the PXRD experiments are consistent with the incorporation of Sc(OTf)₃ as nanocrystalline domains of Sc(OTf)₃•8H₂O/Sc(OTf)₃•xH₂O in ME Sc(OTf)₃,
the degree of which is highly dependent upon the exposure to atmospheric moisture, water, etc. (*vide infra*).

**Figure 6.7.** Experimental PXRD patterns obtained from (a) anhydrous Sc(OTf)$_3$, (b) Sc(OTf)$_3$•8H$_2$O, (c) Sc(OTf)$_3$•xH$_2$O, (d) ME-1, (e) ME-2, and (f) solvent-treated PS.

*Exposure of ME Sc(OTf)$_3$ to Ambient Moisture.* When ME Sc(OTf)$_3$ is employed as a catalyst, it is anticipated that it will be exposed to water contained in the organic solvents employed as the reaction media, as well as atmospheric moisture. Hydrated ME Sc(OTf)$_3$ may be more representative of the structure of the working catalyst. While all of the samples of ME Sc(OTf)$_3$ were handled under an inert atmosphere, it is worthwhile
to examine the influence of moisture adsorption on the catalyst structure. A sample of ME-2 packed into a rotor was exposed to ambient atmosphere by removing the air-tight cap at the top side of the pencil-style rotor. The sample was then left on the bench top for ca. 20 hours, and the sample was then capped and SSNMR spectra were acquired.

Figure 6.8. MAS $^1$H SSNMR spectra (left) and static $^{45}$Sc SSNMR 90°-180° echo spectra (right) of a sample of ambient ME-2 which has been exposed to air. The sample was exposed to air for total times of (a) 0 hours, (b) 20 hours, (c) 2 days and (d) 15 days. For exposure times of 20 hours and 2 days the static $^{45}$Sc SSNMR spectra are shown with and without $^1$H decoupling. For the exposure time of 15 days, the static $^{45}$Sc SSNMR spectra were acquired with selective and non-selective 90° and 180° $^{45}$Sc pulses (and no $^1$H decoupling).
$^1$H and $^{45}$Sc SSNMR spectra of this air-exposed sample of ME-2 are shown in Figure 6.8. After 20 hours of air exposure, an additional relatively sharp resonance is visible in the aromatic region of the MAS $^1$H SSNMR spectrum ($\delta_{\text{iso}} = 6.3$ ppm), indicating that ME-2 has absorbed water from the atmosphere. The observed $\delta_{\text{iso}}$ value indicates that the water is associated with the Sc(OTf)$_3$•8H$_2$O domains, and the narrow width of the resonance intimates that the water possesses significant rotational/translational freedom. The $^{45}$Sc SSNMR spectra are similar to those of ME-2 handled under an inert atmosphere (compare Figure 6.8a with 6.8b). $^1$H-$^{45}$Sc TRAPDOR SSNMR spectra indicate that there is still significant dephasing in the $^{45}$Sc irradiation spectrum (Figure E9), suggesting that the Sc(OTf)$_3$•8H$_2$O domains are still intact and dispersed throughout the polymer.

After two days of total air exposure time the $^1$H resonance corresponding to water is further increased in intensity. The static $^{45}$Sc SSNMR spectra of ME-2 begin to show differences from those of the pristine ME-2. The static powder patterns are similar, which indicates that the eight-coordinate Sc environments are retained; however, the spectrum of ME-2-acquired without decoupling displays a sharp central feature, which may be indicative of self-decoupling of the $^1$H nuclei. The self-decoupling may occur due to rapid exchange of water molecules between the first and second scandium coordination spheres.

Finally, after fifteen days of total exposure time, the MAS $^1$H SSNMR spectra indicate that substantially more water has been absorbed. The water resonance is very narrow and intense, and observed at $\delta_{\text{iso}} = 5.8$ ppm, which is closer to that of liquid water (ca. 4.8 ppm). The static $^{45}$Sc SSNMR spectra show a single relatively narrow resonance
(FWHH of ca. 1 kHz) with $\delta_{\text{iso}} = -6.3$ ppm. The static $^{45}\text{Sc}$ SSNMR spectra were acquired with central transition selective and non-selective 90° pulses, and it is clear that the non-selective 90° pulses give maximum signal. This indicates that the Sc$^{3+}$ ions have entered a solution-like phase where the quadrupolar interaction is averaged to zero.

Further, $^1\text{H}^{-^{45}\text{Sc}}$ TRAPDOR SSNMR spectra show essentially no dephasing when $^{45}\text{Sc}$ irradiation is applied, because the mobility of the Sc(III) ions efficiently averages $^1\text{H}^{-^{45}\text{Sc}}$ dipolar couplings (Figure E9).

PXRD experiments were also performed on a sample of hydrated ME Sc(OTf)$_3$. A sample of ME-2 was packed into a flame sealed glass capillary under an inert atmosphere. The capillary was then mounted in the diffractometer, and the top of the capillary was broken open in order to expose the sample to atmospheric moisture. PXRD patterns were acquired periodically (Figure 6.9). Initially, there are crystalline domains of Sc(OTf)$_3\cdot x\text{H}_2\text{O}$ within the polymer as indicated by the relatively intense diffraction patterns. After ca. 24 minutes of air exposure, conversion to crystalline domains of Sc(OTf)$_3\cdot 8\text{H}_2\text{O}$ occurs. As further moisture is absorbed, the intensities of the diffraction peaks decrease until the pattern matches that of solvent-treated PS (at ca. 13.5 hours), which indicates that the crystalline domains have been converted into amorphous domains. We note that the timings of the structural differences observed by PXRD and SSNMR will be different, since the sample was tightly packed into the rotor for SSNMR experiments, while in the PXRD capillary, the flakes of ME-2 are loosely packed, permitting easy diffusion of air through the PXRD sample and resulting in faster absorption of moisture.
Figure 6.9. PXRD patterns acquired from a sample of ambient ME Sc(OTf)₃ which was exposed to air. The total exposure time is listed to the right of each PXRD pattern.
Figure 6.10. Proposed structural model of ME Sc(OTf)₃. This model is highly schematized and qualitative. Sc(OTf)₃ is hydrated when it undergoes microencapsulation in PS. This results in the formation of nanocrystalline domains of Sc(OTf)₃·8H₂O in the polymer. The PS groups and cyclohexane molecules are spatially proximate to the surface of the nanocrystalline Sc(OTf)₃·8H₂O domains. The cyclohexane molecules undergo translational/rotational motions.

6.4 Conclusions

⁴⁵Sc SSNMR spectra of the pure crystalline forms of Sc(OTf)₃ and Sc(OTf)₃·8H₂O have been acquired, and a new hydrated phase of Sc(OTf)₃, Sc(OTf)₃·ₓH₂O, has been identified. ME Sc(OTf)₃ has been investigated by multinuclear SSNMR and PXRD experiments, and structural model of the ME Sc(OTf)₃ system is now proposed (Figure 6.10). ⁴⁵Sc SSNMR spectra indicate that Sc(OTf)₃ is incorporated into PS as domains of Sc(OTf)₃·8H₂O and/or Sc(OTf)₃·ₓH₂O, the relative amounts of which depend upon the level of hydration. There is no evidence of a direct interaction between the phenyl groups of PS and the scandium centres; rather, it is most likely that Sc(OTf)₃·8H₂O is stabilized in the PS matrix by physisorption (i.e., physical
envelopment). It is possible, though not confirmed directly through our work, that hydrogen bonding interactions between water molecules at the surface of the Sc(OTf)$_3$•8H$_2$O/Sc(OTf)$_3$•xH$_2$O domains and the phenyl groups are key to stabilizing the structure of ME Sc(OTf)$_3$, since contact angle measurements on oriented PS films and AFM studies of PS surfaces indicate that phenyl group surfaces are hydrophilic.\textsuperscript{61,62} $^1$H and $^{13}$C SSNMR spectra show that a substantial amount of cyclohexane is incorporated into ME Sc(OTf)$_3$, but other solvents used in preparation of the ME samples are not present in any significant amounts. \textsuperscript{1}H-$^{45}$Sc TRAPDOR experiments indicate that scandium is dispersed throughout the polymer, consistent with SEM-EDX images previously acquired by Kobayashi. PXRD experiments reveal that the diffraction patterns of ME Sc(OTf)$_3$ are similar to those of the crystalline complexes, Sc(OTf)$_3$•8H$_2$O and Sc(OTf)$_3$•xH$_2$O, and in combination with the reduced $^1$H signal intensities in the TRAPDOR experiments, suggest that there are nanocrystalline domains present. Hence, the structure of this system is best described as a composite material, where nanocrystalline domains of inorganic material are dispersed throughout the polymer.\textsuperscript{63-68}

The newly proposed structural model for ME Sc(OTf)$_3$ is clearly different from previous models, and may provide insight into the structure and chemistry of the numerous heterogeneous scandium catalysts which have been prepared utilizing a number of different schemes.\textsuperscript{19,69-71} The multinuclear SSNMR and PXRD experiments described herein are clearly applicable for the characterization of such systems, and should aid in the future design of new scandium based catalysts, as well a variety of ME catalysts involving different types of metals.\textsuperscript{72-78}
6.5 Bibliography

(44) Bodart, P. R.; Amoueux, J. P.; Dumazy, Y.; Lefort, R., 2000, 98, (19), 1545-1551.


Chapter 7: Probing Lead(II) Bonding Environments in 4-Substituted Pyridine Adducts of (2,6-Me₂C₆H₃S)₂Pb by ²⁰⁷Pb Solid-state NMR

7.1 Introduction

Lead(II) ions are found in a range of materials with interesting optical and electronic properties.¹⁻⁶ For example, lead(II) sulfide (PbS) complexes have many interesting applications in optoelectronic devices as narrow band-gap semi-conducting materials.⁷⁻¹² For this reason, the production of PbS nanocrystals has been extensively studied, and achieved via a variety of synthetic routes.¹³⁻¹⁹ Recently it has been demonstrated that lead(II) thiolates can serve as precursors for the production of thiolate-capped clusters and nanocrystals.²⁰⁻²³ Due to the well known toxicity of lead(II) complexes, there is also much interest in the synthesis of simple thiolate compounds which can be used to model the binding of lead(II) by the cysteine residues of biomolecules.²⁴⁻²⁷ Lead(II) ions may also serve as versatile building blocks for supramolecular frameworks due to the varied coordination geometries observed at the lead(II) centers, with known coordination numbers ranging from three to twelve.¹, ², ⁵, ²⁸⁻⁳⁰ Additionally, lead(II) complexes frequently possess stereochemically active electron lone pairs.³⁰ By altering the ligands bound to the lead(II) center it is possible to alter the activity of the electron lone pair, affording the possibility of precisely controlling the symmetry and bonding environment of the lead(II) site.¹, ², ⁵, ⁶, ²⁸, ²⁹ Therefore, lead(II) centers can act as linkers capable of assuming a number of different geometries and binding modes, which in turn, allows for a variety of structural motifs to be constructed. In this regard, lead(II) thiolates constitute a class of complexes which are known to form
polymeric structures in the solid-state as a result of intermolecular Pb-S contacts. Many of these polymeric lead(II) complexes are insoluble, and even if they can be dissolved, their polymeric structures do not persist in solution. Therefore, the characterization of lead(II) thiolate complexes in the solid state is of great importance.

While refined single-crystal X-ray diffraction is used to accurately determine molecular structure, solid-state $^{207}$Pb NMR spectra can provide information on the electronic environment of the metal atom and the nature of bonding with surrounding ligands. $^{207}$Pb ($I = 1/2$) is the only NMR-active isotope of lead and has a receptivity of 11.8 relative to $^{13}$C. The lead chemical shift range is very large, with a difference of approximately 17000 ppm between lead metal and plumbocene. This large chemical shift range is a direct result of the extremely polarizable lead valence orbitals, which give rise to the large lead chemical shielding anisotropies (CSAs) observed in most solid-state $^{207}$Pb NMR spectra (with the exception of complexes of high spherical or Platonic symmetry). Lead chemical shifts are extremely sensitive probes of atomic/molecular environment and subtle molecular changes induced by chemical (e.g., reactions, solvent coordination) and physical (e.g., temperature, stress) changes.

Once relationships have been established between well-characterized molecular structures and lead chemical shift (CS) tensors, then solid-state NMR can be applied for structural determination of complexes for which single crystal data are not readily available. Given the general insolubility of homoleptic lead(II) thiolate complexes, the lability of their coordination complexes, and the well-known sensitivity of lead CS tensors to subtle changes in molecular structure, solid-state $^{207}$Pb NMR should serve as a formidable probe of molecular structure in these systems. To this end, solid-
state $^{207}$Pb NMR experiments, in tandem with density functional theory (DFT) calculations of CS tensors, are used to measure and theoretically model lead CS tensors for several lead(II) thiolate pyridine adducts (Scheme 1). All of these complexes possess voids in the lead coordination spheres, indicative of the presence of stereochemically active lone pairs. Relationships between the observed $^{207}$Pb CS tensor and structure, symmetry and bonding are constructed.

![Chemical structures](image)

**Scheme 7.1.** Schematic drawings of lead thiolate structures, including (2,6-Me$_2$C$_6$H$_3$S)$_2$Pb(py)$_2$ (1), [(2,6-Me$_2$C$_6$H$_3$S)$_2$Pb(pyOMe)]$_2$ (2) and (2,6-Me$_2$C$_6$H$_3$S)$_2$Pb(pyNMe$_2$) (3) (py = pyridine; pyOMe = 4-methoxypyridine; pyNMe$_2$ = 4-dimethylaminopyridine). Additional views of the structures are shown in Figure 7.3.

### 7.2 Experimental

**General Details.** The characterization, synthesis and single crystal X-ray diffraction analysis of all complexes is described in the original publication.

**Solid-state NMR Spectroscopy.** Solid-state $^{207}$Pb NMR spectra were acquired on a Varian Infinity Plus spectrometer with an Oxford 9.4 T wide-bore magnet [$v_0(^1H) = 399.73$ MHz, $v_0(^{207}Pb) = 83.63$ MHz, $v_0(^{13}C) = 100.51$]. Lead chemical shifts were referenced to Me$_4$Pb ($\delta_{iso} = 0.0$ ppm) by setting the isotropic shift of a secondary standard
of 0.5 M Pb(NO₃)₂(aq) to -2941.0 ppm. Carbon chemical shifts were referenced to tetramethylsilane (δ.iso = 0.0 ppm) by using the high-frequency peak of adamantane as a secondary reference (δ.iso = 38.56 ppm).

All solid-state NMR experiments were performed on a double resonance 4 mm HX Varian/Chemagnetics probe. ¹H-²⁰⁷Pb variable-amplitude cross-polarization/MAS (VACP/MAS) and cross-polarization/Carr-Purcell-Meiboom-Gill (CP/CPMG) experiments were optimized on a sample of lead acetate hydrate [Pb(OAc)₂•xH₂O]. All ¹H-²⁰⁷Pb CP experiments employed 2.0 µs π/2 proton pulses and Hartman-Hahn matching fields of ca. 55 kHz. Individual CP/CPMG sub-spectra were co-added to form the total spectrum (Figure F1). Further details on CP/CPMG experiments are given in the Appendix F (Table F1). Static CP/CPMG ²⁰⁷Pb NMR patterns were simulated using the WSolids program. ²⁰⁷Pb MAS spectra were simulated with the SIMPSON program. The TPPM decoupling scheme was employed in all experiments.

**DFT Calculations.** Theoretical calculations were performed with the EPR and NMR module of the Amsterdam Density Functional (ADF) program suite. The VWN-BP functional was used for electron exchange and correlation for all calculations. Relativistic effects (including spin-orbit) were taken into account with the zeroth-order regular approximation (ZORA). In the current version of ADF, analysis of the contributions to magnetic shielding (MS) from the mixing of molecular orbitals can only be performed for non-relativistic calculations. All-electron gauge including atomic orbitals (GIAO) triple-ζ singly polarized (TZP) and triple-ζ doubly-polarized (TZ2P) basis sets were employed on all atoms for the non-relativistic calculations and ZORA calculations, respectively. However, the largest basis set
available for lead for the non-relativistic calculations was a frozen-core basis set, where the core was extended to the 4d shell for lead (Pb.4d). All calculations were performed using atomic coordinates from single crystal X-ray structures, with H atoms set to idealized positions (e.g., ideal C-H bond lengths and H-C-H angles). All calculations employed a discrete molecular unit, except for those upon 2 for which a dimer was used. Calculations on Me₄Pb (²⁰⁷Pb chemical shift standard) were performed upon atomic coordinates from the previously published low temperature (150 K) crystal structure.⁶⁷

**X-ray Diffraction Experiments.** Powder X-ray diffraction patterns were collected using a Bruker AXS HI-STAR system using a General Area Detector Diffractions System. Compounds 1, 2 and 3 were finely ground, packed into 1.0 mm glass capillary tubes and flame sealed. The X-ray source employed was Cu Kα radiation (1.540598 Å) with an area detector using a 2θ range between 4.0° to 65.0°. Powder X-ray diffraction patterns were simulated with the PowderCell software package.⁶⁸

### 7.3 Results and discussion

**Solid-state ²⁰⁷Pb NMR spectroscopy.** In this section we discuss the acquisition and interpretation of solid-state ²⁰⁷Pb NMR spectra of complexes 1, 2, and 3, in order to examine the electronic structure, bonding environment at the lead centre, and presence and/or influence of the lone pair of electrons on the lead CSA. In many cases, it has been observed that direct detection of ²⁰⁷Pb NMR spectra in solids is challenging, since the ²⁰⁷Pb longitudinal relaxation times ($T_1$) may be very long.⁴², ⁶⁹-⁷¹ In order to circumvent the long ²⁰⁷Pb $T_1$ constants, ¹H–²⁰⁷Pb variable-amplitude cross-polarization (VACP/MAS) NMR experiments⁴⁴, ⁴⁵ were performed on compounds 1, 2 and 3 (Figure 7.1). Normally,
only two spinning speeds are required to differentiate peaks due to spinning sidebands from that of the isotropic chemical shift in the MAS NMR spectra of a spin-1/2 nucleus. However, overlap of spinning sidebands due to large spans ($\Omega$, defined in Table 7.1) requires that the spectrum be acquired at three different spinning speeds (expanded views of spectra given in Figure F2). The isotropic shifts in this series of complexes are similar to that reported from solution $^{207}$Pb NMR experiments on [(PhS)$_3$Pb][Ph$_4$As], $\delta_{\text{iso}} = 2868$ ppm,$^{72}$ which has an $S_3$ lead coordination environment, but are clearly distinct from the $S_2N$ environment in [2-methyl-1-\{methyl(2-pyridin-2-ylethyl)amino\}propane-2-thiolatolead-Pb][ClO$_4$] for which $\delta_{\text{iso}} = 2358$ ppm.$^{25}$

A temperature-dependent chemical shift is observed for compounds 1 and 2 (Figure F2 and Table F2). This behavior is well known, and was previously observed in the $^{207}$Pb NMR spectra of Pb(NO$_3$)$_2$,\textsuperscript{73-77} among other lead-containing systems. Minor impurity peaks are visible in the VACP/MAS NMR spectra and are attributed to hydration of the samples since the MAS spectra were acquired after the static NMR and powder XRD experiments (Figure F3). Relatively accurate values for $\delta_{\text{iso}}$ (Table 7.1) can be obtained from the VACP/MAS spectra; however, the large number of spinning sidebands and the poor signal to noise of the spectra makes extraction of the CS tensor parameters by Herzfeld-Berger analysis difficult and potentially inaccurate.

With this in mind, static (i.e., stationary sample) $^1$H-$^{207}$Pb cross-polarization/Carr-Purcell-Meiboom-Gill (CP/CPMG) experiments were performed.$^{46, 47, 78-80}$ Due to the large breadth of the lead powder patterns, the entire spectrum must be acquired in a piecewise frequency offset fashion (Figure F1), which requires both constant resetting of
Figure 7.1. $^1$H–$^{207}$Pb VACP/MAS NMR spectra of 1, 2 and 3 each acquired at three spinning speeds ($\nu_{\text{rot}}$). Dashed lines indicate $\delta_{\text{iso}}$. A recycle delay of 10 s was used for all spectra and 2004 to 8428 scans were acquired. The relative vertical scaling of the spectra is given on the left.
Table 7.1. Experimental $^{207}$Pb Chemical Shift Parameters.

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<th>$\delta_{33}$ (ppm)</th>
<th>$\delta_{\text{iso}}$ (ppm)$^b$</th>
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</table>

$^a$The chemical shift tensor is described by three principal components ordered such that $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. Shift values for the individual components are calculated from the values of $\Omega$, $\kappa$ and $\delta_{\text{iso}}$. $^b\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$. $\delta_{\text{iso}}$ is given relative to (CH$_3$)$_4$Pb [$\delta_{\text{iso}}$ ($^{207}$Pb) = 0.0 ppm]. All values are taken from VACP/MAS NMR spectra acquired at a spinning speed of 5000 Hz. $^c\Omega = \delta_{11} - \delta_{33}$. Based upon simulations of the static CP/CPMG spectra. $^d\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$, -1.0 $\leq \kappa \leq$ +1.0. Based upon simulations of the static CP/CPMG spectra. $^e$The uncertainty in the last digit of each value is denoted in brackets. Error bounds in the principal CS tensor components (eg. $\delta_{11}$) are of a similar magnitude to those of $\Omega$.

Transmitter frequency and probe retuning. The appearance of “spikelets” in the frequency domain spectra arise from the Fourier transform of the CPMG echo train (alternatively and completely equivalently, one may co-add the echoes and process the summed spin echo to produce a static pattern).$^{81}$ Acquisition of static CP/CPMG spectra is not hindered by a partial averaging of the $^1$H-$^{207}$Pb dipolar interactions that would occur under MAS conditions; hence, high signal to noise static patterns can be acquired very rapidly with respect to VACP/MAS NMR spectra of the same quality. Another clear advantage of the CP/CPMG experiments over their VACP/MAS counterparts is the overall excitation of the $^{207}$Pb NMR powder patterns. Simulations of the VACP/MAS spectra employing the CS tensor parameters extracted from the CP/CPMG spectra clearly demonstrate that the former are not uniformly excited and are unsuitable candidates for accurate measurement of CS tensor parameters via Herzfeld-Berger methods (Figure F4). This is in contrast to direct excitation and detection of broad $^{207}$Pb NMR powder patterns. For instance, Antzutkin et al. recently measured and simulated $^{207}$Pb MAS NMR spectra.
of lead patterns with spans close to 4000 ppm and breadths of ca. 300 kHz (acquisition times of ca. 24-48 hours).\textsuperscript{82}

**Figure 7.2.** $^1$H-$^{207}$Pb CP/CPMG static NMR spectra (black trace) of compounds 1, 2, and 3. Analytical simulations (solid red trace) are overlaid on the experimental spectra. The CS tensor parameters obtained from the simulations are given in Table 7.1.
Co-addition of the sub-spectra and simulation of the observed patterns (Figure 7.2) yield the lead CS tensor parameters (Table 7.1). The $\delta_{\text{iso}}$ is located at the centre of gravity of the powder pattern. The $\Omega$ and $\kappa$ describe the breadth of anisotropic chemical shifts (i.e., the “size” of the CSA) and the degree of axial symmetry of the CS tensor. Though the CS tensor parameters are distinct, they do not vary widely in this series of complexes. This suggests that the orientations of the CS tensors in the molecular frames are related among the three complexes, and that the general modes of bonding and electronic environments at the lead centres are very similar. However, there are some interesting trends in these parameters which can be correlated to molecular structure and symmetry.

First, all three patterns have extremely large spans. The $\Omega$ values observed for complexes 1 and 3 are several hundred ppm larger than those observed for yellow lead oxide ($\Omega = 3917$ to 3995 ppm) and lead(II) dialkyldithiophosphates ($\Omega = 3840$ ppm), which, to the best of our knowledge, are the largest spans previously reported for lead complexes.\textsuperscript{37, 42, 70, 82} Second, all patterns possess positive skews, denoting $\delta_{33}$ as the distinct component in each case, and implying that it must be oriented in a distinct/unique environment within the molecule. Positive skews have previously been observed in the $^{207}$Pb NMR spectra of the several lead(II) complexes, which are also thought to have an electron lone pair molecular orbital (MO) localized at the Pb centres.\textsuperscript{2, 37, 41, 42, 70} Since it is well known that CS tensor components orient along/near symmetry elements, and by virtue of the fact that the $\delta_{33}$ is the distinct component in each complex, it is very likely that $\delta_{33}$ is oriented along/near the direction of the presumed lone pair of electrons. Finally, despite the similarity of the isotropic shifts of 2 and 3, the spectra of their
respective $S_3N$ and $S_2N$ metal bonding environments are readily distinguished by the
differences in $\Omega$ and $\kappa$ (this is visually apparent in comparing these spectra as well,
Figure 7.2). With this limited set of structural parameters and NMR data, two
observations can be made: (i) decreased Pb-S bond lengths are correlated with larger
spans and (ii) the unique four-coordinate environment of 1 leads to a less axial CS tensor.

**DFT Calculations of Lead MS Tensors.** Ab initio and/or pure DFT computational
methods can be used to calculate the nuclear magnetic shielding (MS) tensor parameters,
their orientations within the molecular frames and contributions from individual MOs.
Ramsey’s theory of MS arbitrarilily decomposes the total MS ($\sigma$) at a nucleus into
diamagnetic and paramagnetic terms, such that $\sigma = \sigma_d + \sigma_p$. The diamagnetic and
paramagnetic terms arise from the circulation of electrons in ground state MOs and
mixing of separate MOs, respectively, both of which are induced by the presence of an
external magnetic field. Ziegler and co-workers have developed a DFT-GIAO formalism
for the calculation of MS which further partitions the paramagnetic terms into
contributions from mixing of occupied MOs ($\sigma_p^{occ-occ}$) and mixing of occupied and virtual
MOs ($\sigma_p^{occ-vir}$), the details of which are neatly summarized elsewhere. Furthermore,
for heavy nuclei ($^{207}$Pb, $^{195}$Pt, etc.), it is often necessary to include the relativistic
contributions to the total MS as described by the spin-orbit coupling term ($\sigma_{so}$) in order to
improve agreement between experiment and theory. 

