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By

Meghan Elizabeth Doster

A Dissertation
Submitted to the Faculty of Graduate Studies
Through the Department of Chemistry and Biochemistry
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Ligand Design for the Synthesis of Reactive Nickel(0) Complexes Capable of Inert Bond Activation: C-F and C-H Bond Activation and Catalytic Functionalization

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I. Co-Authorship Declaration

I hereby declare that this thesis incorporates material that is the result of joint research, as follows: Chapter one, contains excerpts from a review entitled “Functionalization of Fluorinated Aromatics by Nickel-Mediated C–H and C–F Bond Activation: Prospects for the Synthesis of Fluorine-Containing Pharmaceuticals” (Johnson, S. A.; Hatnean, J. A.; Doster, M. E. Prog. Inorg. Chem. 2012, 57, 255-352). I wrote sections pertaining to the reactivity of the C–F bond for the manuscript, as well as obtained numerous literature references included in the review. Jillian A. Hatnean tabulated the data on the C–F Activation Products of Fluorinated Aromatics by Ni(0) Complexes. My supervisor Dr. Samuel A. Johnson had a major role in compiling the data and preparing the manuscript. Chapter 3 contains results published in a communication entitled “Catalytic C–H Bond Stannylation: A New Regioselective Pathway to C–Sn Bonds via C–H Bond Functionalization” (Doster, M. E.; Hatnean, J. A.; Jeftic, T.; Modi, S.; Johnson, S. A. J. Am. Chem. Soc. 2010, 132(34), 11923-11925). I was the principal student investigator for the synthesis and catalysis presented with MeNC₆H₄NᵢPr and the mechanistic studies. I had a major role in the preparation of the manuscript. I supervised Tamara Jeftic, and Sunjay Modi who were undergraduates that performed initial NMR studies. Jillian A. Hatnean performed the alternative synthesis and catalysis presented with ᵐPr₃P the results were published as a joint paper, and I have obtained written permission to use this work. Chapter 4 contains results published in the journal article entitled “A Mechanistic Investigation of C–H Bond Stannylation: Synthesis and Characterization of Nickel Catalysts” (Johnson, S. A.; Doster, M. E.; Matthews, J.; Shoshani, M.; Thibodeau, M.; Labadie, A.; Hatnean, J. A. Dalton Trans. 2012, 41(26), 8135-8143). I performed the kinetic and deuterium labeling studies, which provided mechanistic insight. I also played a significant role in the preparation of the supporting information included with the manuscript. I supervised Jacob Matthews who was the undergraduate student that synthesized and characterized the complex (Ph₃P)Ni(η²-CH₂=CHSnPh₃)₂, he also obtained X-ray quality crystals, I have obtained written permission to use this work. I supervised Manar Shoshani who was the undergraduate student that performed the aromatic competition studies, I have obtained written permission
to use this work. Under my supervision Michelle Thibodeau, and Amanda Labadie synthesized a few starting materials, I later used to conduct the kinetic studies. Jillian A. Hatnean identified the complex (Pr3P)Ni(η2-CH2=CHSnBu3)2 in the crude reaction mixture by 1H, 31P and 119Sn NMR spectroscopy. My supervisor Dr. Samuel A. Johnson prepared the manuscript for publication. Chapter 6 is unpublished, it contains joint research with Manar Shoshani and Natalia Mroz. I was the principal investigator on the C–H bond stannylation, mechanistic studies and C–F bond activation of the trifluoromethyl fluorinated benzene derivatives. I had a major role in the preparation of Chapter 6. I supervised Manar Shoshani who was the undergraduate that performed the meta and para substituent competitions, I have obtained written permission to use this work. I supervised Natalia Mroz who performed the initial NMR studies on the C–F bond activation of two of the trifluoromethyl fluorinated benzene derivatives.

For Chapter 2, 5 and 7, I was the sole student investigator on the projects reported and had a major role in the preparation of the manuscripts and chapters. I acknowledge my supervisor as a co-author in Chapters 1–7 as he made significant contribution to the editing of these manuscripts and chapters.

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II. Declaration of Previous Publication

This thesis includes 4 original papers, which have been previously published in peer reviewed journals, as follows:

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A strong neutral-donor, MeNC₆H₄N⁺Pr, with properties analogous to those of N-heterocyclic carbenes was developed to aid in the oxidative addition of challenging substrates to late-transition metals. Selective room-temperature C–F bond activation was observed with partially fluorinated aromatics using a nickel(0) source in the presence of this donor.

Attempts to functionalize the C–F bond of fluorinated aromatics via a Stille coupling reaction with CH₂=CHSnBu₃ and catalytic amounts of MeNC₆H₄N⁺Pr and Ni(COD)₂, failed to produce the expected vinylated product. Rather this reaction provided new C–Sn bonds via C–H bond stannylation to form products of the type C₆F₅H₅-nSnBu₃ and ethylene, at room-temperature with MeNC₆H₄N⁺Pr and at 80 °C with iPr₃P. The scope of fluoroarenes has been examined.

The complex (iPr₃P)Ni(η²-CH₂=CHSnBu₃)₂ was identified as the active species for catalytic C–H bond stannylation. The crystalline complex (iPr₃P)Ni(η²-CH₂=CHSnPh₃)₂ provided a more easily handled analogue, and was also capable of catalytic stannylation. Mechanistic studies involving deuterium labeling, concentration effects and competition reactions with various fluoroarenes were all consistent with the proposed mechanism.

The reaction of CH₂=CHSnR₃ (R = Ph, Bn) and C₆F₅H with MeNC₆H₄N⁺Pr and Ni(COD)₂ produced C₆F₅CH₂CH₂SnR₃. The compound (MeNC₆H₄N⁺Pr)Ni(η²-CH₂=CHSnPh₃)₂, was shown to be a catalyst for C–H alkylation. The isolable complexes cis-(MeNC₅H₄N⁺Pr)₂Ni(C₆F₅)(SnR₃) react with ethylene to give C₆F₅CH₂CH₂SnR₃. Complexes cis-(MeNC₅H₄N⁺Pr)₂Ni(C₆F₅)(SnR₃) are not directly in the catalytic cycle for C–H alkylation, however, they proved to be a resting state for both catalytic C–H stannylation and ethylene carbostannylation. Mechanistic studies involving concentration effects, ligand donor effects and R-group influence of CH₂=CHSnR₃ (R = Ph, Bn, Bu) support the proposed mechanistic manifold.
The scope for C–F activation and C–H stannylation with MeNC₅H₄NⁱPr and Ni(COD)₂ was expanded to trifluoromethyl fluorinated benzene derivatives. The C–H stannylation products undergo further reactivity with MeNC₅H₄NⁱPr and Ni(COD)₂ to form cis-(MeNC₅H₄NⁱPr)₂Ni(2,3,5,6-C₆F₄-4-CF₃)₂, (2,4,5-trifluoro-6-(trifluoromethyl)-1,3-phenylene)bis(tributylstannane) and FSnBu₃. The mechanism of this reactivity was studied and appears to be radical based. Support that *meta*-substituents have an even greater affect on the reaction rate of C–H activation than *para*, was gained from a competition study between various substrates with *meta-* and *para*-substituents.
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xxi
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GLOSSARY OF TERMS

The following abbreviations are used in this thesis.

\( \alpha \) \hspace{1cm} \text{alpha position, or angle label (X-ray crystallography)}

Å \hspace{1cm} \text{Ångström}

AA'BB' \hspace{1cm} \text{second order system, A and A' are chemically equivalent and magnetically in-equivalent, B and B' are chemically equivalent, magnetically in-equivalent and the chemical shift is similar to A and A' (NMR spectroscopy)}

AA'BB'C \hspace{1cm} \text{second order system, A and A' are chemically equivalent and magnetically in-equivalent, B and B' are chemically equivalent, magnetically in-equivalent and have a similar chemical shift to A and A', C couples to A, A', B and B' but has a similar chemical shift to A, A', M and M' (NMR spectroscopy)}

AA'MM' \hspace{1cm} \text{second order system, A and A' are chemically equivalent and magnetically in-equivalent, M and M' are chemically equivalent, magnetically in-equivalent and have a significantly different chemical shift than A and A' (NMR spectroscopy)}

AA'MM'N_3 \hspace{1cm} \text{second order system, A and A' are chemically equivalent and magnetically in-equivalent, M and M' are chemically equivalent, magnetically in-equivalent and have a significantly different chemical shift than A and A', N_3 represents three chemically and magnetically equivalent substituents, which have a significantly different chemical shift than A and A', and a similar chemical shift to M and M' (NMR spectroscopy)}

AA'MM'X \hspace{1cm} \text{second order system, A and A' are chemically equivalent and magnetically in-equivalent, M and M' are chemically equivalent, magnetically in-equivalent and have a significantly different chemical shift than A and A', X couples to A, A', M and M' but has a significantly different chemical shift than A, A', M and M' (NMR spectroscopy)}

acac \hspace{1cm} \text{acetylacetonate}

Anal. \hspace{1cm} \text{analysis}

Ar \hspace{1cm} \text{aryl}

aq \hspace{1cm} \text{aqueous workup}
av  average
\(\beta\)  beta position, or angle label (X-ray crystallography)
Bn  benzyl group, \(-\text{CH}_2\text{(C}_6\text{H}_5)\)
br  broad (NMR spectra)
Bu  butyl group, \(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)
\(^t\)Bu  tertiary butyl group, \(-\text{C(CH}_3)_3\)
cal  calorie
Calcd/calc  calculated
\(^{13}\)C  carbon-13
Cl  chemical ionization
cm  centimetres
cm\(^{-1}\)  wavenumbers (reciprocal centimetres)
COD  cyclooctadiene
Cp  cyclopentadienyl group, \(\text{C}_5\text{H}_5\)
Cy  cyclohexyl group, \(-\text{C}_6\text{H}_{11}\)
Cyp  cyclopentyl group, \(-\text{C}_5\text{H}_9\)
\(\delta\)  chemical shift in ppm (NMR spectra)
\(\Delta\)  delta (difference between variables)
\(\dagger\)  double dagger, transition state
d  doublet (NMR spectra)
dcpe  1,2-bis(dicyclohexylphosphino)ethane, \(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2\)
dd  doublet of doublets (NMR spectra)
dq  doublet of quartets (NMR spectra)
ddm  doublet of doublet of multiplets
dddd  doublet of doublet of doublet of doublets (NMR spectra)
dddq  doublet of doublet of doublet of quartets (NMR spectra)
dddm  doublet of doublet of doublet of multiplets
deg (or °)  degrees
\(\circ\)C  degrees Celsius
dm  doublet of multiplets (NMR spectra)
$d_n$  n-deuterated  
dq  doublet of quartets (NMR spectra)  
D  deuterium  
DFT  density functional theory  
DME  Dimethoxy ethane  
DMSO  dimethyl sulfoxide  
$E$  entgegen, opposite sides  
EA  elemental analysis  
$E_A$  activation energy  
EI  electron impact (mass spectrometry)  
$eq$  equation  
equiv  equivalents  
$F$  structure factors (X-ray crystallography)  
$^{19}F$  fluorine-19  
FW  formula weight  
$\gamma$  angle label (X-ray crystallography)  
g  gram  
GC/MS  gas chromatography/mass spectroscopy  
GOF  goodness of fit  
$\Delta G$  Gibbs free energy  
$\Delta G^\ddagger$  Gibbs free energy of activation  
$\Delta \Delta G^\ddagger$  difference in Gibbs free energy of activation  
$\eta^n$  n-hapto  
h  hour(s)  
H[BPin]  pinacolborane  
$^1$H  proton  
$\{}^1$H$\}$  proton decoupled  
HMDSO  hexamethyldisiloxane  
HMPA  hexamethylphosphoramide  
HRMS  high resolution mass spectrometry  
Hz  Hertz  

xxx
\( \Delta H \) enthalpy
\( \Delta H^\ddagger \) enthalpy of activation
\( \Delta \Delta H^\ddagger \) difference in enthalpy of activation
IR infrared
J Joules
\( ^nJ_{AB} \) n-bond scalar coupling constant between nuclei A and B
\( \kappa^n \) n-kappa
\( k \) rate constant
K Kelvin
kcal kilocalorie
KIE kinetic isotope effect
kJ kilojoules
\( \lambda \) wavelength
L neutral two electron donor
Ln lanthanide
\( \mu \) bridging or absorption coefficient (X-ray crystallography)
M central metal atom (or molar when referring to concentration)
M\(^+\) parent ion
\( m \) meta
m multiplet
MALDI matrix-assisted laser disproportion/ionization
Me methyl, \(-\text{CH}_3\)
Mes mesityl, 2,4,6-trimethylphenyl
mg milligram
MHz Megahertz
min minutes
mL millilitre
mmol millimole
mol mole
MS mass spectroscopy
MW molecular weight
m/z mass/charge (mass spectroscopy unit)
\( \nu \) wavenumber
NHC \( N \)-heterocyclic carbene
NMR nuclear magnetic resonance
No. number
\([\text{NR}_2]^-\) amido donor
\( o \) ortho
ORTEP Oak Ridge Thermal Ellipsoid Plot Program
\( \pi \) pi-bonding
\( p \) para
p pentet
\(^{31}\text{P}\) phosphorus-31
py pyridine
Ph phenyl group, \(-\text{C}_6\text{H}_5\)
\(^i\text{Pr}\) isopropyl, \(-\text{CH}(\text{CH}_3)_2\)
\(^i\text{Pr}_2\text{Im}\) 1,3-di(isopropyl)imidazol-2-ylidene
ppm parts per million
% percent
\( \theta \) theta diffraction/Bragg angle (X-ray crystallography)
q quartet (NMR spectra)
qd quartet of doublets (NMR spectra)
qdd quartet of doublet of doublets (NMR spectra)
qt quartet of triplets (NMR spectra)
R hydrocarbyl
\( R \) reliability factor (X-ray crystallography)
Reflns reflections (X-ray crystallography)
RNA ribonucleic acid
\( \sigma \) estimated standard deviation (X-ray crystallography) or sigma-bonding
s singlet (NMR spectra) or seconds
\(^{119}\text{Sn}\) tin-119
\( \Delta S \) entropy
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>$\Delta S^\circ$</td>
<td>entropy of activation</td>
</tr>
<tr>
<td>syst</td>
<td>system</td>
</tr>
<tr>
<td>t</td>
<td>triplet (NMR spectra) or time</td>
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<tr>
<td>td</td>
<td>triplet of doublets</td>
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<tr>
<td>tm</td>
<td>triplet of multiplets</td>
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<td>tt</td>
<td>triplet of triplets</td>
</tr>
<tr>
<td>T</td>
<td>temperature in Kelvin or °C</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilane</td>
</tr>
<tr>
<td>TON</td>
<td>turn-over-number</td>
</tr>
<tr>
<td>$U(eq)$</td>
<td>equivalent isotropic displacement parameter (one third of the trace of the orthogonalized $U_{ij}$ tensor)</td>
</tr>
<tr>
<td>$V$</td>
<td>unit cell volume</td>
</tr>
<tr>
<td>$W_{1/2}$</td>
<td>width at half height</td>
</tr>
<tr>
<td>X</td>
<td>halide substituent (or donor with a negative charge)</td>
</tr>
<tr>
<td>Y</td>
<td>yttrium</td>
</tr>
<tr>
<td>Z</td>
<td>asymmetric units per unit cell (X-ray crystallography)</td>
</tr>
<tr>
<td>Z</td>
<td>zusammen, same side</td>
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1.1 General Introduction

One of the greatest challenges in chemistry is the development of new pathways for the conversion of typically unreactive species such as alkanes to more reactive and useful species, which can be utilized in the pharmaceutical, agrochemical, natural product, chemical, petrochemical and polymer industries.\textsuperscript{1-20} Traditional methods for functionalizing an alkane typically require a prefunctionalization step, such as halogenation, which requires mediated free-radical activation and extreme conditions.\textsuperscript{6,10,13} The direct activation and functionalization of an alkane C–H bond is highly desirable.\textsuperscript{6,9,10} It would avoid additional steps, which would reduce both the chemical waste and the extreme conditions required to break the C–H bond, and would provide a methodology that is greener, synthetically easier, and more economical for the synthesis of functionalized organics.
The direct activation of an alkane C–H bond is difficult, because the C–H bond is very strong with dissociation energies of about 110 kcal·mol⁻¹, and is therefore typically considered chemically inert.²,⁷,²¹ The search for efficient methodologies for the functionalization of alkane C–H bonds has predominately focused on the late 2nd and 3rd row transition metals. It has been well documented that the 2nd and 3rd row transition metals are capable of reacting with a C–H bond to form new metal-carbon (M–C) and metal-hydrogen (M–H) bonds via C–H bond activation, which is also known as an oxidative addition reaction, and is shown in Scheme 1.1.¹ This reaction is thermodynamically possible because the combination of the M–C and M–H bonds formed is significantly stronger that the C–H bond that was broken. The M–C bond is also more reactive than the C–H bond and can therefore undergo further functionalization.¹⁰

![Scheme 1.1.](image)

**Scheme 1.1.** General reaction scheme for the oxidative addition of an alkane or aryl C–H bond by a transition metal.

Early examples of C–H bond activation with the late transition metals included both intramolecular oxidative addition to both sp² and sp³ C–H bonds of ligands bound to the metal center, and intermolecular oxidative addition to arene C–H bonds, as shown in Scheme 1.2.⁸,¹³,²²,²³ Two generalizations were drawn early on, the first stated that the stronger arene C–H bonds were more readily activated than the weaker alkane C–H bonds because they form stronger M–C bonds.⁸,¹⁴ The second generalization was that the equilibrium for C–H bond activation of alkanes is thermodynamically unfavorable, which indicates that the reverse reaction, reductive elimination, should be favored.⁶ Major breakthroughs by Bergman⁷ and Jones⁶ confirmed that arene C–H bonds are preferentially activated over alkane C–H bonds and disproved that the oxidative addition of alkane C–H bonds is
thermodynamically disfavored, by the observation of C–H oxidative addition of cyclohexane to an iridium complex and C–H oxidative addition of propane to a rhodium complex, as shown in Scheme 1.3.

Scheme 1.2. A) An example of intramolecular C–H bond activation. B) An example of arene C–H bond activation.

Scheme 1.3. A) Example by Bergman of alkane C–H bond activation by Ir complex. B) Example by Jones of alkane C–H bond activation by Rh complex.
Despite a plethora of recent examples of C–H activation with the late transition metals (ex. Rh, Re, Ir, W, Pt, Pd), examples with the 1st row transition metals are relatively rare, but nickel is arguably ahead of the other 1st row metals. The 1st row transition metals form weaker M–C bonds than the 2nd and 3rd row transition metals, which makes the C–H oxidative addition products thermodynamically less favorable. However, developing efficient methodologies for C–H activation with the 1st row transition metals is highly desirable because they are much cheaper and more abundant than the late 2nd and 3rd row metals and would therefore be much more economical for industrial processes.

This dissertation will focus on the development of a strong donor ligand that better promotes the oxidative addition of inert bonds to 1st row transition metals, in particular with nickel. A focus will be on the activation and functionalization of both inert C–F and C–H bonds of partially fluorinated aromatics, due to the demand for functionalized fluorinated organics in the pharmaceutical and agrochemical industries. The decreased tendency for nickel to undergo C–H activation compared to the 2nd and 3rd row transition metals has generated interest with these complexes to activate and functionalize selectively the C–F bond of partially fluorinated aromatics. We will demonstrate that C–H bond activation is actually faster than C–F bond activation, even though it is not thermodynamically favored, and that with the correct choice of substrate, these kinetic C–H activation products can be functionalized by nickel catalysts.

1.2 Overview of Nickel Chemistry

Nickel is an abundant 1st row transition metal found in group 10 of the periodic table. Nickel contains ten d-electrons in a neutral Ni(0) species and can exist in a variety of oxidation states Ni(0)–Ni(IV), the lower oxidation states Ni(0) and Ni(II) are the most common, while Ni(I) and the higher oxidation states Ni(III) and Ni(IV) are quite rare. In the Ni(II) oxidation state a variety of coordination geometries can be observed, square planar or tetrahedral for a coordination number of 4, trigonal bipyramidal or square pyramidal for a coordination number of 5, and octahedral for a coordination number of 6. However, the most frequent geometries adopted by Ni(II) are square planar and octahedral, as shown in Figure 1.1.
Nickel(0) complexes contain two-electron vacant sites, which should make them ideal for oxidative addition reactions. An oxidative addition reaction increases the oxidation state, electron count and coordination number of the metal center by two, as shown in Scheme 1.1.\textsuperscript{1} The oxidative addition of a substrate to a 14 electron Ni(0) complex forms a stable square planar 16 electron Ni(II) complex. These Ni(II) complexes are perfectly suited for reductive elimination, which is the reverse of oxidative addition, and required to complete a catalytic cycle. Sixteen electron Ni(II) complexes are therefore commonly observed in nickel mediated catalytic cross-coupling reactions for this reason.\textsuperscript{56} However, the functionalization of C–H\textsuperscript{57,58} or C–F\textsuperscript{59-63} bonds with nickel is still relatively rare.

When considering C–F bond oxidative addition, nickel has been acknowledged as displaying unique selectivity in the activation of C–F bonds with some substrates, compared to other transition metal, which provides products with fluorine substitution patterns not accessible by other approaches, such as direct fluorination by F\textsubscript{2}.\textsuperscript{64,65} It has also been observed that Ni(0) complexes are less prone to the irreversible oxidative addition of C–H bonds,\textsuperscript{53,54,65,66} and Ni(0) complexes should selectively activate C–F bonds in the presence of typically more reactive C–H bonds. Some recent advances have demonstrated that with appropriate ancillary ligands, nickel complexes can find use in C–H activation, though many of the examples are either chelate-assisted or involve arene C–H bonds that are rendered more reactive by the presence of adjacent substituents, as shown in Scheme 1.4.\textsuperscript{57,58} C–H bond functionalization reactions are more desirable than C–F bond functionalization reactions, as they are more atom efficient, in that the loss of fluoride is not necessary and therefore more economical. A deeper understanding of what controls the selectivity of these reactions is needed inorder to develop optimized nickel catalysts.

1.3 C–H and C–F Bond Activation

1.3.1 General Overview

The C–F bond is the strongest single-bond to carbon, and is often unreactive towards transition metal complexes. The C–X bond strengths in MeX decrease along the series X = F, H, Cl, with values of 481, 439, and 351 kJ·mol$^{-1}$. This bond strength creates thermodynamic issues with respect to C–F bond reactivity, but these bonds are also often unreactive for kinetic reasons. Aromatic C–F bonds are more reactive towards transition metal complexes than aliphatic C–F bonds, despite even higher C–F bond strengths. Similar thermodynamic and kinetic issues also render C–H bonds unreactive.

There are numerous examples of C–H$^{6,7,10,14,16,20,26,27,67-69}$ and C–F$^{70-73}$ bond activation with the 2$^{nd}$ and 3$^{rd}$ row transition metals with a variety of substrates, including polyfluorinated aromatics. In general, the oxidative addition of C–F bonds is more thermodynamically favored than C–H bond oxidative addition, whereas, C–H bond oxidative...
addition is kinetically more facile.\textsuperscript{53} Thus in the presence of C–F and C–H bonds, C–H bond activation is preferred with the 2\textsuperscript{nd} and 3\textsuperscript{rd} row transition metals, as shown in the example with Pt in Scheme 1.5.\textsuperscript{74} A major concern with utilizing the 2\textsuperscript{nd} and 3\textsuperscript{rd} row transition metals for C–H and C–F bond activation is that these metals are very expensive. It would therefore be of interest to find cheaper metals, such as nickel, that have similar reactivity, to make these reactions more economical.

\begin{center}
\includegraphics[width=\textwidth]{scheme15.png}
\end{center}

\textbf{Scheme 1.5.} The C–F and C–H bond activation of fluorinated aromatics with [Pt(PCy\textsubscript{3})\textsubscript{2}].

\subsection*{1.3.2 Theoretical Insight into C–H versus C–F Bond Activation by Ni(0) Complexes}

The oxidative addition chemistry of Ni has been shown to be vastly different from that of its heavier congeners. For example, the platinum complex (dcpe)PtH(CH\textsubscript{2}CMe\textsubscript{3}) reacts thermally in benzene by reductively eliminating neopentane and oxidatively adding a C–H bond of benzene, which produces (dcpe)PtH(Ph) (where dcpe = Cy\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PCy\textsubscript{2} or 1,2-bis(dicyclohexylphosphino)ethane), and is shown in Scheme 1.6.\textsuperscript{26} Related examples of the oxidative addition of the C–H bonds in benzene to Ni complexes are absent in the literature, likely due to subsequent decomposition of the nickel hydride complexes. This difference in reactivity can be attributed to weaker Ni–H bonds formed relative to Pt, which renders oxidative addition of the C–H bond thermodynamically unfavorable compared to the $\eta^2$-intermediate that is formed, Ni(dcpe)($\eta^2$-C\textsubscript{6}H\textsubscript{6}).\textsuperscript{53}

There was an influential paper published in 2004 that took a computational approach to determine the differences between C–H and C–F bond activation of fluorinated aromatics with Ni bis(phosphine) fragments. This report determined that the oxidative addition of C6H6 to the (H2PCH2CH2PH2)Ni fragment should occur via an $\eta^2$-adduct, with a barrier to activation of 85.4 kJ·mol$^{-1}$. Similar calculations were carried out with carbene ligands, which are much stronger donors and might be expected to aid in oxidative addition reactions, however calculations on the oxidative addition of C6H6 to the [iPr2Im]$_2$Ni moiety, where [iPr2Im] = 1,3-di(isopropyl)imidazol-2-ylidene, also reveal that C–H activation reaction is not favorable with respect to the $\eta^2$-adduct, by 45.1 kJ·mol$^{-1}$. The calculational results are summarized in Figure 1.2.
The calculations also revealed that the oxidative addition of a C–F bond in C₆F₆ to a (H₂PCH₂CH₂PH₂)Ni fragment is favorable and that the reaction proceeds through a \( \eta^2 \)-adduct with a \( \sigma \)-complex transition state.⁵³ Similar calculations on the oxidative addition of C₆F₆ to the \([\text{iPr}_2\text{Im}]_2\text{Ni}\) moiety were also carried out and found to be favorable.⁷⁵ The calculational results are summarized in Figure 1.3. The barrier to C–F activation is relatively large, ranging from 94.1 kJ·mol⁻¹ to 111.4 kJ·mol⁻¹, but unlike the C–H bond activation of C₆H₆, these reactions are all thermodynamically downhill. These studies show that Ni(0) mediated C–F bond activations, which occur via \( \eta^2 \)-arenes adducts, should be slow at room temperature and should be irreversible under accessible conditions.

![Figure 1.2](image-url)  
**Figure 1.2.** Calculated energies for the oxidative addition of C₆H₆ to (H₂PCH₂CH₂PH₂)Ni and \([\text{iPr}_2\text{Im}]_2\text{Ni}\) moieties.⁵³,⁷⁵ (Here n/a means trans complex not possible with a chelating ligand.)

<table>
<thead>
<tr>
<th>( \text{L}_2\text{Ni} )</th>
<th>( \sigma )-complex transition state ( \Delta E ) (kJ·mol⁻¹)</th>
<th>cis C–H activation product ( \Delta E ) (kJ·mol⁻¹)</th>
<th>trans C–H activation product ( \Delta E ) (kJ·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2)\text{Ni})</td>
<td>+89.1</td>
<td>+85.4</td>
<td>n/a</td>
</tr>
<tr>
<td>([\text{iPr}_2\text{Im}]_2\text{Ni})</td>
<td>+51</td>
<td>+45.1</td>
<td>+22.9</td>
</tr>
</tbody>
</table>
The thermodynamic preference for Ni(0) complexes to undergo C–F oxidative addition versus C–H bond activation is irrefutable for the systems studied; however, to be utilized in a catalytic cycle, the C–H activation product needs only to be kinetically accessible, with thermodynamically favored products obtained by subsequent reactions. With this in mind, the results of the DFT calculations on the activation of C₆H₆ versus C₆F₆ can be reexamined to determine the kinetic preference for C–H versus C–F activation by Ni(0) complexes. The results indicated that the calculated barrier for C–H activation was 89.1 kJ·mol⁻¹, which is slightly lower than the barrier for C–F bond activation of 94.1 kJ·mol⁻¹; this result suggests that C–H activation should be slightly faster than C–F bond activation. With a suitable trap, such as an alkyne that can insert irreversibly into the Ni–H bond, nickel mediated C–H bond activation could be utilized in catalytic functionalization.  

Figure 1.3. Calculated energies for the oxidative addition of C₆F₆ to (H₂PCH₂CH₂PH₂)Ni and [iPr₂Im]₂Ni moieties. (Here n/a means trans complex not possible with a chelating ligand.)
For the fluorinated aromatics, as opposed to benzene, there are other factors to consider regarding the thermodynamic and kinetic propensity of C–H bonds to undergo oxidative addition. It has been known for some time that the C–H bonds in fluorinated aromatics are more reactive towards oxidative addition than those in benzene.\textsuperscript{124} It has been found that \textit{ortho}-fluorine substituents strongly activate C–H bonds towards oxidative addition. This thermodynamic effect is not caused by a weakening of the C–H bond by adjacent fluorines; on the contrary, these C–H bonds have higher dissociation energies. The presence of \textit{meta}-fluorine substituents does not significantly affect C–H bond strength, and \textit{para}-fluorine substituents increase the C–H bond dissociation energies, but only about one-third as much as the \textit{ortho}-fluorine substituents. Recently, considerable experimental and theoretical work has been undertaken to understand the mechanism of this effect.\textsuperscript{69,76,77}

Fluorine substituents strengthen metal-carbon bonds even more than they strengthen C–H bonds, with \textit{ortho}-fluorine substituents having the largest effect.\textsuperscript{76,77} As with C–H bonds, the influence of \textit{meta}-fluorine and \textit{para}-fluorine substituents is significantly less; however, unlike C–H bonds, the effect of a \textit{meta}-fluorine is nearly equal to that of a \textit{para}-fluorine. From these calculations, it can be proposed that aromatic C–H bonds with \textit{ortho}-fluorines should be easier to activate, and that \textit{meta}-fluorines should also assist C–H bond oxidative addition, though to a lesser degree.

The use of stronger donors, such as carbenes, may even further favor C–H bond activation. It can be hypothesized that stronger donors would create a more electron-rich nickel centre that would further favor oxidative addition. DFT calculations predict that the carbene complex \([i\text{Pr}_2\text{Im}]_2\text{Ni}(\eta^2\text{-C}_6\text{H}_6)\) should have a barrier to C–H activation that is 38.1 kJ\cdot mol\(^{-1}\) lower than with the phosphine complex \((\text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2)\text{Ni}(\eta^2\text{-C}_6\text{H}_6)\) and a barrier to C–F bond activation that is 7.4 kJ\cdot mol\(^{-1}\) higher. These calculations suggest that stronger donors should undergo rapid C–H bond activation, even at room temperature.
1.3.3 C–F Activation with Ni(0) and a Phosphine Ancillary Ligand

The activation of typically inert C–F bonds by transition metal complexes was first reported in 1977. The reaction of (Et₃P)₂Ni(COD) (COD = 1,5-cyclooctadiene) with C₆F₆ provided trans-(Et₃P)₂NiF(C₆F₅), as shown in Scheme 1.7. The product was isolated in a 7 % yield, and characterized by elemental analysis, melting point, and IR spectroscopy. This product was later synthesized by the reaction of (Et₃P)₄Ni with C₆F₆, which takes place over 4 weeks at 25 °C, with an improved isolated yield of 48 %; the low yield was limited primarily by the high solubility of the product in hexane. The presence of excess phosphine produced unwanted difluorophosphorane byproducts, identified in the reaction mixture by their ³¹P resonances.

\[
\text{COD} = 1,5\text{-cyclooctadiene}
\]

\[
\text{Scheme 1.7. C–F activation of C}_6\text{F}_6 \text{ with (Et}_3\text{P)}_2\text{Ni(COD) and (Et}_3\text{P)}_4\text{Ni produced trans-}
\text{(Et}_3\text{P)}_2\text{NiF(C}_6\text{F}_5) \text{ with isolated yields of 7 % and 48 %, respectively.}
\]

1.3.4 C–F Activation of Partially Fluorinated Aromatics

Partially fluorinated aromatics are potentially of greater interest than perfluorinated substrates, particularly in the area of fluorinated pharmaceuticals. However, selective C–F bond activation of partially fluorinated aromatics is relatively rare. An example is shown in Scheme 1.8: the C–F bond activation of C₆F₅H with \textit{in situ} generated (Et₃P)₄Ni in THF was not selective. The mixture was found to contain three C–F activation products in a 7:2:1 ratio by consideration of the ¹⁹F NMR Ni–F resonances. The products were tentatively assigned as products of activation at the \textit{ortho}, \textit{meta}, and \textit{para} sites of C₆F₅H, respectively, one of the major products of the reaction was also found to be 1,2,4,5-tetrafluorobenzene, which was unexpected and not explained by the authors.
Scheme 1.8. C–F bond activation of C₆F₅H with (Et₃P)₄Ni, and the mixture of products formed.

The C–F bond activation of 1,2,4,5-C₆F₄H₂ with the phenanthrene adduct of (Et₃P)₂Ni has been performed.⁵⁴ The presence of C–H bond activation products in equilibrium with dinuclear and mononuclear adducts as kinetic products has been demonstrated.⁶⁶,⁷⁹ This C–F bond activation reaction is slow at room temperature, but is accelerated by added substrate. Although selective C–F bond activation should be easy with this substrate, which features a single fluorine environment, the activation of 1,2,4,5-C₆F₄H₂ yields unexpected byproducts, as shown in Scheme 1.9. This includes the formal hydrodefluorination product 1,2,4-trifluorobenzene and (Et₃P)₂NiF(2,3,5,6-C₆F₄H). The C–F activation product (Et₃P)₂NiF(2,3,5-C₆F₃H₂) was also observed, which is the formal product of the C–F activation of 1,2,3,5-C₆F₄H₂ at the 1-site, despite the fact that no 1,2,3,5-C₆F₄H₂ was present in the reaction mixture.
Scheme 1.9. C–F activation of 1,2,4,5-C₆F₄H₂ with the phenanthrene adduct of (Et₃P)₂Ni and the mixture that results.

It was suggested that the rearrangement product in the reaction could be formed via an intermediate aryne complex.⁵⁴ Recently such a complex has been isolated and characterized in the activation of 1,2,3,5-tetrafluorobenzene.⁶⁶ The activation of 1,2,3,5-tetrafluorobenzene occurs preferentially at the 1-site to give (Et₃P)₂NiF(2,3,5-C₆F₃H₂); but when the phenanthrene adduct (Et₃P)₂Ni(η²-C₁₄H₁₀) was used as the (Et₃P)₂Ni source, the unexpected product (Et₃P)₂NiF(2,4,5-C₆F₃H₂) was also observed. When (Et₃P)₂Ni(η²-CH₂=CHMe₂) was used as a (Et₃P)₂Ni synthon it proved possible to isolate the aryne complex [(Et₃P)₂Ni]₂(μ-η²:η²-3,4,6-C₆F₃H) from a solution containing the C–F activation product and the other intermediates, as shown in Scheme 1.10.
These results suggest that C–F bond activation of partially fluorinated aromatics with Et3P as the ancillary ligand are unselective and produce a complex mixture of products. However, the observation of kinetic C–H bond activation products in solution, which indicates that C–H bond activation with Ni is possible and that C–H functionalization should be achievable with the appropriate choice of ligands and substrates.

1.3.5 C–F Activation with Ni(0) and a Strong Carbene Ancillary Ligand

The N-heterocyclic carbene (NHC) donors have seen extensive use in modern organometallic chemistry. Their donor properties are reminiscent of the most electron-donating trialkylphosphines, and offer a clear alternative to the ubiquitous phosphine donors to promote difficult C–F bond oxidative addition reactions. The NHC ligand, [\textit{i}Pr2Im], has been extensively studied as an ancillary ligand to promote C–F bond activation at nickel. The C–F activation of C6F6 and a variety of partially fluorinated aromatics has been accomplished by the consecutive addition of Ni(COD)2 to two equivalents of [\textit{i}Pr2Im]
followed by C$_6$F$_6$ by the use of the isolated dinuclear COD complex ([I$^2$Pr$_2$Im]$_2$Ni)$_2$(μ-η$^2$:η$^2$-COD)$_{75,80}$ or the mononuclear ethylene adduct [I$^2$Pr$_2$Im]$_2$Ni(η$^2$-C$_2$H$_4$)$_{75}$ followed by the addition of the fluorinated aromatic, as shown in Scheme 1.11.

Scheme 1.11. C–F activation of a variety of partially fluorinated aromatics with a carbene ancillary ligand.

The reactions are all quantitative according to $^{19}$F and $^1$H NMR spectroscopy, with no observation of the kinetic C–H activation products. Pentafluorobenzene and a variety of polyfluorobenzenes all reacted selectively at the para-fluorine position. All three trifluorobenzenes were found to react via C–F bond oxidative addition to nickel. The reactivity of 1,2,4-trifluorobenzene occurred selectively at the 2-position. With 1,2,3-trifluorobenzene the reaction was not completely selective, and 85 % of the product resulted from oxidative addition at the 1-site and 15 % from the 2-site. The less fluorinated arene 1,2-difluorobenzene was found to be a viable substrate, though none of the other difluorobenzenes or any tetrafluorobenzenes were investigated.$^{75}$ This NHC ancillary ligand appears to promote faster C–F activation than the well-studied Et$_3$P ligand; all C–F bond activations utilizing the [I$^2$Pr$_2$Im] ligand were complete overnight at room temperature. These results confirmed that stronger donors, such as carbenes better promote oxidative addition as predicted by the theoretical studies.
1.3.6 Nickel Mediated C–H Bond Activation of Fluorinated Aromatics

The barrier for C–H activation of partially fluorinated aromatics with (H₂PCH₂CH₂PH₂)Ni has been predicted by DFT calculations to be slightly lower than the barrier for C–F activation (Section 1.3.2), which indicated that the C–H oxidative addition products may be kinetically accessible. This was confirmed by the reaction of (Et₃P)₂Ni with 1,2,4,5- or 1,2,3,5-tetrafluorobenzene, when the kinetic C–H activation products were observed by NMR spectroscopy before the thermodynamic C–F activation products formed (Section 1.3.4). Despite observing the kinetic C–H oxidative addition products by NMR, they were not isolable since there was always equilibrium amounts of the mononuclear and dinuclear complexes present in solution. It has been shown recently that increasing the steric bulk of the phosphine ancillary ligand provides enough thermodynamic driving-force to allow for the isolation of the C–H oxidative addition complexes. ⁸¹ The reaction of a slight excess of 1,2,4,5-tetrafluorobenzene with the anthracene adduct (³Pr₃P)₂Ni(η²-C₁₄H₁₀) produced the C–H oxidative addition complex trans-(³Pr₃P)₂NiH(2,3,5,6-C₆H₄H) after 6 hours, as shown in Scheme 1.12. There was no indication of the formation C–F bond activation or fluoroarene products.

![Scheme 1.12. C–H activation of 1,2,4,5-C₆F₄H₂ with (³Pr₃P)₂Ni(η²-C₁₄H₁₀).](image)

To date, the direct observation of C–H oxidative addition products of the fluorobenzenes with ancillary ligands other than phosphines has been curiously absent in the literature. However, catalytic results imply that C–H oxidative addition products are present as kinetic products in solution and precede C–F activation (*vide infra*).
1.4 Potential Application of C–F and C–H Bond Activation of Partially Fluorinated Aromatics

The selective activation and functionalization of C–H and C–F bonds in fluorinated aromatics by transition-metals, has been touted as alternative routes\textsuperscript{82-84} to synthesizing partially fluorinated organics, which have found extensive use in pharmaceuticals\textsuperscript{85-89} and agrochemicals.\textsuperscript{90} Fluorine substituents are only slightly larger than hydrogen, therefore substituting a hydrogen atom for a fluorine will have only minor effects on the size and conformation of molecules, but can cause dramatic effects on many of the physical properties.\textsuperscript{91}

The benefits of partial fluorination on the efficacy of pharmaceutical drugs is well documented, although the exact mechanisms by which fluorination improves drug performance are not always clear.\textsuperscript{85,87,88,92-94} The physical properties affected by the introduction of a fluorine atom include slowed metabolism, improved lipophilicity, and changes in the acidity and basicity of the molecules.

![Fluorouracil, Cipro (Bayer) antibiotic, Paxil (GlaxoSmithKline), Fluconazole (Pfizer) antifungal](image)

Figure 1.4. Four examples of fluorinated organics with medicinal applications.