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Table 7.2. ZORA and Non-relativistic (NR) ADF Calculations of $^{207}$Pb MS and CS Tensor Parameters.

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<th>$\sigma_{22}$ (ppm)</th>
<th>$\sigma_{33}$ (ppm)</th>
<th>$\sigma_{iso}$ (ppm)</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
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$^a$The nuclear magnetic shielding (MS, $\sigma$) tensor is described by three principal components ordered such that $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$ (lowest to highest shielding). The principal chemical shift tensor components ($\delta_{jj}$) are related to the principal magnetic shielding components ($\sigma_{jj}$) by the equation $\delta_{jj} = (\sigma_{iso, ref} - \sigma_{jj})(10^6)/(1 - \sigma_{iso, ref}) \approx \sigma_{iso, ref} - \sigma_{jj}$ where $jj = 11, 22$ or $33$ and $\sigma_{iso, ref}$ refers to the isotropic shielding value of the reference compound ($\sigma_{iso, ref} = \sigma_{iso}(\text{Me}_4\text{Pb})$). $^b$The experimental shift values have been converted to shielding values by subtracting them from the ZORA calculated value of $\sigma_{iso}(\text{Me}_4\text{Pb})$; $\sigma_{jj} = 7531.0 - \delta_{jj}$.

Lead MS parameters from calculations performed with the ADF program suite incorporating ZORA$^{63-65}$ are shown in Table 7.2. In all cases, the ZORA calculations yield values of $\kappa$ which are in good agreement with experimental values. Theoretical
values of $\Omega$ are lower than experimental values in all cases, which arises from consistent underestimation of deshielding along the directions of $\sigma_{11}$ and $\sigma_{22}$. The errors in the calculated $\sigma_{11}$ and $\sigma_{22}$ parameters are unsurprising, given the difficulties associated with accurately calculating the excited electronic states of larger molecules containing Pb atoms. Since the chemical shift range of lead is approximately 17000 ppm, and the spans of the CS tensors are so large, these errors are relatively small (ranging from 15-30%). The calculations also qualitatively predict the relative values of $\delta_{\text{iso}}$ (the $^{207}$Pb nucleus in 1 is predicted to be the most shielded and that in 2 least shielded). While the theoretical tensors are not identical to experimental measurements, they are still extremely useful in understanding the origin of the lead MS in these systems.

Contributions to the principal shielding components of the total shielding tensor have been tabulated for the diamagnetic, paramagnetic and spin-orbit terms for all compounds (Table 7.2). The diamagnetic terms for all compounds are highly isotropic (small $\Omega$ values) and do not contribute to the large shielding anisotropies. The paramagnetic term makes much larger contributions to the isotropic shielding values than the spin-orbit term, but both terms contribute relatively equally to the spans of the CS tensors. Comparison of the ZORA and non-relativistic (NR) calculations make it very clear that the inclusion of relativistic effects for calculations of CS tensors for heavy nuclei is absolutely necessary.

The nature of the CS tensor (i.e. the large span and the positive skews) and its relationship to molecular structure can be rationalized by considering the orientation of the CS tensor in the molecular frame. The lead CS tensor orientations generated from the ZORA calculations are presented in Figure 7.3 for complexes 1, 2 and 3. In all three
systems, the $\sigma_{33}$ component is oriented in the presumed direction of the stereochemically active lone pair and close to the plane of the S-Pb-S bonding arrangement. Conversely, the $\sigma_{11}$ and $\sigma_{22}$ components are not directed along Pb-S or Pb-N bonds, and are oriented as such due to large paramagnetic deshielding contributions arising from mixing of occupied MOs localized on Pb, S and N atoms with an assortment of low-lying virtual MOs.

Figure 7.3. Lead CS tensor orientations for complexes 1, 2 and 3. The tensor orientations have been generated from the ZORA calculations.

Our hypotheses regarding both the large spans and high positive skews and their relation to molecular structure can be confirmed by analyzing the contributions made by individual MOs to the paramagnetic shielding terms. Analyses of the contributions of particular MOs to paramagnetic shielding in simple molecular systems have previously been demonstrated using both the Gaussian software package$^{97-99}$ and ADF software.$^{51,89,100,101}$ The NMR/EPR module of the ADF program suite outputs the paramagnetic shielding contributions arising from mixing of individual occupied-virtual and occupied-occupied MO pairs. However, this analysis is only available for NR calculations in the current implementation of ADF. Despite the fact that the NR calculations show poor
quantitative agreement with experiment, the paramagnetic contributions and CS tensor orientations are very similar to those generated from ZORA calculations (Figure F5). Hence, it is reasonable to examine individual contributions from MO pairs to the paramagnetic terms of the lead CS tensor.

Due to the relatively high local symmetry at the lead atom in complex $1$, we have chosen this as the focus of our discussion of MO contributions to MS (a full MO analysis for all systems is beyond the scope of the current chapter). The contributions from mixing of occupied (occ) and virtual (vir) MOs in complex $1$ are summarized in Table 7.3 (these MOs are depicted in Figures 7.4 and F6) and account for upwards of 90% of the total isotropic shielding contribution from the paramagnetic term. Therefore, occ-occ mixing will not be considered. Due to the enormous number of MO pairs, only those contributing greater than 2% (~77 ppm) of the total isotropic shielding contribution of occ-vir MO mixing (-3865.1 ppm) are listed. In this way, analysis of MO contributions to paramagnetic shielding can be focused upon a select few MOs that are near the HOMO and/or involved in metal-ligand bonding (e.g., MO pairs involving occ MOs from 1 to 120 contribute to only 8.6% of the occ-vir paramagnetic contribution).

Let us consider a specific example to clarify the data in Table 7.3. The mixing of the occ MO 130 (HOMO -3) with virtual orbitals contributes -894.7 ppm to the total paramagnetic shielding ($\sigma_p$) of -4272.2 ppm. Mixing of occ MO 130 with vir MO 138 (denoted as 130-138) accounts for -451.4 ppm of the -894.7 ppm contributed by occ MO 130. The remaining contribution to shielding from occ MO 130 results from its mixing with many other virtual MOs, most notably vir MOs 139 and 144 (an extended data analysis including all occ-vir contributions can be found in the Table F3).
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<th>(\sigma_{\text{iso}}) from occ MO (ppm)</th>
<th>Sum of (\sigma_{\text{iso}}) (ppm)</th>
<th>Major occ-vir Pairs</th>
<th>(\sigma_{\text{iso}}) of MO Pair (ppm)</th>
<th>(\sigma_{11}) (ppm)</th>
<th>(\sigma_{22}) (ppm)</th>
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<td>Total</td>
<td>-1743.0</td>
<td>-2247.4</td>
<td>-1696.8</td>
<td>1284.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a*This column corresponds to the sum of isotropic shieldings of the occ-vir MO pairs that contain the specified occ MO.
Figure 7.4. The occupied and virtual MOs of 1 that make significant contributions to the paramagnetic shielding term. A partial MO diagram indicating the magnetic-dipole allowed transitions between the occupied and virtual orbitals that are pictured is also shown. The MOs are visualized at the 97% electron density level.
The largest contributions to paramagnetic shielding arise from mixing of a variety of occ MOs with vir MOs 138, 139 and 143 (Table 7.3). These virtual MOs are of high lead $p$-orbital character, as demonstrated by the gross populations contributed by individual AOs (Table F4). MO 138 has relatively high Pb $6p_y$ and slight $6s$ characters, but also has significant contributions from C $2p$ orbitals on the neighbouring aromatic rings. MO 139 and MO 143 are comprised of mixtures of large Pb $6p_x$ and $6p_z$ AO contributions. The occupied MOs which mix with these three virtual MOs vary in their relative amounts of Pb, S, N or C AO character. Large deshielding contributions involve occ MOs 130 to 133 (HOMO -3 to HOMO), as well as occ MOs 121, 122, 125 and 126. MO 133 corresponds to the stereochemically active Pb lone pair, whereas MOs 130, 131 and 132 are largely localized on the S atoms. MO 121 describes Pb-N bonding, MO 122 describes S-C $\sigma$-bonding, MO 125 describes Pb-S bonding and S-C $\pi$-bonding, and MO 126 describes S-C $\pi$-bonding and some degree of localized N $2p$ character. Hence, the origin of the lead chemical shielding tensor is relatively complex, and highly dependent upon the characteristics of the Pb lone pair, 3$p$ AOs localized on S atoms, as well as variable types of $\sigma$- and $\pi$-bonding.

Understanding why certain MO pairs make large paramagnetic (de)shielding contributions can be accomplished through relatively simple visualization. MOs which contribute to shielding along the direction of a particular principal component must be relatively close in energy, but also have the appropriate symmetries to interfere or “overlap” with one another when induced to mix by a magnetic field. This type of mixing can be visualized by rotating the appropriate MOs about the axes defining the principal components of the CS tensor. This concept has previously been demonstrated
for several relatively simple systems.$^{51, 98, 99, 101, 102}$ We will use the arbitrary convention of right-handed ninety degree rotations of the virtual MOs about their gauge origin (i.e. contributing AOs are rotated in a right-handed fashion at the nuclear site). Rotations resulting in constructive or destructive overlap of MO lobes generate deshielding and shielding contributions, respectively.$^{99}$ The simplest examples to consider are the 133-143 and 133-139 MO pairs (Figure 7.5). The 133-143 MO pair makes significant deshielding contributions along $\sigma_{11}$ and $\sigma_{22}$. A right handed rotation of 143 about the $\sigma_{11}$ axis results in constructive overlap with 133, and similarly, the same rotation about $\sigma_{22}$ leads to constructive overlap, but to a lesser extent (and hence the smaller deshielding
contribution). In the case of the 133-139 MO pair, rotation about $\sigma_{11}$ does not generate any significant overlap, and the deshielding contribution is minimal. On the other hand, right-handed rotation about $\sigma_{22}$ causes large destructive overlap (i.e. lobes of opposite phase are overlapped), leading to a large shielding contribution. All of the other shielding and deshielding contributions can be rationalized and visualized in this manner, by simple rotations of the virtual orbitals.

7.4 Conclusions

Lead CS tensor parameters have been measured from $^{207}$Pb CP/CPMG solid-state NMR spectra for complexes 1, 2, and 3. The CP/CPMG sequence has been demonstrated to be much more efficient and accurate than MAS methods for the acquisition of the $^{207}$Pb spectra of extremely broad, CSA-dominated powder patterns. Similar lead isotropic chemical shifts are observed within this series of compounds; however, CS tensor parameters are useful for differentiating the three types of lead coordination environments. DFT calculations that account for relativistic effects adequately reproduce the experimental CS tensor parameters and trends. Examination of the individual MOs generated by non-relativistic calculations provides insight into the molecular origins of lead MS, as well as evidence for the existence and position of the stereochemically active lone electron pair. Experimental measurement and theoretical calculations of lead CS tensor parameters are clearly useful for the elucidation of molecular and electronic structure, bonding and symmetry.
7.5 Bibliography


(101) Feindel, K. W.; Ooms, K. J.; Wasylishen, R. E., 2007, 9, (10), 1226-1238.
Chapter 8: The Application of Frequency Swept Pulses for the Acquisition of Nuclear Quadrupole Resonance Spectra

8.1 Introduction

Nuclear quadrupole resonance (NQR) is sometimes referred to as ‘zero-field NMR’ because it involves inducing and observing nuclear spin state transitions in the absence of large static magnetic fields.\(^1\)\(^-\)\(^4\) The NQR phenomenon may be observed for quadrupolar nuclei \((I \geq 1)\) in environments which possess non-zero electric field gradients (EFGs). EFGs arise from non-spherically symmetric charge distributions (e.g., from surrounding atoms and bonds) about a nucleus and are described by second-rank tensors which are symmetric and traceless.\(^3\)\(^,\)\(^4\) Diagonalization of the EFG tensor yields three principal components \((V_{jj})\) which are ordered such that \(|V_{11}| \leq |V_{22}| \leq |V_{33}|\). In turn, the diagonalized EFG tensor may be described by two parameters, the quadrupolar coupling constant \((C_Q = eV_{33}Q/h)\) and the electric field gradient asymmetry parameter \([\eta_Q = (V_{11} - V_{22})/V_{33}]\). In a pure NQR experiment, the quadrupolar resonance frequencies \((\nu_Q)\) are determined by the \(C_Q\) and \(\eta_Q\). For example, there is only one quadrupole resonance frequency for an \(I = 3/2\) nucleus which is given by the expression:

\[
\nu_Q = \frac{C_Q}{2} \sqrt{1 + \frac{(\eta_Q)^2}{3}}
\]

For higher spin nuclei, there are several NQR transitions with distinct values of \(\nu_Q\) which can be related to \(C_Q\) and \(\eta_Q\) via different sets of expressions.\(^5\)

The \(C_Q\) and \(\eta_Q\) values are dependent upon the spherical and axial symmetry, respectively, of the ground state electron distribution about the quadrupolar nucleus;
therefore, knowledge of these parameters can lend insight into the structure and symmetry
of the local nuclear environment. For these reasons, NQR spectroscopy has found
applications in a wide range of areas such as inorganic chemistry, materials science and
pharmaceuticals.\textsuperscript{6-15} There is also much interest in the use of NQR for the detection of
explosives and illicit narcotics (\textsuperscript{14}N NQR).\textsuperscript{16-22} NQR is particularly useful when values of
\(C_Q\) are extremely large; in such cases, NMR spectra of quadrupolar nuclei are broadened
such that detection of an NMR signal can become very difficult.

\textbf{Figure 8.1.} Schematic representations of the pulse sequences employed for the
acquisition of NQR spectra. (a) Hahn-Echo with 90° excitation pulse and 180° or 90°
refocusing pulse. (b) QCPMG sequence with 90° excitation pulse and a train of 180°
refocusing pulses (reference 35). (c) The composite echo sequence of Odin (reference
54). (d) WURST-QCPMG sequence with excitation and refocusing pulses with 90°
pulses of equal length and sweep rate. Note that for WURST echo spectra the WURST-
QCPMG sequence (reference 64) was employed with only a single refocusing pulse and
the first echo was acquired (\(N = 1\)).
In the past, frequency-swept continuous wave irradiation was utilized for acquiring NQR spectra.\textsuperscript{1-4} However, pulsed Fourier transform techniques, such as the standard Hahn-echo sequence\textsuperscript{23} and quadrupolar echo sequences\textsuperscript{24-26} (Figure 8.1a), are now the preferred methods for acquiring NQR spectra. Pulse sequences such as the Carr-Purcell Meiboom-Gill (CPMG) sequence\textsuperscript{27-29} (Figure 8.1b) have also been employed for signal enhancement.\textsuperscript{30, 31} These sequences have enabled the acquisition of NQR spectra of nuclei such as $^{14}$N, which typically possesses low resonance frequencies and inherently low signal to noise (S/N).\textsuperscript{21, 22, 32, 33} It should also be noted that CPMG-type sequences have found applications for the signal enhancement of solid-state NMR spectra.\textsuperscript{34-38}

While these techniques are successful at increasing the S/N of NQR spectra, there are several commonly encountered problems in NQR spectroscopy. The $C_Q$ and $\eta_Q$ values are related to the symmetry of the atoms surrounding a nucleus and are characteristic of the particular system under investigation. Therefore, for a given quadrupolar nucleus, resonance frequencies of near 0 MHz to 1000’s of MHz are possible. The NQR experiment can be very onerous due to this large range of resonance frequencies, and most often, the experimentalist must spend a great deal of time searching for the NQR resonance(s). If the experimentalist has some prior knowledge of the approximate values of the quadrupolar parameters, the frequency search range may be reduced, and the experimental time decreased. Such information is available from a variety of sources, including previous NQR experiments on analogous systems and from theoretically calculated quadrupolar parameters (i.e., from first principles calculations). However, for many systems, such information is either unavailable or unreliable.
Another commonly encountered problem in NQR spectroscopy is the acquisition of spectra which are severely broadened due to a distribution of resonance frequencies, which most often arise in systems that are disordered at the atomic or molecular level. For example, Taylor et al. have extensively studied arsenic-containing glasses with $^{75}$As NQR and have found that the resonances of some samples span several MHz in breadth, as opposed to resonances in ordered solids which are typically several kHz in breadth.$^{39-43}$ The limited excitation bandwidths associated with standard, high-power, rectangular pulses utilized in the Hahn-echo sequence make it necessary to increment the transmitter frequency in order to collect such broad NQR spectra.$^{44}$ Incrementing of the transmitter frequency requires re-tuning and/or re-configuration of the probe, which can be extremely time consuming. Automated NQR systems capable of scanning a wide range of frequencies have been developed to address this problem,$^{45-49}$ though they are not widely available. Both manual and automated experiments benefit from broadband excitation pulses, which serve to reduce the number of frequency increments, and may aid in mapping out broad distributions of quadrupolar frequencies. In this light, several authors have discussed the development of echo sequences constructed from composite pulses which are capable of exciting broad frequency ranges.$^{50-54}$ For example, the composite echo sequence of Odin et al. is shown in Figure 8.1c.$^{54}$

Recently, there has been much interest in broadband excitation pulse sequences in solid-state NMR spectroscopy; in particular, the application of frequency swept pulses seems to hold significant promise. Bodenhausen et al. first demonstrated the application of echo sequences employing frequency swept pulses for the acquisition of solution $^1$H NMR spectra.$^{55}$ Similar pulses have been employed for the excitation and signal enhancement of solid-state NMR spectra of quadrupolar nuclei$^{56-58}$ and for broadband
decoupling and inversion in solution NMR experiments.\textsuperscript{59-62} Recently, Bhattacharya and Frydman have demonstrated the application of frequency swept (wideband uniform rate smooth truncated, WURST)\textsuperscript{61} pulses for the uniform excitation of wideline solid-state NMR spectra of quadrupolar nuclei.\textsuperscript{63} The WURST pulse is applied at a fixed transmitter frequency, with the frequency sweep achieved via simultaneous modulation of the pulse amplitude and phase. WURST pulses differ from conventional rectangular pulses not only in their amplitude and phase modulation over the duration of the pulse, but also because of their generally lower power requirements and longer lengths (typically ca. 50 µs to several ms). Our research group has recently introduced the WURST-QCPMG pulse sequence (Figure 8.1d).\textsuperscript{64} We have demonstrated that this sequence is useful for acquiring high quality ultra-wideline NMR spectra of quadrupolar nuclei; this is due in part to the large excitation bandwidths offered by the WURST pulses, and in part to the increased S/N ratios afforded by the CPMG protocol.\textsuperscript{65}

Theoretical and experimental investigations have suggested that shaped pulses suitable for NMR experiments can be readily applied to NQR experiments.\textsuperscript{66} For instance, frequency modulated (FM) pulses have previously been applied in NQR experiments by Schurrer and Pérez,\textsuperscript{67} however, these FM pulses possess a non-uniform “zipper”-like excitation profile limited to distinct offset frequencies. Spectral ranges greater than 500 kHz can routinely be uniformly excited with WURST pulses,\textsuperscript{64,65,68} with excitation breadth limited by a combination of the resonance frequency and probe bandwidth, suggesting that WURST echo and WURST-QCPMG sequences may find use in NQR experiments for a variety of quadrupolar nuclei.
Herein, we investigate the use of WURST-echo and WURST-QCPMG sequences for the acquisition of NQR spectra. The superior excitation bandwidths of WURST pulse sequences may be helpful in locating NQR resonances during the initial stages of NQR experimentation on samples with unknown resonance frequencies. In order to mimic the search for an NQR signal of unknown frequency, spectra have been acquired with various transmitter offsets (of several hundreds of kHz) from the resonance frequencies. The signals of the NQR spectra obtained with 90°-90° echo, 90°-180° echo, Odin’s composite echo sequence, and WURST echo pulse sequences are monitored as a function of transmitter offset frequency. The use of the CPMG protocol for signal enhancement of NQR spectra acquired with WURST pulses is investigated. The utility of the WURST pulses for the acquisition of wideline NQR spectra is also demonstrated. To this end, we have acquired a portion of the wideline $^{63/65}$Cu NQR spectrum of copper(I) cyanide (CuCN), which is a disordered solid possessing a wide distribution of $^{63/65}$Cu nuclear quadrupole resonances.

### 8.2 Experimental

All samples were purchased from Sigma-Aldrich Inc., and packed into shortened 5 mm glass NMR tubes. All experiments were performed on a Varian Chemagnetics triple resonance T3 MAS NMR probe with a 5 mm coil interfaced with a Varian InfinityPlus console running Spinsight software. Radiofrequency field strengths and pulse lengths were calibrated with on resonance Bloch decay experiments on the respective powdered samples. Note that we refer to the pulses which give maximum signal as “90° pulses”; however, since all experiments are performed on powdered
samples these actually correspond to pulse angles of ca. 57.3° (1 radian). All “180°” pulses were double the length of “90°” pulses. For all echo experiments, the interpulse delays, τ₁ and τ₂, were set such that the full echo was acquired. Hahn-echo and QCPMG sequences employed 16 step phase cycles, while the composite echo sequence employed an 8 step phase cycle. The WURST-QCPMG sequence with N set equal to 1 was used for all WURST echo experiments (Figure 8.1d) and an 8 step phase cycle was employed. The required RF field strength (in kHz) for the WURST pulse can be approximated by, $\nu_{\text{WURST}} = A \cdot R^{1/2} (I + 1/2)^{-1}$, where $R$ is the sweep rate which is equal to 2 times the WURST offset in kHz (e.g., a WURST offset of ±1000 kHz corresponds to a sweep range of 2 MHz) divided by the pulse length (in ms). $A$ is a factor which ranges between 0.5 and 0.1 and is inversely proportional to the $\gamma$ of the nucleus. For all WURST experiments, the RF field strength of the pulse ($\nu_{\text{WURST}}$) was experimentally optimized, starting from the theoretical value. The value of $\nu_{\text{WURST}}$ which gave maximum S/N was utilized. In all cases, WURST-80 pulse shapes were used with pulse lengths of 50 µs. The WURST pulses were constructed from 900 individual pulse elements (ca. 55.6 ns in length) whose phases and amplitudes were varied to attain the desired waveform. The minimum pulse element length of the InfinityPlus waveform tool is 50 ns. The value of $\tau_1$ for WURST experiments was set according to the formula $\tau_1 = 0.5 \cdot (\tau_{\text{WURST}} + \tau_{\text{acq}})$, where $\tau_{\text{WURST}}$ and $\tau_{\text{acq}}$ are the WURST pulse length and acquisition time of each echo, respectively. Spectral widths of 2 MHz, 1 MHz and 2.5 MHz were employed for $^{35}\text{Cl}$, $^{63/65}\text{Cu}$, and $^{75}\text{As}$ NQR, respectively. A spectral width of 200 kHz was employed for the point-by-point $^{63/65}\text{Cu}$ NQR spectrum. Recycle delays of 0.2 s, 0.4 s and 0.08 s were employed for $^{35}\text{Cl}$, $^{75}\text{As}$ and $^{63/65}\text{Cu}$ NQR experiments, respectively.
Recycle delays were experimentally optimized on each sample to ensure complete longitudinal relaxation of the magnetization was obtained. All other relevant experimental parameters are listed in Appendix G (Tables G1-G3). **CAUTION:** Due to the lengths of the WURST pulses and the short recycle delays typical of NQR experiments, the duty cycle of the probe should be carefully monitored. All spectra were processed by applying three zero fills followed by Fourier transformation. For all echo spectra the full echo was acquired and Fourier transformed and the spectrum was then magnitude calculated. The S/N and integrated intensity (II) were measured with the default algorithms in the Spinsight software package. The S/N corresponds to the ratio of the peak intensity of the resonance divided by the average absolute intensity of the baseline regions. The baseline regions on either side of the NQR resonance were employed for S/N measurements. WURST-QCPMG pulse sequences for Varian (InfinityPlus - Spinsight) and Bruker (Avance - TopSpin) spectrometers are available from the authors upon request.

### 8.3 Results and Discussion

$^{35}$Cl, $^{63/65}$Cu and $^{75}$As were chosen for this work due to their high natural abundances and relatively high quadrupolar frequencies (between 34 and 116 MHz) in a variety of structural motifs. The relevant nuclear properties are listed in Table 8.1. All of the samples discussed herein have previously been characterized by NQR spectroscopy.
Table 8.1. Nuclear Properties

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Nuclear Spin</th>
<th>Natural Abundance (%)</th>
<th>Quadrupole Moment (Q/fm²)</th>
<th>Magnetogyric Ratio (γ/10⁷ rad s⁻¹ T⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>³⁵Cl</td>
<td>3/2</td>
<td>75.8</td>
<td>-8.2</td>
<td>2.624198</td>
</tr>
<tr>
<td>⁶³Cu</td>
<td>3/2</td>
<td>69.2</td>
<td>-22.0</td>
<td>7.111789</td>
</tr>
<tr>
<td>⁶⁵Cu</td>
<td>3/2</td>
<td>30.8</td>
<td>-20.4</td>
<td>7.60435</td>
</tr>
<tr>
<td>⁷⁵As</td>
<td>3/2</td>
<td>100.0</td>
<td>31.4</td>
<td>4.596163</td>
</tr>
</tbody>
</table>

⁷⁵As NQR. ⁷⁵As NQR spectra of As₂O₃ (arsenolite phase) were previously acquired by Taylor over a range of temperatures. We observed a resonance at 116.234 MHz at 294 K which is close to the frequency of 116.222 MHz (300 K) reported by Taylor. In order to mimic the initial stages of NQR experiments on a sample with unknown resonance frequencies (i.e., searching a large frequency range for a single quadrupolar resonance frequency), ⁷⁵As NQR spectra have been acquired at variable transmitter offset frequencies. The transmitter frequency was incremented in steps of 100 kHz for frequencies close to the NQR frequency, while a larger increment of 200 kHz was employed for offsets of 600 kHz and above. At each transmitter frequency the probe was tuned and ⁷⁵As NQR spectra were then acquired with the four different pulse sequences (spectra are pictured in Fig. G1 for on-resonance irradiation). The integrated intensity (II) of the NQR spectra as a function of transmitter offset is shown in Figure 8.2 (numerical values of S/N and II of the spectra are listed in Table G4).

Before the effects of transmitter offsets are reviewed it is important to discuss the factors which will influence the II and S/N of the NQR spectra acquired with the transmitter on resonance (e.g., the intensity points in Figure 8.2 with 0 kHz transmitter offsets). The main factor which affects the II and S/N of all spectra acquired with echo pulse sequences is the length of time between the excitation and refocusing pulses, during which transverse relaxation (T₂) of the magnetization occurs (i.e., the τ₁ time period in the
Figure 8.2. Integrated intensity of the $^{75}$As NQR spectra of As$_2$O$_3$ (arsenolite) as a function of transmitter offset from the resonance frequency for the 90°-180° echo, 90°-90° echo, composite echo and WURST echo pulse sequences. For each transmitter offset the probe was tuned using reflected power measurements available in Spinsight, followed by acquisition of the spectra with the five pulse sequences. For clarity the intensity points have been connected by lines for the 90°-180° echo and WURST echo spectra.
echo sequences, Figure 8.1). The $\tau_1$ values listed in Appendix G are those that were input into the pulse sequences on the spectrometer. These values are corrected within the pulse sequence programs and do not describe the total time for which the signal is allowed to dephase after the excitation pulse. For this reason, we will refer to the total dephasing time period as $\tau_d$. Values of $\tau_d$ employed for experiments are also listed in Appendix G.

In the case of the echo sequences employing conventional pulse sequences, $\tau_d$ will be close in value to $\tau_1$ due to the relatively short pulse widths of conventional refocusing pulses. However, the WURST echo sequence utilizes pulse widths which are much longer than conventional pulses (i.e., 50 $\mu$s). Subsequently, significantly more transverse relaxation occurs from the time a particular frequency isochromat is excited by a WURST pulse to the time it is refocused by the next WURST pulse, in comparison to conventional echo sequences. For these reasons the $\tau_1$ values are corrected within the pulse sequence to account for lengths of the WURST pulses and for the WURST echo sequence and $\tau_d = \tau_1 + \tau_2$. The S/N and II of the 90°-180° echo sequences and WURST echo sequences with various $\tau_d$ times are listed in Table G5. The value of $\tau_d$ dramatically affects the II and S/N of the 90°-180° echo and WURST echo spectra due to the relatively short $T_2(^{75}\text{As})$ value for As$_2$O$_3$ at room temperature. For example, NQR spectra acquired with the 90°-180° echo sequence using $\tau_d$ values of 145.7 $\mu$s and 78.35 $\mu$s, yield II values of 286 and 443, respectively. It should be noted that if $\tau_d$ is too short, it is not possible to acquire the full echo, and this truncation leads to lineshape and baseline distortions, making it difficult to obtain meaningful II and S/N measurements. For these reasons, we set $\tau_d$ for all echo experiments such that the full echo was acquired and the values of $\tau_d$ are approximately equal.
There are several key observations that can be made from Figure 8.2. First, we will consider the case where the transmitter is on resonance or close to the resonance frequency (less than a 100 kHz offset). It is clear that NQR spectra acquired with the 90°-180° echo and composite echo sequences possess higher II (II > 280) and S/N (S/N > 1200) than those acquired with the WURST echo sequence (II = 186, S/N = 871). For the WURST spectra acquired on resonance we tested the effects of the RF field of the WURST pulse on the II and S/N of NQR spectra. Experiments conducted with variable WURST pulse widths (and different experimentally optimized RF field strengths) show no appreciable variation in II (Table G6). We therefore attribute the reduced II and S/N of the WURST echo to the fact that the refocusing pulse is acting as a 90° pulse since it is the same length and power as the initial pulse (e.g., the II and S/N of the WURST echo sequence are similar to the 90°-90° echo sequence).

In order to try and improve the S/N of the WURST echo spectra we have attempted to implement a 90°-180° WURST echo sequence. Bhattacharya and Frydman previously outlined several approaches for obtaining a WURST 180° (π) refocusing pulse for solid-state NMR of quadrupolar nuclei. The first approach is to employ a WURST π-pulse which sweeps over the range of frequencies at double the rate of the excitation pulse \( R_{\text{ref}} = 2R_{\text{exc}} \). This can be accomplished in two ways: (1) by employing a WURST π-pulse which is half the time length of the excitation pulse \( \tau_{\text{exc}} = 2\tau_{\text{ref}} \) and sweeps over the same frequency range, or, (2) by employing a WURST refocusing pulse which is identical in length to the excitation pulse \( \tau_{\text{exc}} = \tau_{\text{ref}} \), but sweeps over double the frequency range. They found that the optimal RF field for the refocusing WURST π-pulse \( v_{\text{ref}} \) was ca. 4.7 times higher than that of the excitation pulse \( v_{\text{exc}} \), while we
found experimentally optimized $\nu_{\text{ref}}$ values which were ca. 1.5 to 1.7 times higher than $\nu_{\text{exc}}$ (Table G7). In both cases, our “90°-180°” WURST echo spectra are similar to the corresponding 90°-90° WURST echo spectra in terms of S/N and II (Table G7). A second approach for obtaining a WURST $\pi$-pulse is to utilize a refocusing pulse of the same length ($\tau_{\text{exc}} = \tau_{\text{ref}}$) and same sweep rate ($R_{\text{ref}} = R_{\text{exc}}$); however, $\nu_{\text{ref}}$ is set to ca. 3.2 times larger than $\nu_{\text{exc}}$. In this case, we found that maximum signal is obtained when $\nu_{\text{exc}} \approx \nu_{\text{ref}}$ (identical to a 90°-90° WURST echo spectrum), consistent with our previous results obtained from the solid-state NMR spectra of quadrupolar nuclei. It is worth noting that the WURST pulses employed herein are much shorter (less than 100 $\mu$s) than those employed by Bhattacharya and Frydman (ca. 1 – 2 ms), and hence, the pulses may be operating in different adiabatic regimes (this may account for the differences in ratios of $\nu_{\text{ref}}$: $\nu_{\text{exc}}$ between our experiments and Frydman’s experiments). It may be possible to obtain WURST $\pi$-pulses by employing longer pulse widths, however, this would necessitate the use of much longer echo delays and result in NQR spectra with lower S/N.

At relatively large transmitter offsets (i.e., 200 kHz and greater) the WURST echo sequence affords higher II and S/N NQR spectra than those acquired with conventional echo sequences. For instance, with WURST pulses, NQR spectra with II > 48 are observed for transmitter offsets as large as 1000 kHz. Clearly, the WURST pulses offer superior excitation bandwidths in comparison to the conventional rectangular pulses. Considering these observations, a strategy for the observation of NQR resonances of unknown frequencies emerges. The frequency range of interest can be surveyed with a WURST echo or WURST-QCPMG sequence using large transmitter offset increments. In this case, transmitter increments of ca. 2000 kHz could be reasonably employed with
the WURST echo sequence in the search for an NQR resonance of unknown frequency, while the composite echo sequence would be limited to transmitter increments of ca. 800 kHz. Once the approximate frequency of the NQR resonance is identified, the transmitter could be set to the resonance frequency and a high quality spectrum could then be obtained with a conventional sequence.

Another important observation is the distinct asymmetry in the peak intensities in Figure 8.2. For all of the pulse sequences, higher intensities are observed for spectra acquired with positive transmitter offsets in comparison to those acquired with negative transmitter offsets of the same magnitude. This asymmetry is particularly pronounced for the WURST echo spectra. For example, for the WURST echo spectrum acquired at an offset of +300 kHz, II = 212, while at an offset of -300 kHz, II = 134. Additionally, the WURST echo NQR spectra unexpectedly possess higher II when the transmitter is +300 kHz from resonance (II = 212), rather than when the transmitter is on resonance (II = 186).

What is the origin of this asymmetry in II and S/N for equally spaced transmitter offsets of opposite sign? Initially, we thought this asymmetry may be due to the sweep direction of WURST pulses. Given the lengths of the WURST pulses (50 µs) and the fact that the pulse is linearly swept across the specified frequency range, it is possible that transverse relaxation \((T_2)\) of the resonance may occur if the resonance is excited near the start of the first WURST pulse waveform; however, when a pulse with opposite sweep direction was applied, spectra with an identical intensity profile were obtained (not shown). Our research group has previously observed similar asymmetries in \(^{14}\text{N}\) WURST-QCPMG NMR spectra, which were found to result from frequency sweep
induced population transfers.\textsuperscript{68} However, this is very unlikely, given that there are only two quantized energy levels, and that this asymmetry is observed in spectra using WURST pulses with opposite sweep directions. Both of these mechanisms are unlikely, given that this asymmetry in intensities is observed for the all of the other pulse sequences, although, the asymmetry is not as pronounced as for the WURST echo spectra.

Therefore, we attribute the asymmetry in Figure 8.2 to a difference in the characteristic impedance values of the excitation circuit and receiver circuit of the spectrometer (which we refer to as an “impedance mismatch”). This phenomenon has recently been reported by Marion and Desvaux\textsuperscript{72} and Muller et al.\textsuperscript{73} In both manuscripts, the authors describe the observation of an impedance mismatch via the acquisition of spin-noise NMR spectra. It was found the S/N of the spin-noise NMR spectra improved when the probe was detuned (as indicated by standard tuning protocols). This is because the standard tuning procedures available with most commercial spectrometers result in tuning of the probe such that it is optimized for excitation (e.g., matched and tuned to the amplifier circuit), rather than for receiving of signals.\textsuperscript{72,73} These impedance mismatches are readily detected in spin-noise NMR spectra, because they require no excitation pulses and their S/N and phases are only dependent upon impedance matching the probe to the receiver.

In our work the probe was coarsely tuned by observing an impedance-frequency response curve (e.g., a ‘wobble’ curve) and fine tuned by minimizing the level of reflected power. This method optimizes the tuning of the probe for excitation only. Figure 8.2 indicates that there is an approximate difference of 300 kHz between the optimal receiver and excitation tuning of the probe, which is consistent with the
frequency differences of several hundred kilohertz observed by Desvaux and Muller et al.\textsuperscript{72,73} In order to confirm that there was an impedance mismatch, the probe was tuned in the usual manner to 116.534 MHz, which is 300 kHz higher than the resonance frequency. The transmitter frequency was then placed on resonance (116.234 MHz), and spectra with the five different pulse sequences were acquired. This yielded spectra with higher II and S/N, except for the spectrum acquired with 90°-90° echo sequence (Figure 8.3, spectra are shown in Figure G2). Finally, additional experiments were conducted which involved re-calibration of the pulse widths to account for the de-tuning of the probe (the 90° pulse width increases from 1.6 µs to 2.1 µs). These experiments yield S/N and II values which are between 1.3 to 1.4 times larger than those obtained when the probe is tuned to the transmitter frequency (i.e., on-resonance). These gains are observed for all of the pulse sequences (compare first data set to last data set for each pulse sequence in Figure 8.3).

We have also investigated the influence of the receiver gain setting on the II and S/N values when the probe is optimized for excitation (tuned on resonance) and when the probe is optimized for reception (tuned +300 kHz off resonance) and re-calibrated pulse widths are employed (Table G8). The II is observed to steadily increase with the receiver gain level, while the S/N ratio remains constant. Marion and Desvaux have observed that at higher receiver gain settings, the S/N ratio of solution $^1$H NMR spectra is progressively lowered and balances the gains in signal (II), due to uniform digitization of the probe noise at higher receiver gain settings.\textsuperscript{72} However, they also point out that if the pre-amplifier noise level is significant, then it is expected that tuning the probe to the receiver optimum will always lead to improved S/N ratios.\textsuperscript{72} This suggests that in our system, the
Figure 8.3. Integrated intensity of the $^{75}$As NQR spectra of As$_2$O$_3$ acquired when the probe has been tuned on resonance (116.234 MHz), tuned +300 kHz off resonance (116.534 MHz), and when the probe is tuned +300 kHz off resonance and the pulse widths have been re-calibrated. The transmitter was set to the resonant frequency (116.234 MHz) in all cases. Spectra were acquired with the four different pulse sequences. When the probe is tuned +300 kHz off resonance and re-calibrated pulses are employed, the II of the NQR spectra is 1.3 to 1.4 times larger.
pre-amplifier is the predominant noise source, as we observe improved S/N ratios when
the probe is tuned to the receiver optimum for a range of receiver gain settings.

The superior excitation bandwidths of the WURST pulses enable experiments
which allow for the detection of impedance mismatches between reception and excitation
pathways, even when the differences are on the order of several hundred kHz. WURST
echo spectra could be acquired with variable offsets and the II or S/N can be plotted in a
manner similar to that presented herein to detect the optimal receiver tuning. Marion and
Desvaux have demonstrated that this mismatch can be eliminated by altering the
impedance of the amplifier pathway by changing the lengths of transmission cables.72  In
the future, we intend to utilize the WURST echo sequence in order to better impedance
match our reception and excitation pathways. This approach should be applicable to
NQR, as well as solution and solids NMR experiments, and would be much faster than
acquiring spin-noise NMR spectra. It would also be possible to detect impedance
mismatches by monitoring the S/N of a spectrum acquired with conventional pulses while
the transmitter is placed on resonance and the probe tuning frequency is varied.
However, if there is a large impedance mismatch, the pulse widths of the conventional
pulses will increase due to reflection of power by the probe.72  This necessitates time
consuming pulse width calibrations for each probe tuning increment. Therefore, WURST
pulses should be better suited to detect impedance mismatches.

**Signal Enhancement with the CPMG Protocol.** Marino and Klainer first
demonstrated in 1977 that the CPMG pulse sequence affords large S/N gains in NQR.31
CPMG type sequences are now frequently employed in order to enhance the signal of
unreceptive NQR nuclei such as $^{14}$N.18, 21, 22, 30  For these reasons, the S/N of $^{75}$As NQR
spectra acquired with the QCPMG35 and WURST-QCPMG sequences64 (Figure 8.1) are
compared to the corresponding single echo sequences. In order to obtain “spikelet-free”
spectra, the spin echoes obtained from the $^{75}$As QCPMG and WURST-QCPMG FIDs
were summed into a single time domain echo. These single time domain echoes were
then Fourier transformed to produce spectra which are similar in appearance to
conventional echo spectra. The QCPMG and WURST-QCPMG spectra are compared
to echo spectra in Figure G3 and II and S/N measurements are shown in Table 8.2. The
QCPMG spectra are of higher II and S/N than the WURST-QCPMG when the number of
echoes (MG loops) and echo size is the same. This is consistent with the II and S/N
observed for the corresponding echo sequences.

<table>
<thead>
<tr>
<th>Echo Size</th>
<th>$\tau_{acq}$ (µs)</th>
<th>MG Loops (N)$^a$</th>
<th>WURST-QCPMG$^b$</th>
<th>QCPMG$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>512</td>
<td>204.8</td>
<td>1</td>
<td>186 871</td>
<td>286 2506</td>
</tr>
<tr>
<td>512</td>
<td>204.8</td>
<td>8</td>
<td>624 2064</td>
<td>904 3293</td>
</tr>
<tr>
<td>256</td>
<td>102.4</td>
<td>24</td>
<td>2294 4700</td>
<td>3834 5741</td>
</tr>
<tr>
<td>140</td>
<td>56.0</td>
<td>80</td>
<td>5227 4117</td>
<td>9172 5427</td>
</tr>
</tbody>
</table>

$^a$This is the number of refocusing pulses and echoes that were acquired. For the case of
MG Loops = 1 the II and S/N from the 90°-180° echo and WURST echo spectra were
used. $^b$For all WURST-QCPMG experiments $\tau_2 = 20$ µs. $\tau_1$ can be determined using the
formula given in the Experimental section. $^c$For all QCPMG experiments $\tau_2 = 30$ µs and
$\tau_3 = \tau_4 = 20$ µs. $^d$Small echo sizes lead to truncation of the individual echoes in the time
domain. This causes lineshape and baseline distortions leading to skewed II and S/N
values.

While the $T_2(75\text{As})$ and $T_1(75\text{As})$ time constants are relatively short for As$_2$O$_3$ at
room temperature it is possible to acquire multiple echoes for ca. 4.5 ms. It can be readily
seen that the acquisition of multiple echoes yields significant improvements in II and S/N
of the NQR spectra. For example the acquisition of 8 MG loops leads to ca. three-fold
increase in the II values for both the WURST-QCPMG and QCPMG pulse sequences, in
comparison to the corresponding single echo experiments. As expected for CPMG experiments, the largest signal enhancements are obtained when a large number of tightly spaced echoes are acquired. When the echo size is 256 points and 24 echoes are acquired the II is observed to increase by factors of 12.3 and 13.4 for WURST-QCPMG and QCPMG, respectively. Acquisition of 80 echoes (with each echo consisting of 140 points) leads to gains in the II by factors of 28 and 32 for the WURST-QCPMG and QCPMG sequences, respectively (last entries, Table 8.2). However, it should be noted that when the echo size is small, truncation of the individual echoes results in broadening of the NQR resonances as well as baseline distortions (Figure G3), rendering the measured II and S/N values unreliable. Clearly, the CPMG protocol can be used to enhance the signal of NQR spectra acquired with WURST pulses. The WURST-QCPMG sequence can provide significant signal enhancement and should make WURST pulses more competitive with conventional pulses, while still retaining their larger excitation bandwidths.

$^{35}$Cl NQR. A series of experiments similar to that described above has been conducted for the acquisition of $^{35}$Cl NQR spectra of 4-chloropyridine. This was done in order to test the use of WURST pulses for the acquisition of spectra of a less receptive NQR nucleus and the performance of the sequence at a lower resonance frequency. The $^{35}$Cl NQR spectrum of 4-chloropyridine at a temperature of 77 K was acquired by Bray et al. and a resonance at 34.789 MHz was observed. We observed a resonance at 35.352 MHz at a temperature of 294 K. In Figure 8.4, the II of the $^{35}$Cl NQR spectra as a function of transmitter offset is shown (II and S/N values given in Table G9) for the four different pulse sequences. Spectra acquired with the four pulse sequences and the transmitter on resonance are pictured in Figure G4. This sample possesses a relatively
Figure 8.4. Integrated intensity of the $^{35}$Cl NQR spectra of 4-chloropyridine as a function of transmitter offset from the resonance frequency for the 90°-180° echo, 90°-90° echo, composite echo and WURST echo. For each transmitter offset the probe was tuned using reflected power measurements available in Spinsight. Spectra with the four pulse sequences were then acquired. For clarity the intensity points have been connected by lines for the 90°-180° echo and WURST echo spectra.
long $T_2^\ast(\text{Cl})$, and hence, a fairly long $\tau_d$ value (ca. 275 $\mu$s) is required to acquire the full echo.

From Figure 8.4 it is once again clear that conventional echo pulse sequences provide superior S/N in comparison to the WURST sequence for spectra acquired with small transmitter frequency offsets (less than 100 kHz). At large frequency offsets (150 kHz and higher) the WURST pulses are much more efficient. $^{35}\text{Cl}$ NQR spectra of II and S/N of 18 and 13, respectively, may be observed with WURST pulses at transmitter offsets as large as 600 kHz. Therefore, in an NQR experiment involving the search for an unknown quadrupolar resonance of a similar frequency to this, it would be possible to use 1.2 MHz transmitter increments to locate the resonance, as opposed to ca. 600 kHz with conventional echoes, effectively reducing the total number of experiments by a factor of two.

The $^{35}\text{Cl}$ NQR configuration of the spectrometer components once again displays an impedance mismatch between the excitation and receiving pathways. In this case the receiving optimum is located at ca. -200 kHz from the excitation optimum as indicated in Figure 8.4. The II was measured for the peaks in the $^{35}\text{Cl}$ NQR spectra acquired with the probe tuned on resonance (35.352 MHz) and tuned -200 kHz off resonance (35.152 MHz), with the transmitter fixed on resonance in both cases (Figure 8.5). II and S/N increases of ca. 1.6 are observed when the probe is tuned to -200 kHz from the resonance frequency and the pulse widths are re-calibrated. These gains in II and S/N are once again relatively constant for a variety of receiver gain settings (Table G10). Although there is a smaller frequency difference between the receiving and excitation optimum for the $^{35}\text{Cl}$ NQR probe configuration, the drop off in signal to noise is more severe than that
observed for the $^{75}\text{As}$ NQR spectra. We attribute this to the decreased bandwidth of the probe for the $^{35}\text{Cl}$ NQR configuration (vide infra).

**Figure 8.5.** Integrated intensity of the $^{35}\text{Cl}$ NQR spectra of 4-chloropyridine acquired when the probe has been tuned on resonance (35.352 MHz), tuned -200 kHz off resonance (35.152 MHz) and when the probe is tuned -200 kHz off resonance and the pulse widths have been re-calibrated. The transmitter was set to the resonant frequency (35.352 MHz) in all cases. Spectra were acquired with the four different pulse sequences. When the probe is tuned -200 kHz off resonance and re-calibrated pulses are employed, the II of the NQR spectra is 1.64 to 1.67 times larger.
Factors Limiting the Excitation Bandwidth of WURST Pulses. While the
WURST pulses display impressive excitation bandwidths, it is worthwhile to consider the
factors which limit them. For example, $^{35}\text{Cl}$ and $^{75}\text{As}$ NQR experiments employed
WURST pulses with a sweep range of ±1000 kHz and ±1400 kHz, respectively, while
resonances with offsets larger than 600 kHz and 1200 kHz, respectively, possess very low
S/N. In these cases, the bandwidth and quality factor (Q-factor) of the probe are the main
limitations on the apparent excitation bandwidth of the WURST pulses. The Q-factor of
the probe determines the power profile of the probe, which affects both the efficiency of
excitation pulses as well as the detection of signal(s).

Muller et al. have suggested that the Q-factor of the probe can be approximated by
dividing the resonance frequency ($\nu_Q$) by the FWHH measured from the inflection of the
wobble curve. For the $^{35}\text{Cl}$ NQR configuration of the probe (35.346 MHz) a FWHH
value of approximately 350 kHz was observed in the wobble curve giving a Q-factor of
approximately 101 (Figure G6). For the $^{75}\text{As}$ NQR probe configuration (116.234 MHz) a
FWHH value of approximately 600 kHz was observed in the wobble curve giving a Q-
factor of approximately 194. The large probe bandwidth of the $^{75}\text{As}$ NQR experiments
enables resonances to be detected at offsets larger than ±1000 kHz, whereas the smaller
probe bandwidth in the $^{35}\text{Cl}$ configuration limits detection of signals to offsets of ca. ±600
kHz. For a given resonance frequency lower Q-factor values will lead to larger probe
bandwidths; however, the signal is also proportional to the Q-factor of the probe. For
nuclei such as $^{75}\text{As}$ and $^{35}\text{Cl}$ which are highly abundant and typically possess high
resonance frequencies (and high S/N), it may be worthwhile to attempt experiments with
lower Q-factor probes. This could afford larger excitation and detection bandwidths at
Aside from limitations imposed by the probe, the required power for the WURST pulses also increases with increasing sweep width, necessitating the use of high powers and/or longer pulses. Large sweep widths and/or long pulse lengths may lead to unacceptably high transmitter duty cycles, although sweep widths of ±1.5 MHz can be safely achieved for almost all nuclei with 50 µs WURST pulses.

**Acquisition of Wideline NQR Spectra.** Systems such as amorphous glasses, semiconductors, polymers and high temperature superconductors possess varying degrees of disorder at the atomic level which results in distributions in $C_Q$ and $\eta_Q$. This in turn gives rise to distributions of NQR frequencies and correspondingly broad NQR spectra. Two methods for acquiring wideline NQR spectra are commonly employed. The traditional method involves stepping the transmitter frequency in evenly spaced increments and acquiring a spin-echo at each frequency (we will refer to this as the “point-by-point” method). The echo intensities are then plotted as a function of transmitter frequency and used to construct the NQR spectrum. The second approach is similar to the first approach in that spin-echoes are acquired at evenly spaced transmitter increments; however, each echo is Fourier transformed and then co-added in the frequency domain to form the total spectrum. Wideline solid-state NMR spectra are frequently acquired in this manner as well. This method is advantageous because it enables sharp spectral features to be detected while requiring fewer transmitter offsets than the point-by-point method. The superior excitation bandwidths of the WURST pulses should make them ideal for acquiring wideline NQR spectra in a similar manner.
Figure 8.6. Wideline $^{63/65}$Cu NQR spectrum of the broad resonance of CuCN centered around 37.9 MHz. (a) “Point-by-point” spectrum (see text for details) acquired with the QCPMG pulse sequence and low power pulses (10 µs 90° pulse). A transmitter increment of 120 kHz was employed and 15 echoes were acquired (1.3 hours total acquisition time). (b) QCPMG spikelet spectrum and echo spectrum formed from time domain co-addition of the echoes. A transmitter increment of 120 kHz and high-power 90° pulses (0.7 µs) were employed. 12 sub-spectra were required to form the total pattern (1.3 hours total acquisition time). (c) WURST-QCPMG spikelet spectrum and echo spectrum formed from time domain co-addition of the echoes. A transmitter increment of 250 kHz was employed and 6 sub-spectra were required to form the total pattern (0.8 hours total acquisition time).
In order to investigate the utility of WURST pulses for the acquisition of wideline NQR spectra, we have acquired a portion of the $^{63/65}$Cu NQR spectrum of copper(I) cyanide. The $^{63/65}$Cu NQR spectrum of CuCN consists of four broad peaks (FWHH > 400 kHz) separated by several MHz with some of the peaks containing overlapping $^{65}$Cu and $^{63}$Cu resonances from distinct chemical environments. We have acquired the approximately 1 MHz broad $^{63/65}$Cu resonance centered at 37.9 MHz (Figure 8.6). The QCPMG sequence was used to acquire a point-by-point spectrum (Figure 8.6a) by summing the echoes in the QCMPG echo train in the time domain. The resultant echo was then magnitude calculated and the II was measured and plotted as a function of transmitter frequency. Echo intensities were measured at 15 transmitter offset frequencies, with 4000 scans per sub-spectrum (0.08 s recycle delay) and a total experimental time of 1.3 hours. The asymmetric shape of the point-by-point spectrum is consistent with the previously reported spectrum.