Some examples of common fluorine containing pharmaceuticals are shown in Figure 1.4. Pharmaceutical drugs with a single fluorine substituent are the most common, but drugs containing two fluorinated positions are also ubiquitous in the literature. An example is provided by Fluconazole, which contains an aromatic ring with fluorine substituents at the 2- and 4-positions. The analogous compounds with substitution in either the 2- or 4- positions
showed good activity, but only the 2,4-difluorophenyl isomer had the desired solubility. There are also numerous drugs with anticancer properties that contain aromatic rings bearing two fluorine substituents in the 2,6- or 3,4-positions.\textsuperscript{89}

Compounds with higher degrees of fluorination on aromatic rings are less common in pharmaceutical applications. Pentafluorophenyl rings readily undergo nucleophilic attack, which in most cases would be an undesirable reactivity, but this property has been exploited in the design of anticancer agents,\textsuperscript{88,95} an example is shown in Figure 1.5.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1_5.png}
\caption{An example of an anticancer agent with reactive pentafluorophenyl substituent.}
\end{figure}

Tetra- and trifluorinated aromatic substituents are also rare in pharmaceuticals. It is not clear if this is attributed to lower activities, undesirable physical properties, or simply increased difficulty of synthesis. Sitagliptin, shown in Figure 1.6, is an example where partial optimization of the fluorine substitution pattern on the aromatic substituent was used to determine that the 3,4,5-trifluorophenyl substitution pattern performed better than those with 3,4- or 2,5-difluorophenyl substituents. Further X-ray crystallography was used to study the interaction of this drug with the active site, results revealed that the 3,4,5-trifluorophenyl group completely occupies the hydrophobic pocket, which is consistent with its increased potency relative to its difluorophenyl analogues.\textsuperscript{96}
In order to conduct fluorine scans of possible fluorine substitution patterns when designing drugs, libraries containing selectively functionalized fluorinated building blocks with a variety of fluorine substituent patterns need to be developed. There is potential for the use of transition metal complexes as catalysts for the selective conversion of available fluorinated substrates into these versatile building blocks via either C–H or C–F bond activation. Traditionally expensive 2nd and 3rd row transition metals are utilized for C–H and C–F activation, however nickel has proven useful as a much cheaper alternative for C–F bond activation and potential for C–H bond activation. Developing nickel catalysts capable of C–F and C–H bond functionalization will be a much more economical alternative to the 2nd and 3rd row transition metals.

1.5 Catalytic Functionalization by Nickel Complexes

There are two potential pathways partially fluorinated aromatics can be functionalized. The first pathway is catalytic C–F bond functionalization, as shown in Figure 1.7. This pathway involves the cleavage of one of the C–F bonds of the fluorinated aromatic and the formation of new Ni–F and Ni–C bonds, via oxidative addition. The Ni–F bond can then undergo a transmetallation step, in this case with the hypothetical reagent RY, to form Ni–R and YF. This is followed by a cis/trans isomerization if required and reductive elimination of R and the aryl group from nickel to produce a product functionalized at the site of C–F activation.

Figure 1.6. An example of pharmaceutical containing a trifluorophenyl substituents.

Sitagliptin (Januvia) Merck & Co. treatment of type 2 diabetes
The second possible pathway is catalytic C–H bond functionalization, as shown in Figure 1.8. This pathway involves the cleavage of one of the C–H bonds of the fluorinated aromatic and the formation of new Ni–H and Ni–C bonds. The Ni–H bond can then undergo a transmetallation, in this case with the hypothetical reagent RZ, to form Ni–R and HZ. Reductive elimination of R and the aryl group from nickel produces a product functionalized at the site of C–H bond activation. The two pathways provide very different products, which differ both in the number of fluorines present and the fluorine substitution pattern.

**Figure 1.7.** Catalytic pathway for C–F bond functionalization of a fluorinated aromatic and fictional reagent RY utilizing a Ni(0) catalyst.
1.5.1 C–F Functionalization by Nickel Complexes

Although there are a plethora of stoichiometric reactivities observed with C–F activation products, catalytic C–F bond functionalization reactions are rare. For example, reactions such as the replacement of fluoride with other halides are unlikely to result in carbon-halogen bond formation, due to the strength of the Ni–F bond. Many of the stoichiometric reactions studied with the Ni–F complexes could have potential in catalysis, particularly where the Ni–F bond is replaced with a Ni–C bond; however, strongly basic or nucleophilic reagents such as MeLi may not be compatible with the polyfluoroarene substrates. Some examples of catalytic C–F functionalization are presented *vide infra*, and it should be noted that the organotin and organoboron reagents used in Stille and Suzuki-Miyaura coupling are the most common reagents for converting Ni–F to Ni–C bonds in catalysis.

1.5.1.1 Stille Coupling

The Stille cross-coupling reaction involves the coupling of an organostannane and an organic electrophile, to form a new C–C $\sigma$-bond, typically using a Pd(0) catalyst.$^{98-100}$ Recently, there have been a few examples of Stille cross-coupling utilizing nickel...
The reaction of pentafluoropyridine with CH₂=CHSnBu₃ is catalyzed by the product of C–F activation, (Et₃P)₂NiF(2-C₅F₄N), and added Et₃P, albeit with high catalyst loadings and a modest number of turnovers, as shown in Scheme 1.13. A base was necessary for catalysis, possibly to scrub small amounts of HF from side reactions. A significant byproduct in the reaction is 2,3,5,6-tetrafluoropyridine. In addition, it proved possible to use 2,3,5,6-tetrafluoropyridine as a substrate in this reaction with similar efficiency and afforded a turn-over number (TON) of 5. The scope of this methodology with respect to the use of a wider range of fluorinated organics and organotin reagents, as well as more capable nickel catalysts, has yet to be fully elaborated. Reagents capable of selective C–F rather than C–H bond activation may be necessary to extend this reactivity to partially fluorinated aromatics.\(^{58}\)

![Scheme 1.13. An example of a Stille cross-coupling reaction utilizing a nickel catalyst.](image)

### 1.5.1.2 Suzuki-Miyaura Coupling

The Suzuki-Miyaura cross-coupling reaction involves the coupling of organoboranes with organic halides or triflates to form new C–C bonds, typically using a Pd(0) catalyst.\(^{102-104}\) The substrate 5-chloro-2,4,6-trifluoropyridine has been found to undergo a catalytic C–C bond coupling reaction with arylboronic acids to produce disubstituted products, as shown in Scheme 1.14.\(^ {105}\) The catalyst is the C–F activation product obtained initially by reacting Ni(COD)₂ and Ph₃P with 5-chloro-2,4,6-trifluoropyridine.
Similar catalytic cross-coupling reactions have been reported with the perfluorinated arenes, octafluorotoluene and decafluorobiphenyl. The catalyst \( ([\text{iPr}_2\text{Im}])_2\text{Ni})_2(\text{COD}) \) in this system operates with a much lower catalyst loading than the previous example (2 mol % vs 10 mol %), and significantly better TONs, though direct comparison of ancillary ligand effects is impossible due to the difference in substrates.

**1.5.2 C–H Bond Functionalization with Ni(0)**

The functionalization of C–H bonds in fluorinated aromatics is very appealing. It avoids the production of fluoride containing byproducts, which are formed during C–F bond functionalization, and thus is more atom-efficient. It also avoids the problems associated with the formation of kinetically inert C–H bond activation products in catalytic cycles intended to operate by C–F activation.

**1.5.2.1 C–H Alkenylation and Alkylation of Fluorinated Aromatics**

It has recently been shown that with the appropriate choice of phosphine ancillary ligands, it is possible to catalytically functionalize C–H bonds in fluoroarenes by trapping the nickel-hydrides with suitable alkynes and alkenes. The reaction of pentafluorobenzene with PrC≡CPr with catalytic amounts of Ni(COD)\(_2\) and Cyp\(_3\)P produced (\(E\))-pentafluoro(octen-4-yl)benzene, as shown in Scheme 1.15. The use of tri(sec-alkyl)phosphines as ancillary ligands appears crucial in these reactions; the phosphines \(\text{iPr}_3\)P,
Cy₃P, and Cyp₃P all generate active catalysts, whereas Me₃P, Bu₃P, and 'Bu₃P do not. Other symmetrical alkynes are also catalytically inserted into the C–H bond of pentafluorobenzene, though with poorer yields. Sterically unsymmetrical alkynes insert regioselectively, to produce products with the larger of the two substituents *trans* to the pentafluorophenyl group.

The mechanism was originally suggested to involve the formation of an $\eta^2$-arene adduct of the nickel-phosphine, followed by C–H bond activation, regioselective insertion of the alkyne into the Ni–H bond, and reductive elimination to form a new C–C bond. However, computational studies were later conducted that disputed the proposed mechanism and suggested an alternative more favorable mechanism, involving the coordination of the alkyne to the metal center followed by a H-transfer from the $\sigma$-coordinated arene to the alkyne, and reductive elimination to form the desired C–H alkenylation product.¹⁰⁶

![Reaction scheme](image)

Scheme 1.15. General reaction scheme for C–H alkenylation of fluorinated aromatics.

This reaction has been extended to other partially fluorinated arenes using the most reactive alkyne, PrC≡CPr. Figure 1.9 shows a selection of accessible products, as well as yields. In general, the less fluorinated substrates were found to be less reactive, and the reaction with both 1,2-difluorobenzene and monofluorobenzene are obtained with less than a single catalyst turnover under the conditions employed. In compounds with multiple C–H bonds, the hydrogens with the most *ortho*-fluorine substituents were selectively activated, consistent with the thermodynamic preferences for C–H activation.⁷⁷
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**Figure 1.9.** A selection of polyfluorinated substrates functionalized by 4-octyne.

### 1.6 Optimization of Nickel Catalysts for Inert Bond Activation

Studies have proven that nickel is capable of promoting oxidative additions and functionalizations of inert C–F and C–H bonds with unique selectivity compared to the 2\textsuperscript{nd} and 3\textsuperscript{rd} row transition metals, though this area is still relatively unexplored. It has been indicated that the choice of ancillary ligand is crucial for determining the feasibility, selectivity and rate of inert bond activation with nickel, and further investigation is needed for the optimization of nickel catalysts. This section will discuss the development of a strong amido donor ancillary ligand for the promotion of C–H and C–F bond activation with nickel.

#### 1.6.1 Amido Donor Ligands

It should be noted that the term amide has two different meanings in chemistry. In organic chemistry, amide takes on the meaning of a functional group that contains a carbonyl carbon that bears an alkyl or aryl group and an amino group, RCONR\textsubscript{2}.\textsuperscript{107} In inorganic chemistry, the term amide commonly represents an amino group that bears two alkyl or aryl groups and a negative charge, [NR\textsubscript{2}]\textsuperscript{−}.\textsuperscript{1} The second version is the one that will be considered throughout this section.

Amido donors have proven themselves to be a highly diversified and valuable class of ligands for the formation of transition metal and main group complexes.\textsuperscript{108} Amido transition metal chemistry expanded into a major field of study in the 1960s and 1970s and can be
connected with early pioneers of the field including Bürger, Wannagat, Bradley and Lappert. The reactivity differences of the metal-amido bond compared to the metal-carbon bond were the focus of many of the original investigations. However, it was found that the metal-amido bond was not as synthetically useful as initially thought, since the metal amido bond proved to be kinetically inert and thermodynamically more stable than the metal-carbon bond for the early transition metal complexes formed. More recent advances have proven that the stable metal-amido bond can be exploited in such a way that the reactivity of the metal center can be defined and the chemistry of the complexes formed can be tuned as required.

Amido donor ligands also are popular due to their unique $\sigma$- and $\pi$-donor capabilities and the availability of two substituent positions at the amido N-donor atom. This double substitution pattern is ideal for ligand design, as amido groups can easily be combined into complex polydentate ligand designs and with other donor functionalities. Amido ligands have proven useful for the stabilization of early transition metals in the medium to high oxidation states due to their $\pi$-donating capabilities, although there are also several examples of low oxidation state late transition metal complexes bearing amido donors.

![Figure 1.10. Amido donor $\sigma$ and $\pi$ orbitals.](image)

Each amido donor only has one $\pi$ lone pair, therefore they are known as single faced $\pi$-donors, and the orientation of the substituents will control the position of the lone pair orbital. The orientation of the ligands about a single faced $\pi$-donor will cause differences in the electronic structures of formed complexes. The orbitals available for amido $\sigma$- and $\pi$-donation are shown in Figure 1.10. Amide functional groups are most commonly found in a nearly planar geometry. A few examples of amido donors can be seen in Figure 1.11.
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Figure 1.11. Examples of some possible types of amido donors.

1.6.2 Modification of 4-Aminopyridine

Amido donors bear a formal negative charge, but the introduction of a peripheral positive charge to these anionic donors would expand the chemistry that is possible by modifying the net charge on the complexes formed. An overall neutral charge on the nitrogen donor will allow for the stabilization of higher oxidation state metals, without taking away crucial reaction sites. There are many related examples that undergo similar modifications to change the reactivity of the systems such as with cyclopentadienyl and phosphine donors. 4-aminopyridine will be used as a precursor, to form a nitrogen donor that is overall neutral but still has amido-donor-like properties, via alkylation of the pyridine and amino nitrogens, followed by deprotonation of the amino nitrogen to form 1.1, as shown in Figure 1.12.

![Resonance structures of the potential zwitterionic amido donor 1.1.](image)

Figure 1.12. Resonance structures of the potential zwitterionic amido donor 1.1.

The free ligand can be described as a neutral imine, which minimizes charge separation as shown in structure 1.1a, or as zwitterionic amide, structure 1.1b, which has the benefit of aromatic stabilization despite a separation of charge. It is hard to predict which resonance form will be the most stable and therefore the dominate structure the nitrogen donor will reside in. The resonance structures should allow for the stabilization of a wider variety of transition metals. The imine form of the nitrogen ligand should be able to stabilize...
low oxidation state metals, and the zwitterionic form should stabilize high oxidation state metals. The combination of both forms of stabilization may lead to facile oxidative additions of inert bonds with late transition metal complexes of these ligands.

These ligands may have several different possible applications, though the exact applications of these ligands are not yet known because the exact reactivity has yet to be determined. Applications that will be investigated in this dissertation include inert bond activation, alternative synthetic methods for synthesizing fluorinated pharmaceuticals and nickel chemistry, both the formation of stable complexes and catalysis.

1.6.3 The Stabilization of Nickel Complexes for the Promotion of C–H Bond Activation

A plausible route upon which the modified 4-aminopyridine nitrogen ligand may be able to promote C–H bond activation with transition metals, through its resonance structures, is shown in Scheme 1.16. It can be envisioned that the imino resonance structure will render the low-valent transition metal complexes stable, whereas the amido resonance structure will render the oxidative addition step thermodynamically viable.

\[ \text{Scheme 1.16. General reaction of C–H activation of substrate R–H with a transition metal stabilized by ligand 1.1} \]

1.7 Scope of Dissertation

This dissertation contains six additional chapters that discuss C–F activation and C–H functionalization reactions possible with a novel nitrogen donor ligand and the chapters provide detailed mechanistic studies of these processes. Chapter 2 details the design and synthesis of a new nitrogen donor ligand (MeNC_5H_4N^{iPr}) with N-heterocyclic donor properties, which provides the first example of selective C–F bond activation of
tetrafluorobenzenes with Ni(0). Chapter 3 discusses the C–H stannylation of a wide range of fluorinated aromatics with CH$_2$=CHSnBu$_3$, utilizing Ni(0) and an ancillary ligand (MeNC$_5$H$_4$N$i$Pr or $i$Pr$_3$P). Chapter 4 describes the resting state for C–H bond stannylation ($i$Pr$_3$P)Ni($\eta^2$-CH$_2$=CHSnBu$_3$)$_2$ and provides a detailed mechanistic study of this reaction. Chapter 5 contains details of the catalytic C–H bond alkylation of fluorinated aromatics with CH$_2$=CHSnPh$_3$, and the catalytic carbostannylation of ethylene with organostannanes of the type C$_6$F$_5$SnR$_3$ (R = Ph or Bn), utilizing catalytic amounts of Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr. Chapter 6 examines the expansion of C–F bond activation and catalytic C–H bond stannylation of trifluoromethyl fluorinated benzene derivatives; as well as the reactivity of these products and insight into how the CF$_3$ moiety influences the rate of C–H bond stannylation relative to variety of other substituents. Chapter 7 provides a summary of the various projects discussed in the dissertation, and offers several related projects for future work in this area utilizing Ni(0) and MeNC$_5$H$_4$N$i$Pr.
1.8 References


(10) Lyons, T. W.; Sanford, M. S. Chem. Rev. 2010, 110, 1147-1169.
(20) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. Chem. Rev. 2010, 110, 890-931.


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Chapter 1 - Ligand Design for the Promotion of Inert Bond Activation and Catalysis


2.1 Introduction

$N$-heterocyclic carbenes (NHCs) have gained recent prominence as alternatives to the ubiquitous phosphine donors as ancillary ligands for both stoichiometric and catalytic transformations. The strong $\sigma$-donor abilities of this class of ligands has a profound effect on reactivity; for example, the use of these donors often permits the oxidative addition of substrates that are otherwise unreactive. Although these donors are commonly described as predominantly carbene-like in character, ylid resonance structures with carbanion character may also be drawn, as shown in Scheme 2.1.
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Scheme 2.1. Carbene structure A and zwitterionic resonance structures B. Mes = 2,4,6–Me₃C₆H₂.

We sought to modify nitrogen donors using a similar strategy. Amido donors (R₂N⁻) are well known to stabilize high-oxidation-state early-transition-metal complexes by virtue of the fact that they are hard donors capable of both σ and π donation. These donors should be ideal for promoting oxidative addition reactions with the late transition metals. However, the excessively hard donor properties of amido ligands and the strongly π-antibonding interactions between the occupied metal d-orbitals and the nitrogen-based lone pair often renders these donors too reactive for use as ancillary ligands with these low-valent soft metals. The anionic charge of amido donors also impedes the utility of these donors in catalysis; the low oxidation state of the majority of active species in late-transition-metal catalysis mandates the use of neutral ancillary ligands to maintain sufficient reactive sites. A nitrogen-donor ligand with amido-donor-like properties, but a net neutral charge and diminished π-donor abilities could have an impact similar to NHCs.

2.2 Results and Discussion

2.2.1 Ligand Design

A synthetic route to such a nitrogen donor is shown in Scheme 2.2 and Scheme 2.3. Initial attempts to alkylate the amino nitrogen of 4-aminopyridine to form 4-(isopropylamino)pyridine involved a condensation reaction with acetone. Unfortunately this method was unsuccessful due to the auto-ionization of acetone, since acetone was used as both solvent and reactant, the concentration of water was too great thus driving the equilibrium of the desired condensation reaction towards the reactants. A second approach by Burmistrov and Krasovskii involved the alkylation of the amino nitrogen of 4-aminopyridine with isopropanol and 80 % sulfuric acid, as shown in Scheme 2.2. This approach seemed...
superior on paper, however, the reaction was inconsistent and several modifications had to be made. The modifications made to the procedure included adding double the amount of the reactants 4-aminopyridine and isopropanol and only half the amount of acid, which helped to increase the yield obtained. The original procedure called for the solution to be neutralized to pH 7 as part of the workup; however, a slightly basic solution of pH 8–9 gave higher yields. The neutralized product was then to be extracted into toluene, however, by filtering off the salt and extracting the product into diethyl ether the process was greatly simplified. The original procedure called for the 4-(isopropylamino)pyridine dissolved in toluene or ether to be dried with NaSO₄, however yields were extremely low. It was later determined that the Na⁺ was binding to 4-(isopropylamino)pyridine and the problem was rectified by changing the drying reagent to 4 Å MS. The final modification made was the solvent the product was recrystallized from. The procedure originally called for heptane but the product was found to be nearly insoluble. Toluene was used as the solvent and clear crystals of pure 4-isopropylaminopyridine were obtained, in a 77 % isolated yield, by cooling the saturated solution to −40 °C.

Scheme 2.2. Synthesis of 4-(isopropylamino)pyridine.