The QCPMG and WURST-QCPMG spectra are shown in Figure 8.6b and 6c, respectively. Both spectra were formed by Fourier transforming the individual sub-spectra and co-adding them in the frequency domain. Spikelet spectra and echo spectra are shown for both pulse sequences. Spikelet spectra were obtained by directly Fourier transforming the train of echoes from the CPMG spectra. Echo spectra were obtained from the QCPMG spectra in the manner described in the “Signal Enhancement with the CPMG Protocol” section. A transmitter increment of 120 kHz was employed for the QCPMG sequence (90° pulses of 0.7 µs); while a transmitter increment of 250 kHz was employed with the WURST-QCPMG sequence (±1000 kHz sweep ranges). This enabled
the WURST-QCPMG spectrum to be acquired with only 6 sub-spectra while the QCPMG spectrum required 12 sub-spectra to form the total pattern. However, the lower S/N of the WURST spectra required that 6000 scans be acquired for each sub-spectrum, while only 4800 scans were required with the QCPMG sequence to obtain similar S/N ratios. It can also be seen that the spikelet and echo versions of the QCPMG and WURST-QCPMG spectra provide an excellent overall match with the shape of the point-by-point spectrum, indicating that accurate lineshapes can be obtained with either sequence. However, despite the lower S/N of the WURST-QCPMG spectra the pattern could be acquired in a total time of 0.8 hours, while 1.3 hours of time were required for the QCPMG sequence. This also does not include the additional time required for the spectrometer operator to step the transmitter frequency and re-tune the probe. WURST-QCPMG is clearly the most efficient method for acquiring broad NQR spectra. It should also be noted that due to the high $\gamma$ of the $^{63,65}$Cu nuclei only ca. 100 W of input power were required for the WURST pulses, compared to ca. 750 W of input power utilized for the QCPMG spectra.

### 8.4 Conclusions

WURST echo and WURST-QCPMG experiments possess several advantages in comparison to standard pulsed experiments for the acquisition of NQR spectra. The large uniform excitation bandwidths of the WURST pulses should enable NQR signals of unknown frequency to be located in a more efficient manner than conventional pulsed NQR experiments. The broadband excitation of the WURST pulses makes them useful for samples which possess broad distributions of NQR frequencies, as evidenced by acquisition of $^{63,65}$Cu NQR spectra of CuCN. WURST pulses could also potentially be
useful for examining samples containing multiple sites which possess disparate NQR frequencies that can not be uniformly excited by conventional pulse techniques.

However, WURST pulses are not ideally suited for samples which possess very short transverse relaxation times ($T_2$) and/or nuclei which possess inherently low signal spectra due to low resonance frequency and/or low natural abundance. Clearly, spectra acquired with WURST pulses are of lower S/N than those acquired with conventional echo sequences; therefore WURST experiments may be limited to nuclei which are highly receptive to NQR experiments. Impedance mismatches between receiving and excitation pathways within NQR and NMR spectrometer systems can also be readily detected with WURST pulse sequences. This may afford a straightforward method for optimizing the performance of a variety of NQR and NMR spectrometers. This is especially important for NMR or NQR experiments performed on unreceptive nuclei where it is desirable to maximize inherently weak signals.

While this work has been limited to $I = 3/2$ nuclei, it is anticipated that WURST pulses may be useful for higher spin nuclei (e.g., $I = 1, 2, 5/2$, etc.); however, due to scaling of the pulse widths, the higher spin nuclei possess inherently shorter 90° pulse widths with large excitation bandwidths. Pre-polarization schemes where the sample is shuttled in and out of high field magnets should also be compatible with WURST pulses. The large excitation bandwidths afforded by the WURST pulses in combination with their low power requirements may also make them attractive for portable NQR systems where small power supplies are desirable and/or for experiments conducted with large-diameter sample coils.
8.5 Bibliography

(80) $T_2$ was measured for several QCPMG sub-spectra acquired at different transmitter frequencies (Table G11) and $T_2$ values were found to be relatively constant, suggesting that the shape of the pattern is not strongly influenced by $T_2$. 

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Chapter 9: General Conclusions and Future Outlook

In this thesis it is demonstrated that multinuclear solid-state NMR (SSNMR) can be employed as a powerful probe of structure and bonding in inorganic and organometallic complexes, and can be readily applied to characterize complex heterogeneous catalyst systems. As detailed in Chapter 6, multinuclear SSNMR experiments, complemented by powder XRD data, have allowed for the development of a structural model for microencapsulated (ME) Sc(OTf)$_3$ catalysts, which will provide much needed insight for the preparation and development of improved ME catalytic systems. Similarly, the combination of $^{35}$Cl and $^{91}$Zr SSNMR can act as a powerful probe of structure for zirconocene-based catalysts, as demonstrated in Chapters 2 and 3. Quantum chemical calculations of NMR interaction tensors, when taken along side of experimental SSNMR data of well-characterized systems, enable the NMR spectroscopist to gain a deep comprehension not only of the origin of the NMR interactions, but also an understanding of the relationships between these interactions and molecular structure and symmetry. This in turn can be used to make structural predictions for systems with unknown or ambiguous structures, as well as shedding light on the local electronic structure, including details like molecular orbitals, bonding and internuclear distances. This approach is demonstrated in Chapter 7, where the experimentally determined lead chemical shift anisotropies were demonstrated to arise from the presence of stereochemically active electron lone pairs centred on the lead atoms. It is hoped that this thesis will encourage the more general application of SSNMR for the characterization of inorganic and organometallic complexes, and related catalysts.
A continuing goal of the research presented herein will be to demonstrate that multinuclear SSNMR can be applied to probe the structure of heterogeneous catalysts which possess ambiguous molecular structures. In this regard, metallocenes serve as an ideal system to demonstrate this approach. As recounted in Chapters 2 and 3, the exact nature and structure of both homogeneous and heterogeneous activated metallocene olefin polymerization catalysts remain poorly understood.\textsuperscript{1-3} The difficulties in probing the structure of these complexes arise from the fact that highly active catalysts are only obtained when the metallocenes have been treated with a stoichiometric excess of methylaluminoxane (MAO). Furthermore, heterogeneous versions of the catalysts are especially challenging to study due their lack of long-range order and the small number of active sites which reside at the surface of the support material. Given the inherent insensitivity of SSNMR experiments, the dilution of the active sites/species currently represents a considerable challenge for NMR spectroscopists. This is not terribly problematic when acquiring SSNMR spectra of highly receptive nuclei and/or nuclei which possess relatively narrow resonances or powder patterns. For example, in Chapter 6, it was shown that $^{45}$Sc SSNMR spectra of ME Sc(OTf)$_3$ samples (which are ca. 1 \% Sc by mass) could be acquired in several hours at a moderate magnetic field strength of 9.4 T. However, many important catalysts possess unreceptive nuclei; in these cases, the dilution of the active catalyst or precursor in the abundant support material can lead to unreasonably lengthy experiment times if signal enhancement techniques are not employed.

The signal of the NMR experiment is described by the following equation:
Hence, it is clear that the application of high magnetic fields and/or very low temperatures can lead to large signal enhancements. Herein, it was demonstrated that SSNMR spectra of unreceptive nuclei, such as $^{35}\text{Cl}$ and $^{91}\text{Zr}$, in crystalline metallocenes, can be acquired in times on the order of minutes at high magnetic fields. For zirconocenes possessing narrow powder patterns (such as $\text{Cp}_2\text{ZrCl}_2$), a high quality $^{91}\text{Zr}$ SSNMR spectrum can be acquired with a standard quadrupolar echo sequence in a matter of minutes at 21.1 T. However, we have also demonstrated that it is very likely that many SSNMR spectra of quadrupolar nuclei in heterogeneous catalysts will possess ultra-wideline (UW) powder patterns. UW SSNMR spectra are very challenging to acquire due to dispersion of the NMR signal intensity over the broad powder patterns. In Chapters 2 and 3, it was shown that the QCPMG and WURST-QCPMG pulse sequences allow for the acquisition of $^{91}\text{Zr}$ and $^{35}\text{Cl}$ UW SSNMR spectra of metallocenes in a matter of minutes at 21.1 T. This suggests that the examination of heterogeneous catalysts with dilute nuclear contents and broad powder patterns is feasible; however, depending upon the exact dilution factors and natures of the systems, it will be a considerable challenge.

9.1 Preliminary Characterization of Model Heterogeneous Catalysts by $^{91}\text{Zr}$ SSNMR Spectroscopy

In the remaining portions of this final chapter, a recently initiated $^{91}\text{Zr}$ SSNMR
study of model heterogeneous zirconocene catalysts consisting of zirconocenes immobilized on silica, is described. This study is being conducted in collaboration with Drs. Paul Ellis and Andrew Lipton (Pacific Northwest National Labs, Richland WA) and Prof. Christophe Copéret (CNRS, Lyon, France and ETH Zurich).

The two model catalysts were obtained by contacting Cp₂ZrMeCl and Cp₂ZrMe₂ with the silica surface (Scheme 9.1). A reaction between the methyl groups of the zirconocene complexes and the hydroxyl groups of the surface occurs, leading to the formation of Zr-O bonds. The surface species have been characterized by ¹H MAS SSNMR and IR spectroscopy (results not shown). The structures shown in Scheme 9.1 are consistent with this data and previously proposed structures.²⁻⁷

Scheme 9.1. Preparation of surface-supported zirconocenes. Molecular analogs of the surface-supported species are shown to the right.
Elemental analysis (EA) indicates that 1-Cl and 2-Me are 3.02 % Zr by mass and 1.99 % Zr by mass, respectively, which are ca. one tenth of those of the crystalline species, Cp₂ZrCl₂ (31.2 % Zr by mass) and Cp₂ZrMe₂ (36.3 % Zr by mass). As a result, ⁹¹Zr SSNMR experiments on 1-Cl and 2-Me will be challenging. In addition to the direct reduction in Zr mass %, a further reduction of Zr occurs in 1-Cl and 2-Me due to low densities of the support material (tamped densities of ca. 0.3 g/cm³); for comparison, the densities predicted from the single crystal X-ray structures of Cp₂ZrCl₂ and Cp₂ZrMe₂ are 1.82 g/cm³ and 1.46 g/cm³, respectively. Therefore, the number of ⁹¹Zr spins in the 1-Cl and 2-Me samples is reduced by a factor of ca. 30-60, depending upon the tamped densities of the powdered crystalline samples. One might naively assume that the reduction in Zr content could be made up by acquiring more transients, however, the signal to noise of NMR experiments is proportional to the square root of the number of transients. Therefore, in order to acquire ⁹¹Zr SSNMR spectra of similar S/N to those of the crystalline complexes, 900 to 3600 times the number of transients would be needed. Clearly, signal enhancement techniques are absolutely necessary for any ⁹¹Zr SSNMR experiments conducted on such systems.

In this regard, Ellis and Lipton have previously demonstrated that the SSNMR spectra of unreceptive metal nuclei in metalloproteins can be acquired by employing cryogenic temperatures, in conjunction with NMR experiments which employ cross-polarization (CP) from ¹H and the QCPMG pulse sequence (CP/QCPMG).⁸⁻¹⁴ For example, when this pulse sequence was utilized on isotopically enriched samples at 10 K, it was possible to acquire ⁶⁷Zn SSNMR spectra of a 32 kDa protein (0.21 % Zn by mass)
and $^{25}$Mg SSNMR spectra of 35 kDa protein (0.07% Mg by mass). A similar approach was employed for the acquisition of the $^{91}$Zr SSNMR spectra of 1-Cl and 2-Me.

The $^{91}$Zr QCPMG SSNMR spectra of 1-Cl and 2-Me acquired at 10 K with direct polarization of the $^{91}$Zr nuclei are shown in Figure 9.1. Cooling the sample to 10 K provides signal enhancement of a factor of ca. 30, which partially offsets the loss in signal from reduced Zr content. A preliminary $^{91}$Zr SSNMR spectrum of a molecular analog to the surface supported species, Cp$_2$ZrClOSiMe$_3$, was also acquired at 9.4 T (Figure 9.1c). The synthesis and characterization of a corresponding methyl derivative, Cp$_2$ZrMe(OSiMe$_3$), is currently underway. Spectra were acquired in a piece-wise manner, with 11 and 13 sub-spectra acquired for 1-Cl and 2-Me, respectively. A 30 s pulse delay was employed for all experiments and the complete UW SSNMR spectra of 1-Cl and 2-Me were acquired in total experiment times of ca. 2 days each. Cross-polarization from $^1$H was attempted, as this could provide a theoretical signal gain of $\gamma_{1H}/\gamma_{91Zr} \approx 17$. Unfortunately, signal was not observed, most likely due to an increase in the $^1$H longitudinal relaxation times $[T_1(^1H)]$ at 10 K. It was possible to acquire $^1$H-$^{91}$Zr CP/QCPMG SSNMR spectra of crystalline Cp$_2$ZrCl$_2$; however, CP could only be observed at temperatures below ca. 200 K, presumably due to an increase in the rotating frame relaxation time constants $[T_{1p}({^{91}Zr})]$. Measurements of the optimal $^1$H recycle delays for crystalline Cp$_2$ZrCl$_2$ at 140 K reveal that recycle delays of ca. 12 s are necessary to obtain complete longitudinal relaxation. This is consistent with our hypothesis that the $T_1(^1H)$ is very long for 1-Cl and 2-Me at 10 K. Future experiments should be attempted with pentamethylcyclopentadienyl (Cp*) complexes, as the presence of mobile methyl
Figure 9.1. Static $^{91}\text{Zr}$ SSNMR spectra of (a) Cp$_2$ZrCl-(SiO$_2$) ($1$-Cl) and (b) Cp$_2$ZrMe-(SiO$_2$) ($2$-Me) acquired at 18.8 T. Analytical simulations are overlaid on the experimental spectra (solid red traces). Both spectra were acquired with sample temperatures of 10 K, 30 second recycle delays and 512 transients (4.3 hours) per sub-spectrum (50 kHz transmitter offset). 11 sub-spectra and 13 sub-spectra were acquired to form the total spectra of Cp$_2$ZrCl-(SiO$_2$) and Cp$_2$ZrMe-(SiO$_2$), respectively. A simulation with $\Omega = 0$ ppm (dashed blue trace) is shown for Cp$_2$ZrMe-(SiO$_2$). (c) Static $^{91}\text{Zr}$ SSNMR WURT-QCPMG spectrum of Cp$_2$ZrCl(OSiMe$_3$) at 9.4 T (black trace). The asterisk denotes a small amount of Cp$_2$ZrCl$_2$. Partway through the acquisition of sub-spectra it was necessary to alter the probe configuration, resulting in uneven intensities in the individual sub-spectra, and leading to intensity differentials between the experimental and simulated spectra.
<table>
<thead>
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<th>Compound</th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>$C_Q$ (MHz)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>$\eta_Q$&lt;sup&gt;c&lt;/sup&gt;</th>
<th>$\Omega$ (ppm)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>$\kappa$&lt;sup&gt;e&lt;/sup&gt;</th>
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<th>$\beta$ ($^\circ$)</th>
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<sup>a</sup> The complex name has been bolded for experimental values. The “X-ray” and “geom” labels indicate that calculations were performed with atomic coordinates taken from single crystal X-ray structures and geometry optimized models, respectively. <sup>b</sup> $C_Q = eQV_3/h$. Only the magnitude of $C_Q$ can be obtained from SSNMR experiments, while the sign of $C_Q$ is obtainable only from theoretical calculations. <sup>c</sup> $\eta_Q = (V_{11} - V_{22})/V_{33}$. <sup>d</sup> $\Omega = \delta_{13} - \delta_{11}$. <sup>e</sup> $\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$. <sup>f</sup>The uncertainties associated with the CS tensor parameters and Euler angles are very large; however, inclusion of parameters similar to those obtained from calculated values results in improved fits of the experiment spectra.
groups may afford more efficient $^1$H relaxation and enable CP experiments to be performed.

From the simulations of the static $^{91}$Zr SSNMR spectra of 1-Cl, 2-Me and Cp$_2$ZrCl(OSiMe$_3$) it is possible to obtain the $^{91}$Zr electric field gradient (EFG) tensor parameters ($C_Q$ and $\eta_Q$, Table 9.1). The lineshapes of static powder patterns are also influenced by the chemical shift (CS) tensor parameters ($\Omega$, $\kappa$ and $\delta_{so}$) and Euler angles; however, given the magnitude of the quadrupolar interactions in 1-Cl, 2-Me and Cp$_2$ZrCl(OSiMe$_3$), and the low S/N of the spectra of 1 and 2, it is difficult to obtain accurate values for these parameters. For comparison, the $^{91}$Zr CS and EFG tensor parameters of several previously studied crystalline zirconocene complexes (Chapter 3) are also listed in Table 9.1.

Large values of $C_Q$ are obtained for all complexes, and can most likely be attributed to the relatively short O-Zr bond lengths (ca. 1.90 to 2.00 Å, vide infra). In Chapter 3, it is demonstrated that $C_Q$ increases for Cp$_2$ZrX$_2$ complexes (X = Cl, Me) as the Zr-X bond lengths are shortened. Therefore, from the values of $C_Q$ obtained from the spectra of 1-Cl and 2-Me, and the similarly large value of $C_Q$ observed for Cp$_2$ZrCl(OSiMe$_3$), one can conclude that there is an interaction between the Zr centres and surface oxygen atoms in 1-Cl and 2-Me. The $\eta_Q$ value of 1-Cl is near 1 ($\eta_Q = 0.85$), while those of 2-Me and Cp$_2$ZrCl(OSiMe$_3$) are closer to 0.50 ($\eta_Q = 0.40$ and 0.50, respectively). The differences in the $\eta_Q$ values for 1-Cl and 2-Me can probably be attributed to differences in the Zr-Cl and Zr-Me bond lengths, but the origin of the differences in the $C_Q$ and $\eta_Q$ values for 1-Cl and Cp$_2$ZrCl(OSiMe$_3$) is not immediately
clear.

Quantum chemical calculations were performed in order to obtain structural models of 1-Cl and 2-Me. There is no known crystal structure for Cp₂ZrCl(OSiMe₃); however, a structure for the closely related CpZrCl(OSiMe₂(CH₂Cl)) complex is known.¹⁵ Atomic coordinates for calculations on Cp₂ZrCl(OSiMe₃) were obtained by replacing the Cl atom in CpZrCl(OSiMe₂(CH₂Cl)) with an H atom. Calculations of NMR tensor parameters were performed on this model, as well as a model in which all atomic positions were optimized (Figure 9.2). In both cases the calculations successfully predict the large \( C_Q \) values and the intermediate \( \eta_Q \) values that were obtained from simulations of the spectra, although \( C_Q \) is slightly underestimated in each case.

**Figure 9.2.** (a) Structure of Cp₂ZrCl(OSiMe₃) with coordinates based upon the single crystal XRD structure of Cp₂ZrCl(OSiMe₂(CH₂Cl)). (b) Geometry optimized structure of Cp₂ZrCl(OSiMe₃). (c) Geometry optimized model of 1-Cl. The Cp₂ZrCl fragment was bonded to a SiO₂ cluster based upon the structure of β-cristabolite. Atomic coordinates for the SiO₂ fragment were taken from Blanc et al.⁸ Each of the terminal oxygen atoms was capped with a single H atom.
Eisenstein and Coperet have recently presented computational studies of organometallic complexes bound to silica surfaces.\textsuperscript{6,7} One of the major findings of these studies is that the SiO\textsubscript{2} surface essentially acts as a sterically congested anionic ligand. Quantum chemical calculations were performed on models of 1-Cl and 2-Me constructed by binding the metallocene fragments to the surface oxygen atom of an SiO\textsubscript{2} cluster derived from the (110) surface structure of β-cristabolite. These calculations predict that there are relatively minor differences in the O-Zr bond lengths and Zr-O-Si angles of 1-Cl and Cp\textsubscript{2}ZrCl(OSiMe\textsubscript{3}). The slight differences in this angle may explain the differences in the observed $C_Q$ and $\eta_Q$ values for 1-Cl and Cp\textsubscript{2}ZrCl(OSiMe\textsubscript{3}), although additional calculations are required to test this. The quantum chemical calculations also predict that 2-Me should possess a larger value of $C_Q$ and lower value of $\eta_Q$ than 1-Cl.

**Future Work**

Silica is one of the most commonly employed support materials for heterogeneous organometallic catalysts; therefore, investigating the structures of silica-supported catalysts is of great importance.\textsuperscript{2-4,6} In the future, it will be worthwhile to attempt experiments on surface-supported Cp* zirconocenes, as the methyl groups may lead to efficient $^1$H relaxation, which may enable $^1$H-$^91$Zr CP experiments. This could result in substantial increases in S/N bringing total experiment times down to the order of hours.

Another exciting possibility is the application of dynamic nuclear polarization (DNP) for signal enhancement.\textsuperscript{16-20} In DNP experiments the spin polarization of unpaired electrons is transferred to $^1$H nuclei by irradiating the sample with microwave frequencies.
In order to accomplish this the sample is usually dissolved into a solution which is doped with a stable radical species. The solutions are then frozen and DNP SSNMR experiments are conducted. The low temperatures are also necessary in order to obtain efficient DNP enhancements. In order to apply this approach to heterogeneous catalysts it would be necessary to develop sample preparation protocols which are capable of bringing the polarization transfer agent in contact with the catalyst surface. While the development of these protocols would be a non-trivial, the potential signal enhancements available from DNP experiments warrant their development.

The theoretical signal gain of DNP experiments is proportional to $\gamma_e/\gamma_X$ where, $\gamma_e$ is the gyromagnetic ratio of the electron. For $^1\text{H}$ this ratio is equal to $-658$, while for $^{91}\text{Zr}$ this ratio is equal to $7051$. Recently, commercial DNP SSNMR spectrometers operating at fields of $9.4\ \text{T}$ and $14.1\ \text{T}$ have become available.$^{17}$ With these systems, $^1\text{H}$ DNP signal enhancement factors of $30$ to $60$ are typical. Therefore, if the polarization of the $^1\text{H}$ nuclei could be enhanced and then subsequently transferred to $^{91}\text{Zr}$ nuclei via CP, $^{91}\text{Zr}$ signal enhancement factors of ca. $321$ to $642$ are feasible. These DNP SSNMR experiments would not be limited to zirconium, as many of the other transition metals possess NMR active nuclei with low receptivities (e.g., $^{47/49}\text{Ti}$, $^{53}\text{Cr}$, $^{57}\text{Fe}$, $^{67}\text{Zn}$, $^{95}\text{Mo}$, $^{99}\text{Ru}$, $^{109}\text{Ag}$, $^{183}\text{W}$ and $^{189}\text{Y}$).$^{21}$ Therefore, DNP experiments could enable the characterization of a variety of heterogeneous catalysts by SSNMR spectroscopy of unreceptive metal nuclei.
9.5 Bibliography

(14) Ellis, P. D.; Lipton, A. S., Low-temperature solid-state NMR spectroscopy. A strategy for the direct observation of quadrupolar nuclides of biological interest. In Annual
Appendix A: Supplementary Figures and Tables for Chapter 2

Table A1. QCPMG Acquisition Parameters For Spectra Acquired at 9.4 T

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<sup>a</sup>1 = Cp<sub>2</sub>TiCl<sub>2</sub>, 2 = CpTiCl<sub>3</sub>, 3 = Cp<sub>2</sub>ZrCl<sub>2</sub>, 4 = Cp<sup>*</sup><sub>2</sub>ZrCl<sub>2</sub>, 5 = Cp<sub>2</sub>HfCl<sub>2</sub>, 6 = Cp<sub>2</sub>ZrMeCl, 7 = (Cp<sub>2</sub>ZrCl)<sub>2</sub>µ-O, 8 = Cp<sup>*</sup>ZrCl<sub>3</sub>, 9 = CpZrCl<sub>3</sub>, 10 = Cp<sub>2</sub>ZrHCl 

<sup>b</sup>This includes sub-spectra that were acquired in the region of the <sup>35</sup>Cl satellite transitions.
Table A2. QCPMG Acquisition Parameters For Spectra Acquired at 21.1 T

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$^a$2 = CpTiCl3, 3 = Cp$_2$ZrCl$_2$, 8 = Cp*ZrCl$_3$, 10 = Cp$_2$ZrHCl

$^b$The spectrum of this compound was acquired with a hahn-echo type sequence in a piecewise manner.
Figure A1. Static $^{35}$Cl NMR spectra acquired at 9.4 T and a comparison of simulations. The dashed traces are simulations which include the effects of CSA, while the solid trace does not include CSA. At this field there is very little difference between the two simulations for all spectra. The fit with four independent sites is shown for Cp*ZrCl$_3$. 

CpTiCl$_3$

Cp$_2$ZrCl$_2$

Cp*ZrCl$_3$
Figure A2. The $^{35}$Cl spectrum of Cp*ZrCl$_3$ and a comparison of simulations which utilize two sites (one bridging and one terminal) and four independent sites (two bridging and two terminal). In the two site fit the terminal site is shown with the dashed trace. The simulation which uses four sites provides a better fit of the intensity in the central part of the pattern and reproduces the “shoulder” features at both sides of the central transitions. In both the two and four site fits the intensity of the bridging sites has been set to half of those of the terminal sites.
Figure A3. Experimental powder X-ray diffraction pattern of Cp₂ZrHCl. The top simulation is based upon the single-crystal X-ray diffraction structure of Cp₂ZrHMe. The middle trace is a simulation based upon the structure Cp₂ZrHMe where the methyl group has been removed and a chlorine atom has been placed at the position of the methyl carbon. The middle trace provides an excellent match with the experimental pattern.
Figure A4. FIDs and the corresponding fourier transformed $^{35}$Cl NMR spectra of Cp$_2$ZrHCl. The FIDs have been magnitude calculated in order to make the echo tops more visible. The application of $^1$H decoupling greatly increases the number of echoes which may be acquired and results in large gains in signal to noise.
### Table B1. Acquisition Parameters for $^{91}$Zr MAS SSNMR Spectra Acquired at 9.4 T

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<tr>
<td>$180^\circ$ pulse widths $[\pi]$ (µs)</td>
<td>4.0</td>
<td>3.72</td>
<td>11.0</td>
<td>11.0</td>
<td>11.0</td>
</tr>
<tr>
<td>Ring-down delays $[\tau_1]$ (µs)</td>
<td>100.0</td>
<td>100</td>
<td>90.91</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Ring-down delays $[\tau_2]$ (µs)</td>
<td>50</td>
<td>50</td>
<td>53.41</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>DFS Start Frequency (MHz)</td>
<td>-</td>
<td>-</td>
<td>0.900</td>
<td>0.65</td>
<td>-</td>
</tr>
<tr>
<td>DFS End Frequency (MHz)</td>
<td>-</td>
<td>-</td>
<td>0.150</td>
<td>0.12</td>
<td>-</td>
</tr>
<tr>
<td>Length of DFS Sweep (ms)</td>
<td>-</td>
<td>-</td>
<td>0.800</td>
<td>0.600</td>
<td>-</td>
</tr>
<tr>
<td>Number of Steps in DFS Waveform</td>
<td>-</td>
<td>-</td>
<td>1800</td>
<td>1800</td>
<td>-</td>
</tr>
<tr>
<td>DFS Step Length (µs)</td>
<td>-</td>
<td>-</td>
<td>0.44</td>
<td>0.33</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Echo refers to a 16-step Hahn echo sequence. DFS/Echo or FAM/Echo refers to a sequence where the Hahn echo portion is prefaced by a double frequency sweep (DFS) waveform or fast amplitude modulated (FAM) waveform [see main text for references].
### Table B2. Acquisition Parameters for Static $^{91}$Zr SSNMR Spectra Acquired at 9.4 T

<table>
<thead>
<tr>
<th></th>
<th>Cp$_2$ZrCl$_2$</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pulse Sequence</strong></td>
<td>DFS/Echo</td>
<td>DFS/Echo</td>
<td>Echo</td>
<td>DFS/Echo</td>
<td>DFS/Echo</td>
</tr>
<tr>
<td><strong>Number of scans</strong></td>
<td>153600</td>
<td>90167</td>
<td>110608</td>
<td>54000</td>
<td>64800</td>
</tr>
<tr>
<td><strong>Recycle Delay (s)</strong></td>
<td>0.75</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>Dwell (µs)</strong></td>
<td>3.5</td>
<td>25.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td><strong>Spectral width (kHz)</strong></td>
<td>285.71</td>
<td>40</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td><strong>Acquisition length (number of points)</strong></td>
<td>256</td>
<td>512</td>
<td>512</td>
<td>2048</td>
<td>2048</td>
</tr>
<tr>
<td>90° pulse width $[\pi/2]$ (µs)</td>
<td>1.17</td>
<td>2.00</td>
<td>1.86</td>
<td>4.16</td>
<td>2.71</td>
</tr>
<tr>
<td>180° pulse widths $[\pi]$ (µs)</td>
<td>2.34</td>
<td>4.00</td>
<td>3.72</td>
<td>4.16$^b$</td>
<td>5.42</td>
</tr>
<tr>
<td><strong>Ring-down delays $[\tau_1]$ (µs)</strong></td>
<td>84.5</td>
<td>100</td>
<td>65</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td><strong>Ring-down delays $[\tau_2]$ (µs)</strong></td>
<td>53.0</td>
<td>50</td>
<td>35</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td><strong>DFS Start Frequency (MHz)</strong></td>
<td>2.000</td>
<td>0.800</td>
<td>-</td>
<td>1.000</td>
<td>1.250</td>
</tr>
<tr>
<td><strong>DFS End Frequency (MHz)</strong></td>
<td>0.185</td>
<td>0.110</td>
<td>-</td>
<td>0.100</td>
<td>0.100</td>
</tr>
<tr>
<td><strong>Length of DFS Sweep (ms)</strong></td>
<td>0.800</td>
<td>0.700</td>
<td>-</td>
<td>1.250</td>
<td>1.600</td>
</tr>
<tr>
<td><strong>Number of Steps in DFS Waveform</strong></td>
<td>5920</td>
<td>2380</td>
<td>-</td>
<td>6400</td>
<td>6400</td>
</tr>
<tr>
<td><strong>DFS Step Length (µs)</strong></td>
<td>0.135</td>
<td>0.294</td>
<td>-</td>
<td>0.195</td>
<td>0.25</td>
</tr>
</tbody>
</table>

$^a$Echo refers to a 16-step Hahn echo sequence. DFS/Echo or FAM/Echo refers to a sequence where the Hahn echo portion is prefaced by a double frequency sweep (DFS) waveform or fast amplitude modulated (FAM) waveform [see main text for references].

$^b$In this case the a 90°-90° echo was employed.
<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Table B3.</strong> Acquisition Parameters for Ultra-wideline $^{91}$Zr SSNMR Spectra Acquired at 9.4 T</td>
<td><strong>6</strong></td>
<td><strong>7</strong></td>
<td><strong>8</strong></td>
</tr>
<tr>
<td>Pulse Sequence</td>
<td>QCPMG</td>
<td>WURST-QCPMG</td>
<td>WURST-QCPMG</td>
</tr>
<tr>
<td>Number of scans per sub-spectrum</td>
<td>70000</td>
<td>36000</td>
<td>10800</td>
</tr>
<tr>
<td>Transmitter offset per piece (kHz)</td>
<td>80</td>
<td>192</td>
<td>200</td>
</tr>
<tr>
<td>Number of sub-spectra acquired</td>
<td>40</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Recycle delay (s)</td>
<td>0.2</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Number of Meiboom-Gill loops [N]</td>
<td>24</td>
<td>16</td>
<td>163</td>
</tr>
<tr>
<td>Real points per loop</td>
<td>40</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Spectral width of sub-spectra (kHz)</td>
<td>800</td>
<td>800</td>
<td>1000</td>
</tr>
<tr>
<td>Dwell (µs)</td>
<td>1.25</td>
<td>1.25</td>
<td>1.0</td>
</tr>
<tr>
<td>Spikelet separation (kHz) [1/τ_a]</td>
<td>20.0</td>
<td>16.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Acquisition length (number of points)</td>
<td>980</td>
<td>800</td>
<td>16300</td>
</tr>
<tr>
<td>90º pulse width [π/2] (µs)</td>
<td>1.95</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>180º pulse widths [π] (µs)</td>
<td>3.90</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>QCPMG ring-down delays [τ_1 = τ_2 = τ_3 = τ_4] (µs)</td>
<td>40</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WURST-QCPMG ringdown delay [τ_1] (µs)</td>
<td>-</td>
<td>56.25</td>
<td>75</td>
</tr>
<tr>
<td>WURST-QCPMG ringdown delay [τ_2 = τ_3] (µs)</td>
<td>-</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Offset of WURST pulse (kHz)*</td>
<td>-</td>
<td>800</td>
<td>1000</td>
</tr>
<tr>
<td>Sweep Rate of WURST pulse (MHz/ms)</td>
<td>-</td>
<td>32</td>
<td>40</td>
</tr>
</tbody>
</table>

*The WURST pulse sweeps over a total frequency range equal to two times the offset of the WURST pulse.
<table>
<thead>
<tr>
<th>Pulse Sequence&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Cp₂ZrCl₂</th>
<th>1</th>
<th>2</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Echo</td>
<td>Echo</td>
<td>Echo</td>
<td>Echo</td>
<td>Echo</td>
</tr>
<tr>
<td>Number of scans</td>
<td>1024</td>
<td>9832</td>
<td>12730</td>
<td>28816</td>
</tr>
<tr>
<td>Recycle Delay (s)</td>
<td>0.5</td>
<td>1.0</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Dwell (µs)</td>
<td>10.0</td>
<td>5.0</td>
<td>2.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Spectral width (kHz)</td>
<td>100.0</td>
<td>200.0</td>
<td>500.0</td>
<td>250.0</td>
</tr>
<tr>
<td>Acquisition length</td>
<td>1024</td>
<td>512</td>
<td>256</td>
<td>512</td>
</tr>
<tr>
<td>(number of points)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90° pulse width [π/2] (µs)</td>
<td>4.2</td>
<td>5.7</td>
<td>2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>180° pulse widths [π] (µs)</td>
<td>4.2</td>
<td>5.7</td>
<td>4.6</td>
<td>2.0</td>
</tr>
<tr>
<td>Ring-down delays [τ₁] (µs)</td>
<td>100</td>
<td>30</td>
<td>30</td>
<td>98</td>
</tr>
<tr>
<td>Ring-down delays [τ₂] (µs)</td>
<td>50</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

<sup>a</sup>Echo refers to a 16-step Hahn echo sequence. DFS/Echo or FAM/Echo refers to a sequence where the Hahn echo portion is prefaced by a double frequency sweep (DFS) waveform or fast amplitude modulated (FAM) waveform [see main text for references].

<sup>b</sup>In this case the a 90°-90° echo was employed.
<table>
<thead>
<tr>
<th>Pulse Sequence</th>
<th>4</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>WURST-QCPMG</td>
<td>WURST-QCPMG</td>
<td>WURST-QCPMG</td>
<td>WURST-QCPMG</td>
<td>WURST-QCPMG</td>
<td>WURST-QCPMG</td>
</tr>
<tr>
<td>Number of scans per sub-spectrum</td>
<td>19161</td>
<td>40960</td>
<td>32768</td>
<td>8192</td>
<td>8192</td>
</tr>
<tr>
<td>Transmitter offset per piece (kHz)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>200.0</td>
</tr>
<tr>
<td>Number of sub-spectra acquired</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>Recycle delay (s)</td>
<td>2.0</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Number of Meiboom-Gill loops [N]</td>
<td>25</td>
<td>32</td>
<td>32</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>Real points per loop</td>
<td>200</td>
<td>250</td>
<td>250</td>
<td>500</td>
<td>125</td>
</tr>
<tr>
<td>Spectral width of sub-spectra (kHz)</td>
<td>500</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Dwell (µs)</td>
<td>2.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Spikelet separation (kHz) [1/τₐ]</td>
<td>2.5</td>
<td>4.0</td>
<td>4.0</td>
<td>2.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Acquisition length (number of points)</td>
<td>5000</td>
<td>8000</td>
<td>8000</td>
<td>16000</td>
<td>4000</td>
</tr>
<tr>
<td>WURST pulse width (µs)</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>WURST-QCPMG ringdown delay [τ₁] (µs)</td>
<td>130</td>
<td>112</td>
<td>112</td>
<td>192</td>
<td>2.5</td>
</tr>
<tr>
<td>WURST-QCPMG ringdown delay [τ₂ = τ₃] (µs)</td>
<td>20</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>Offset of WURST pulse (kHz)*</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Sweep Rate of WURST pulse (MHz/ms)</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
</tbody>
</table>

*The WURST pulse sweeps over a total frequency range equal to two times the offset of the WURST pulse.
Figure B1. ORTEP depiction of the solid-state molecular structure of \( \text{Cp}_2\text{ZrMeCl} \) shown with 30\% probability thermal ellipsoids. The structure features a ~60:40 occupational disorder of the Cl and CH\(_3\) sites, with a greater occupation of Cl at the Cl(1a) site. Bonds between the cyclopentadienyl carbons and Zr are omitted for clarity.
Table B6. Crystal Data and Structure Refinement for Cp₂ZrMeCl (7).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₁₁H₁₃ClZr</td>
</tr>
<tr>
<td>Formula weight</td>
<td>271.88</td>
</tr>
<tr>
<td>Temperature</td>
<td>173(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(1)/n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 6.7624(6) Å, b = 11.7215(10) Å, c = 13.6347(11) Å</td>
</tr>
<tr>
<td></td>
<td>α = 90°, β = 92.3670(10)°, γ = 90°.</td>
</tr>
<tr>
<td>Volume</td>
<td>1079.84(16) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.672 mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.216 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>544</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.42 × 0.4 × 0.19 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.99 to 27.47°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>–8≤h≤8, –15≤k≤14, –17≤l≤17</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>11766</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2447 [R(int) = 0.0234]</td>
</tr>
<tr>
<td>Completeness to theta = 27.47°</td>
<td>98.6 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.794 and 0.653</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2447 / 0 / 139</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.047</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R₁ = 0.0226, wR₂ = 0.0509</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0261, wR₂ = 0.0532</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.623 and –0.391 e.Å⁻³</td>
</tr>
</tbody>
</table>
Figure B2. ORTEP depiction of the solid-state molecular structure of O(\text{Me}_2\text{SiC}_5\text{H}_4)_2\text{ZrBr}_2 (4) shown with 50% probability thermal ellipsoids.
Table B7. Crystal data and structure refinement for O(Me$_2$SiC$_5$H$_4$)$_2$ZrBr$_2$ (4).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>cs905</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C$<em>{14}$H$</em>{20}$Br$_2$OSi$_2$Zr</td>
</tr>
<tr>
<td>Formula weight</td>
<td>511.52</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P\ 2_1/c$</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>$a = 13.5792(5)$ Å, $b = 8.5955(3)$ Å, $c = 15.3894(5)$ Å</td>
</tr>
<tr>
<td>Volume</td>
<td>1784.40(10) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.904 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>5.222 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>1000</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.44 x 0.21 x 0.12 mm$^3$</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>4.18 to 30.03°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-16&lt;=$h&lt;=$19, -12&lt;=$k&lt;=$8, -21&lt;=$l&lt;=$21</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>16281</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>5194 [R(int) = 0.0444]</td>
</tr>
<tr>
<td>Completeness to theta = 30.03°</td>
<td>99.7 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Gaussian</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.583 and 0.293</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>5194 / 0 / 185</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>0.867</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0286, wR2 = 0.0537</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0459, wR2 = 0.0554</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.165 and -0.623 e.Å$^{-3}$</td>
</tr>
</tbody>
</table>
Figure B3. ORTEP depiction of the solid-state molecular structure of $(1,3$-$\text{C}_5\text{H}_3)(\text{SiMe}_2\text{OSiMe}_2)_2(1,3$-$\text{C}_5\text{H}_3)$ZrBr$_2$ (5) shown with 50% probability thermal ellipsoids.
**Table B8.** Crystal Data and Structure Refinement for $(1,3\text{-C}_5\text{H}_3)(\text{SiMe}_2\text{O}\text{SiMe}_2)_2(1,3\text{-C}_5\text{H}_3)\text{ZrBr}_2$ (5)

Table 1. Crystal data and structure refinement for JSM-STRAP2.

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<th>Identification code</th>
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<td>Empirical formula</td>
<td>$\text{C}<em>{18}\text{H}</em>{30}\text{Br}_2\text{O}_2\text{Si}_4\text{Zr}$</td>
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<tr>
<td>Formula weight</td>
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<tr>
<td>Wavelength</td>
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</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P\ b\ c\ a$</td>
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| Unit cell dimensions  | $a = 14.9355(13)$ Å  |
|                       | $\alpha = 90^\circ$. |
|                       | $b = 14.682(3)$ Å     |
|                       | $\beta = 90^\circ$.   |
|                       | $c = 24.174(2)$ Å     |
|                       | $\gamma = 90^\circ$.  |
| Volume                | 5301.0(12) Å³        |
| Density (calculated)  | 1.608 Mg/m³          |
| Absorption coefficient| 3.622 mm⁻¹           |
| $F(000)$              | 2560                 |
| Crystal size          | 0.6 x 0.2 x 0.08 mm³ |
| Theta range for data collection | 2.12 to 22.50°. |
| Index ranges          | -1<=$h$<=$16$, -1<=$k$<=$15$, -26<=$l$<=$1$ |
| Reflections collected | 3879                 |
| Independent reflections| 3202 [R(int) = 0.0548] |
| Completeness to theta = 22.50° | 92.5 % |
| Absorption correction | Empirical            |
| Max. and min. transmission | 0.8107 and 0.3614 |
| Refinement method     | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3202 / 0 / 253 |
| Goodness-of-fit on $F^2$ | 0.993 |
| Final R indices [I>2sigma(I)] | R1 = 0.0508, wR2 = 0.0788 |
| R indices (all data)  | R1 = 0.1200, wR2 = 0.0966 |
| Extinction coefficient| 0.00061(6)           |
| Largest diff. peak and hole | 0.415 and -0.430 e.Å⁻³ |
Table B9. Calculated $^{91}$Zr EFG and CS Tensor Parameters for Cp$_2$ZrCl$_2$ using Coordinates Determined from Single Crystal X-ray Structures (Site 1 Only)

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<th>$\Omega$ (ppm)</th>
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12s11p7d

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12s11p7d - ii

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12s9p5d

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</table>

The 6-31G** basis set was employed on C and H unless otherwise noted. For some of the calculations CS tensor parameters were not calculated. All calculations were performed with Gaussian 03. References and explanations of the basis set labels can be found in the main text.
Table B10. Calculated $^{91}\text{Zr}$ EFG and CS Tensor Parameters for Cp$_2$ZrBr$_2$ (2) Using Coordinates Determined from Single Crystal X-ray Structures (Both Sites)

<table>
<thead>
<tr>
<th>Zr Basis/Site</th>
<th>Method</th>
<th>Br Basis</th>
<th>$\sigma_{iso}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
<th>$V_{33}$ (a.u.)</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
</tr>
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<td></td>
<td>0.058</td>
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<tr>
<td>6s3p3d</td>
<td>RHF</td>
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<td>447</td>
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<td>-0.236</td>
<td>-9.77</td>
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</tr>
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<td>562</td>
<td>-0.58</td>
<td>0.162</td>
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<tr>
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<td>1820</td>
<td>821</td>
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<td></td>
<td>B3LYP</td>
<td>6-311G**</td>
<td>1806</td>
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<td>0.86</td>
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<tr>
<td></td>
<td></td>
<td>Br-11s7p4d-QZV</td>
<td>1817</td>
<td>821</td>
<td>-0.61</td>
<td>-0.141</td>
<td>-5.82</td>
<td>0.93</td>
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<tr>
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<td>-0.97</td>
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<tr>
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<td>B3LYP</td>
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<td>Br-11s7p4d-QZV</td>
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<td>Br-1S2</td>
<td>2482</td>
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<td>-0.72</td>
<td>0.163</td>
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<td>0.49</td>
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<td>574</td>
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<td>0.151</td>
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<td>0.75</td>
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<td>Br-1S2</td>
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<td>0.186</td>
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<tr>
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<td>B3LYP</td>
<td>6-311G**</td>
<td>1781</td>
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<td>748</td>
<td>-0.65</td>
<td>-0.027</td>
<td>-1.12</td>
<td>0.93</td>
</tr>
</tbody>
</table>
Note: There are two crystallographic sites for Cp₂ZrBr₂. One Cp ring of site 2 has been modelled with disorder and possesses two conformations. Calculations are shown for both conformations.

**Table B11.** Calculated ⁹¹Zr EFG and CS Tensor Parameters for Cp₂ZrCl₂ using Coordinates With Idealized Cp Rings (Both Sites)

<table>
<thead>
<tr>
<th>Zr Basis</th>
<th>Method</th>
<th>Cl Basis</th>
<th>Site</th>
<th>σ_{iso} (ppm)</th>
<th>Ω (ppm)</th>
<th>κ V_{33} (a.u.)</th>
<th>C_Q (MHz)</th>
<th>η_Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td></td>
<td></td>
<td>1</td>
<td>340</td>
<td>-0.60</td>
<td>0.150</td>
<td>6.2</td>
<td>0.18</td>
</tr>
<tr>
<td>Experiment</td>
<td></td>
<td></td>
<td>2</td>
<td>350</td>
<td>-0.70</td>
<td>0.158</td>
<td>6.5</td>
<td>0.30</td>
</tr>
<tr>
<td>6s3p3d</td>
<td>RHF</td>
<td>cc-pVDZ</td>
<td>1</td>
<td>2562 343</td>
<td>-0.41</td>
<td>0.0142</td>
<td>0.59</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>RHF</td>
<td>cc-pVDZ</td>
<td>2</td>
<td>2562 349</td>
<td>-0.42</td>
<td>0.0188</td>
<td>0.78</td>
<td>0.42</td>
</tr>
<tr>
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<td>cc-pVTZ</td>
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<td>0.0677</td>
<td>2.80</td>
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<tr>
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<td>RHF</td>
<td>cc-pVTZ</td>
<td>2</td>
<td>2573 378</td>
<td>-0.56</td>
<td>0.0812</td>
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<td>0.71</td>
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<td>6-31G** on C,H</td>
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<td>B3LYP</td>
<td>cc-pVDZ</td>
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<td>cc-pVDZ</td>
<td>2</td>
<td>1917 456</td>
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<td>-0.1472</td>
<td>-6.09</td>
<td>0.30</td>
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<td>B3LYP</td>
<td>cc-pVTZ</td>
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<td>1925 471</td>
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<tr>
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<td>B3LYP</td>
<td>cc-pVTZ</td>
<td>2</td>
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<td>-0.65</td>
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<td>0.48</td>
</tr>
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<td>6-31G** on C,H</td>
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<td>6-31G**</td>
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<td>0.40</td>
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<td>cc-pVDZ</td>
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<td>cc-pVDZ</td>
<td>2</td>
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<td>cc-pVTZ</td>
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<td>B3LYP</td>
<td>cc-pVTZ</td>
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The 6-31G** basis set was employed on C and H unless otherwise noted. For some of the calculations CS tensor parameters were not calculated. All calculations were performed with Gaussian 03.
Table B12. Calculated $^{91}$Zr EFG and CS Tensor Parameters for Cp$_2$ZrBr$_2$ (2) Using Coordinates With Idealized Cp rings (Both Sites)

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<th>Zr Basis/Site Method Br Basis</th>
<th>Zr Basis/Site Method Br Basis</th>
<th>Zr Basis/Site Method Br Basis</th>
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<th>Zr Basis/Site Method Br Basis</th>
<th>Zr Basis/Site Method Br Basis</th>
<th>Zr Basis/Site Method Br Basis</th>
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<td>Ω (ppm)</td>
<td>κ</td>
<td>$V_{33}$ (a.u.)</td>
<td>$C_Q$ (MHz)</td>
<td>η$_Q$</td>
<td>σ$_{iso}$ (ppm)</td>
<td>Ω (ppm)</td>
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<td>0.058</td>
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<td>Site 2/Cp Conformation 1</td>
<td>Site 2/Cp Conformation 2</td>
<td>Site 2/Cp Conformation 2</td>
<td>Site 2/Cp Conformation 2</td>
<td>Site 2/Cp Conformation 2</td>
<td>Site 2/Cp Conformation 2</td>
<td>Site 2/Cp Conformation 2</td>
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<td>0.91</td>
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Site 2/Cp Conformation 1

| 6s3p3d RHF Br-1S2          | 2411                        | 379                        | -0.14                       | 0.310                      | 12.83                      | 0.20                       |
| RHF 6-31G** Br-1S2         | 2490                        | 493                        | -0.56                       | 0.154                      | 6.37                       | 0.06                       |
| B3LYP Br-1S2               | 1747                        | 515                        | -0.43                       | 0.120                      | 4.97                       | 0.31                       |
| B3LYP 6-31G** Br-11s7p4d-QZV | 1811                        | 698                        | -0.68                       | -0.025                     | -1.03                      | 0.31                       |
| B3LYP 6-311G** Br-11s7p4d-QZV | 1797                        | 692                        | -0.68                       | -0.038                     | -1.57                      | 0.39                       |
| 12s9p5d RHF Br-1S2         | 2517                        | 399                        | -0.52                       | -0.099                     | -4.10                      | 0.83                       |
| RHF 6-31G** Br-1S2         | 2517                        | 399                        | -0.52                       | -0.099                     | -4.10                      | 0.83                       |
| B3LYP Br-1S2               | 1839                        | 380                        | -0.36                       | 0.042                      | 1.73                       | 0.19                       |
| B3LYP 6-31G** Br-1S2       | 1938                        | 545                        | -0.67                       | 0.082                      | 3.38                       | 0.40                       |
| Zr-5F3 RHF Br-1S2          | 2400                        | 345                        | -0.09                       | 0.202                      | 8.34                       | 0.12                       |
| RHF 6-31G** Br-1S2         | 2517                        | 399                        | -0.52                       | -0.099                     | -4.10                      | 0.83                       |
| B3LYP Br-1S2               | 1839                        | 380                        | -0.36                       | 0.042                      | 1.73                       | 0.19                       |
| B3LYP 6-31G** Br-1S2       | 1938                        | 545                        | -0.67                       | 0.082                      | 3.38                       | 0.40                       |
| 12s9p5d RHF Br-1S2         | 2479                        | 501                        | -0.75                       | 0.199                      | 8.22                       | 0.59                       |
| RHF 6-31G** Br-1S2         | 2529                        | 528                        | -0.78                       | -0.080                     | -3.33                      | 0.43                       |
| B3LYP Br-1S2               | 1742                        | 794                        | -0.67                       | 0.232                      | 9.60                       | 0.19                       |
| B3LYP 6-31G** Br-1S2       | 1796                        | 861                        | -0.73                       | -0.057                     | -2.36                      | 0.67                       |

Site 2/Cp Conformation 2

| 6s3p3d RHF Br-1S2          | 2402                        | 386                        | -0.16                       | 0.299                      | 12.35                      | 0.22                       |
| RHF 6-31G** Br-1S2         | 2483                        | 513                        | -0.57                       | 0.148                      | 6.14                       | 0.07                       |
| B3LYP Br-1S2               | 1726                        | 523                        | -0.44                       | 0.107                      | 4.42                       | 0.36                       |
| B3LYP 6-31G** Br-1S2       | 1793                        | 721                        | -0.69                       | -0.046                     | -1.92                      | 0.17                       |
| B3LYP 6-311G** Br-11s7p4d-QZV | 1777                        | 707                        | -0.69                       | -0.049                     | -2.03                      | 0.16                       |
| B3LYP Br-11s7p4d-QZV       | 1794                        | 730                        | -0.71                       | -0.059                     | -2.45                      | 0.16                       |
Note: There are two crystallographic sites for Cp$_2$ZrBr$_2$. One Cp ring of site 2 has been modelled with disorder and possesses two conformations. Calculations are shown for both conformations.