The next step in the synthesis was the alkylation of the pyridine nitrogen. It was initially decided to alkylate the pyridine nitrogen with 2-bromopropane, yielding 1-isopropyl-4-(isopropylamino)pyridinium bromide, as an oily product which was insoluble in most solvents, except for highly polar chlorinated solvents, DMSO and HMPA thus making it very impractical for future reactions in the glove box and for isolating organometallic compounds. Finding a better alkylation group would increase solubility and thus give more flexibility for solvent choice. It was later determined that MeI was a superior choice, alkylation of 4-(isopropylamino)pyridine at the pyridine nitrogen with MeI provides 2.1 and subsequent deprotonation of the amino nitrogen atom with NaH, provides 2.2 as a colorless, sublimable,
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toluene-soluble powder in an 85 % yield, as shown in Scheme 2.3. Species **2.2** has two viable resonance structures that could describe its ground state. The imine form has minimized charge separation, whereas the zwitterionic form benefits from aromatic stabilization.

Scheme 2.3. Synthesis of donor **2.1** and **2.2**.

Figure 2.1. Structure of **2.1** as determined by X-ray crystallography.

The solid-state structure of **2.1** was determined by X-ray crystallography and an ORTEP depiction is shown in Figure 2.1. The C(4)–N(1) bond distance of 1.3332(2) Å confirms that the cationic fragment of **2.1** displays partial imine character; typical bond distances for a single and double C–N bond are 1.47 Å and 1.28 Å, respectively.**51,52** Similarly, the C(4)–C(5), C(5)–C(6) and C(6)–N(2) bond lengths of the nitrogen-containing
ring are 1.417(2), 1.351(3) and 1.358(2) Å, respectively, confirming the ring is not completely aromatic. The crystallographic data indicates that hydrogen is in the vicinity of N(1) and a weak interaction is possible between I− and N+–H. The hydrogen-iodide bond length of 2.95(2) Å is significantly longer than a typical H–I bond length of 2.53 Å. The 1H NMR of 2.1 in C₆D₆ displays four proton environments for the nitrogen containing ring, due to the considerable double bond character of the C(4)–N(1) bond, demonstrating that the solution structure is consistent with the solid-state structure.

The solid-state structure of the neutral compound 2.2 was determined by X-ray crystallography and an ORTEP depiction is shown in Figure 2.2. The C(4)–N(1) bond distance of 1.3044(15) Å confirms that 2.2 displays considerable imine character. Likewise, the C(4)–C(5) bond length of 1.4532(16) Å is longer than a typical aromatic C–C bond, and the C(5)–C(6) bond length of 1.3474(17) Å is much shorter. The C(6)–N(2) bond length of 1.3709(15) Å is longer than the expected bond length of 1.34 Å for pyridine N–C bonds. The 1H NMR of 2.2 in C₆D₆ displays four proton environments for the nitrogen containing ring, due to the considerable double bond character of the C(4)–N(1) bond. Irrespective of this considerable imine character, the reactivity of 2.2 resembles that of an amido salt, as exemplified by its behavior as a strong base in aqueous solution.

![Figure 2.2. Structure of 2.2 as determined by X-ray crystallography.](image)
2.2.2 Synthesis of \(\text{cis-}(\text{CO})_2\text{RhCl}(\text{MeNC}_5\text{H}_4\text{NiPr})\) and Determination of Ligand Donor Strength

Adducts generated from \([\text{(CO)}_2\text{Rh}(\mu-\text{Cl})]_2\) have been used to determine the donor properties of NHCs by measurement of the CO stretching frequencies.\(^{16}\) To provide a comparison, donor 2.2 was treated with half an equivalent of \([\text{(CO)}_2\text{Rh}(\mu-\text{Cl})]_2\) to generate \(\text{cis-}(\text{CO})_2\text{RhCl}(\text{MeNC}_5\text{H}_4\text{NiPr})\) (2.3), as shown in Scheme 2.4. The solid-state structure of 2.3 was determined by X-ray crystallography, shown in Figure 2.3, and confirms binding of the nitrogen donor to the rhodium centre with minimal perturbation of the C–N and C–C bond lengths compared to those of the free ligand 2.2. The IR spectrum of 2.3 displays two CO stretching frequencies at 2077 and 1998 cm\(^{-1}\) (av 2038 cm\(^{-1}\)). By this measure, 2.2 is a significantly stronger donor than the pyridine analogue, which displays an average \(v_{\text{CO}}\) of 2052 cm\(^{-1}\).\(^{17}\) Remarkably, the average \(v_{\text{CO}}\) value for 2.3 is similar to that of the analogous complex of the \(N\)-heterocyclic carbene A, which displays \(v_{\text{CO}}\) values of 2081 and 1996 cm\(^{-1}\) (av 2039 cm\(^{-1}\)).\(^{18}\) This comparison indicates that the donor properties of 2.2 could resemble those of the NHCs. It should be noted that though it is widely accepted that the donor properties of ligands can be determined by measuring the CO stretching frequency, there has been some skeptical criticism in a recent computational study suggesting it may not be suitable to compare different ligand types in systems of the type \(\text{Ni(CO)}_3\text{L}\) and \(\text{IrCl(CO)}_2\text{L}\),\(^{19}\) and another recent paper by Goldman indicates that electrostatic issues can also impact the CO stretching frequency.\(^{49,50}\)

\[ \text{N} = \text{N} + 1/2 [\text{(CO)}_2\text{Rh}(\mu-\text{Cl})]_2 \rightarrow \text{cis-}(\text{CO})_2\text{RhCl}(\text{MeNC}_5\text{H}_4\text{NiPr}) \]

\textbf{Scheme 2.4.} Synthesis of rhodium carbonyl complex 2.3.
2.2.3 Synthesis and Characterization of C‒F Bond Activation Products with Hexafluorobenzene, Pentafluorobenzene and the Tetrafluorobenzene Derivatives

To test the ability of these ligands to aid in the oxidative addition of challenging substrates, we investigated the activation of the strong and relatively inert C‒F bonds in fluorinated aromatics by nickel(0). It is known that sources of the $[(\text{Et}_3\text{P})_2\text{Ni}]$ moiety react with the tetrafluorobenzenes, but the reaction takes weeks at room temperature and can provide unwanted byproducts by rapid and reversible C‒H bond activation or radical reactions. Very recently it has been shown that the use of $N$-heterocyclic carbenes rather than phosphines as the ancillary ligand in these reactions allows for faster selective activation of C‒F bonds in a variety of polyfluorobenzene species; however, at the time of publication no nickel complex capable of the selective activation of the tetrafluorobenzenes had been reported.

As monitored by $^1$H NMR spectroscopy, toluene solutions of [Ni(COD)$_2$] (COD = 1,5-cyclooctadiene) and 2.2 showed no significant replacement of the 1,5-cyclooctadiene
donors, as might be expected for a hard donor such as 2.2. However, solutions of two equivalents of 2.2 and one equivalent of [Ni(COD)]2 react over the course of 0.5–5 h at room temperature with C₆F₆, C₆F₅H, 1,2,4,5-, 1,2,3,4-, and 1,2,3,5-tetrafluorobenzene to form C–F bond activated products 2.4–2.8, respectively, as shown in Scheme 2.5. The products precipitated from the reaction mixtures as red crystalline solids and were isolated in 70–80 % yields.
Scheme 2.5. C–F bond activation with C₆F₅, C₆F₅H and all three isomers of C₆F₄H₂. Site of selective activations are circled; chemical shifts from $^{19}$F{¹H} NMR spectra are given with respect to CFCl₃ at δ 0.0.

All three components (Ni⁰ source, ligand and fluorinated substrate) are necessary to observe a reaction; no reaction was observed in solutions of either [Ni(COD)]₂ with the polyfluoroaromatics or 2.2 with the polyfluoroaromatics. Also, no reaction was observed in these systems when alternate nitrogen donors such as bipyridine or the imine iBuCHNPh³⁵ were used in place of 2.2.
The solid-state structure of 2.4 was determined by X-ray crystallography and an ORTEP depiction is shown in Figure 2.4. Product 2.4 is square-planar, with the ancillary ligands \textit{trans} disposed. The nitrogen-containing and pentafluorophenyl rings all lie out of the coordination plane and the isopropyl substituents of the ancillary ligands are situated opposite faces of the square plane. The Ni(1)–N(1) bond distance is 1.9256(15) Å, which lies within the range of nickel amide bonds (1.93–1.82 Å)\(^3\).

**Figure 2.4.** Structure of 2.4 as determined by X-ray crystallography.\(^{\text{15}}\) Selected bond lengths [Å]: Ni(1)–N(1), 1.9256(15); Ni(1)–F(1), 1.8589(15); Ni(1)–C(10), 1.903(3).

Suitable crystals of 2.6 and 2.8 suitable for analysis by X-ray crystallography were obtained by layering the reagents in toluene, Ni(COD)\(_2\) in the bottom layer and 2.2 and the fluorinated aromatic in the top layer; an ORTEP of the solid-state molecular structures are shown in Figure 2.5. There is disorder in both 2.6 and 2.8 due to the two possible orientations of the fluorinated aryl ring; the molecules pack with little discrimination to the orientation of the 2,4,5-C\(_6\)F\(_3\)H\(_2\) and 2,3,5-C\(_6\)F\(_3\)H\(_2\) moieties of 2.6 and 2.8, respectively, most likely due to the similar sizes of hydrogen and fluorine. The disorder limits the reliability of some of the bond lengths, but the connectivity of these molecules can be confirmed without doubt. Complexes 2.6 and 2.8 have similar structures to that of 2.4, where the geometry is square.
planar with the ligands trans disposed. The Ni(1)–N(1) bond distance of 2.6 and 2.8 were found to be 1.954(10) and 1.9240(15) Å respectively and the Ni(1)–N(3) bond distance of 2.6 was found to be 1.897(10) Å.

![Figure 2.5](image.png)

**Figure 2.5.** Structures of 2.6 and 2.8 as determined by X-ray crystallography. Selected bond lengths for 2.6 [Å]: N(1)–Ni(1), 1.954(10); N(3)–Ni(1), 1.897(10); F(1)–Ni(1), 1.871(5); C(19)–Ni(1) 1.896(10). Selected bond lengths for 2.8 [Å]: Ni(1)–N(1), 1.9240(15); Ni(1)–F(1), 1.8693(16); Ni(1)–C(10), 1.884(3).

Both the $^1$H and $^{19}$F{$^1$H} NMR spectra for 2.4–2.8 in CD$_2$Cl$_2$ are consistent with regioselective C–F bond activation, with no detectable impurities or byproducts. The $^{19}$F{$^1$H} NMR shifts for 2.4–2.8 are summarized in Scheme 2.6. Notably, the chemical shift for the fluoride resonance is dramatically affected by the substitution pattern of the fluoroaryl group, with the presence of ortho and meta fluorine substituents having a larger effect than the para fluorine substituents on the fluoride shift. The similarity of the $^1$H NMR spectra for the ancillary ligand resonances in 2.4–2.8 suggests that these complexes are isostructural to the structurally characterized 2.4, the $^1$H NMR spectra of 2.5 is shown in Figure 2.6.
These C–F bond activation complexes 2.4–2.8 are stable in CD₂Cl₂ solutions at room temperature for several hours, before decomposing gradually. These complexes are stable for months in an inert atmosphere at −40 °C, and moderately stable in CH₂Cl₂ at −40 °C, before gradually rearranging to cis-(MeNC₅H₄NⁱPr)₂Ni(C₆F₅)₂ (2.9) as a yellow crystalline solid and an unidentifiable nickel fluoride species, with no evidence for the formation of (MeNC₅H₄NⁱPr)₂NiF₂ by ¹⁹F{¹H} NMR spectroscopy. The structure of 2.9 was confirmed by X-ray crystallography and is shown in Figure 2.7. The Ni(1)–N(1) bond length was 1.9256(15) Å which is comparable to the Ni–N bond lengths found in complexes 2.4, 2.6 and 2.8 where MeNC₅H₄NⁱPr ligands were trans disposed. The room temperature ¹⁹F{¹H} NMR spectrum in d₈-toluene revealed four resolved resonances at δ −115.4, −164.6, −165.2 and −166.8 corresponding to the two overlapping ortho-fluorines, the para-fluorine and the two meta-fluorine environments respectively. The overlapping resonances associated with the ortho-fluorine environments are second order multiplets, the two meta-fluorines environments are complex multiplets, doublets of second order multiplets, while the para-fluorine is a triplet, with coupling to the two meta-fluorine environments with a ³JFF value of 20.2 Hz.
2.2.4 Expanding the Scope of Substrates for C–F Bond Activation to Tri-, Di- and Monofluorobenzene

Given the successful C–F bond activation of the tetrafluorobenzene derivatives with \( \text{2.2} \) and \( \text{Ni(COD)}_2 \), these reactions were expanded to include 1,2,3-, 1,3,5- and 1,2,4-trifluorobenzene, 1,2-, 1,3- and 1,4-difluorobenzene and monofluorobenzene. The reaction of \( \text{2.2} \), \( \text{Ni(COD)}_2 \) and 1,3,5-trifluorobenzene, shown in Scheme 2.6, proved to be very slow, with only a 12% conversion to the C–F bond activation product, \( \text{trans}-(\text{MeNC}_5\text{H}_4\text{N}^\text{iPr})_2\text{NiF}(3,5-\text{C}_6\text{F}_2\text{H}_3) \) (\textbf{2.10}), after 1 week at room temperature. Single crystals of \textbf{2.10} suitable for structural analysis by X-ray crystallography were obtained by layering the reagents in an NMR tube in C\(_6\)H\(_6\), the bottom layer contained Ni(COD)\(_2\) and the top layer consisted of \textbf{2.2} and 1,3,5-C\(_6\)F\(_3\)H\(_3\); an ORTEP of the solid-state molecular structure is shown in Figure 2.8. Complex \textbf{2.10} has a similar structure to that of \textbf{2.4}, \textbf{2.6} and \textbf{2.8} where the geometry about the nickel center is square planar with the ligands \textit{trans} disposed. The Ni(1)–N(1) bond distance was found to be 1.9261(14) Å. Compound \textbf{2.10} was also characterized by multinuclear NMR spectroscopy, unfortunately due to the low yield of \textbf{2.10} good quality...
NMR spectra could not be obtained and the coupling constants could not be resolved. The room temperature $^1$H NMR spectrum has chemical resonances consistent with the solid-state molecular structure and confirms that $\textbf{2.10}$ is isostructural to compounds $\textbf{2.4–2.8}$. The $^{19}$F{$^1$H} NMR spectra confirms the presence of a broad nickel-fluoride resonance at $\delta$ – 320.9.

$\textbf{Scheme 2.6.}$ Synthesis of compound $\textbf{2.10}$.

![Scheme 2.6](image)

$\textbf{Figure 2.8.}$ Structure of $\textbf{2.10}$ as determined by X-ray crystallography. Selected bond lengths for $\textbf{2.10}$ [Å]: Ni(1)–N(1), 1.9261(14); Ni(1)–F(1), 1.8836(14); Ni(1)–C(10), 1.873(2).

The reaction of $\textbf{2.2}$, Ni(COD)$_2$ and 1,2,4-trifluorobenzene in toluene afforded a mixture of C–F bond activation products with activation at the 2-site as the major product
(2.11), as shown in Scheme 2.7, this reaction was slow with less than a 12 % conversion to the mixture of C–F bond activation products after 10 days. The reaction mixture was analyzed by multinuclear NMR, however, due to the low yields good quality data was not obtained and the coupling constants could not be resolved. The $^1$H NMR spectra confirms that the structures of the mixture of products are isostructural to compounds 2.4–2.8. The $^{19}$F{${}^1$H} NMR spectra confirms the presence of fluoride shifts at $\delta$ –330.3, –331.5 and –329.5 with integrals of 1:0.08:0.06, for 2.11, 2.12 and 2.13 respectively.

Scheme 2.7. Mixture of C–F bond activation products from the reaction with 1,2,4-trifluorobenzene.

The reaction of 2.2, Ni(COD)$_2$ and 1,2,3-trifluorobenzene in toluene afforded a mixture of C–F bond activation products, as shown in Scheme 2.8, this reaction was slow undergoing only a 10 % conversion to the C–F bond activation products after 2 weeks at room temperature. The reaction mixture was analyzed by multinuclear NMR, however the low yields made it impossible to obtain good quality NMR data and the coupling constants could not be resolved. The $^1$H NMR spectra confirms that the structures of the mixture of products are isostructural to compounds 2.4–2.8. The $^{19}$F{${}^1$H} NMR spectra confirms that both possible activation isomers are present in the mixture, with activation at the 1-site (2.14) and 2-site (2.15) in a 1:0.73 ratio respectively.
Chapter 2 – Selective C–F Bond Activation of Tetrafluorobenzenes by Nickel(0) with a Nitrogen Donor Analogous to N-heterocyclic Carbenes

**Scheme 2.8.** Mixture of C–F bond activation products from the reaction with 1,2,3-trifluorobenzene.

The reactions of 1,2-, 1,3- and 1,4-difluorobenzene or monofluorobenzene with \[ \text{Ni(COD) _2} \] and \[ \text{Ni(COD)} \] _2_, failed to produce the desired C–F bond activation products, \( \text{trans}-(\text{MeNC}_5\text{H}_4\text{N}^+\text{Pr})_2\text{NiF(C}_6\text{H}_4\text{)} \) or \( \text{trans}-(\text{MeNC}_5\text{H}_4\text{N}^+\text{Pr})_2\text{NiF(C}_6\text{H}_5) \), at room temperature after several weeks, either as an isolable product or as evidence by NMR spectroscopy.

**2.2.5 Deuterium Labelling Study to Confirm Site of C–F Bond Activation.**

The site of activation in 2.5–2.8 and 2.11–2.15 was confirmed by reaction with a solution of 10 % HCl in D_2O and subsequent extraction into C_6D_6 and filtration through silica gel to remove any protonated 2.2 and nickel-containing byproducts. The site of deuteration in the resultant fluorobenzene derivatives was readily determined by NMR spectroscopy by using the deuterium isotope effect on the ^19F chemical shifts, as shown in Scheme 2.9. The regioselectivity observed is identical to the preferred products of typical nucleophilic aromatic substitution reactions with these substrates, but with significantly improved regioselectivity.^[37]
Scheme 2.9. Fluoroaromatic products from the reaction of 2.5–2.8 and 2.11–2.15 with acidified D$_2$O.
2.3 Conclusions

This donor set facilitates regioselective C–F bond activation, which includes the first example of selective C–F bond activation of the tetrafluorobenzenes by a nickel complex. These results illustrate the strong N-heterocyclic-carbene-like $\sigma$-donor properties of 2.2 and the ability of this hard ligand to facilitate difficult oxidative additions. In light of the remarkable scope and impact of N-heterocyclic carbenes, the investigation of these simple nitrogen donors as alternative ligands in similar applications is warranted.

2.4 Experimental

2.4.1 General Procedures

All reactions were performed under an atmosphere of dry oxygen-free dinitrogen by means of standard Schlenk or glovebox techniques, although ligand 2.2, its precursor salt 2.1 and its complexes were not particularly oxygen-sensitive. Toluene-$d_8$ and CD$_2$Cl$_2$ were dried by refluxing with Na/K and CaH$_2$, respectively, and were then vacuum transferred and degassed by three freeze-pump-thaw cycles. All other solvents were purchased anhydrous from Aldrich and further purified using a Grubbs’ type column system$^{38}$ produced by Innovative Technology. $^1$H, $^{13}$C{$^1$H}, and $^{19}$F{$^1$H} were recorded on a Bruker AMX Spectrometer operating at 300 MHz with respect to proton nuclei. $^1$H NMR spectra were referenced to residual protons (CD$_2$Cl$_2$, $\delta$ 5.32; toluene-$d_8$, $\delta$ 2.09) with respect to tetramethylsilane at $\delta$ 0.00. $^{13}$C{$^1$H} spectra were referenced relative to solvent resonances (CD$_2$Cl$_2$, $\delta$ 53.8; C$_7$D$_8$, $\delta$ 20.4). $^{19}$F{$^1$H} NMR spectra were referenced to an external sample of 80 % CCl$_3$F in CDCl$_3$ at $\delta$ 0.0. Toluene-$d_8$, and CD$_2$Cl$_2$ were purchased from Cambridge Isotope Laboratory. The compounds 4-aminopyridine, isopropanol, iodomethane, NaH, hexafluorobenzene, pentafluorobenzene, 1,2,3,4- and 1,2,3,5-, and 1,2,4,5-tetrafluorobenzene, 1,2,3- and 1,2,4- and 1,3,5-trifluorobenzene, 1,2-, 1,3-, and 1,4-difluorobenzene and monofluorobenzene were purchased from Aldrich. The compounds 4-(iso-propylamino)pyridine$^{14}$ and Ni(COD)$_2$$^{39}$ were prepared by literature procedures. Elemental analysis was performed at the University of Windsor, Windsor, Ontario, Canada and at Atlantic Microlab Inc. Norcross, Georgia, USA.
2.4.2 Synthesis, Characterization and Reactivity of Complexes

**Synthesis of 4-(isopropylamino)-1-methylpyridinium iodide (2.1).** To a room-temperature solution of (4-isopropylamino)pyridine (1.00 g, 7.30 mmol), in 15 mL of toluene was added methyl iodide (6 mL, large excess). The mixture was stirred for 24 h, which provided a white precipitate that was filtered and dried under vacuum (1.55 g, 76 % yield). ¹H NMR (CD₂Cl₂ 27 °C, 300.13 MHz): δ 1.11 (d, 6H, NCH(CH₃)₂, ³J_HH = 7.0 Hz); 3.58 (septet, 1H, NCH, ³J_HH = 7.0 Hz); 3.81 (s, 3H, NCH₃); 6.39 (d, 1H, NH, ³J_HH = 7.7 Hz); 7.37 (d, 1H, C₅H₄N, ³J_HH = 7.7 Hz); 7.77 (d, 1H, C₅H₄N, ³J_HH = 7.7 Hz); 7.88 (d, 1H, C₅H₄N, ³J_HH = 7.7 Hz); 8.13 (d, 1H, C₅H₄N, ³J_HH = 7.7 Hz). ¹³C{¹H} NMR (CD₂Cl₂, 27 °C, 75.47 MHz): δ 21.8 (s, NCH(CH₃)₂); 45.4 and 45.6 (s, NCH₃ and CH); 105.5 (s, C₅H₄N); 111.4 (s, C₅H₄N); 143.7 (s, C₅H₄N); 155.9 (s, C₅H₄N). Anal. Calcd. C, 38.86; H, 5.44; N, 10.07. Found C, 38.70; H, 5.42; N, 10.10.