**Table B13.** Calculated $^{91}\text{Zr}$ NMR Tensor Parameters for Cp*$_2$ZrCl$_2$ (1) Using Coordinates From the Single Crystal X-ray Structure of (CpMe$_4$Et)$_2$ZrCl$_2$ and Structures With Idealized Cp rings

<table>
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<th>Method</th>
<th>Cl Basis</th>
<th>$\sigma_{iso}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
<th>$V_{33}$ (a.u.)</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
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**Table B14.** Calculated EFG Tensor Parameters for the Central Molecule of a 12 Molecule Cluster of Cp$_2$ZrMeCl.

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<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
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<td>Cluster 2</td>
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Figure B4. MAS $^{91}$Zr SSNMR spectra of Cp$_2$ZrCl$_2$ acquired at 21.1 T (top) and 9.4 T (bottom). Analytical simulations are overlaid on top of the experimental spectra. Two sites were employed in the simulations. A de-convolution of the individual simulated sites is also shown for both fields. The spectrum acquired at 21.1 T was acquired with a sample spinning speed ($v_{rot}$) of 10 kHz.
Figure B5 $^{91}$Zr triple quantum-MQMAS NMR spectrum of Cp$_2$ZrBr$_2$ at 9.4 T. Although the direct dimension clearly exhibits NMR patterns for more than one $^{91}$Zr site, it is not possible to separate them at an applied magnetic field of 9.4 T. A spinning speed of $\nu_{\text{rot}} = 10000$ Hz was employed.
Figure B6. MAS $^{91}$Zr SSNMR spectrum of Cp$_2$ZrBr$_2$ (2) acquired at a sample spinning speed ($\nu_{\text{rot}}$) of 5000 Hz at 21.1 T. The asterisk denotes the isotropic peak. All other peaks are spinning sidebands. A numerical simulation performed with the SIMPSON program is overlaid on top of the experimental spectrum. The simulation employs the CS tensor parameters and Euler angles obtained from the static spectra. Inset: The spectrum that results from adding each of the spinning sidebands to the isotropic peak. An analytical simulation generated with the WSolids program is overlaid on the experimental spectrum. The simulation employs two sites which possess the same EFG tensor parameters as those employed for simulations of the 9.4 T MAS spectrum. $\delta_{\text{iso}}$ values of 128 ppm and 130 ppm were employed for the two sites in the simulation.
Figure B7. Solution NMR spectra of Ind$_2$ZrCl$_2$ (6). (a) $^{13}$C($^1$H) NMR spectrum in CH$_2$Cl$_2$. The indenyl ligand fragment is pictured. (b) $^1$H NMR spectrum in CD$_2$Cl$_2$. 
Figure B8. Experimental powder X-ray diffraction pattern (bottom trace) measured from 6 at room temperature. The simulated powder pattern (top trace) has been calculated from the previously determined single crystal X-ray diffraction structure (Repo, T.; Klinga, M.; Mutikainen, I.; Su, Y.; Leskela, M.; Polamo, M., Acta Chem. Scand. 1996, 50, (12), 1116-1120). The single crystal X-ray diffraction structure was determined at a temperature of 153 K. Temperature dependent polymorphism may account for the discrepancy in the measured and observed powder patterns.
Figure B9. Solution $^1$H and $^{13}$C NMR spectra of 7 in C$_6$D$_6$. These spectra were collected immediately after the sample was synthesized. (a) $^1$H NMR (b) $^{13}$C NMR.
Figure B10. $^1$H and $^{13}$C solution NMR spectra of the sample of 7 which was employed for experiments at 21.1 T. These spectra were acquired several months after the solid-state $^{91}$Zr NMR spectrum had been acquired. (a) $^1$H NMR spectrum. (b) $^{13}$C NMR spectra with and without $^1$H decoupling are shown. C$_6$D$_6$ was employed as the solvent. The methyl peak is not visible in the $^{13}$C NMR spectrum without decoupling due to low signal to noise.
Figure B11. $^1$H and $^{13}$C solution NMR spectra of the sample of 7 which was employed for experiments at 9.4 T. These spectra were recorded after the sample had been characterized by $^{91}$Zr SSNMR. (a) $^1$H NMR spectrum. (b) $^{13}$C NMR spectra with and without $^1$H decoupling are shown. The peaks visible at $\delta_{iso}(^1H) = 0.05$ ppm and $\delta_{iso}(^{13}C) = 1.04$ ppm are attributed to silicone grease which was used to seal the top of glass tubes used for SSNMR experiments. CH$_2$Cl$_2$ was employed as the solvent. All CH$_2$Cl$_2$ resonances have been truncated.
Figure B12. Solid-state $^{13}$C NMR spectra of 7 acquired with the variable amplitude cross-polarization sequence (top trace) and the Bloch decay sequence (bottom trace). Spectra were acquired from the sample employed for experiments at 9.4 T. Both spectra were acquired with spinning speeds of $\nu_{\text{rot}} = 6000$ Hz. The silicone grease signal observed in the solution $^{13}$C NMR spectra is visible near 0 ppm in the solid-state $^{13}$C Bloch decay NMR spectrum. The silicone grease signal is not visible in the cross-polarization spectrum due to the averaging of $^1$H-$^{13}$C dipolar coupling by translational/rotational motion of the grease molecules. Two peaks corresponding to cyclopentadienyl carbons are visible (114.7 and 114.1 ppm, shown in bottom inset). Two peaks in the methyl region are visible (36.1 ppm and 32.6 ppm). The top inset shows an expansion of the methyl region with a linefitting simulation overlaid. The integrated intensity of the two methyl peaks matches that expected from the fractional occupancies listed in the single crystal X-ray diffraction structure.
Figure B13. Solution $^{91}$Zr NMR spectra of zirconocenes dissolved in CH$_2$Cl$_2$. (a) Cp$_2$ZrCl$_2$ [δ$_{iso}$ = 0.0 ppm, FWHM = 224 Hz]. (b) Cp$_2$ZrMeCl (7) [δ$_{iso}$ = 240.4 ppm, FWHM = 1214 Hz]. (c) Cp$_2$ZrMe$_2$ (8) [δ$_{iso}$ = 493 ppm, FWHM = 2524 Hz]. Based upon solution $^{91}$Zr NMR spectra there appears to be a significant amount of Cp$_2$ZrCl$_2$ within the sample of Cp$_2$ZrMeCl. Integration of the peaks in the $^{91}$Zr spectrum reveals an approximate ratio of 100:21 of Cp$_2$ZrMeCl to Cp$_2$ZrCl$_2$; however, this ratio is misleading as the narrower $^{91}$Zr signal of Cp$_2$ZrCl$_2$ will decay much more slowly due to a much longer $T_2$. This leads to a relatively high intensity for the Cp$_2$ZrCl$_2$ resonance; much of the signal corresponding to Cp$_2$ZrMeCl is lost during ring down delays. Solution $^1$H NMR spectra indicated that the ratio of Cp$_2$ZrMeCl to Cp$_2$ZrCl$_2$ is closer to 100:2.
Figure B14. Experimental powder X-ray diffraction pattern (bottom trace) measured from 7 at room temperature. The simulated powder pattern (top trace) has been calculated with the single crystal X-ray diffraction structure reported in this work. These diffraction patterns were acquired before solid-state NMR spectra had been acquired.
Figure B15. The two different 12-molecule clusters employed for the calculation of $^{91}$Zr EFG tensor parameters of 7. The cyclopentadienyl (Cp) ligands have been removed and the centroids (blue) of the Cp rings are included for clarity. The position of some of the Me carbon (grey) and Cl atoms (green) vary between the two clusters. The Me carbon and Cl atoms which are located in different positions in Cluster 2 are circled. Interatomic distances are shown for these Me carbon and Cl distances. The EFG tensor parameters for the central atom are reported in Table B14.
Appendix C: Supplementary Figures and Tables for Chapter 4

**Table C1.** Acquisition Parameters for MAS $^{47/49}$Ti SSNMR Spectra Acquired at 21.1 T$^a$

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$^a$All MAS spectra acquired at 21.1 T were acquired on a Bruker 4mm HX MAS probe. $^b$Echo refers to a 16-step Hahn echo sequence.

**Table C2.** Acquisition Parameters for MAS $^{47/49}$Ti SSNMR Spectra Acquired at 9.4 T

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$^a$MAS spectra at 9.4 T were acquired on Chemagnetics T3 MAS probes. $^b$DFS/Echo and DFS/QCPMG refers to a sequence where the Hahn echo and QCPMG portions, respectively, are prefaced by a double frequency sweep (DFS) waveform [see main text for references].
Table C3. Acquisition Parameters for Static $^{47/49}$Ti SSNMR Spectra Acquired at 21.1 T

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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</thead>
<tbody>
<tr>
<td>Probe</td>
<td>5 mm</td>
<td>7 mm</td>
<td>4 mm</td>
<td>7 mm</td>
</tr>
<tr>
<td>Pulse Sequence&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Echo</td>
<td>Echo</td>
<td>Echo</td>
<td>Echo</td>
</tr>
<tr>
<td>Number of scans</td>
<td>8898</td>
<td>20951</td>
<td>35218</td>
<td>16764</td>
</tr>
<tr>
<td>Recycle Delay (s)</td>
<td>1.0</td>
<td>2.0</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Dwell (µs)</td>
<td>2.5</td>
<td>5.0</td>
<td>10.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Spectral width (kHz)</td>
<td>400.0</td>
<td>200.0</td>
<td>100.0</td>
<td>200.0</td>
</tr>
<tr>
<td>Acquisition length (number of points)</td>
<td>1024</td>
<td>512</td>
<td>1024</td>
<td>512</td>
</tr>
<tr>
<td>90º pulse width [$\pi$/2] (µs)</td>
<td>2.1</td>
<td>1.4</td>
<td>8.4</td>
<td>1.4</td>
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<tr>
<td>180º pulse widths [$\pi$] (µs)</td>
<td>4.2</td>
<td>2.8</td>
<td>16.8</td>
<td>2.8</td>
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<tr>
<td>Ring-down delays [$\tau_1$] (µs)</td>
<td>100.0</td>
<td>80.0</td>
<td>60.0</td>
<td>80.0</td>
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<tr>
<td>Ring-down delays [$\tau_2$] (µs)</td>
<td>20.0</td>
<td>10.0</td>
<td>10.0</td>
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<sup>a</sup>Static spectra at 21.1 T were acquired on a Bruker 4mm MAS probe or a home built single channel 5mm coil or 7 mm coil static transverse coil probes. DFS/Echo and DFS/QCPMG refers to a sequence where the Hahn echo and QCPMG portions, respectively, are prefaced by a double frequency sweep (DFS) waveform [see main text for references].
Table C4. Acquisition Parameters for Static $^{47/49}$Ti SSNMR Spectra Acquired at 9.4 T

<table>
<thead>
<tr>
<th>Probe</th>
<th>1</th>
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<tbody>
<tr>
<td>Pulse Sequence $^d$</td>
<td>DFS/QCPMG</td>
<td>DFS/QCPMG</td>
<td>Echo</td>
<td>DFS/Echo</td>
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<tr>
<td>Number of scans</td>
<td>30592</td>
<td>30240</td>
<td>150752</td>
<td>34644</td>
</tr>
<tr>
<td>Recycle Delay (s)</td>
<td>2.0</td>
<td>2.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Dwell (µs)</td>
<td>10.0</td>
<td>6.2</td>
<td>5.0</td>
<td>6.2</td>
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<tr>
<td>Spectral width (kHz)</td>
<td>100.0</td>
<td>160.0</td>
<td>200.0</td>
<td>160.0</td>
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<tr>
<td>Acquisition length (number of points)</td>
<td>2048</td>
<td>4096</td>
<td>1024</td>
<td>4096</td>
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<tr>
<td>90° pulse width [π/2] (µs)</td>
<td>2.50</td>
<td>2.10</td>
<td>6.00</td>
<td>2.75</td>
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<tr>
<td>180° pulse widths [π] (µs)</td>
<td>5.00</td>
<td>4.20</td>
<td>12.00</td>
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<tr>
<td>Ring-down delays [τ1] (µs)</td>
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<td>100.0</td>
<td>100.0</td>
<td>140.0</td>
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<td>Ring-down delays [τ2] (µs)</td>
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<td>Number of Meiboom-Gill loops [N]</td>
<td>19</td>
<td>25</td>
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<tr>
<td>Real points per loop</td>
<td>100</td>
<td>160</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Spikelet Separation [1/τ_a] (Hz)</td>
<td>1000.0</td>
<td>1000.0</td>
<td>-</td>
<td>-</td>
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<tr>
<td>DFS Start Frequency (MHz)</td>
<td>1.000</td>
<td>1.300</td>
<td>-</td>
<td>1.000</td>
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<tr>
<td>DFS End Frequency (MHz)</td>
<td>0.250</td>
<td>0.320</td>
<td>-</td>
<td>0.250</td>
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<tr>
<td>Length of DFS Sweep (ms)</td>
<td>0.200</td>
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<td>0.200</td>
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<tr>
<td>Number of Steps in DFS Waveform</td>
<td>800</td>
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<td>800</td>
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<tr>
<td>DFS Step Length (µs)</td>
<td>0.25</td>
<td>0.25</td>
<td>-</td>
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$^d$DFS/Echo and DFS/QCPMG refers to a sequence where the Hahn echo and QCPMG portions, respectively, are prefaced by a double frequency sweep (DFS) waveform [see main text for references].
Table C5. Quantum Chemical Calculations of $^{49}$Ti CS and EFG Tensor Parameters for 1 with Variable Ti Basis Sets.

### Site 1 – RHF Calculations

<table>
<thead>
<tr>
<th>Structure</th>
<th>Ti Basis</th>
<th>$\sigma_{iso}$ (ppm)</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal Cp</td>
<td>cc-pVTZ</td>
<td>559</td>
<td>-600</td>
<td>109</td>
<td>0.9</td>
<td>2.55</td>
<td>0.80</td>
</tr>
<tr>
<td>X-ray Cp</td>
<td>cc-pVTZ</td>
<td>585</td>
<td>-642</td>
<td>170</td>
<td>0.3</td>
<td>6.44</td>
<td>0.32</td>
</tr>
<tr>
<td>Ideal Cp</td>
<td>cc-pVQZ</td>
<td>558</td>
<td>-596</td>
<td>107</td>
<td>0.9</td>
<td>3.61</td>
<td>0.64</td>
</tr>
<tr>
<td>X-ray Cp</td>
<td>cc-pVQZ</td>
<td>584</td>
<td>-637</td>
<td>168</td>
<td>0.3</td>
<td>7.60</td>
<td>0.30</td>
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<tr>
<td>Ideal Cp</td>
<td>ahlrichs-pVDZ</td>
<td>409</td>
<td>-689</td>
<td>166</td>
<td>0.7</td>
<td>-6.14</td>
<td>0.21</td>
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<td>X-ray Cp</td>
<td>ahlrichs-pVDZ</td>
<td>437</td>
<td>-737</td>
<td>252</td>
<td>0.2</td>
<td>-2.05</td>
<td>0.55</td>
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<tr>
<td>Ideal Cp</td>
<td>ahlrichs-VTZ</td>
<td>564</td>
<td>-623</td>
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<td>2.09</td>
<td>0.48</td>
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<tr>
<td>X-ray Cp</td>
<td>ahlrichs-VTZ</td>
<td>591</td>
<td>-667</td>
<td>216</td>
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<td>6.64</td>
<td>0.15</td>
</tr>
<tr>
<td>Ideal Cp</td>
<td>6-311G**</td>
<td>572</td>
<td>-630</td>
<td>143</td>
<td>0.4</td>
<td>2.10</td>
<td>0.55</td>
</tr>
<tr>
<td>X-ray Cp</td>
<td>6-311G**</td>
<td>599</td>
<td>-674</td>
<td>209</td>
<td>0.0</td>
<td>6.75</td>
<td>0.18</td>
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### Site 1 – B3LYP Calculations

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<th>Structure</th>
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<th>$\delta_{iso}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal Cp</td>
<td>cc-pVTZ</td>
<td>-98</td>
<td>-690</td>
<td>473</td>
<td>-0.2</td>
<td>1.86</td>
<td>0.97</td>
</tr>
<tr>
<td>X-ray Cp</td>
<td>cc-pVTZ</td>
<td>-62</td>
<td>-744</td>
<td>538</td>
<td>-0.3</td>
<td>5.60</td>
<td>0.35</td>
</tr>
<tr>
<td>Ideal Cp</td>
<td>cc-pVQZ</td>
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<td>-690</td>
<td>472</td>
<td>-0.2</td>
<td>-1.83</td>
<td>0.85</td>
</tr>
<tr>
<td>X-ray Cp</td>
<td>cc-pVQZ</td>
<td>-76</td>
<td>-744</td>
<td>536</td>
<td>-0.3</td>
<td>5.43</td>
<td>0.41</td>
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<tr>
<td>Ideal Cp</td>
<td>ahlrichs-pVDZ</td>
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<td>-678</td>
<td>526</td>
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<td>3.85</td>
<td>0.16</td>
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<td>X-ray Cp</td>
<td>ahlrichs-pVDZ</td>
<td>-57</td>
<td>-729</td>
<td>588</td>
<td>-0.4</td>
<td>7.82</td>
<td>0.07</td>
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<td>Ideal Cp</td>
<td>ahlrichs-VTZ</td>
<td>-82</td>
<td>-688</td>
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<td>-2.42</td>
<td>0.48</td>
</tr>
<tr>
<td>X-ray Cp</td>
<td>ahlrichs-VTZ</td>
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<td>-743</td>
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<td>-0.4</td>
<td>5.84</td>
<td>0.58</td>
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<tr>
<td>Ideal Cp</td>
<td>6-311G**</td>
<td>-97</td>
<td>-701</td>
<td>517</td>
<td>-0.3</td>
<td>-2.45</td>
<td>0.41</td>
</tr>
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<td>X-ray Cp</td>
<td>6-311G**</td>
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<td>-757</td>
<td>583</td>
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<td>5.61</td>
<td>0.67</td>
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### Site 2 – RHF Calculations

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<th>$\delta_{iso}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
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<tr>
<td>Ideal Cp</td>
<td>cc-pVTZ</td>
<td>560</td>
<td>-602</td>
<td>112</td>
<td>0.9</td>
<td>2.46</td>
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<tr>
<td>X-ray Cp</td>
<td>cc-pVTZ</td>
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<td>0.22</td>
</tr>
<tr>
<td>Ideal Cp</td>
<td>cc-pVQZ</td>
<td>560</td>
<td>-597</td>
<td>111</td>
<td>0.9</td>
<td>3.53</td>
<td>0.57</td>
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<tr>
<td>X-ray Cp</td>
<td>cc-pVQZ</td>
<td>564</td>
<td>-618</td>
<td>153</td>
<td>0.5</td>
<td>8.35</td>
<td>0.21</td>
</tr>
<tr>
<td>Ideal Cp</td>
<td>ahlrichs-pVDZ</td>
<td>412</td>
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<td>1.99</td>
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<td>X-ray Cp</td>
<td>ahlrichs-VTZ</td>
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<td>-647</td>
<td>198</td>
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<td>6-311G**</td>
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<td>-631</td>
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<td>1.99</td>
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<td>6-311G**</td>
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<td>-654</td>
<td>192</td>
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### Site 2 – B3LYP Calculations

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<th>$\sigma_{iso}$ (ppm)</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal Cp</td>
<td>cc-pVTZ</td>
<td>-96</td>
<td>-692</td>
<td>476</td>
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<td>-1.81</td>
<td>0.91</td>
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<td>X-ray Cp</td>
<td>cc-pVTZ</td>
<td>-85</td>
<td>-721</td>
<td>522</td>
<td>-0.3</td>
<td>6.82</td>
<td>0.29</td>
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<td>-0.2</td>
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<td>ahlrichs-VTZ</td>
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<td>-733</td>
<td>567</td>
<td>-0.3</td>
<td>7.24</td>
<td>0.49</td>
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Table C6. Quantum Chemical Calculations of $^{49}$Ti CS and EFG Tensor Parameters for 2 with Variable Ti Basis Sets.

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<th>Ti Basis</th>
<th>$\sigma_{iso}$ (ppm)</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
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<tr>
<td>Ideal Cp</td>
<td>cc-pVTZ</td>
<td>364</td>
<td>-405</td>
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<td>0.1</td>
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<td>cc-pVTZ</td>
<td>347</td>
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<td>117</td>
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<td>7.44</td>
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<td>cc-pVQZ</td>
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<td>cc-pVQZ</td>
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<td>118</td>
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<td>0.33</td>
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<td>ahlrichs-pVDZ</td>
<td>198</td>
<td>-478</td>
<td>101</td>
<td>-0.1</td>
<td>-5.86</td>
<td>0.40</td>
</tr>
<tr>
<td>X-ray Cp</td>
<td>ahlrichs-pVDZ</td>
<td>180</td>
<td>-479</td>
<td>138</td>
<td>-0.4</td>
<td>-6.49</td>
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<td>Ideal Cp</td>
<td>ahlrichs-VTZ</td>
<td>384</td>
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<td>-3.03</td>
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<td>6-311G**</td>
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<td>-453</td>
<td>63</td>
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<td>6-311G**</td>
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<td>-453</td>
<td>90</td>
<td>-0.5</td>
<td>7.67</td>
<td>0.61</td>
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<table>
<thead>
<tr>
<th>Structure</th>
<th>Ti Basis</th>
<th>$\sigma_{iso}$ (ppm)</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
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<tbody>
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<td>-386</td>
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<td>-387</td>
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Table C7. Quantum Chemical Calculations of $^{49}$Ti CS and EFG Tensor Parameters for 3 with Variable Ti Basis Sets.

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<th>$\delta_{iso}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
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<tr>
<td>X-ray Cp</td>
<td>cc-pVTZ</td>
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<td>9.00</td>
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<td>6-311G**</td>
<td>88</td>
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<th>$\kappa$</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
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<td>-550</td>
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<td>ahlrichs-pVDZ</td>
<td>-533</td>
<td>-253</td>
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<td>X-ray Cp</td>
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<td>-532</td>
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<td>396</td>
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<td>400</td>
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Table C8. Quantum Chemical Calculations of $^{49}$Ti CS and EFG Tensor Parameters for 4 with Variable Ti Basis Sets.

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<th>$\Delta_{\text{iso}}$ (ppm)</th>
<th>$\Omega$ (ppm)</th>
<th>$\kappa$</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
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<td>cc-pVQZ</td>
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<td>-33</td>
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<td>0.9</td>
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Table C9. Plane-wave Calculations of $^{49}$Ti NMR Tensor Parameters (CASTEP)$^a$

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<th>$\kappa$</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
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<td>I (site 1)</td>
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<td>685</td>
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$^a$Ab initio plane-wave density functional theory calculations for 1-4 were performed with the CASTEP NMR program in the Materials Studio 5.0 environment. Ultrasoft pseudopotentials were used for $^{49}$Ti EFG calculations with a plane wave basis set cutoff of 350 eV for fine accuracy basis sets with Monkhorst-Pack $k$-space grid sizes of (3×1×1), (1×2×1), (2×1×2), and (2×1×1) employed for 1, 2, 3 and 4, respectively. The Perdew, Burke and Ernzerhof (PBE) functionals were used in the generalized gradient approximation (GGA) for the exchange-correlation energy.$^{1,2}$ The magnetic shielding (MS) for $^{49}$Ti was calculated with fine accuracy using the projector-augmented wave method (GIPAW) implemented in the CASTEP code.$^{3,4}$ The previously reported single crystal X-ray diffraction structures were employed for all calculations. Prior to EFG and MS calculations the H atom positions were optimized.

Figure C1. Experimental (black traces) and simulated (blue and red traces) static $^{47/49}$Ti SSNMR spectra of 1-4 acquired at 21.1 T. The top simulations (blue traces) employ $\Omega = 0$ ppm, while the bottom simulations (red traces) employ the $\Omega$ value determined from fits of the static spectra at both fields. From these simulations it is clear that titanium CSA is substantial for 1-4.
Figure C2. SIMPSON simulations of the MAS $^{47/49}$Ti spectra of 4. The value of $\Omega$ was changed for each simulation while all other parameters were fixed to those given in Table 4.1. This shows the sensitivity of the lineshape of the isotropic peak and spinning sideband manifold to the magnitude of the $^{47/49}$Ti CSA.
### Appendix D: Supplementary Figures and Tables for Chapter 5

#### Table D1. Experimental Pulse Sequence Settings

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values Employed</th>
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<td><strong>Solid-state $^{45}$Sc NMR experiments</strong></td>
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<tr>
<td>$\pi/2$ pulse widths (µs)</td>
<td>1.5 to 6.5</td>
</tr>
<tr>
<td>$\nu$, Rf fields (kHz)</td>
<td>41.7 to 9.7</td>
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<tr>
<td>Recycle Delays (s)</td>
<td>0.5 to 4.0</td>
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<tr>
<td>$\nu_{rot}$, Sample spinning speeds (kHz)</td>
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<td>Spectral widths for static spectra (kHz)</td>
<td>50.0 to 400.0</td>
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<tr>
<td>Spectral widths for MAS spectra (kHz)</td>
<td>200 to 1000</td>
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<tr>
<td>Number of scans for static spectra</td>
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<tr>
<td>Number of scans for MAS spectra</td>
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<td><strong>Solid-state $^{13}$C MAS NMR experiments</strong></td>
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<td>$^{13}$C $\pi/2$ pulse width (µs)</td>
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<td>Recycle delay (s)</td>
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<tr>
<td>$\nu_{rot}$, Sample spinning speeds (kHz)</td>
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<td>Spectral widths (kHz)</td>
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<td>Number of scans</td>
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<td>$^1$H/$^19$F decoupling fields (kHz)</td>
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<td><strong>Solid-state $^1$H→$^{13}$C VACP/MAS NMR experiments</strong></td>
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</tr>
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<td>$^1$H $\pi/2$ pulse widths (µs)</td>
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<tr>
<td>Hartman-Hahn matching fields (kHz)</td>
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<tr>
<td>Recycle delays (s)</td>
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<tr>
<td>$\nu_{rot}$, Sample spinning speeds (kHz)</td>
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<td>Spectral widths (kHz)</td>
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<td>$^1$H decoupling fields (kHz)</td>
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<td><strong>Solid-state $^{19}$F→$^{13}$C VACP/MAS NMR experiments</strong></td>
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<td>Number of scans</td>
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Figure D1. Static $^{45}$Sc Spectra of Sc(OAc)$_3$ and Sc(acac)$_3$. The rf field used to acquire the spectra is shown to the right of each spectrum. The bottom (red) spectrum has been acquired with a Hahn echo of the form \{\pi/2 - \tau - \pi/2 - \tau - \text{acquire}\}, denoted as 90°-90° echo in the figure. All other spectra were acquired with an echo of the form \{\pi/2 - \tau - \pi - \tau - \text{acquire}\}. The sensitivity of the spectra to the rf field and pulse sequence is visible. For these samples a 90°-90° echo employing an rf field equal to approximately half the width of the static pattern produces the best lineshape.
Figure D2. Static $^{45}$Sc NMR spectra at 9.4 T and simulations. All simulations neglect the effects of scandium CSA ($\Omega = 0$ ppm), illustrating that scandium CSA is substantial for all complexes. (a) Sc(acac)$_3$ (b) Sc(TMHD)$_3$ (c) Sc(OAc)$_3$ (d) Sc(NO$_3$)$_3$•5H$_2$O, (e) ScCl$_3$•6H$_2$O (f) ScCl$_3$•3THF (g) ScCp$_3$ (h) Sc(OTf)$_3$. 
Figure D3. Powder X-Ray diffraction patterns of ScCl$_3$·3THF, Sc(OAc)$_3$ and Sc(OTf)$_3$. The calculated patterns were generated from known single crystal X-ray structures using the PowderCell computer program.
Figure D4. Static $^{45}$Sc NMR spectrum of ScCl$_3$·6H$_2$O without $^1$H decoupling at 11.7 T. The simulation parameters are $C_Q = 13.0$, $\eta_Q = 0.55$, $\delta_{iso} = 145.0$ ppm. Without the acquisition of MAS spectra and/or $^1$H decoupled static spectra incorrect $^{45}$Sc NMR parameters could be obtained from simulation.
Figure D5. Variable Temperature $^{13}$C VACP/MAS NMR spectra of ScCp$_3$ at 9.4 T with a spinning speed of 5 kHz. Spinning sidebands are visible at both sides of the spectra. These spectra indicate that there is fluxional motion of the Cp ligands.
**Figure D6.** $^{19}$F and $^{13}$C NMR spectra at 9.4 T. Asterisks and crosses denote spinning sidebands. (a) $^{19}$F Hahn-echo MAS spectra of ME Sc(OTf)$_3$ (top) and Sc(OTf)$_3$ (bottom) at spinning speeds of 12 kHz and 10 kHz, respectively. (b) $^{13}$C NMR spectra of Sc(OTf)$_3$; $^{19}$F-$^{13}$C VACP/MAS at 5 kHz (top); Hahn-Echo at 10 kHz (bottom). (c) $^{13}$C NMR spectra of ME Sc(OTf)$_3$, $^{1}$H-$^{13}$C VACP/MAS at 13 kHz (top); $^{19}$F-$^{13}$C VACP/MAS at 5 kHz (middle); $^{13}$C Hahn-Echo at 14 kHz (bottom). The loading level of Sc(OTf)$_3$ in the polystyrene is approximately 10% by mass, which accounts for the observation of the normally weak Teflon signal of the rotor spacer in the $^{13}$C and $^{19}$F spectra.
Figure D7. Static $^{45}\text{Sc}$ NMR spectrum of ME Sc(OTf)$_3$ without $^1\text{H}$ decoupling at 9.4 T. The spectrum is the result of ~ 35000 scans. The strong $^1\text{H}$—$^{45}\text{Sc}$ dipole coupling indicates the relatively close proximity of protons to the scandium nucleus.
Appendix E: Supplementary Figures and Tables for Chapter 6

Table E1. Acquisition Parameters for MAS $^{45}$Sc SSNMR Spectra Acquired at 9.4 T (Figure 6.1)

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<th>Sample</th>
<th>Sc(OAc)$_3$</th>
<th>Sc(OTf)$_3$</th>
<th>Sc(OTf)$_3$•8H$_2$O</th>
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<td>Echo</td>
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<td>Number of scans</td>
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<td>64</td>
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<td>2.0</td>
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<td>Dwell (µs)</td>
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</tr>
<tr>
<td>Spectral width (kHz)</td>
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<td>500.0</td>
<td>400.0</td>
</tr>
<tr>
<td>Spinning Speed (Hz)</td>
<td>8000</td>
<td>5000</td>
<td>8000</td>
</tr>
<tr>
<td>Acquisition length (number of points)</td>
<td>32768</td>
<td>65536</td>
<td>16384</td>
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<tr>
<td>90º pulse width [$\pi$/2] (µs)</td>
<td>0.60</td>
<td>2.90</td>
<td>2.90</td>
</tr>
<tr>
<td>180º pulse widths [$\pi$] (µs)</td>
<td>1.20</td>
<td>2.90</td>
<td>2.90</td>
</tr>
<tr>
<td>Ring-down delays [$\tau_1$] (µs)</td>
<td>125.0</td>
<td>200.0</td>
<td>125.0</td>
</tr>
<tr>
<td>Ring-down delays [$\tau_2$] (µs)</td>
<td>75.0</td>
<td>30.0</td>
<td>30.0</td>
</tr>
</tbody>
</table>

$^a$Echo refers to a 16-step echo sequence.

Table E2. Acquisition Parameters for Static $^{45}$Sc SSNMR Spectra Acquired at 9.4 T (Figure 6.1)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sc(OAc)$_3$</th>
<th>Sc(OTf)$_3$</th>
<th>Sc(OTf)$_3$•8H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse Sequence$^a$</td>
<td>Echo</td>
<td>Echo</td>
<td>Echo</td>
</tr>
<tr>
<td>Number of scans</td>
<td>3392</td>
<td>1024</td>
<td>96</td>
</tr>
<tr>
<td>Recycle Delay (s)</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Dwell (µs)</td>
<td>5.0</td>
<td>2.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Spectral width (kHz)</td>
<td>200.0</td>
<td>500.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Acquisition length (number of points)</td>
<td>2048</td>
<td>4096</td>
<td>2048</td>
</tr>
<tr>
<td>90º pulse width [$\pi$/2] (µs)</td>
<td>10.00</td>
<td>5.80</td>
<td>2.90</td>
</tr>
<tr>
<td>180º pulse widths [$\pi$] (µs)</td>
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<td>2.90</td>
</tr>
<tr>
<td>Ring-down delays [$\tau_1$] (µs)</td>
<td>60.0</td>
<td>140.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Ring-down delays [$\tau_2$] (µs)</td>
<td>25.0</td>
<td>20.0</td>
<td>20.0</td>
</tr>
</tbody>
</table>

$^a$Echo refers to a 16-step echo sequence.
Table E3. Acquisition Parameters for MAS $^{45}$Sc SSNMR Spectra Acquired at 9.4 T (Figure 6.3)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sc(O Tf)$_3$·8H$_2$O</th>
<th>ME Sc(O Tf)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse Sequence$^a$</td>
<td>Echo</td>
<td>Echo</td>
</tr>
<tr>
<td>Number of scans</td>
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<td>115568</td>
</tr>
<tr>
<td>Recycle Delay (s)</td>
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<td>0.5</td>
</tr>
<tr>
<td>Dwell (µs)</td>
<td>2.5</td>
<td>20.0</td>
</tr>
<tr>
<td>Spectral width (kHz)</td>
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<td>12000</td>
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<tr>
<td>Acquisition length (number of points)</td>
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<td>2048</td>
</tr>
<tr>
<td>$90^\circ$ pulse width [$\pi/2$] (µs)</td>
<td>2.90</td>
<td>1.50</td>
</tr>
<tr>
<td>$180^\circ$ pulse widths [$\pi$] (µs)</td>
<td>2.90</td>
<td>3.00</td>
</tr>
<tr>
<td>Ring-down delays [$\tau_1$] (µs)</td>
<td>125.0</td>
<td>83.33</td>
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<tr>
<td>Ring-down delays [$\tau_2$] (µs)</td>
<td>30.0</td>
<td>43.33</td>
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</table>

$^a$Echo refers to a 16-step echo sequence.

Table E4. Acquisition Parameters for Static $^{45}$Sc SSNMR Spectra Acquired at 9.4 T (Figure 6.3)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sc(O Tf)$_3$·8H$_2$O</th>
<th>ME Sc(O Tf)$_3$</th>
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</thead>
<tbody>
<tr>
<td>Pulse Sequence$^a$</td>
<td>DFS/Echo</td>
<td>DFS/Echo</td>
</tr>
<tr>
<td>Number of scans</td>
<td>256</td>
<td>44272</td>
</tr>
<tr>
<td>Recycle Delay (s)</td>
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<td>0.5</td>
</tr>
<tr>
<td>Dwell (µs)</td>
<td>12.5</td>
<td>12.5</td>
</tr>
<tr>
<td>Spectral width (kHz)</td>
<td>80.0</td>
<td>80.0</td>
</tr>
<tr>
<td>Acquisition length (number of points)</td>
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<td>512</td>
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<tr>
<td>$90^\circ$ pulse width [$\pi/2$] (µs)</td>
<td>3.30</td>
<td>5.00</td>
</tr>
<tr>
<td>$180^\circ$ pulse widths [$\pi$] (µs)</td>
<td>6.60</td>
<td>10.00</td>
</tr>
<tr>
<td>Ring-down delays [$\tau_1$] (µs)</td>
<td>75.0</td>
<td>75.0</td>
</tr>
<tr>
<td>Ring-down delays [$\tau_2$] (µs)</td>
<td>20.0</td>
<td>25.0</td>
</tr>
<tr>
<td>DFS Start Frequency (MHz)</td>
<td>1.600</td>
<td>1.600</td>
</tr>
<tr>
<td>DFS End Frequency (MHz)</td>
<td>0.100</td>
<td>0.100</td>
</tr>
<tr>
<td>Length of DFS Sweep (µs)</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Number of Steps in DFS Waveform</td>
<td>1024</td>
<td>1024</td>
</tr>
<tr>
<td>DFS Step Length (µs)</td>
<td>0.059</td>
<td>0.059</td>
</tr>
</tbody>
</table>

$^a$DFS/Echo refers to a sequence where the Hahn echo portion is prefaced by a double frequency sweep (DFS) waveform [see main text for references].
Table E5. Acquisition Parameters for MAS $^{45}$Sc SSNMR Spectra Acquired at 9.4 T (Figure 6.4)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sc(OTf)$_3$·8H$_2$O</th>
<th>ME-1</th>
<th>ME-2</th>
<th>ME-3</th>
<th>ME Sc(OTf)$_3$·d$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse Sequence$^a$</td>
<td>DFS/Echo</td>
<td>DFS/Echo</td>
<td>DFS/Echo</td>
<td>DFS/Echo</td>
<td>DFS/Echo</td>
</tr>
<tr>
<td>Number of scans</td>
<td>32</td>
<td>752</td>
<td>304</td>
<td>1040</td>
<td>720</td>
</tr>
<tr>
<td>Recycle Delay (s)</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Dwell (μs)</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>5.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Spectral width (kHz)</td>
<td>400.0</td>
<td>400.0</td>
<td>400.0</td>
<td>200.0</td>
<td>400.0</td>
</tr>
<tr>
<td>Spinning Speed (Hz)</td>
<td>8000</td>
<td>10000</td>
<td>8000</td>
<td>10000</td>
<td>10000</td>
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<tr>
<td>Acquisition length (number of points)</td>
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<td>4096</td>
<td>4096</td>
<td>4096</td>
<td>4096</td>
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<td>90º pulse width [$\pi/2$] (μs)</td>
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<td>2.90</td>
<td>2.90</td>
<td>2.90</td>
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</tr>
<tr>
<td>180º pulse widths [$\pi$] (μs)</td>
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<td>5.80</td>
<td>5.80</td>
<td>5.80</td>
<td>5.80</td>
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<tr>
<td>Ring-down delays [$\tau_1$] (μs)</td>
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<td>100.0</td>
<td>125.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Ring-down delays [$\tau_2$] (μs)</td>
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<td>30.0</td>
<td>30.0</td>
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<td>1.100</td>
<td>1.100</td>
</tr>
<tr>
<td>DFS End Frequency (MHz)</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
</tr>
<tr>
<td>Number of Steps in DFS Waveform</td>
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<td>4000</td>
<td>4000</td>
</tr>
<tr>
<td>DFS Step Length (μs)</td>
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<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
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</table>

$^a$DFS/Echo refers to a sequence where the Hahn echo portion is prefaced by a double frequency sweep (DFS) waveform [see main text for references].
Table E6. Acquisition Parameters for Static $^{45}$Sc SSNMR Spectra Acquired at 9.4 T (Figure 6.4)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sc(OTf)$_3$·8H$_2$O</th>
<th>ME Sc(OTf)$_3$·8H$_2$O</th>
<th>Ambient ME Sc(OTf)$_3$</th>
<th>ME Sc(OTf)$_3$·d$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse Sequence$^a$</td>
<td>DFS/Echo</td>
<td>DFS/Echo</td>
<td>DFS/Echo</td>
<td>DFS/Echo</td>
</tr>
<tr>
<td>Number of scans</td>
<td>208</td>
<td>3120</td>
<td>3400</td>
<td>44272</td>
</tr>
<tr>
<td>Recycle Delay (s)</td>
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<td>2.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Dwell (µs)</td>
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<td>10.0</td>
<td>10.0</td>
<td>12.5</td>
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<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>80.0</td>
</tr>
<tr>
<td>Acquisition length (number of points)</td>
<td>1024</td>
<td>1024</td>
<td>1024</td>
<td>1024</td>
</tr>
<tr>
<td>90º pulse width [π/2] (µs)</td>
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<td>2.90</td>
<td>2.90</td>
<td>5.00</td>
</tr>
<tr>
<td>180º pulse widths [π] (µs)</td>
<td>2.90</td>
<td>2.90</td>
<td>2.90</td>
<td>10.00</td>
</tr>
<tr>
<td>Ring-down delays [τ$_1$] (µs)</td>
<td>125.0</td>
<td>100.0</td>
<td>100.0</td>
<td>75.0</td>
</tr>
<tr>
<td>Ring-down delays [τ$_2$] (µs)</td>
<td>25.0</td>
<td>30.0</td>
<td>30.0</td>
<td>25.0</td>
</tr>
<tr>
<td>DFS Start Frequency (MHz)</td>
<td>1.100</td>
<td>1.100</td>
<td>1.100</td>
<td>1.600</td>
</tr>
<tr>
<td>DFS End Frequency (MHz)</td>
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<td>0.100</td>
<td>0.100</td>
</tr>
<tr>
<td>Length of DFS Sweep (µs)</td>
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<td>2000</td>
<td>2000</td>
<td>60</td>
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<tr>
<td>Number of Steps in DFS Waveform</td>
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<td>4000</td>
<td>4000</td>
<td>1024</td>
</tr>
<tr>
<td>DFS Step Length (µs)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.059</td>
</tr>
</tbody>
</table>

$^a$DFS/Echo refers to a sequence where the Hahn echo portion is prefaced by a double frequency sweep (DFS) waveform [see main text for references].
Figure E1. Static solid-state $^{45}$Sc NMR spectra of Sc(OTf)$_3$ and Sc(OTf)$_3$•8H$_2$O acquired at magnetic fields of 11.7 T and 9.4 T. The EFG and CS tensor parameters and Euler angles employed for the simulations are given in Table 1 of the manuscript. All spectra were acquired with 90°-90° echo sequences. It should be noted that a sample of Sc(OTf)$_3$•8D$_2$O was employed for experiments at 11.7 T in order reduce the effects of $^1$H dipolar coupling on the static $^{45}$Sc powder pattern. The 11.7 T spectrometer did not possess an amplifier capable of fully removing the effects of dipolar coupling to $^1$H. For this reason the deuterated compound was employed. Both spectra were acquired with 90°-90° echo sequences.
Figure E2. (a) Powder X-ray diffraction (PXRD) patterns of a sample of Sc(OTf)$_3$ acquired with a capillary which is open to air. The times listed next to the PXRD patterns correspond to the amount of time for which the sample was exposed to air. From the PXRD patterns it is clear that anhydrous Sc(OTf)$_3$ adsorbs water and is converted to Sc(OTf)$_3$$\times$H$_2$O followed by adsorption of additional water to form Sc(OTf)$_3$$\times$8H$_2$O. (b) MAS $^{45}$Sc SSNMR spectra of Sc(OTf)$_3$$\times$H$_2$O and Sc(OTf)$_3$$\times$8H$_2$O. The MAS spectra of the two phases are identical in appearance. Static $^{45}$Sc SSNMR spectra of the two phases are also identical in appearance (not shown). (c) MAS $^1$H SSNMR spectra of Sc(OTf)$_3$$\times$H$_2$O and Sc(OTf)$_3$$\times$8H$_2$O acquired with $\nu_{\text{rot}} = 12500$ Hz and a 20s pulse delay. The MAS $^1$H SSNMR spectrum of Sc(OTf)$_3$$\times$H$_2$O is substantially broader than that of Sc(OTf)$_3$$\times$8H$_2$O.
Figure E3. MAS $^{13}$C SSNMR spectra of polystyrene samples treated with various solvents and ME Sc(OTf)$_3$. (a) pure polystyrene (PS), $\nu_{\text{rot}} = 13500$ Hz, (b) PS recovered from cyclohexane, $\nu_{\text{rot}} = 13500$ Hz (c) PS recovered from cyclohexane and hexanes, $\nu_{\text{rot}} = 13500$ Hz (d) PS recovered from cyclohexane, hexanes, and acetonitrile, $\nu_{\text{rot}} = 6500$ Hz and (e) PS recovered from cyclohexane, hexanes, and acetonitrile, $\nu_{\text{rot}} = 11500$ Hz, and (f) ME-2. The spectrum depicted in (e) was acquired with a Bloch decay pulse sequence (90° pulse-acquire) and a recycle delay of 4 s and all other spectra were acquired with VACP. A 1 ms contact time was employed for all VACP experiments. These spectra show that cyclohexane in adsorbed by the polystyrene and is present in the samples of ME Sc(OTf)$_3$. 
**Figure E4.** \(^1\text{H}-^{13}\text{C}\) dipolar correlation spectrum of ME-2 acquired with \(v_{\text{rot}} = 13669\) Hz. Frequency switched Lee-Goldberg (FSLG) was applied during the \(t_1\) evolution period in order to provide homonuclear \(^1\text{H}\) decoupling. The spectrum was acquired with a 12 s pulse delay and a 1 ms contact time. 48 \(t_1\) increments were acquired. TPPI phase cycling was employed to obtain absorption lineshapes.
Figure E5. MAS $^1$H SSNMR spectra acquired with $\nu_{\text{rot}}$ = 12500 kHz. (a) pure polystyrene, (b) ambient ME Sc(OTf)$_3$, (c) Sc(OTf)$_3$$\cdot$8H$_2$O, (d) Sc(OTf)$_3$$\cdot$xH$_2$O. The resonances of the water $^1$H nuclei are extremely broad in comparison to those of the polystyrene and cyclohexane resonances. Given the relatively low loading levels of Sc(OTf)$_3$$\cdot$8H$_2$O within ambient ME Sc(OTf)$_3$ it is anticipated that the water $^1$H nuclei will contribute negligible amounts of signal to the $^1$H SSNMR spectrum of ambient ME Sc(OTf)$_3$. Therefore, it can be assumed that all signal observed in the MAS $^1$H SSNMR spectrum of ambient ME Sc(OTf)$_3$ can be attributed to the $^1$H nuclei of polystyrene and cyclohexane.
Figure E6. MAS \(^1\)H-\(^{45}\)Sc TRAPDOR SSNMR spectra of ME Sc(OTf)_3-d_8. All pulse sequence parameters were identical to those employed to acquire the TRAPDOR MAS spectrum of ambient ME Sc(OTf)_3. Integrated intensities are shown to the right of each spectrum. The most intense resonance at ca. 1.4 ppm corresponds to cyclohexane.
Figure E7. VACP/MAS $^{19}$F→$^{13}$C{$^{19}$F} SSNMR spectra of (a) Sc(OTf)$_3$•$^8$H$_2$O (MAS $^{19}$F SSNMR spectrum inset), (b) ambient ME Sc(OTf)$_3$ and (c) ME Sc(OTf)$_3$-$^8$d$_8$. A broad resonance centered around the $^{13}$C phenyl group resonances is visible in the spectrum of ME Sc(OTf)$_3$-$^8$d$_8$. A contact time of 2 ms, $v_{rot} = 10000$ Hz and a recycle delay of 5 s were employed for all VACP/MAS $^{19}$F→$^{13}$C spectra. 13260 and 17880 transients were collected for the spectra of ambient ME Sc(OTf)$_3$ and ME Sc(OTf)$_3$-$^8$d$_8$, respectively. (d) The $^1$H→$^{13}$C{$^1$H} SSNMR spectrum of ambient ME Sc(OTf)$_3$ is shown for comparison.
Figure E8. MAS $^1$H (top) and $^2$H (bottom) SSNMR spectra of ME Sc(OTf)$_3$-$d_8$ and PS-$d_8$. MAS $^1$H SSNMR spectra were acquired with $\nu_{\text{rot}} = 12.5$ kHz and a 20 s recycle delay. MAS $^2$H spectra of both complexes were acquired with $\nu_{\text{rot}} = 8$ kHz. An expansion of the isotropic peaks is shown in the bottom set of $^2$H spectra.
$^{19}$F-$^{13}$C Cross-polarization experiments. VACP/MAS $^{19}$F→$^{13}$C{$^{19}$F} SSNMR experiments were conducted on ME Sc(OTf)$_3$-d$_8$ because $^1$H nuclei directly bound to $^{13}$C nuclei will be absent; this eliminates the need to apply $^1$H decoupling to observe any potential cross-polarization from the $^{19}$F nuclei of the triflate groups to the $^{13}$C nuclei of polystyrene. MAS $^{13}$C{$^{19}$F} Bloch decay SSNMR spectra of ME Sc(OTf)$_3$-D$_8$, Sc(OTf)$_3$•8H$_2$O, and ambient ME ScOTf$_3$ are shown in Figure E7. However, there are no resonances visible in the phenyl regions or aliphatic regions of the VACP/MAS $^{19}$F→$^{13}$C{$^{19}$F} SSNMR spectrum of ME Sc(OTf)$_3$-d$_8$. The $^{19}$F spectra of Sc(OTf)$_3$•8H$_2$O are relatively narrow, indicative of substantial rotational motion of the –CF$_3$ groups. This suggests that the lack of polystyrene signals in the VACP/MAS $^{19}$F→$^{13}$C spectrum can most likely be attributed to the efficient averaging of $^{19}$F-$^{13}$C dipolar interactions by rotational motion of the triflate groups.

MAS $^1$H and $^2$H SSNMR Experiments on ME Sc(OTf)$_3$-d$_8$. MAS $^2$H SSNMR is often employed to acquire high resolution MAS SSNMR spectra of deuterated species. MAS $^2$H SSNMR spectra are particularly useful because the $^2$H chemical shifts ($\delta_{iso}$) are approximately identical to those observed in the $^1$H SSNMR spectra of the same complex. Therefore, the $^2$H SSNMR spectrum can serve as a “high-resolution” $^1$H SSNMR spectrum of the complex. The MAS $^2$H and $^1$H SSNMR spectra of the sample of pristine deuterated polystyrene (PS-d$_8$) and ME Sc(OTf)$_3$ prepared with deuterated polystyrene (ME Sc(OTf)$_3$-d$_8$) are shown in Figure E8. The spectra of the deuterated complexes show two distinct chemical shifts which correspond to those expected for aromatic and aliphatic deuterons. The isotropic $^2$H resonances of ME Sc(OTf)$_3$-d$_8$ are substantially narrowed in comparison to those of PS-d$_8$. This suggests that ME Sc(OTf)$_3$-d$_8$ is more crystalline than PS-d$_8$. This increased crystallinity probably arises from the dissolution and subsequent precipitation of the PS which occurs during the synthetic procedure of ME Sc(OTf)$_3$.  

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Figure E9. $^1$H-$^{45}$Sc TRAPDOR SSNMR spectra of a sample of ME-2 which has been exposed to air for (a) 20 hours and (b) 15 days. Integrated intensities are shown to the right of each spectrum.
Appendix F: Supplementary Figures and Tables for Chapter 7

### Table F1. CP/CPMG Acquisition Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Compound 1</th>
<th>Compound 2</th>
<th>Compound 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of sub-spectra acquired</td>
<td>16</td>
<td>15</td>
<td>17</td>
</tr>
<tr>
<td>Number of scans per sub-spectrum</td>
<td>80</td>
<td>144</td>
<td>64</td>
</tr>
<tr>
<td>Transmitter offset per piece (kHz)</td>
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<td>30.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Recycle Delay (s)</td>
<td>20.0</td>
<td>20.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Number of Meiboom-Gill loops [N]</td>
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<td>163</td>
<td>163</td>
</tr>
<tr>
<td>Real points per loop</td>
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<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Spectral window of sub-spectra (kHz)</td>
<td>1000.0</td>
<td>1000.0</td>
<td>1000.0</td>
</tr>
<tr>
<td>Dwell (µs)</td>
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<td>10.0</td>
<td>10.0</td>
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<td>Proton 90° pulse width [π/2] (µs)</td>
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<td>Lead 180° pulse widths [π] (µs)</td>
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<td>3.3</td>
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<tr>
<td>Contact time (ms)</td>
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<td>12.0</td>
<td>9.0</td>
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<td>Ring-down delays [τ₁ = τ₂ = τ₃ = τ₄] (µs)</td>
<td>40.0</td>
<td>30.0</td>
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Elements in square-brackets [ ] are defined in the schematic of the CP/CPMG sequence (Figure S2).