**Synthesis of MeNC₅H₄N°Pr, (2.2).** To a room temperature stirred solution of 2.1 (5 g, 0.02 mol) in 50 mL of THF was added NaH (0.485 g, 0.02 mol). The solution was stirred for 5 h and the solvent was removed under vacuum. The product was then sublimed under dynamic vacuum onto a ice-cooled cold finger at 100 °C to yield a colorless solid (2.62 g, 86 % yield). ¹H NMR (d₈-toluene, 27 °C, 300.13 MHz): δ 1.44 (d, 6H, NCH(CH₃)₂, ³J_HH = 6.4 Hz); 2.01 (s, 3H, NCH₃); 3.71 (septet, 1H, NCH, ³J_HH = 6.4 Hz); 5.58 (dd, 1H, C₅H₄N, ³J_HH = 8.3 Hz, ⁴J_HH = 2.6 Hz); 5.71 (dd, 1H, C₅H₄N, ³J_HH = 8.3 Hz, ⁴J_HH = 2.6 Hz); 6.20 (dd, 1H, C₅H₄N, ³J_HH = 8.3 Hz, ⁴J_HH = 2.6 Hz). ¹³C{¹H} NMR (d₈-toluene, 27 °C, 75.47 MHz): δ 24.3 (s, (NCH(CH₃)₂); 40.6 and 48.7 (s, NCH₃ and CH); 104.6 (s, C₅H₄N); 117.3 (s, C₅H₄N); 134.1 (s, C₅H₄N); 137.1 (s, C₅H₄N); 153.2 (s, C₅H₄N). Anal. Calcd. C, 71.96; H, 9.39; N, 18.65. Found C, 72.22; H, 9.25; N, 19.04. IR (KBr) ν = 2975, 1655, 1581, 1431, and 1388 cm⁻¹.

**Synthesis of cis-(MeNC₅H₄N°Pr)RhCl(CO)₂, (2.3).** To a solution of 2.2 (0.193 g, 1.29 mmol) in 15 mL of toluene was added [(CO)₂Rh(μ-Cl)]₂ (0.250 g, 0.643 mmol). A crystalline colorless precipitate was obtained by cooling the solution to –40 °C for 5 h. The solid was filtered, rinsed with toluene, and then dried. (0.370 g, 84 % yield). ¹H NMR (CD₃CN, 25 °C, 300.13 MHz): δ 1.22 (d, 3H, NCH(CH₃)₂, ³J_HH = 6.6 Hz); 1.36 (d, 3H, NCH(CH₃)₂, ³J_HH =
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6.6 Hz); 3.52 (s, 3H, NCH3); 3.75 (septet, 1H, NCH, 3J_{HH} = 6.6 Hz); 6.36 (dd, 1H, C5H4N, 3J_{HH} = 7.5 Hz, 4J_{HH} = 3.1 Hz); 7.19 and 7.24 (AA'BB' second order m, 2H, C5H4N, 3J_{HH} = 7.5 Hz, 4J_{HH} = 3.1 Hz). 13C{1H} NMR (CD3CN, 25 °C, 75.47 MHz): δ 23.7 (s, (NCH(C2H5))2); 25.0 (s, (NCH(C2H5))2); 43.8 and 51.9 (s, NCH3 and CH); 107.4 (s, C5H4N); 116.8 (s, C5H4N); 138.8 (s, C5H4N); 140.9 (s, C5H4N); 161.0 (s, C5H4N); 183.1 (d, CO, 1J_{RhC} = 74.7 Hz); 187.0 (d, CO, 1J_{RhC} = 65.4 Hz). IR (KBr) ν = 2962, 2077, 1998, 1656, 1492, 1210, and 811 cm⁻¹. Anal. Calcd. C, 38.34; H, 4.09; N, 8.13. Found C, 38.04; H, 4.47; N, 8.24.

Synthesis of trans-(MeNC5H4NiPr)2NiF(C6F5), (2.4). To a solution of 2.2 (0.250 g, 1.67 mmol) and Ni(COD)2 (0.229 g, 0.84 mmol) in 10 mL of toluene was added hexafluorobenzene (0.156 g, 0.84 mmol). The solution was left undisturbed for 1 h, which yielded a crystalline red-orange solid. The solid was filtered, rinsed with toluene and pentane, and then dried. (0.371 g, 81 % yield). 1H NMR (CD2Cl2, 25 °C, 300.13 MHz): δ 0.14 (d, 3H, NCH(C2H5)2, 3J_{HH} = 3.8 Hz); δ 2.61 (d, 3H, NCH(C2H5)2, 3J_{HH} = 3.8 Hz); 3.02 (septet, 1H, NCH, 3J_{HH} = 3.8 Hz); 3.53 (s, 3H, NCH3); 5.92 (dd, 1H, C5H4N, 3J_{HH} = 8.3 Hz, 4J_{HH} = 3.8 Hz); 6.81 (d, 1H, C5H4N, 3J_{HH} = 8.3 Hz;); 7.24 (d, 1H, C5H4N, 3J_{HH} = 8.3 Hz); 10.11 (br, 1H, C5H4N). 19F{1H} NMR (CD2Cl2, 25 °C, 282.40 MHz): –116.6 (AA'BB' apparent d, 2F, ortho–F, 3J_{FF} = 21.5 Hz); –164.8 (t, 1F, para–F, 3J_{FF} = 21.5 Hz); –168.0 (AA'BB'C apparent t, 2F, meta–F, 3J_{FF} = 21.5 Hz); –355.0 (br, 1F, Ni–F). 13C{1H} NMR (CD2Cl2, 25 °C, 75.47 MHz): δ 19.1 and 24.9 (s, (NCH(C2H5))2); 42.4 and 50.3 (s, NCH3 and CH); 106.7 (s, C5H4N); 118.1 (s, C5H4N); 134.1 (dm, Ar–C, 1J_{CF} = 280.3 Hz); 135.0 (s, C5H4N); 137.0 (s, C5H4N); 150.3 (dm, Ar–C, 1J_{CF} = 219.0 Hz); 155.9 (dm, Ar–C, 1J_{CF} = 180.3 Hz); 158.1 (s, C5H4N). Anal. Calcd. C, 52.87; H, 5.18; N, 10.28. Found C, 51.9; H, 5.28; N, 10.04.

Synthesis of trans-(MeNC5H4NiPr)2NiF(2,2′,3,3′-C6F4H), (2.5). To a solution of 2.2 (0.450 g, 3 mmol) and Ni(COD)2 (0.413 g, 1.5 mmol) in 10 mL of toluene was added pentafluorobenzene (0.252 g, 1.5 mmol). The solution was left undisturbed for 2 h, which yielded a crystalline red-orange solid. The solid was filtered, rinsed with toluene and pentane, and then dried. (0.632 g, 80 % yield). 1H NMR (CD2Cl2, 25 °C, 300.13 MHz): δ 0.13 (d, 3H, NCH(CH3)2, 3J_{HH} = 4.2 Hz); 2.62 (d, 3H, NCH(CH3)2, 3J_{HH} = 4.2 Hz); 3.05 (septet, 1H,
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NCH, $^3J_{HH} = 4.2$ Hz); 3.52 (s, 3H, NCH3); 5.93 (dd, 1H, C5H4N, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 2.8$ Hz); 6.37 (tt, 1H, Ar–H, $^3J_{HF} = 7.5$, Hz, $^4J_{HF} = 2.8$ Hz); 6.80 (d, 1H, C5H4N, $^3J_{HH} = 7.5$ Hz); 7.23 (d, 1H, C5H4N, $^3J_{HH} = 7.5$ Hz); 10.11 (br, 1H, C5H4N). 19F{1H} NMR (CD2Cl2, 25 °C, 282.40 MHz): –118.8 (AA'BB' apparent dd, 1F, Ar–3–F, $^3J_{FF} = 31.2$ Hz, $^4J_{FF} = 16.0$ Hz); –146.1 (AA'BB' apparent dd, 1F, Ar–1–F, $^3J_{FF} = 31.2$ Hz, $^4J_{FF} = 16.0$ Hz); –351.9 (br, 1F, Ni–F).

Synthesis of trans-(MeNC5H4N\text{iPr})2NiF(2,4,5-C6F3H2), (2.6). To a solution of 2.2 (0.450 g, 3 mmol) and Ni(COD)2 (0.413 g, 1.5 mmol) in 10 mL of toluene was added 1,2,4,5-tetrafluorobenzene (0.225 g, 1.5 mmol). The solution was left undisturbed for 5 h, which yielded a crystalline red-orange solid. The solid was filtered, rinsed with toluene and pentane, then dried. (0.569 g, 74 % yield). 1H NMR (CD2Cl2, 25 °C, 300.13 MHz): $\delta$ 0.22 (d, 3H, NCH(C\text{H}3)2), $^3J_{HH} = 3.8$ Hz); $\delta$ 2.53 (d, 3H, NCH(CH\text{H}3)2), $^3J_{HH} = 3.8$ Hz); 3.32 (septet, 1H, NCH, $^3J_{HH} = 3.8$ Hz); 3.52 (s, 3H, NCH3); 5.94 (dd, 1H, C5H4N, $^3J_{HH} = 9.6$ Hz, $^4J_{HH} = 4.8$ Hz); 6.10 (m, 1H, C6F4H2); 6.80 (dd, 1H, C5H4N, $^3J_{HH} = 9.6$ Hz, $^4J_{HH} = 4.8$ Hz); 7.00 (td, 1H, C6F4H2, $^3J_{HH} = 12$ Hz, $^4J_{HH} = 3.0$ Hz); 7.22 (d, 1H, C5H4N, $^3J_{HH} = 9.6$ Hz); 10.17 (d, 1H, C5H4N, $^3J_{HH} = 9.6$ Hz). 19F{1H} NMR (CD2Cl2, 25 °C, 282.40 MHz): –95.4 (d, 1F, Ar–5–F, $^3J_{FF} = 25.4$ Hz); –147.2 (dd, 1F, Ar–4–F, $^3J_{FF} = 19.8$ Hz, $^4J_{FF} = 2.8$ Hz); –149.7 (dd, 1F, Ar–2–F, $^3J_{FF} = 25.4$ Hz, $^4J_{FF} = 19.8$ Hz); –325.8 (br s, 1F, Ni–F).

Synthesis of trans-(MeNC5H4N\text{iPr})2NiF(2,3,6-C6F3H2), (2.7). To a solution of 2.2 (0.450 g, 3 mmol) and Ni(COD)2 (0.413 g, 1.5 mmol) in 10 mL of toluene was added 1,2,3,4-tetrafluorobenzene (0.225 g, 1.5 mmol). The solution was left undisturbed for 5 h, which

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yielded a crystalline red-orange solid. The solid was filtered, rinsed with toluene and pentane, and then dried. (0.538 g, 70 % yield). $^1$H NMR (CD$_2$Cl$_2$, 25 °C, 300.13 MHz): $\delta$ 0.12 (d, 3H, NCH(CH$_3$)$_2$), $^{3}$J$_{HH}$ = 5.5 Hz); $\delta$ 2.62 (d, 3H, NCH(CH$_3$)$_2$), $^{3}$J$_{HH}$ = 5.5 Hz); 3.09 (septet, 1H, NCH, $^{3}$J$_{HH}$ = 5.5 Hz); 3.52 (s, 3H, NCH$_3$); 5.92 (dd, 1H, C$_2$H$_4$N, $^{3}$J$_{HH}$ = 8.2 Hz, $^{4}$J$_{HH}$ = 2.9 Hz); 6.07 (br m, 1H, C$_6$F$_4$H$_2$); 6.46 (m, 1H, C$_6$F$_4$H$_2$); 6.79 (d, 1H, C$_5$H$_4$N, $J$ = 8.2 Hz); 7.22 (d, 1H, C$_3$H$_4$N, $J$ = 8.2 Hz); 10.09 (br d, 1H, C$_5$H$_4$N, $J$ = 8.2 Hz). 19F{1H} NMR (CD$_2$Cl$_2$, 25 °C, 282.40 MHz): –93.4 (d, 1F, Ar–3–F, $^{3}$J$_{FF}$ = 16.4 Hz); –112.2 (dd, 1F, Ar–1–F, $^{3}$J$_{FF}$ = 31.9 Hz, $^{5}$J$_{FF}$ = 16.4 Hz, $^{4}$J$_{FF}$ = 3.3 Hz); –142.2 (d, 1F, Ar–5–F, $^{3}$J$_{CF}$ = 31.1 Hz); –333.5 (br s, 1F, Ni–F). 13C{1H} NMR (CD$_2$Cl$_2$, 25 °C, 75.47 MHz): $\delta$ 19.1 and 25.0 (s, (NCH(CH$_3$)$_2$); 42.4 and 50.6 (s, NCH$_3$ and CH); 106.3 (s, C$_5$H$_4$N); 106.8 (br m, Ar–C); 110.4 (dd, Ar–C, $^{2}$J$_{CF}$ = 19.0 Hz, $^{2}$J$_{CF}$ = 11.3 Hz); 118.2 (s, C$_5$H$_4$N); 134.9 (s, C$_3$H$_4$N); 137.5 (s, C$_5$H$_4$N); 140.0 (dd, Ar–C, $^{1}$J$_{CF}$ = 230.0 Hz, $^{2}$J$_{CF}$ = 19.0 Hz); 156.1 (dm, Ar–C, $^{1}$J$_{CF}$ = 260 Hz); 158.0 (s, C$_3$H$_4$N); 165.9 (dd, Ar–C, $^{1}$J$_{CF}$ = 230.0 Hz, $^{2}$J$_{CF}$ = 19.0 Hz). Anal. Caled. C, 56.61; H, 5.94; N, 11.00. Found C, 54.04; H, 6.32; N, 10.71.

Synthesis of trans-(MeNC$_5$H$_4$N$(t$Pr)$_2$)NiF(2,3,5-C$_6$F$_3$H$_2$), (2.8). To a solution of 2.2 (0.450 g, 3 mmol) and Ni(COD)$_2$ (0.413 g, 1.5 mmol) in 10 mL of toluene was added 1,2,3,5-tetrafluorobenzene (0.225 g, 1.5 mmol). The solution was left undisturbed for 5 h, which yielded a crystalline red-orange solid. The solid was filtered, rinsed with toluene and pentane, then dried. (0.586 g, 76 % yield). $^1$H NMR (CD$_2$Cl$_2$, 25 °C, 300.13 MHz): $\delta$ 0.22 (d, 3H, NCH(CH$_3$)$_2$), $^{3}$J$_{HH}$ = 6.5 Hz); $\delta$ 2.55 (d, 3H, NCH(CH$_3$)$_2$), $^{3}$J$_{HH}$ = 6.5 Hz); 3.33 (septet, 1H, NCH, $^{3}$J$_{HH}$ = 6.5 Hz); 3.54 (s, 3H, NCH$_3$); 5.97 (dd, 1H, C$_2$H$_4$N, $^{3}$J$_{HH}$ = 7.7 Hz, $^{4}$J$_{HH}$ = 3.3 Hz); 6.18 (multiplet, 2H, o–Ar–H and p–Ar–H, $^{3}$J$_{HF}$ = 7.7 Hz and $^{4}$J$_{HF}$ = 3.2 Hz); 6.82 (dd, 1H, C$_3$H$_4$N, $^{3}$J$_{HH}$ = 7.7 Hz and $^{4}$J$_{HF}$ = 2.0 Hz); 7.28 (dd, 1H, C$_5$H$_4$N, $^{3}$J$_{HH}$ = 7.7 Hz); 10.18 (d, 1H, C$_5$H$_4$N, $^{3}$J$_{HH}$ = Hz). 19F NMR (CD$_2$Cl$_2$, 25 °C, 282.40 MHz): –122.5 (d, 1F, Ar–3–F, $^{3}$J$_{FF}$ = 16.4 Hz); –124.1 (dd, 1F, Ar–3–F, $^{3}$J$_{FF}$ = 31.9 Hz, $^{4}$J$_{FF}$ = 16.4 Hz, $^{5}$J$_{FF}$ = 3.3 Hz); –142.2 (d, 1F, Ar–5–F, $^{3}$J$_{CF}$ = 31.1 Hz); –333.5 (br s, 1F, Ni–F). 13C{1H} NMR (CD$_2$Cl$_2$, 25 °C, 75.47 MHz): $\delta$ 19.5 and 24.8 (s, (NCH(CH$_3$)$_2$); 42.5 and 50.3 (s, NCH$_3$ and CH); 98.1 (dd, Ar–C, $^{2}$J$_{CF}$ = 28.3 Hz, $^{3}$J$_{CF}$ = 21.4 Hz); 107.2 (s, C$_3$H$_4$N); 117.3 (s, C$_3$H$_4$N); 120.5 (t, p–Ar–C, $^{2}$J$_{CF}$ = 22.6 Hz); 135.4 (s, C$_5$H$_4$N); 137.2 (s, C$_5$H$_4$N); 146.9 (dm, Ar–C, $^{1}$J$_{CF}$ = 259.9 Hz);
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153.9 (dm, Ar–C, \( J_{CF} = 240.4 \) Hz); 156.2 (dm, Ar–C, \( J_{CF} = 201.2 \) Hz); 157.3 (s, C\(_5\)H\(_4\)N). Anal. Calcd. C, 56.61; H, 5.94; N, 11.00. Found C, 56.53; H, 6.01; N, 10.71.

**Characterization of cis-(MeNC\(_5\)H\(_4\)N\(^i\)Pr)\(_2\)Ni(C\(_6\)F\(_5\))\(_2\) (2.9).** \(^{19}\)F NMR (CD\(_2\)Cl\(_2\), 25 °C, 282.40 MHz): –115.4 (br, 2F, o–Ar–F); –164.6 (t, 1F, p–Ar–F, \( J_{FF} = 20.2 \) Hz); –165.2 (m, 1F, m–Ar–F); –166.8 (m, 1F, m–Ar–F).

**Reaction of 2.2, Ni(COD)\(_2\) and 1,3,5-trifluorobenzene.**

To a solution of 2.2 (0.250 g, 1.67 mmol) and Ni(COD)\(_2\) (0.229 g, 0.833 mmol) in 10 mL of toluene was added 1,3,5-trifluorobenzene (0.180 g, 0.833 mmol). The solution was left undisturbed for 1 week, which yielded a crystalline dark-orange solid (2.10). The solid was filtered, rinsed with toluene and pentane, then dried. (0.049 g, 12 % yield). \(^1\)H NMR (CD\(_2\)Cl\(_2\), 25 °C, 300.13 MHz): \( \delta \) 2.38 (d, 12H, NCH(CH\(_3\))\(_2\), \( J_{HH} = 6.5 \) Hz); 3.22 (septet, 2H, NC\(_3\)H\(_2\), \( J_{HH} = 6.3 \) Hz); 3.54 (s, 6H, NCH\(_3\)); 6.03 (d, 2H, C\(_5\)H\(_4\)N, \( J_{HH} = 7.7 \) Hz, \( J_{HH} = 3.3 \) Hz); 6.72 (d, 2H, C\(_5\)H\(_4\)N, \( J_{HH} = 7.4 \) Hz); 6.83 (d, 2H, C\(_5\)H\(_4\)N, \( J_{HH} = 7.74 \) Hz); 7.20 (m, 3H, Ar–H); 10.17 (d, 2H, C\(_5\)H\(_4\)N, \( J_{HH} = 7.9 \) Hz). \(^{19}\)F NMR (CD\(_2\)Cl\(_2\), 25 °C, 282.40 MHz): –320.9 (br s, 1H, Ni–F).

**Reaction of 2.2, Ni(COD)\(_2\) and 1,2,4-trifluorobenzene.**

To a solution of 2.2 (0.250 g, 1.67 mmol) and Ni(COD)\(_2\) (0.229 g, 0.833 mmol) in 10 mL of toluene was added 1,2,4-trifluorobenzene (0.180 g, 0.833 mmol). The solution was left undisturbed for 10 days, yielding a mixture of products which precipitated as a dark-orange solid (2.11, 2.12 and 2.13). The solid was filtered, rinsed with toluene and pentane, then dried. (0.049 g, 12 % yield). All NMR data provided is for the major isomer 2.11 activation at the 2-position. \(^1\)H NMR (CD\(_2\)Cl\(_2\), 25 °C, 300.13 MHz): \( \delta \) 0.2 (6H, NCH(CH\(_3\))\(_2\)); 2.5 (6H, NCH(CH\(_3\))\(_2\)); 3.2 (2H, NCH\(_2\)); 3.4 (6H, NCH\(_3\)); 5.9 (2H, C\(_5\)H\(_4\)N); 6.2 (1H, Ar–H); 6.8 (2H, C\(_5\)H\(_4\)N); 7.0 (2H, Ar–H); 7.3 (2H, C\(_5\)H\(_4\)N); 10.2 (2H, C\(_5\)H\(_4\)N). \(^{19}\)F NMR (CD\(_2\)Cl\(_2\), 25 °C, 282.40 MHz): –99.1 (1F, Ar–F); –125.9 (1F, Ar–F); –330.2 (br s, 1F, Ni–F).
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Reaction of 2.2, Ni(COD)₂ and 1,2,3-trifluorobenzene.

To a solution of 2.2 (0.250 g, 1.67 mmol) and Ni(COD)₂ (0.229 g, 0.833 mmol) in 10 mL of toluene was added 1,2,3-trifluorobenzene (0.180 g, 0.833 mmol). The solution was left undisturbed for 2 weeks, which yielded a mixture of isomers which precipitated as a dark-orange solid (2.14 and 2.15). The solid was filtered, rinsed with toluene and pentane, then dried. (0.049 g, 12 % yield). \(^{19}\text{F}\{^1\text{H}\} \text{NMR data for activation at the 1-site, 2.14.} \) \(^{19}\text{F}\{^1\text{H}\} \text{NMR (CD}_2\text{Cl}_2, 25 \degree \text{C, 282.40 MHz): } -119.4 \text{ (d, 1F, Ar–2–F, } ^3J_{FF} = 32.0 \text{ Hz); } -145.2 \text{ (d, 1F, Ar–3–F, } ^3J_{FF} = 32.5 \text{ Hz), } -328.7 \text{ (br s, 1F, Ni–F).} \) \(^{19}\text{F}\{^1\text{H}\} \text{NMR data for activation at the 2-site 2.15.} \) \(^{19}\text{F}\{^1\text{H}\} \text{NMR (CD}_2\text{Cl}_2, 25 \degree \text{C, 282.40 MHz): } -87.5 \text{ (s, 2F, Ar–F), } -340.3 \text{ (br s, 1F, Ni–F).} \)

Reaction of 2.5–2.8 and 2.11–2.15 with D₂O.

A solution of 0.2 mL of 10 % HCl in D₂O is added to a vial containing compound 2.5, 2.6, 2.7, 2.8, 2.11, 2.12, 2.13, 2.14, or 2.15 in C₆D₆. The solution is mixed and then filtered through a silica column to remove any nickel byproducts, and protonated ligand. The filtrate contains the deuterated and protonated organic products in C₆D₆, the \(^{19}\text{F}\) NMR shifts are shown in Scheme 2.9. The site activated during C–F bond activation contains a mixture of isotopomers 10 % H; 90 % D, which can be distinguished by \(^{19}\text{F}\{^1\text{H}\} \text{NMR, and confirmed by a 0.3 ppm shift of any fluorine coupled to deuterium in complexes 2.5–2.8 and 2.11–2.15.} \)

2.4.3 Elemental Analysis

Products 2.1–2.8 were dried overnight under vacuum, \(^1\text{H} \text{NMR was used to confirm that no water or solvents remained cocrystallized within the lattice. Combustion of 2.1–2.3 gave experimental values within } \pm 0.4 \text{ %}. \) Combustions of products 2.4–2.8 gave accurate \% values for N and H, however, the C \% values were found to be consistently low after multiple trials. The samples were analyzed at two locations Atlantic Micolabs in Atlanta, Georgia and at the University of Windsor in Windsor, Canada which resulted in consistent results of acceptable H and N values and low C values. The inconsistent % C values are expected for 2.4–2.8, because combustion of fluorocarbon compounds often result in
incompatible % C values for elemental analysis.\textsuperscript{40,41} High resolution mass spectrometry was attempted at the McMaster Regional Centre for Mass Spectrometry for products 2.4–2.8. Despite using a variety of methods, which included HREI-MS, HRCI-MS and MALDI, no parent peaks were observed for the desired products.

2.5 X-ray Crystallography

2.5.1 General Collection and Refinement Information

The X-ray structures were obtained at –130 °C, with the crystal covered in Paratone and placed rapidly into the cold N\textsubscript{2} stream of the Kryo-Flex low-temperature device. The data were collected using the SMART\textsuperscript{42} software on a Bruker APEX CCD diffractometer using a graphite monochromator with Mo K\textalpha\ radiation (\(\lambda = 0.71073 \text{ Å}\)). A hemisphere of data was collected using a counting time of 10-30 s per frame. Details of crystal data, data collection, and structure refinement are listed in Tables 1-3. Data reductions were performed using the SAINT\textsuperscript{43} software, and the data were corrected for absorption using SADABS.\textsuperscript{44} The structures were solved by direct methods using SIR97\textsuperscript{45} and refined by full-matrix least-squares on \(F^2\) with anisotropic displacement parameters for the non-H atoms, unless otherwise stated, using SHELXL-97\textsuperscript{46} and the WinGX\textsuperscript{47} software package, and thermal ellipsoid plots were produced using ORTEP3\textsuperscript{2.48}

2.5.2 Crystallographic Data

\textit{Table 2.1. Crystallographic Data for 4-(isopropylamino)-1-methylpyridinium iodide, 2.1.}

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C\textsubscript{9}H\textsubscript{15}IN\textsubscript{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>278.13</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)/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 8.3498(10) Å            (\alpha = 90^\circ).</td>
</tr>
</tbody>
</table>
Chapter 2 – Selective C–F Bond Activation of Tetrafluorobenzenes by Nickel(0) with a Nitrogen Donor Analogous to N-heterocyclic Carbenes

\[ b = 10.5660(13) \, \text{Å} \quad \beta = 104.9350(10)^\circ. \]
\[ c = 13.1122(16) \, \text{Å} \quad \gamma = 90^\circ. \]

Volume \[1117.7(2) \, \text{Å}^3\]

\( b = 10.5660(13) \, \text{Å} \quad \beta = 104.9350(10)^\circ. \]
\( c = 13.1122(16) \, \text{Å} \quad \gamma = 90^\circ. \]

\text{Density (calculated)} \quad 1.653 \, \text{Mg/m}^3

Absorption coefficient \quad 2.821 \, \text{mm}^{-1}

\( b = 10.5660(13) \, \text{Å} \quad \beta = 104.9350(10)^\circ. \]
\( c = 13.1122(16) \, \text{Å} \quad \gamma = 90^\circ. \]

\text{F(000)} \quad 544

Crystal size \quad 0.11 \times 0.09 \times 0.06 \, \text{mm}^3

Theta range for data collection \quad 2.51 \text{ to } 27.99^\circ.

Index ranges \quad -10 \leq h \leq 10, -13 \leq k \leq 13, -16 \leq l \leq 17

Reflections collected \quad 12091

Independent reflections \quad 2581 [R(int) = 0.0213]

Completeness to theta = 27.99° \quad 96.2 \%

Absorption correction \quad \text{None}

Max. and min. transmission \quad 0.8490 \text{ and } 0.7467

Refinement method \quad \text{Full-matrix least-squares on } F^2

Data / restraints / parameters \quad 2581 / 0 / 116

Goodness-of-fit on \( F^2 \) \quad 1.040

Final R indices \([I>2\sigma(I)]\) \quad R1 = 0.0176, wR2 = 0.0412

R indices (all data) \quad R1 = 0.0208, wR2 = 0.0423

Largest diff. peak and hole \quad 0.366 \text{ and } -0.336 \, \text{e.Å}^{-3}

\textbf{Table 2.2. Crystallographic Data for 1-methyl-4-isopropyliminopyridine, 2.2.}

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>( \text{C}<em>3\text{H}</em>{14}\text{N}_2 )</td>
</tr>
<tr>
<td>Formula weight</td>
<td>150.22</td>
</tr>
<tr>
<td>Temperature</td>
<td>140(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Space group</td>
<td>I4(1)/a</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>( a = 14.5158(10) , \text{Å} \quad \alpha = 90^\circ. )</td>
</tr>
</tbody>
</table>
Chapter 2 – Selective C–F Bond Activation of Tetrafluorobenzenes by Nickel(0) with a Nitrogen Donor Analogous to N-heterocyclic Carbenes

\[ b = 14.5158(10) \, \text{Å} \quad \beta = 90^\circ. \]
\[ c = 16.885(2) \, \text{Å} \quad \gamma = 90^\circ. \]

Volume \[ 3557.9(6) \, \text{Å}^3 \]

Z \[ 16 \]

Density (calculated) \[ 1.122 \, \text{Mg/m}^3 \]

Absorption coefficient \[ 0.068 \, \text{mm}^{-1} \]

F(000) \[ 1312 \]

Crystal size \[ 0.38 \times 0.33 \times 0.18 \, \text{mm}^3 \]

Theta range for data collection \[ 2.81 \text{ to } 27.50^\circ. \]

Index ranges \[ -18 \leq h \leq 18, -18 \leq k \leq 18, -21 \leq l \leq 21 \]

Reflections collected \[ 19524 \]

Independent reflections \[ 2042 \, [R(\text{int}) = 0.0228] \]

Completeness to theta = 27.50\(^{\circ}\) \[ 99.6 \% \]

Absorption correction \[ \text{Semi-empirical from equivalents} \]

Max. and min. transmission \[ 0.9878 \text{ and } 0.9746 \]

Refinement method \[ \text{Full-matrix least-squares on } F^2 \]

Data / restraints / parameters \[ 2042 / 0 / 103 \]

Goodness-of-fit on \( F^2 \) \[ 1.070 \]

Final R indices \([I>2\sigma(I)]\) \[ R1 = 0.0444, \, wR2 = 0.1191 \]

R indices (all data) \[ R1 = 0.0494, \, wR2 = 0.1243 \]

Largest diff. peak and hole \[ 0.258 \text{ and } -0.184 \, \text{e.Å}^{-3} \]

**Table 2.3. Crystallographic Data for cis–(MeNC}_5\text{H}_4\text{N}^i\text{Pr})\text{RhCl(CO)}_2, 2.3.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>( \text{C}<em>{11}\text{H}</em>{14}\text{ClN}_2\text{O}_2\text{Rh} )</td>
</tr>
<tr>
<td>Formula weight</td>
<td>344.60</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>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pna2(1)</td>
</tr>
</tbody>
</table>
| Unit cell dimensions      | \( a = 11.979(3) \, \text{Å} \) \quad \alpha = 90^\circ. \]

References begin on page 70
Volume \[ 2800.7(12) \text{ Å}^3 \]

\[ b = 8.405(2) \text{ Å} \quad \beta = 90^\circ. \]

\[ c = 27.817(7) \text{ Å} \quad \gamma = 90^\circ. \]

Z \[ 8 \]

Density (calculated) \[ 1.635 \text{ Mg/m}^3 \]

Absorption coefficient \[ 1.402 \text{ mm}^{-1} \]

F(000) \[ 1376 \]

Crystal size \[ 0.19 \times 0.15 \times 0.06 \text{ mm}^3 \]

Theta range for data collection \[ 1.46 \text{ to } 27.50^\circ. \]

Index ranges \[ -14 \leq h \leq 15, -10 \leq k \leq 10, -35 \leq l \leq 34 \]

Reflections collected \[ 27119 \]

Independent reflections \[ 6251 \{R(int) = 0.0503\} \]

Completeness to theta \[ 27.50^\circ \] \[ 99.4 \% \]

Absorption correction \[ \text{Semi-empirical from equivalents} \]

Max. and min. transmission \[ 0.9206 \text{ and } 0.7766 \]

Refinement method \[ \text{Full-matrix least-squares on } F^2 \]

Data / restraints / parameters \[ 6251 / 1 / 313 \]

Goodness-of-fit on \[ F^2 \] \[ 1.094 \]

Final R indices \[ [I>2\sigma(I)] \]

\[ R1 = 0.0723, wR2 = 0.1624 \]

R indices (all data) \[ R1 = 0.0863, wR2 = 0.1715 \]

Absolute structure parameter \[ 0.20(11) \]

Largest diff. peak and hole \[ 2.266 \text{ and } -2.399 \text{ e.Å}^{-3} \]

**Table 2.4. Crystallographic Data for trans-(MeNC$_5$H$_4$N$_i$Pr)$_2$NiF(C$_6$F$_5$), 2.4.**

Empirical formula \[ C_{24}H_{28}F_{6}N_{4}Ni, 2(C_6H_6) \]

Formula weight \[ 701.43 \]

Temperature \[ 143(2) \text{ K} \]

Wavelength \[ 0.71073 \text{ Å} \]

Crystal system \[ \text{Monoclinic} \]

Space group \[ \text{C2/c} \]
Chapter 2 – Selective C–F Bond Activation of Tetrafluorobenzenes by Nickel(0) with a Nitrogen Donor Analogous to N-heterocyclic Carbenes

Unit cell dimensions
\[ a = 16.436(2) \, \text{Å} \quad \alpha = 90^\circ. \]
\[ b = 22.687(3) \, \text{Å} \quad \beta = 125.0670(10)^\circ. \]
\[ c = 11.4519(16) \, \text{Å} \quad \gamma = 90^\circ. \]

Volume
\[ 3495.1(8) \, \text{Å}^3 \]

Z
4

Density (calculated)
\[ 1.333 \, \text{Mg/m}^3 \]

Absorption coefficient
\[ 0.618 \, \text{mm}^{-1} \]

F(000)
1464

Crystal size
\[ 0.39 \times 0.20 \times 0.08 \, \text{mm}^3 \]

Theta range for data collection
1.76 to 27.49°.

Index ranges
\(-20 \leq h \leq 20, -29 \leq k \leq 29, -14 \leq l \leq 14\)

Reflections collected
19372

Independent reflections
3957 \([R(\text{int}) = 0.0291]\)

Completeness to theta = 27.49°
98.5 %

Absorption correction
Semi-empirical from equivalents

Max. and min. transmission
0.9523 and 0.7947

Refinement method
Full-matrix least-squares on \(F^2\)

Data / restraints / parameters
3957 / 0 / 218

Goodness-of-fit on \(F^2\)
1.179

Final R indices \([I>2\sigma(I)]\)
\(R1 = 0.0393, \, wR2 = 0.0942\)

R indices (all data)
\(R1 = 0.0491, \, wR2 = 0.1094\)

Largest diff. peak and hole
0.515 and –0.298 \, e\text{.Å}^{-3}\)

Table 2.5. Crystallographic Data for trans-(MeNC5H4N\textit{i}Pr)2NiF(2,4,5-C6F3H2), 2.6.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>(\text{C}<em>{24}\text{H}</em>{30}\text{F}_4\text{N}_4\text{Ni}, 2(\text{C}_7\text{H}_8))</td>
</tr>
<tr>
<td>Formula weight</td>
<td>693.50</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>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pna2(1)</td>
</tr>
</tbody>
</table>
Unit cell dimensions

- \( a = 11.701(4) \, \text{Å} \)  
  \( \alpha = 90^\circ \)
- \( b = 22.922(7) \, \text{Å} \)  
  \( \beta = 90^\circ \)
- \( c = 13.684(4) \, \text{Å} \)  
  \( \gamma = 90^\circ \)

Volume

- \( 3670(2) \, \text{Å}^3 \)

Z

- 4

Density (calculated)

- 1.255 \( \text{Mg/m}^3 \)

Absorption coefficient

- 0.580 \( \text{mm}^{-1} \)

F(000)

- 1464

Crystal size

- 0.45 x 0.06 x 0.05 mm\(^3\)

Theta range for data collection

- 2.46 to 20.00\(^\circ\)

Index ranges

- \(-11 \leq h \leq 11, -22 \leq k \leq 22, -13 \leq l \leq 13\)

Reflections collected

- 14850

Independent reflections

- 3377 \([R(\text{int}) = 0.0541]\)

Completeness to \( \theta \) = 20.00\(^\circ\)

- 99.2 \%

Absorption correction

- Semi-empirical from equivalents

Max. and min. transmission

- 0.9716 and 0.7804

Refinement method

- Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters

- 3377 / 2 / 189

Goodness-of-fit on \( F^2 \)

- 1.148

Final R indices \([I>2\sigma(I)]\)

- \( R1 = 0.0904, wR2 = 0.2157 \)

R indices (all data)

- \( R1 = 0.0961, wR2 = 0.2193 \)

Absolute structure parameter

- 0.49(6)

Largest diff. peak and hole

- 0.764 and -0.744 e.Å\(^{-3}\)

Table 2.6. Crystallographic Data for trans-(MeNC\(_5\)H\(_4\)N\(^i\)Pr)\(_2\)NiF(2,3,5-C\(_6\)F\(_3\)H\(_2\)), 2.8.

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>( C_{24}H_{30}F_4N_4Ni, 2(C_6H_6) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>665.45</td>
</tr>
<tr>
<td>Temperature</td>
<td>143(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
</tbody>
</table>
Space group  
C2/c

Unit cell dimensions 
\[ a = 16.4271(19) \text{ Å} \quad \alpha = 90^\circ. \]
\[ b = 21.856(3) \text{ Å} \quad \beta = 124.3640(10)^\circ. \]
\[ c = 11.5064(13) \text{ Å} \quad \gamma = 90^\circ. \]

Volume  
3410.1(7) Å³

Z  
4

Density (calculated)  
1.296 Mg/m³

Absorption coefficient  
0.621 mm⁻¹

F(000)  
1400

Crystal size  
0.38 x 0.21 x 0.18 mm³

Theta range for data collection  
2.02 to 27.49°.

Index ranges  
\[-21<=h<=21, -27<=k<=28, -14<=l<=14\]

Reflections collected  
18920

Independent reflections  
3859 \([R(\text{int}) = 0.0287]\)

Completeness to theta = 27.49°  
98.6 %

Absorption correction  
Semi-empirical from equivalents

Max. and min. transmission  
0.8964 and 0.7982

Refinement method  
Full-matrix least-squares on \(F^2\)

Data / restraints / parameters  
3859 / 0 / 213

Goodness-of-fit on \(F^2\)  
1.045

Final R indices \([I>2\sigma(I)]\)  
R1 = 0.0419, wR2 = 0.0994

R indices (all data)  
R1 = 0.0494, wR2 = 0.1053

Largest diff. peak and hole  
0.577 and –0.470 e.Å⁻³

Table 2.7. Crystallographic Data for \(\text{cis-(MeNC}_5\text{H}_4\text{N}^\text{iPr})_2\text{Ni(2,3,4,5,6-C}_6\text{F}_5)_2\), 2.9.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>(\text{C}<em>{35}\text{H}</em>{28}\text{F}_{10}\text{N}_4\text{Ni})</td>
</tr>
<tr>
<td>Formula weight</td>
<td>753.32</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>
</tbody>
</table>
Chapter 2 – Selective C–F Bond Activation of Tetrafluorobenzenes by Nickel(0) with a Nitrogen Donor Analogous to N-heterocyclic Carbenes

Space group: P2(1)/c

Unit cell dimensions:
- \( a = 12.5947(18) \, \text{Å} \)  
- \( \alpha = 90^\circ \)
- \( b = 15.938(2) \, \text{Å} \)  
- \( \beta = 93.454(2)^\circ \)
- \( c = 17.499(3) \, \text{Å} \)  
- \( \gamma = 90^\circ \)

Volume: 3506.1(9) Å³

Z: 4

Density (calculated): 1.427 Mg/m³

Absorption coefficient: 0.637 mm⁻¹

F(000): 1536

Crystal size: 0.39 x 0.20 x 0.08 mm³

Theta range for data collection: 1.62 to 27.50°.

Index ranges: \(-15 \leq h \leq 16, -20 \leq k \leq 20, -22 \leq l \leq 22\)

Reflections collected: 36894

Independent reflections: 7859 [R(int) = 0.1594]

Completeness to theta = 27.50°: 97.3 %

Absorption correction: Semi-empirical from equivalents

Max. and min. transmission: 0.9508 and 0.7893

Refinement method: Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters: 7859 / 0 / 270

Goodness-of-fit on \( F^2 \): 1.202

Final R indices [I>2sigma(I)]: \( R1 = 0.1423, \ wR2 = 0.2990 \)

R indices (all data): \( R1 = 0.2180, \ wR2 = 0.3299 \)

Largest diff. peak and hole: 1.263 and -0.910 e.Å⁻³

Table 2.8. Crystallographic Data for trans-(MeNC₅H₄N^iPr)₂NiF(3,5-C₆F₂H₃), 2.10.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₂₄H₃₁N₄F₃Ni, 2(C₆H₆)</td>
</tr>
<tr>
<td>Formula weight</td>
<td>647.45</td>
</tr>
<tr>
<td>Temperature</td>
<td>143(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
</tbody>
</table>
Chapter 2 – Selective C–F Bond Activation of Tetrafluorobenzenes by Nickel(0) with a Nitrogen Donor Analogous to N-heterocyclic Carbenes

Space group C2/c
Unit cell dimensions
\[ a = 16.4489(16) \, \text{Å} \quad \alpha = 90^\circ. \]
\[ b = 21.747(2) \, \text{Å} \quad \beta = 124.3990(10)^\circ. \]
\[ c = 11.5372(11) \, \text{Å} \quad \gamma = 90^\circ. \]
Volume \[ 3405.3(6) \, \text{Å}^3 \]
Z 4
Density (calculated) 1.263 Mg/m\(^3\)
Absorption coefficient 0.616 mm\(^{-1}\)
F(000) 1368
Crystal size 0.39 x 0.11 x 0.10 mm\(^3\)
Theta range for data collection 2.84 to 27.50°.
Index ranges \(-21 \leq h \leq 20, -28 \leq k \leq 27, -14 \leq l \leq 14\)
Reflections collected 18565
Independent reflections 3842 [R(int) = 0.0255]
Completeness to theta = 27.50° 98.4 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.9410 and 0.7952
Refinement method Full-matrix least-squares on F\(^2\)
Data / restraints / parameters 3842 / 0 / 204
Goodness-of-fit on F\(^2\) 1.097
Final R indices [I>2sigma(I)] R1 = 0.0387, wR2 = 0.0912
R indices (all data) R1 = 0.0436, wR2 = 0.0951
Largest diff. peak and hole 0.508 and –0.221 e.Å\(^{-3}\)
Chapter 2 – Selective C–F Bond Activation of Tetrafluorobenzenes by Nickel(0) with a Nitrogen Donor Analogous to N-heterocyclic Carbenes

2.6 References


(15) CCDC-712083 (1), CCDC-712085 (2), and CCDC-712084 (3) contain the supplementary crystallographic data for this chapter. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data_request/cif.
Chapter 2 – Selective C–F Bond Activation of Tetrafluorobenzenes by Nickel(0) with a Nitrogen Donor Analogous to N-heterocyclic Carbenes


(42) SMART Molecular analysis research tool; Bruker AXS Inc. Madison, WI, 2001.

(43) SAINTPlus Data reduction and correction program; Bruker AXS Inc.: Madison, WI, 2001.


Chapter 3 - Catalytic C–H Bond Stannylation: A New Regioselective Pathway to C–Sn Bonds via C–H Bond Functionalization

3.1 Introduction

In the past few decades, transition metal C–H bond activation\textsuperscript{1–15} and catalytic functionalization have gone from an exotic branch of transition-metal reactivity without practical application to cutting-edge technology in catalytic organic transformations.\textsuperscript{16–19} Reactions that convert C–H bonds into molecules bearing versatile functional groups, such as regioselective borylations,\textsuperscript{20} have been extensively utilized to generate functionalized organics such as arylboronic esters directly from hydrocarbons and B–H or B–B bond cleavage, as depicted in Scheme 3.1; these compounds serve as versatile starting materials used in reactions such as Miyaura–Suzuki coupling.\textsuperscript{21,22}
Chapter 3 – Catalytic C–H Bond Stannylation: A New Regioselective Pathway to C–Sn Bonds via C–H Bond Functionalization

Scheme 3.1. Examples of aryl C–H bond borylation with transition metal catalysts.

Unfortunately, extensions of the C–H bond borylation methodology are limited in scope. For example, although the oxidative addition of Sn–H bonds to transition metals has precedent, the catalytic conversion of trialkyltin hydrides, HSnR₃, to R₃SnSnR₃ and H₂ is often instantaneous. The oxidative addition of Sn–Sn bonds have also been reported; to date, however, this reactions has been utilized only in catalytic coupling to carbon–halide bonds and additions to carbon–carbon multiple bonds.²³ This pair of currently unsuccessful approaches to catalytic C–H bond stannylation, which are analogous to those used in borylation chemistry, are shown in Scheme 3.2. A new method for forming C–Sn bonds from C–H bonds could have significant impact as a facile route to reagents for the Stille coupling reaction,²⁴⁻²⁶ which is widely utilized because of the air and moisture stability and functional group tolerance of the organonotin compounds it employs. The syntheses of these organotin reagents typically involve multiple steps from expensive functional-group-containing precursors.

Scheme 3.2. Examples of analogous organostannane reagents to the borylation reaction do not undergo C–H bond stannylation.
3.2 Results and Discussion

3.2.1 C–H Bond Stannylation of Fluorinated Aromatics

We have previously shown in Chapter 2 that stoichiometric amounts of Ni(COD)$_2$ (COD = 1,5-cyclooctadiene) and the ancillary ligand MeNC$_5$H$_4$N$i$Pr react with a variety of partially fluorinated aromatics, such as C$_6$F$_5$H, via selective C–F bond activation at room temperature.$^{27}$ The addition of CH$_2$=CHSnBu$_3$ and a partially fluorinated arene to catalytic amounts of Ni(COD)$_2$, and MeNC$_5$H$_4$N$i$Pr would be expected to result in catalytic C–F bond functionalization via the Stille coupling reaction to produce a partially fluorinated styrene, as shown in Scheme 3.3.$^{28}$

![Scheme 3.3](image)

Scheme 3.3. Expected Stille coupling reaction was not observed.

Remarkably, these reactions at room temperature yielded no C–F activation products and practically quantitative conversions to the product of C–H functionalization, C$_6$F$_{n}$H$_{5-n}$SnBu$_3$, as shown in Scheme 3.4. The stoichiometric production of ethylene as a byproduct was positively identified by $^1$H and $^{13}$C{$_^1$H} NMR spectroscopy when the reaction was performed in C$_6$D$_6$ in a sealed NMR tube. The reaction was found to go to completion with as little as 1 mol % Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr and provided practically pure product, as monitored by $^{19}$F, $^1$H, and $^{119}$Sn NMR spectroscopy. These reactions could also be performed without the addition of solvent.
The $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of the crude reaction mixture of the C–H stannylation of C$_6$F$_5$H in C$_6$D$_6$ is shown in Figure 3.1. The $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum displayed three resonances at $\delta$ –121.3, –153.0, and –160.7 and the structure of 3.1 was confirmed by the presence of Sn satellites. The ortho ($\delta$ –121.3) and meta ($\delta$ –160.7) fluorine resonances displayed AA'MM'X second order coupling patterns while the para fluorine ($\delta$ –153.0) was a triplet of triplets. If the expected Stille coupling product, 1,2,4,5-tetrafluoro-3-vinylbenzene, was formed, then only two fluorine environments would have been present in the $^{19}\text{F}$ NMR spectrum.

Scheme 3.4. General reaction scheme for the catalytic stannylation of C–H bonds.
Figure 3.1. \(^{19}\text{F}\{^1\text{H}\}\) NMR spectrum of \(\text{C}_6\text{F}_5\text{SnBu}_3\) (3.1) in the crude reaction mixture from the reaction of \(\text{C}_6\text{F}_5\text{H}, \text{CH}_2=\text{CHSnBu}_3\) with catalytic amounts of \(\text{Ni(COD)}_2\) and \(\text{MeNC}_5\text{H}_4\text{N}^\text{iPr}\).

To investigate the generality of this catalytic functionalization, we examined the scope of fluorinated aromatics that undergo this reaction. A summary is shown in Table 3.1. Aromatic substrates with C–H bonds *ortho* to two fluorines, such as \(\text{C}_6\text{F}_5\text{H}, 1,2,4,5-\text{C}_6\text{F}_4\text{H}_2, 1,2,3,5-\text{C}_6\text{F}_4\text{H}_2, 1,2,4-\text{C}_6\text{F}_3\text{H}_3, 1,3,5-\text{C}_6\text{F}_3\text{H}_3\) and \(1,3-\text{C}_6\text{F}_2\text{H}_4\) proved to be the most reactive. The monostannylated compounds 3.1, 3.2, 3.4, 3.7 and 3.10 were obtained with good selectivity (>91 \%) using a modest excess of fluorinated aromatic (~2 equivalents); the only significant impurities were the distannylated compounds 3.3, 3.5, 3.8 and 3.11, which were readily separated. The \(^1\text{H}\) and \(^{19}\text{F}\{^1\text{H}\}\) NMR spectra of isolated 3.2 are shown in Figure 3.2 and 3.3, respectively. The \(^1\text{H}\) NMR spectrum displayed four butyl environments at \(\delta\ 0.86, 1.19, 1.30\) and \(1.52\) as expected and one aromatic resonance at \(\delta\ 6.37\), as a triplet of triplets. The \(^{19}\text{F}\{^1\text{H}\}\) NMR spectrum exhibited two fluorine resonances at \(\delta\ –122.4\) and \(–138.4\), as second order multiplets with Sn satellites.
Figure 3.2. $^1$H NMR spectrum of isolated 2,3,5,6-C$_6$F$_4$H-1-SnBu$_3$ (3.2) from the reaction of 1,2,4,5-C$_6$F$_4$H$_2$, CH$_2$=CHSnBu$_3$ with catalytic amounts of Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr.

Figure 3.3. $^{19}$F{$^1$H} NMR spectrum of isolated 2,3,5,6-C$_6$F$_4$H-1-SnBu$_3$ (3.2) from the reaction of 1,2,4,5-C$_6$F$_4$H$_2$, CH$_2$=CHSnBu$_3$ with catalytic amounts of Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr.
The distannylated compounds 3.3, 3.5 and 3.11 could be obtained with good selectivity themselves by using 2.5 equivalents of CH$_2$=CHSnBu$_3$. Attempts to form the tristannylated compound 1,3,5-(SnBu$_3$)-2,4,6-C$_6$F$_3$ (3.12) with MeNC$_5$H$_4$NiPr as the ancillary ligand proved to be unsuccessful. The activation of heterocycles such as 2,3,5,6-tetrafluoropyridine, 2,3,5- and 2,4,6-trifluoropyridine also proved to be possible with MeNC$_5$H$_4$NiPr as the ancillary ligand, the monostannylated compounds 3.13, 3.14 and 3.15 were obtained with good yields (>85 %) with the only significant impurity being the distannylated compound 1,3-(SnBu$_3$)-2,4,6-C$_5$F$_3$N (3.16).

A decrease in rate was observed with substrates with a lesser degree of fluorination; however, it proved possible to increase the turnover rate by increasing the temperature from 25 to 45 °C using the ancillary ligand MeNC$_5$H$_4$NiPr. The reactions of substrates where only one fluorine substituent is disposed ortho to a C–H bond were slow and even at elevated temperatures were not efficiently catalyzed using the ancillary ligand MeNC$_5$H$_4$NiPr. Temperatures higher than 60 °C resulted in rapid decomposition of Ni(COD)$_2$ to nickel metal, and the yields dropped off significantly. In the cases where data for the analogous borylation reactions were available for comparison, these stannylation reactions were found to occur under milder conditions, produce higher yields, and be more selective, with no C–F functionalization products observed.$^{29}$

### 3.2.2 Comparison in Reactivity with $^3$Pr$_3$P as the Ancillary Ligand.

Note: The results presented in this section, with $^3$Pr$_3$P as the ancillary ligand, were performed by Jillian A. Hatnean and published in a joint paper, under the supervision of Dr. Samuel Johnson.

Replacing MeNC$_5$H$_4$NiPr with traditional phosphine donors, such as $^3$Pr$_3$P, led to slower rates for the substrates investigated under the same conditions, however, the thermal stability of the catalyst improved, which allowed for efficient functionalization at higher temperatures. For example, with $^3$Pr$_3$P as the ancillary ligand, the functionalization of 1,2,3,4-C$_6$F$_4$H$_2$ occurs in 4 h at 80 °C and provided selective conversion to the monostannylated product 3.6. Similar results were observed when 1,2,3-trifluorobenzene was used as the
substrate, providing the monosubstituted product 3.17. The distannylated product 3.18 was also obtained selectively in the presence of excess CH₂=CHSnBu₃ and was present as a slight impurity in the synthesis of 3.17. The tristannylated compound 3.12, was not observed with MeNC₅H₄NⁱPr as the ancillary ligand but was synthesized with iPr₃P in a 95 % yield.

The monostannylated compounds 3.19, 3.20, and 3.22 were obtained from 1,3-, 1,2-, and 1,4-difluorobenzene, respectively, in >90 % yields at 80 °C when iPr₃P was employed as the ligand. The only significant impurities were the distannylated compounds 1,4-(SnBu₃)₂-2,3-C₆F₂H₂ (3.21), 1,4-(SnBu₃)₂-2,5-C₆F₂H₂ (3.23), and 1,3-(SnBu₃)₂-2,5-C₆F₂H₂ (3.24). With fluorobenzene, only 15 % conversion to the monostannylated complex 1-(SnBu₃)-2-C₆FH₃ (3.25) was achieved. These di- and monofluorinated aromatics proved to be poor substrates when MeNC₅H₄NⁱPr was used as the ancillary ligand.

Table 3.1. Summary of catalytic C–H bond functionalization of fluorinated arenes with CH₂=CHSnBu₃. aNMR yield from integration of ¹⁹F{¹H} NMR spectra. bIsolated yield after chromatography. c2.5 equivalents of CH₂=CHSnBu₃. d3.5 equivalents CH₂=CHSnBu₃. e10-fold excess of fluorinated aromatic.

<table>
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<th>Reagent</th>
<th>Ancillary Ligand and Ni(COD)₂ Loading (%)</th>
<th>Conditions</th>
<th>Yield (%)</th>
<th>Products and #</th>
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<td>MeNC₅H₄NⁱPr 3 %</td>
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<td>iPr₃P, 5 %</td>
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<td>F F F SnBu₃</td>
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<td>MeNC₅H₄NⁱPr 3 %</td>
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<td>95a (4a of 3.3)</td>
<td>F F F SnBu₃</td>
</tr>
<tr>
<td></td>
<td>iPr₃P, 5 %</td>
<td>80 °C, 0.2 h</td>
<td>93a (7a of 3.3)</td>
<td>F F F SnBu₃</td>
</tr>
</tbody>
</table>
Chapter 3 – Catalytic C–H Bond Stannylation: A New Regioselective Pathway to C–Sn Bonds via C–H Bond Functionalization

1,2,4,5–\( C_6F_4H_2 \)  
\[ \text{MeNC} \text{5H}_2N^\text{iPr} \]  
3 %  
\( ^3\text{Pr}_3\text{P}, \) 5 %  
80 °C, 6 h\(^c\)  
85\(^a\) (11\(^a\) of 3.2)

1,2,3,5–\( C_6F_4H_2 \)  
\[ \text{MeNC} \text{3H}_2N^\text{iPr} \]  
3 %  
\( ^3\text{Pr}_3\text{P}, \) 5 %  
80 °C, 0.7 h  
95\(^a\) (82\(^b\))

1,2,3,5–\( C_6F_4H_2 \)  
\[ \text{MeNC} \text{3H}_2N^\text{iPr} \]  
5 %  
\( ^3\text{Pr}_3\text{P}, \) 5 %  
80 °C, 12 h\(^c\)  
95\(^a\)

1,2,3,4–\( C_6F_3H_3 \)  
\[ \text{MeNC} \text{3H}_2N^\text{iPr} \]  
3 %  
\( ^3\text{Pr}_3\text{P}, \) 5 %  
80 °C, 7 h  
98\(^a\)

1,2,4–\( C_6F_3H_3 \)  
\( ^3\text{Pr}_3\text{P}, \) 5 %  
80 °C, 48 h\(^c\)  
50\(^a\)  
(40\(^a\) of 3.7 and \( \text{Bu}_6\text{Sn}_2 \))
Chapter 3 – Catalytic C–H Bond Stannylation: A New Regioselective Pathway to C–Sn Bonds via C–H Bond Functionalization

1,3,5–C₆F₃H₃

MeNC₅H₄N′iPr

3 %

³Pr₃P, 5 %

40 °C, 4 h

91 a (83 b)

1,3,5–C₆F₃H₃

MeNC₅H₄N′iPr

5 %

³Pr₃P, 5 %

80 °C, 0.5 h

83 a (17 a of 3.11)

1,3,5–C₆F₃H₃

³Pr₃P, 5 %

80 °C, 18 h c

38 a (55 a of 3.10)

1,3,5–C₆F₃H₃

³Pr₃P, 5 %

80 °C, 18 h d

95 a (5 a of 3.11)

2,3,5,6–C₅F₄HN

MeNC₅H₄N′iPr

5 %

³Pr₃P, 5 %

80 °C, 2 h

98 a (87 b)

2,3,5–C₅F₃H₂N

MeNC₅H₄N′iPr

5 %

³Pr₃P, 5 %

80 °C, 1 h

85 a (62 b)

2,4,6–C₅F₃H₂N

MeNC₅H₄N′iPr

5 %

³Pr₃P, 5 %

80 °C, 12 h

96 a (4 a of 3.16)
Chapter 3 – Catalytic C–H Bond Stannylation: A New Regioselective Pathway to C–Sn Bonds via C–H Bond Functionalization

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ligand</th>
<th>Temperature</th>
<th>Time</th>
<th>Yield (%)</th>
<th>Reference</th>
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</thead>
<tbody>
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<td>2,4,6–C₅F₃H₂N</td>
<td>MeNC₅H₄NPr</td>
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<td>99</td>
<td>3.15</td>
</tr>
<tr>
<td></td>
<td>iPr₃P, 5 %</td>
<td>80 °C, 24 h</td>
<td>56</td>
<td>99</td>
<td>3.15</td>
</tr>
<tr>
<td>1,2,3–C₆F₃H₃</td>
<td>iPr₃P, 5 %</td>
<td>80 °C, 48 h</td>
<td>50</td>
<td>30</td>
<td>3.18</td>
</tr>
<tr>
<td></td>
<td>iPr₃P, 5 %</td>
<td>80 °C, 72 h</td>
<td>30</td>
<td>40</td>
<td>3.17</td>
</tr>
<tr>
<td>1,3–C₆F₂H₄</td>
<td>iPr₃P, 5 %</td>
<td>80 °C, 18 h</td>
<td>90</td>
<td></td>
<td>3.19</td>
</tr>
<tr>
<td>1,2–C₆F₂H₄</td>
<td>iPr₃P, 5 %</td>
<td>80 °C, 18 h</td>
<td>92</td>
<td></td>
<td>3.20</td>
</tr>
<tr>
<td>1,4–C₆F₂H₄</td>
<td>iPr₃P, 5 %</td>
<td>80 °C, 18 h</td>
<td>90</td>
<td></td>
<td>3.21</td>
</tr>
</tbody>
</table>
3.2.3 Mechanistic Studies

Both an ancillary ligand and Ni(COD)$_2$ are necessary for the desired catalytic reaction to proceed under the conditions used. Catalysis was observed even in the presence of added Hg, which argues against Ni metal particles from the decomposition of Ni(COD)$_2$ acting as the active catalyst. No direct reaction was observed between pentafluorobenzene and CH$_2$=CHSnBu$_3$ even when a toluene solution was heated to 100 °C. Similarly, no reaction was observed with the addition of the ligand MeNC$_5$H$_4$N$i$Pr in the absence of the metal-containing catalyst precursor Ni(COD)$_2$.

The reagents CH$_2$=CHSnMe$_3$, cis-(1-propenyl)SnBu$_3$, and trans-(1-propenyl)SnBu$_3$ all proved to be successful reagents for C–H bond functionalization. The replacements of these reagents with SnBu$_4$, SnPh$_4$, Me$_3$SnSnMe$_3$ and PhSnBu$_3$ were unsuccessful, as no conversion to the desired products was observed even at elevated temperatures. The reaction of HSnBu$_3$ and C$_6$F$_5$H using catalytic Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr or $i$Pr$_3$P did not yield 3.1 but instead produced Sn$_2$Bu$_6$ instantaneously with the liberation of H$_2$ gas. The ratio of C–H-functionalized product to C–D-functionalized product in the reaction of the monodeuterated substrate 1,2,4,5-C$_6$F$_4$HD with CH$_2$=CHSnBu$_3$ using catalytic Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr was found to be 2.1:1 at 298 K by integration of the $^{19}$F{$^1$H} NMR resonances of the products. This kinetic isotope effect is consistent with the equilibrium isotope effect previously observed in the oxidative addition of 1,2,4,5-C$_6$F$_4$HD to a Ni(PEt$_3$)$_2$ synthon,$^{30}$ it supports a mechanism where oxidative cleavage of the C–H bond occurs at the transition metal during the catalytic cycle$^{30-32}$ and eliminates the possibility that the mechanism involves simple deprotonation of the fluoroarene.

Two plausible mechanistic manifolds for the functionalization of C$_6$F$_5$D with cis-(1-propenyl)SnBu$_3$ that invoke the oxidative addition product L$_2$NiD(C$_6$F$_5$), where L is the ancillary ligand, are shown in Figure 3.4. One possibility is that the reaction occurs by oxidative addition of C–H and Sn–C bonds to Ni centers, pure $\sigma$-bond metathesis, or some combination of these processes.$^{33}$ An example of this mechanistic manifold showing oxidative addition of the C–H bond of the fluoroarene and $\sigma$-bond metathesis to form the new C–Sn bond is shown in Figure 3.4 as mechanism A. In this mechanism, the double bond
of the propenyl group coordinates to the metal, which brings the SnBu$_3$ and C$_6$F$_5$ substituents into close enough proximity to undergo $\sigma$-bond metathesis. Reductive elimination of cis-propene-$d_1$ followed by oxidative addition of C$_6$F$_5$D regenerates L$_2$NiD(C$_6$F$_5$). Mechanism B involves 1,2-insertion of the vinyl moiety into Ni–D bond or a step H-transfer, followed by $\beta$-elimination of the SnBu$_3$ group. Mechanism B would produce trans-propene-$d_1$ and thus can be differentiated from mechanism A.
Figure 3.4. Two possible reaction pathways for C–Sn bond formation.

Experimentally, the functionalization of C₆F₅D with cis-(1-propenyl)SnBu₃ was observed to liberate almost exclusively trans-propene-d₁ at 50 % conversion, as identified by NMR spectroscopy. The ¹H NMR spectrum of the reaction mixture features two resonances
for \textit{trans}-propene-\textit{d}_1. The hydrogen attached to C–1 that is \textit{cis} to the methyl group was at \(\delta\) 4.99, with a 17.0 Hz coupling to C–2 hydrogen, and a 1.7 Hz quartet coupling to the methyl group. The C–2 hydrogen geminal to the methyl group further revealed the location of the deuterium label, with a 1.5 Hz \textit{cis} HD coupling, as expected when the gyromagnetic ratios for hydrogen and deuterium are considered, providing a small 1:1:1 triplet splitting of the 17 Hz doublet and 6.4 Hz quartet splitting. The \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum was also definitive regarding the carbon to which the deuterium is attached. Only C–1 has a \(^1J_{\text{CD}}\) coupling, which was a 1:1:1 triplet with a distinctive 24.5 Hz coupling at \(\delta\) 115.6. The C–2 carbon at \(\delta\) 115.6 was a singlet at \(\delta\) 133.6. Reaction with a mixture of pentafluorobenzene-\textit{d}_1 and a mixture of \textit{cis}- and \textit{trans}-1-propenyl-tributyltin catalysed by Ni(COD)\textsubscript{2} and MeNC\textsubscript{5}H\textsubscript{4}Ni\textsubscript{\textit{i}Pr} provided both \textit{cis}- and \textit{trans}-1-deuteropropene, which confirmed that the single isotopomer of deuteropropene obtained using \textit{cis}-(1-propenyl)SnBu\textsubscript{3} is not due to initial isomerization of the vinyl reagent. The formation of \textit{trans}-propene-\textit{d}_1 supports mechanistic manifold B, where oxidative addition, \(\beta\)-elimination of syn-coplanar SnBu\textsubscript{3}, and reductive elimination or a combination of these processes accounts for Sn–C bond formation. This reaction pathway provides an unexpected route to facile C–H bond functionalization under mild conditions.

### 3.3 Conclusions

Although the past decade has seen significant progress in the direct conversion of C–H bonds to C–C, C–N, and C–O bonds, few reactions are available that can function with a wide range of substrates and convert hydrocarbons to versatile functional-group-containing materials. The stannylation reaction reported here provides a facile route to fluorinated arenes with a range of substitution patterns from commercially available chemicals. The stannanes produced here have the potential to serve as a library of compounds for the synthesis of fluorinated pharmaceuticals bearing a variety of substitution patterns\textsuperscript{34-36} among many possible applications. It has been noted that although fluorine substituents adjacent to aromatic C–H bonds thermodynamically favor oxidative addition because of stronger carbon–metal bonds, it has been proposed that these bonds are actually more difficult to catalytically functionalize because of this increased bond strength\textsuperscript{37}. A greater scope of substrates may be accessible with catalysts involving second- and third-row metals, which are capable of C–H bond activation of unactivated arenes such as those commonly used in
Also of interest is the extension of the scope of this methodology to the synthesis of other carbon–heteroatom bonds. Efforts to identify active catalysts and substrates are underway.

### 3.4 Experimental

#### 3.4.1 General Procedures

All reactions were performed under an atmosphere of dry oxygen-free dinitrogen by means of standard Schlenk or glovebox techniques. Benzene-$d_6$ was dried by refluxing with Na/K and was then vacuum transferred and degassed by three freeze-pump-thaw cycles. All other solvents were purchased anhydrous from Aldrich and further purified using a Grubbs’ type column system, produced by Innovative Technology. $^1$H, $^{13}$C{$^1$H}, $^{19}$F{$^1$H}, and $^{119}$Sn{$^1$H} NMR spectra were recorded on a Bruker AMX Spectrometer operating at 300 MHz or where stated at 500 MHz with respect to proton nuclei. $^1$H NMR spectra were referenced to residual protons (C$_6$D$_6$, δ 7.15, CDCl$_3$, δ 7.24) with respect to tetramethylsilane at δ 0.00. $^{13}$C{$^1$H} spectra were referenced relative to solvent resonances (C$_6$D$_6$, δ 128.0). $^{19}$F{$^1$H} NMR spectra were referenced to an external sample of 80 % CCl$_3$F in CDCl$_3$ at δ 0.0. $^{119}$Sn{$^1$H} NMR spectra were referenced to an external sample of SnMe$_4$ at δ 0.0. C$_6$D$_6$ was purchased from Cambridge Isotope Laboratory. The compounds pentafluorobenzene, 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-tetrafluorobenzene, 1,3,5-, 1,2,4-, and 1,2,3-trifluorobenzene, 1,2-, 1,3-, and 1,4-difluorobenzene, fluorobenzene, 2,3,5,6-tetrafluoropyridine, CH$_2$=CHSnBu$_3$, and Sn$_2$Me$_6$ were purchased from Aldrich. The compounds 2,4,6- and 2,3,5-trifluoropyridine, cis-(1-propenyl)SnBu$_3$ and cis-trans-(1-propenyl)SnBu$_3$ were purchased from Alfa Aesar. The compounds $^3$Pr$_3$P, Et$_3$P, Cy$_3$P, and $^3$Bu$_3$P were purchased from Strem Chemicals. The compounds MeNC$_5$H$_4$N$i$Pr, CH$_2$=CHSnMe$_3$, Ni(COD)$_2$, Pt(COD)$_2$, Pt(PCy$_3$)$_2$, C$_6$F$_5$D$_4$ and C$_6$F$_4$HD$_4$ were prepared by literature procedures. High Resolution Mass Spectrometry was performed at McMaster University, Hamilton, Ontario, Canada. Note the method used for HRMS was positive-ion electron impact (EI), this is a high impact method and the loss of a butyl group for compounds 3.1–3.22 can be expected as EI often brings about the loss of R from R’SnR$_3$.45,46
It should be noted that reactions where a single product was obtained, passing the crude mixture through a silica plug and removal of volatiles in vacuo was sufficient in purifying the resulting oil as confirmed by $^1$H, $^{19}$F{$^1$H}, and $^{31}$P{$^1$H} NMR spectroscopy. This technique suitably removed all of the nitrogen donor or $^i$Pr$_3$P, and COD. In the reactions where multiple products were obtained, such as in the synthesis of the di- or tri-substituted products, further purification by a C$_{18}$ reverse-phase silica column was used to separate the mono-substituted product from the di- or tri-substituted products. The mono-substituted products elute from the column first through numerous methanol washes; subsequent washes with toluene suitably removed the di- and tri-substituted products from the column. Removal of the volatiles in vacuo resulted in pure products as confirmed by $^1$H and $^{19}$F{$^1$H} NMR spectroscopy.

3.4.2 Synthesis, Characterization and Reactivity of Complexes

Synthesis of tributyl(2,3,4,5,6-pentafluorophenyl)stannane (3.1). A solution of C$_6$F$_5$H (0.187 g, 1.11 mmol) and CH$_2$=CHSnBu$_3$ (0.176 g, 0.555 mmol) in 0.6 g of C$_6$D$_6$ was added to MeNC$_5$H$_4$iPr (0.005 g, 0.033 mmol) and Ni(COD)$_2$ (0.004 g, 0.017 mmol). The solution was heated at 35 °C for 1 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (95 % yield by NMR spectroscopy; isolated 0.178 g, 70 % yield). $^1$H NMR (C$_6$D$_6$, 25 °C, 300.13 MHz): $\delta$ 0.88 (t, 9H, CH$_3$, $^3$J$_{HH}$ = 7.0 Hz); 1.16 (m with Sn satellites, 6H, SnCH$_2$H, $^2$J$_{HSn}$ = 54.0 Hz, $^3$J$_{HH}$ = 8.3 Hz); 1.31 (dt, 6H, SnCH$_2$CH$_2$CH$_2$, $^3$J$_{HH}$ = 7.7 Hz, $^3$J$_{HH}$ = 7.2 Hz); 1.51 (tt, 6H, SnCH$_2$CH$_2$H, $^3$J$_{HH}$ = 8.5 Hz, $^3$J$_{HH}$ = 7.7 Hz). $^{19}$F{$^1$H} NMR (C$_6$D$_6$, 25 °C, 282.40 MHz): $\delta$ –121.3 (AA'MM'N second order with Sn satellites, 2F, 2,6–Ar–F, $^3$J$_{FSn}$ = 7.7 Hz); –153.0 (tt with Sn satellites, 1F, 4–Ar–F, $^3$J$_{FF}$ = 19.9 Hz, $^4$J$_{FF}$ = 1.8 Hz, $^5$J$_{FSn}$ = 7.4 Hz); –160.7 (AA'MM'N second order, 2F, 3,5–Ar–F). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 25 °C, 75.47 MHz): $\delta$ 11.7 (t with Sn satellites, SnCH$_2$, $^1$J$_{CSn(119)}$ = 359 Hz, $^1$J$_{CSn(117)}$ = 343 Hz, $^4$J$_{CF}$ = 2.0 Hz); 13.7 (s, CH$_3$); 27.5 (s with Sn satellites, SnCH$_2$CH$_2$, $^2$J$_{CSn(119)}$ = 65.9 Hz, $^2$J$_{CSn(117)}$ = 63.1 Hz); 29.2 (s with Sn satellites, SnCH$_2$CH$_2$CH$_2$, $^3$J$_{CSn}$ = 21.3 Hz); 110.9 (t, 1–Ar–C, $^2$J$_{CF}$ = 53.7 Hz); 137.2 (dm, Ar–C, $^1$J$_{CF}$ = 254.9 Hz); 141.7 (dm, Ar–C, $^1$J$_{CF}$ = 251.1 Hz); 149.0 (dm, Ar–C, $^1$J$_{CF}$ = 234.1 Hz).
Alternate synthesis of tributyl(2,3,4,5,6-pentafluorophenyl)stannane (3.1). A solution of C₆F₅H (0.057 g, 0.335 mmol) in toluene was added to a mixture of CH₂=CHSnBu₃ (0.106 g, 0.335 mmol), iPr₃P (0.0054 g, 0.033 mmol), and Ni(COD)₂ (0.0046 g, 0.017 mmol). The solution is heated at 80 °C for 3 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (98 % yield by NMR spectroscopy).

Synthesis of tributyl(2,3,5,6-tetrafluorophenyl)stannane (3.2). To a solution of 1,2,4,5-C₆F₄H₂ (0.417 g, 2.76 mmol) and CH₂=CHSnBu₃ (0.176 g, 0.55 mmol) in 0.6 g of C₆D₆ was added MeNC₅H₄N iPr (0.005 g, 0.033 mmol) and Ni(COD)₂ (0.004 g, 0.0167 mmol). The solution was heated at 35 °C for 30 min, filtered through silica and the solvent was removed, leaving a colourless oil. (95 % yield by NMR spectroscopy). 

Alternate synthesis of tributyl(2,3,5,6-tetrafluorophenyl)stannane (3.2). A solution of 1,2,4,5-C₆F₄H₂ (0.250 g, 1.7 mmol) in toluene was added to a mixture of CH₂=CHSnBu₃ (0.106 g, 0.335 mmol), iPr₃P (0.0054 g, 0.033 mmol), and Ni(COD)₂ (0.0046 g, 0.017 mmol). The solution was heated at 80 °C for 10 min. The reaction mixture was filtered
through silica and the solvent was removed, leaving a colourless oil. (93 % yield by NMR spectroscopy, 7 % of 3.3).

**Synthesis of 2,3,5,6-tetrafluorophenyl-1,4-bis(tributylstannane) (3.3).** To a solution of 1,2,4,5-C₆F₄H₂ (0.083 g, 0.55 mmol) and CH₂=CHSnBu₃ (0.440 g, 1.39 mmol) in 0.6 g of C₆D₆ was added MeNC₅H₄N iPr (0.005 g, 0.033 mmol) and Ni(COD)₂ (0.004 g, 0.017 mmol). The solution was heated to 45 °C for 6 h, filtered through silica and the solvent removed, leaving a colourless oil. (85 % yield by NMR spectroscopy, 11% of 3.2). 

**Alternate synthesis of 2,3,5,6-tetrafluorophenyl-1,4-bis(tributylstannane) (3.3).** A solution of 1,2,4,5-C₆F₄H₂ (0.051 g, 0.335 mmol) and CH₂=CHSnBu₃ (0.265 g, 0.835 mmol) in toluene was added to a mixture of iPr₃P (0.0054 g, 0.033 mmol) and Ni(COD)₂ (0.0046 g, 0.017 mmol). The solution was heated at 80 °C for 8 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (99 % yield by NMR spectroscopy).

**Synthesis of tributyl(2,3,4,6-tetrafluorophenyl)stannane (3.4).** To a solution of 1,2,3,5-C₆F₄H₂ (0.417 g, 2.76 mmol) and CH₂=CHSnBu₃ (0.176 g, 0.55 mmol) in 0.6 g of C₆D₆ was added MeNC₅H₄N iPr (0.005 g, 0.033 mmol) and Ni(COD)₂ (0.004 g, 0.017 mmol). The solution was heated to 35 °C for 40 min, filtered through silica and the solvent was removed, leaving a colourless oil. (95 % yield by NMR spectroscopy; isolated 0.200 g, 82 % yield).
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Alternate synthesis of tributyl(2,3,4,6-tetrafluorophenyl)stannane (3.4). A solution of 1,2,3,5-C₆F₄H₂ (0.151 g, 1.01 mmol) and CH₂=CHSnBu₃ (0.106 g, 0.335 mmol) in toluene was added to a mixture of iPr₃P (0.0054 g, 0.033 mmol) and Ni(COD)₂ (0.0046 g, 0.017 mmol). The solution was heated at 80 °C for 30 min. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (90 % yield by NMR spectroscopy, 10 % of 3.5).

Synthesis of 2,4,5,6-tetrafluorophenyl-1,3-bis(tributylstannane) (3.5). To a solution of 1,2,3,5-C₆F₄H₂ (0.083 g, 0.55 mmol) and CH₂=CHSnBu₃ (0.440 g, 1.39 mmol) in 0.6 g of C₆D₆ was added MeNC₅H₄N₅Pr (0.005 g, 0.033 mmol) and Ni(COD)₂ (0.004 g, 0.0167 mmol). The solution was heated to 40 °C for 18 h, filtered through silica and the solvent was removed, leaving a colourless oil. (84 % yield by NMR spectroscopy, 12 % of 3.4). ¹H NMR (C₆D₆, 25 °C, 300.13 MHz): δ 0.89 (t, 9H, CH₃, ³J_HH = 7.3 Hz); 1.23 (m, 6H, SnCH₂CH₂CH₂, ³J_HH = 8.6 Hz); 1.34 (qd, 6H, SnCH₂CH₂CH₂, ³J_HH = 7.3 Hz, ³J_HH = 7.4 Hz); 1.58 (tt, 6H, SnCH₂CH₂CH₂, ³J_HH = 7.6 Hz, ³J_HH = 8.6 Hz). ¹⁹F{¹H} NMR (C₆D₆, 25 °C, 282.40 MHz): δ –
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77.5 (d, 1F, 2–Ar–F, $^3J_{FF} = 15.2$ Hz); –115.9 (d, 2F, 4,6–Ar–F, $^3J_{FF} = 25.3$ Hz); –165.7 (td with Sn satellites, 1F, 5–Ar–F, $^3J_{FF} = 25.3$ Hz, $^4J_{F_{Sn}} = 3.1$ Hz, $^5J_{FF} = 15.2$ Hz). $^{13}$C{${^1}$H} NMR (C$_6$D$_6$, 25 ºC, 75.47 MHz): $\delta$ 11.2 (s with Sn satellites, SnCH$_2$, $^1J_{CSn(119)} = 358$ Hz, $^1J_{CSn(117)} = 342$ Hz); 13.5 (s, CH$_3$); 27.2 (s with Sn satellites, SnCH$_2$CH$_2$, $^2J_{CSn} = 20.7$ Hz); 100.0 (ddm, 1,3–Ar–C, $^2J_{CF} = 50.5$ Hz, $^2J_{CF} = 64.2$ Hz); 133.7 (dm, Ar–C, $^1J_{CF} = 262.8$ Hz); 155.6 (dm, Ar–C, $^1J_{CF} = 237.0$ Hz); 164.9 (dm, Ar–C, $^1J_{CF} = 237.8$ Hz). $^{119}$Sn{${^1}$H} NMR (C$_6$D$_6$, 25 ºC, 111.96 MHz): $\delta$ –28.7 (m AA'XX'YZ second order, $^4J_{Sn_{Sn}} = 3.1$ Hz). Calcd for C$_{30}$H$_{54}$F$_4$Sn$_2$: [M+ – C$_4$H$_9$], 673.1501. Found: m/z 673.1502.

Alternate synthesis of 2,4,5,6-tetrafluorophenyl-1,3-bis(tributylstannane) (3.5). A solution of 1,2,3,5-C$_6$F$_4$H$_2$ (0.051 g, 0.335 mmol) and CH$_