### Table F2. ²⁰⁷Pb isotropic chemical shift of (2,6-Me₂C₆H₃S)₂Pb(py)₂ (1) and [(2,6-Me₂C₆H₃S)₂Pb(pyOMe)]₂ (2) at three spinning speeds.

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<th>Spinning Speed (Hz)</th>
<th>Temperature (K)ᵃ</th>
<th>δₐiso of 1 (ppm)ᵇ</th>
<th>δₐiso of 2 (ppm)ᵇ</th>
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<td>2878</td>
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<td>8000</td>
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ᵃ The temperature of the sample in the rotor was calibrated by recording the ¹¹⁹Sn spectrum of Sn₂Sm₂O₇ at various spinning speeds according to the procedure given by Grimmer, A.; Kretschmer, A.; Cajipe, V. B. Magnetic Resonance in Chemistry 1997, 35, 86. ᵇ Given the breadth of the peaks in the MAS spectra there are significant errors of approximately 5 ppm for all of the listed shifts.
Table F3. Paramagnetic shielding arising from mixing of occ.-vir. MOs in 1.
Occ.
MO
48
48
48
48
49
49
49
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53
54
54
56
75
76
87
87
93
93
94
95
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105
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110
110
111
111
111
111
112
114
114
114
118
119
119
120
120
120
120
120
120
120
120
120

σiso

Vir.
MO
143
144
145
146
139
143
146
210
210
144
334
139
139
144
139
148
139
143
139
138
143
143
139
143
139
146
139
143
138
143
138
144
146
155
143
138
144
152
143
139
143
138
139
143
144
147
148
153
155
156

-23.435
11.838
-4.696
28.675
-24.882
-21.408
15.539
4.346
-5.516
-8.208
-9.329
1.217
8.357
-7.298
17.161
-9.575
-5.472
28.958
8.451
6.406
-1.829
29.049
10.021
-43.08
3.688
10.502
4.072
1.707
-16.494
-34.799
-10.351
-5.881
-14.569
-5.907
-25.374
-45.568
6.5
1.966
-18.34
-20.134
2.838
29.184
-125.88
-44.645
15.106
38.461
-6.895
-14.679
56.185
-39.049

Occ.
MO
122
122
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125
125
125
125
125
125
125
125
125
125
126

σiso

Vir.
MO
138
139
143
144
145
147
149
154
155
156
157
163
164
192
193
252
138
139
143
144
145
146
147
152
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155
157
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161
162
164
165
166
167
169
188
191
209
220
246
248
252
262
295
307
324
351
353
359
138

389

-81.601
19.602
-76.395
-39.537
-29.738
20.57
-29.603
-7.962
13.617
17.947
-45.666
-10.073
-8.018
-33.844
-8.519
-0.633
19.687
34.247
-135.605
-64.748
-19.491
-7.528
-16.791
-12.349
4.583
-23.511
-18.003
1.013
3.78
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14.425
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7.378
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5.069
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9.879
2.097
4.256
10.816
-7.298
-5.455
-26.28
5.401
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-13.12
-33.903

Occ.
MO

σiso

Vir.
MO
130
131
131
131
131
131
131
131
131
131
131
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131
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131
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350
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309
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139
140
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158
164

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-33.977
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7.226
6.93
31.198
-22.549
-17.674
19.868
19.458
-8.764
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430.36
-155.367
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-45.895
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13.92
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27.553
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27.122


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<td></td>
<td>2.50</td>
<td></td>
<td>2p_z</td>
<td>1.00</td>
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</table>

*Occ stands for occupancy. **SFO:** symmetrized fragment orbitals. *C1 and C2 are bound to S1 and S2 respectively. *p* and *o* refer to carbon atoms para and ortho to C1 and C2. *d* Occupied MOs are fully occupied by two electrons, vir MOs contain no electrons. *e* The “p” and “o” labels refer to the carbon atoms ortho and para to the carbon bound to sulfur. The “2” in “C2p” indicates that it is located in the phenyl group bound to “S2”.
Figure F1. Sixteen CP/CPMG sub-spectra of compound 1 are shown along with the resultant spectrum produced by co-addition of the individual pieces.
**Figure F2.** Magnified views of the $^1$H-$^{207}$Pb VACP/MAS NMR spectra of 1, 2 and 3 found in Figure 5 of the manuscript. Further expansions of the areas highlighted in the boxed areas are shown in the right columns of the figure. The dependence of the isotropic chemical shifts of 1 and 2 on the temperature (spinning speed) of the sample is evident (Table F2). Minor impurities that are visible are believed to result from hydration of the samples, since the VACP/MAS NMR spectra were acquired 21 days after the static spectra. The width of the peaks is increased by the amount of gaussian line broadening applied in processing (minimum 300 Hz).
Figure F3. Powder X-ray diffraction patterns of compounds 1, 2 and 3. Simulated patterns were generated from the single crystal X-ray diffraction structures with the Powdercell program.
**Figure F4.** SIMPSON simulations of the VACP/MAS spectra employing the CS tensor parameters extracted from simulation of the CP/CPMG spectra. The simulations employ ideal pulses. The vertical scaling factors of the experimental spectra are indicated in the figure. In all instances the experimental spectra display incomplete excitation and/or lack of signal to noise for resolving lower-intensity portions of the patterns. The discontinuities (eg. high and low points of the sideband manifolds) of the experimental spectra match those of the simulations. The incomplete excitation arises from a combination of the large chemical shielding anisotropy and small excitation profiles characteristic of cross-polarization experiments.
Figure F5. Chemical shielding tensor orientations generated from ZORA [closed-head (🔴) red arrows] and non-relativistic (NR) [open-head (○) black arrows] ADF calculations for complexes 1, 2 and 3. For all cases the position of $\sigma_{33}$ is placed in approximately the same direction by the NR and ZORA calculations; the $\sigma_{33}(\text{ZORA})$-Pb-$\sigma_{33}(\text{NR})$ angles are ~0°, 8° and 6° for 1, 2, and 3 respectively. In complex 2 the positions of $\sigma_{11}$ and $\sigma_{22}$ generated by the NR calculations are switched relative to those produced by the ZORA calculation [i.e., $\sigma_{11}(\text{NR})$ is directed closer to $\sigma_{22}(\text{ZORA})$ than $\sigma_{11}(\text{ZORA})$].
Figure F6. MOs generated from non-relativistic DFT calculations on complex 1. The MOs pictured make large contributions to the paramagnetic shielding term, and are visualized at the 97% electron density level with the ADFview program. Hydrogen atoms omitted for clarity.
A Note on the Generation of the Contributions of the Individual Shielding Terms to the Total Principal Shielding Components

The ADF program outputs principal shielding components for the diamagnetic ($\sigma^d$), paramagnetic ($\sigma^p$), and spin-orbit terms ($\sigma^{so}$). In order to determine the contributions from the individual shielding terms (e.g. paramagnetic) to the principal components of the total shielding tensor ($\sigma$) the principal components of the shielding terms as output by the ADF program cannot be used. This is because the principal axis system (PAS) of each of the individual shielding terms is not necessarily coincident with the PAS of the total shielding tensor; if one tries to sum the principal components of each of the individual shielding terms the values of the principal components of the total tensor will not be obtained. In order to gauge the contributions of the individual shielding terms to the principal components of $\sigma$ one must translate the individual shielding terms into the PAS of the total shielding tensor. This is done by determining the eigenvectors (which correspond to the columns of the 3 x 3 matrix $X$) of the total shielding tensor. Eigenvectors for the total shielding tensor can be found in ADF output file and are labelled as “Principal Axis System” near the tensor output. Alternatively they can be found by solving for the eigenvalues of the total shielding tensor with a standard mathematical computing program.

$$\sigma X = \sigma_{PAS} X$$

where, $\sigma = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{xy} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} \end{pmatrix}$ $\sigma_{PAS} = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}$

The inverse of the eigenvectors ($X^{-1}$) then needs to be found. The product of $X^{-1}$, $\sigma$ and $X$ will yield the principal shielding components of the total CS tensor (the diagonal elements of $\sigma_{PAS}$).

$$X^{-1} \sigma X = \sigma_{PAS}$$

The contributions to the principal components of the total shielding tensor from the individual shielding terms can then be determined by finding the product of $X$, $\sigma^x$ and $X^{-1}$ (where $\sigma^x$ corresponds to the tensor of the shielding term in question).
The diagonal elements of the $3 \times 3$ matrix $\sigma_{PAS}^x$ correspond to the contributions to the principal components of the total shielding tensor from the tensor $\sigma^x$.

By applying this routine to the diamagnetic, paramagnetic, and spin-orbit shielding tensors their contributions to the principal components of the total shielding tensor can be determined. This same procedure is also applied to determine the contributions of the individual MO pairs (Table 5 of the manuscript) to the total shielding tensor.
## Appendix G: Supplementary Figures and Tables for Chapter 8

### Table G1. Experimental $^{75}$As NQR Parameters

<table>
<thead>
<tr>
<th>Pulse Sequence</th>
<th>Bloch Decay</th>
<th>90°-180° Echo</th>
<th>90°-90° Echo</th>
<th>Composite Echo</th>
<th>WURST Echo</th>
</tr>
</thead>
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<tr>
<td>Number of Scans</td>
<td>32</td>
<td>32</td>
<td>32</td>
<td>32</td>
<td>32</td>
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<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
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<td>1.65</td>
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<td>2500</td>
<td>2500</td>
<td>2500</td>
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<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
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<td>147.4</td>
<td>147.4</td>
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<td>147.4</td>
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<td>512</td>
<td>512</td>
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<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
<td>56000</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>57</td>
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</table>

*The first time listed for the 180° pulse width corresponds to the length of the 31.5° pulse and the second time listed gives the length of the 189° pulse.

$\tau_d$ is the total time between excitation of a signal and the time at which it is refocused. For WURST echo experiments $\tau_d = \tau_1 + \tau_2$. For the echo sequences $\tau_d = \tau_1 - 0.5*(180° pulse width).
### Table G2. Experimental $^{35}$Cl NQR Parameters

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<th>90°-90° Echo</th>
<th>Composite Echo</th>
<th>WURST Echo</th>
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<td>256</td>
<td>256</td>
<td>256</td>
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<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
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<td>2.20</td>
<td>2.20</td>
<td>50</td>
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<td>2.20</td>
<td>0.76, 4.62*</td>
<td>50</td>
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<td>Dwell (µs)</td>
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<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
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<td>276</td>
<td>281</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
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*The first time listed for the 180° pulse width corresponds to the length of the 31.5° pulse and the second time listed gives the length of the 189° pulse.

$^\dagger \tau_d$ is the total time between excitation of a signal and the time at which it is refocused. For WURST echo experiments $\tau_d = \tau_1 + \tau_2$. For the echo sequences $\tau_d = \tau_1 - 0.5\ast(180°$ pulse width).
Table G3. Experimental $^{63/65}$Cu NQR Parameters

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<th>QCPMG (Co-Add of FT Spectra)</th>
<th>WURST-QCPMG (Co-Add of FT Spectra)</th>
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<td>250</td>
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<td>1.0</td>
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<td>-</td>
</tr>
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<td>100</td>
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<tr>
<td>WURST sweep rate (kHz/ms)</td>
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<td>-</td>
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*The first time listed for the 180° pulse width corresponds to the length of the 31.5° pulse and the second time listed gives the length of the 189° pulse.*
**Table G4.** Integrated Intensity and Signal to Noise of $^{75}$As NQR Spectra of As$_2$O$_3$ as a Function of Transmitter Offset

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<th>Offset from Resonance (kHz)</th>
<th>90-180 Echo</th>
<th>90-90 Echo</th>
<th>Comp. Echo</th>
<th>WURST Echo</th>
<th>Bloch Decay</th>
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<td>II</td>
<td>S/N</td>
<td>II</td>
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<td>0</td>
<td>0</td>
<td>3</td>
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<tr>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>49</td>
</tr>
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<td>0</td>
<td>0</td>
<td>1</td>
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<td>0</td>
<td>0</td>
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<td>14</td>
<td>72</td>
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<td>30</td>
<td>47</td>
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<td>26</td>
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<td>96</td>
<td>496</td>
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<tr>
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<td>530</td>
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**Table G5.** Integrated Intensity and Signal to Noise of $^{75}$As NQR Spectra of As$_2$O$_3$ as a Function of the Echo Delay ($\tau_d$)

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<th>(\tau_d) (MHz)</th>
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<th>90°-180° Echo</th>
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<tr>
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</tr>
<tr>
<td>185</td>
<td>136</td>
<td>554</td>
</tr>
<tr>
<td>165</td>
<td>160</td>
<td>690</td>
</tr>
<tr>
<td>147.4</td>
<td>186</td>
<td>871</td>
</tr>
</tbody>
</table>

*When \(\tau_d\) becomes short only a portion of the full echo is acquired (e.g., the echo is truncated in the time domain). This leads to baseline and lineshape distortions which make II and S/N measurements unreliable.
**Table G6.** Integrated Intensity and Signal to Noise of $^{75}$As NQR Spectra of As$_2$O$_3$ as a Function of WURST Pulse Width

<table>
<thead>
<tr>
<th>WURST Pulse Width (µs)</th>
<th>RF Field of Pulse (kHz)</th>
<th>Echo Size (# of points) *</th>
<th>$\tau_1$ (µs)</th>
<th>$\tau_2$ (µs)</th>
<th>$\tau_d$ (µs)</th>
<th>II</th>
<th>S/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>57</td>
<td>1024</td>
<td>229.8</td>
<td>20</td>
<td>249.8</td>
<td>69</td>
<td>250</td>
</tr>
<tr>
<td>100</td>
<td>44</td>
<td>900</td>
<td>230.0</td>
<td>20</td>
<td>250.0</td>
<td>72</td>
<td>271</td>
</tr>
<tr>
<td>200</td>
<td>31</td>
<td>650</td>
<td>230.0</td>
<td>20</td>
<td>250.0</td>
<td>72</td>
<td>312</td>
</tr>
</tbody>
</table>

*The echo size was decreased for longer pulse widths in order to retain similar values of $\tau_1$ and $\tau_d$.

**Table G7.** Pulse Sequence Parameters and Performance of 90°-180° and 90°-90° WURST Echo Sequences for the Acquisition of $^{75}$As NQR Spectra.

<table>
<thead>
<tr>
<th>WURST Pulse Sequence</th>
<th>90°-90°</th>
<th>90°-90°</th>
<th>90°-180°</th>
<th>90°-180°</th>
<th>90°-180°</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_{exc}$ (µs)</td>
<td>50</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>$\tau_{ref}$ (µs)</td>
<td>50</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>Offset$_{exc}$ (kHz)</td>
<td>800</td>
<td>800</td>
<td>800</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td>Offset$_{ref}$ (kHz)</td>
<td>800</td>
<td>800</td>
<td>800</td>
<td>1600</td>
<td>800</td>
</tr>
<tr>
<td>$R_{exc}$ (kHz/ms)</td>
<td>32000</td>
<td>16000</td>
<td>16000</td>
<td>16000</td>
<td>16000</td>
</tr>
<tr>
<td>$R_{ref}$ (kHz/ms)</td>
<td>32000</td>
<td>16000</td>
<td>16000</td>
<td>32000</td>
<td>32000</td>
</tr>
<tr>
<td>$\nu_{exc}$ (kHz)</td>
<td>52</td>
<td>37</td>
<td>37</td>
<td>37</td>
<td>37</td>
</tr>
<tr>
<td>$\nu_{ref}$ (kHz)</td>
<td>52</td>
<td>37</td>
<td>37$^b$</td>
<td>56</td>
<td>63</td>
</tr>
<tr>
<td>$\tau_d$ (µs)</td>
<td>147.4</td>
<td>172.4</td>
<td>172.4</td>
<td>172.4</td>
<td>147.4</td>
</tr>
<tr>
<td>II</td>
<td>149</td>
<td>116</td>
<td>-$^b$</td>
<td>122</td>
<td>153$^c$</td>
</tr>
<tr>
<td>S/N</td>
<td>730</td>
<td>541</td>
<td>-</td>
<td>579</td>
<td>753</td>
</tr>
</tbody>
</table>

$^a$All other experimental parameters not listed here were the same as those listed in Table S1.

$^b$The rf field of the refocusing pulse was experimentally optimized and it was found that using an rf field equal in magnitude to the excitation pulse gave maximum signal. Therefore, the sequence and resulting spectra are identical to the corresponding 90°-90° WURST echo case.

$^c$This 90°-180° WURST echo sequence yields II and S/N comparable to that obtained from the 90°-90° sequence, which employs an identical echo dephasing period ($\tau_d$).
Table G8. S/N and II of $^{75}$As NQR WURST Echo Spectra at Different Receiver Gain Settings.

<table>
<thead>
<tr>
<th>Receiver Gain</th>
<th>Probe Tuned on Resonance</th>
<th>Probe Tuned +300 kHz Off Resonance$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>II</td>
<td>S/N</td>
</tr>
<tr>
<td>10</td>
<td>98</td>
<td>950</td>
</tr>
<tr>
<td>20$^b$</td>
<td>186</td>
<td>955</td>
</tr>
<tr>
<td>30</td>
<td>299</td>
<td>950</td>
</tr>
<tr>
<td>40</td>
<td>377</td>
<td>944</td>
</tr>
<tr>
<td>50</td>
<td>473</td>
<td>910</td>
</tr>
<tr>
<td>70</td>
<td>596</td>
<td>950</td>
</tr>
<tr>
<td>80</td>
<td>757</td>
<td>838</td>
</tr>
<tr>
<td>90$^c$</td>
<td>904</td>
<td>934</td>
</tr>
</tbody>
</table>

$^a$Re-calibrated pulse widths were also employed (the 90° pulse was found to increase from 1.65 µs to 2.1 µs).

$^b$This receiver gain setting was employed for all other experiments in the manuscript.

$^c$At a receiver gain setting greater than 90 the signal saturates the digitizer.

Table G9. Integrated Intensity and Signal to Noise of $^{35}$Cl NQR Spectra of 4-chloropyridine as a Function of Transmitter Offset

<table>
<thead>
<tr>
<th>Transmitter Frequency (MHz)</th>
<th>Offset from Resonance (kHz)</th>
<th>90°-180° Echo $^b$</th>
<th>90°-90° Echo $^b$</th>
<th>Comp. Echo</th>
<th>WURST Echo</th>
<th>Bloch Decay</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>S/N</td>
<td>II</td>
<td>S/N</td>
<td>II</td>
</tr>
<tr>
<td>36.052</td>
<td>700</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>35.952</td>
<td>600</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>35.852</td>
<td>500</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>9</td>
</tr>
<tr>
<td>35.752</td>
<td>400</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td>35.652</td>
<td>300</td>
<td>17</td>
<td>8</td>
<td>17</td>
<td>20</td>
<td>24</td>
</tr>
<tr>
<td>35.552</td>
<td>200</td>
<td>0</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>42</td>
</tr>
<tr>
<td>35.502</td>
<td>150</td>
<td>7</td>
<td>28</td>
<td>11</td>
<td>9</td>
<td>46</td>
</tr>
<tr>
<td>35.452</td>
<td>100</td>
<td>43</td>
<td>47</td>
<td>53</td>
<td>45</td>
<td>53</td>
</tr>
<tr>
<td>35.402</td>
<td>50</td>
<td>108</td>
<td>64</td>
<td>113</td>
<td>90</td>
<td>65</td>
</tr>
<tr>
<td>35.352</td>
<td>0</td>
<td>167</td>
<td>79</td>
<td>156</td>
<td>112</td>
<td>83</td>
</tr>
<tr>
<td>35.302</td>
<td>-50</td>
<td>162</td>
<td>88</td>
<td>162</td>
<td>122</td>
<td>94</td>
</tr>
<tr>
<td>35.252</td>
<td>-100</td>
<td>105</td>
<td>107</td>
<td>127</td>
<td>101</td>
<td>115</td>
</tr>
<tr>
<td>35.202</td>
<td>-150</td>
<td>24</td>
<td>84</td>
<td>41</td>
<td>37</td>
<td>124</td>
</tr>
<tr>
<td>35.152</td>
<td>-200</td>
<td>10</td>
<td>57</td>
<td>10</td>
<td>6</td>
<td>121</td>
</tr>
<tr>
<td>35.052</td>
<td>-300</td>
<td>14</td>
<td>10</td>
<td>30</td>
<td>20</td>
<td>93</td>
</tr>
<tr>
<td>34.952</td>
<td>-400</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>56</td>
</tr>
<tr>
<td>34.852</td>
<td>-500</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>33</td>
</tr>
<tr>
<td>34.752</td>
<td>-600</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>18</td>
</tr>
<tr>
<td>34.652</td>
<td>-700</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>15</td>
</tr>
</tbody>
</table>

II* correspond to II values which have been corrected by multiplying the measured II values by the ratio of the FWHH of the echo spectra to the Bloch decay spectra [e.g., a scaling factor of (3.7 kHz/4.7 kHz = 0.80) has been applied].
### Table G10. S/N and II of $^{35}$Cl NQR WURST Echo Spectra at Different Receiver Gain Settings.

<table>
<thead>
<tr>
<th>Receiver Gain</th>
<th>Probe Tuned on Resonance</th>
<th>Probe Tuned +300 kHz Off Resonance$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>II</td>
<td>S/N</td>
</tr>
<tr>
<td>10</td>
<td>7</td>
<td>60</td>
</tr>
<tr>
<td>70</td>
<td>41</td>
<td>61</td>
</tr>
<tr>
<td>130$^b$</td>
<td>89</td>
<td>64</td>
</tr>
<tr>
<td>190</td>
<td>138</td>
<td>58</td>
</tr>
<tr>
<td>250</td>
<td>188</td>
<td>58</td>
</tr>
<tr>
<td>310</td>
<td>228</td>
<td>58</td>
</tr>
<tr>
<td>490$^c$</td>
<td>284</td>
<td>60</td>
</tr>
</tbody>
</table>

$^a$ Re-calibrated pulse widths were also employed (the 90° pulse was found to increase from 2.2 $\mu$s to 2.5 $\mu$s).

$^b$ This receiver gain setting was employed for all other experiments in the manuscript.

$^c$ At a receiver gain setting greater than 90 the signal saturates the digitizer.

### Table G11. Transverse Relaxation ($T_2$) Time Constants as a Function of Resonance Frequency for $^{63/65}$Cu NQR of CuCN.

<table>
<thead>
<tr>
<th>Frequency (MHz)</th>
<th>$T_2$ (µs)</th>
<th>Deviation ($\chi^2$, µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37.64</td>
<td>500</td>
<td>76</td>
</tr>
<tr>
<td>37.88</td>
<td>498</td>
<td>77</td>
</tr>
<tr>
<td>38.12</td>
<td>474</td>
<td>84</td>
</tr>
<tr>
<td>38.36</td>
<td>532</td>
<td>96</td>
</tr>
</tbody>
</table>
Figure G1. $^{75}$As NQR spectra of As$_2$O$_3$ acquired with the transmitter on resonance and the probe tuned to the resonance frequency. Spectra acquired with five different pulse sequences are shown. The vertical scaling of the spectra has not been altered. The full width at half height (FWHH) of the resonance is approximately 13 kHz in all spectra.
As NQR spectra of As$_2$O$_3$ acquired with the transmitter on resonance. Spectra acquired with the probe tuned to the resonance frequency (blue spectra) are compared to spectra acquired with the probe tuned to a frequency +300 kHz from the resonance frequency (green spectra), and the probe tuned +300 kHz off resonance and with re-calibrated pulse widths (red spectra). The S/N and II of the spectra are between 1.3 to 1.4 times higher when the probe is tuned +300 kHz off resonance and re-calibrated pulses are employed than when the probe is tuned on resonance.
Figure G3. $^{75}\text{As}$ QCPMG and WURST-CPMG NQR spectra. The numbers of refocusing pulses and echoes acquired are given next to the spectra. Large gains in signal are realized for both QCPMG and WURST-QCPMG when 80 echoes are acquired, however truncation of the individual echoes leads to broadening of the signal and lineshape distortions.
Figure G4. $^{35}$Cl NQR spectra of 4-chloropyridine acquired with the transmitter on resonance and the probe tuned to the resonance frequency. Spectra acquired with five different pulse sequences are shown. The vertical scaling of the spectra has not been altered. The full width at half height (FWHH) of the resonance is approximately 3.6 kHz for all echo spectra. The FWHH of the Bloch decay spectra is approximately 4.7 kHz. This will lead to artificially higher II values for Bloch decay spectra. From comparison of the spectra above it is clear that the intensity of the Bloch decay spectra is actually similar to that of the 90°-180° echo spectra.
Figure G5. $^{35}$Cl NQR spectra of 4-chloropyridine acquired with the transmitter on resonance. Spectra acquired with the probe tuned to the resonance frequency (blue spectra) are compared to spectra acquired with the probe tuned to a frequency +300 kHz from the resonance frequency (green spectra), and the probe tuned +300 kHz off resonance and with re-calibrated pulse widths (red spectra). The S/N and II of the spectra are ca. 1.6 times higher when the probe is tuned -200 kHz off resonance and re-calibrated pulses are employed than when the probe is tuned on resonance.
Figure G6. The wobble curves (blue trace) obtained from the NQR probe when it was configured for (A) $^{35}$Cl (35.346 MHz) and (B) $^{75}$As (116.234 MHz). Lorentzian line fits (red trace) generated with the NUTS NMR processing software are overlaid on the wobble curves (blue trace). The full widths at half maximum of the fits are approximately 350 kHz and 600 kHz for $^{35}$Cl and $^{75}$As, respectively.
Vita Auctoris

Aaron J. Rossini was born in Brantford, Ontario, Canada. He graduated from St. Anne’s High School in Tecumseh, Ontario in June of 2001, and the University of Windsor in May 2005 with a B.Sc. (Honours) in Chemistry. He is currently a PhD. candidate at the University of Windsor and is planning on graduating in October 2010.

Publications:


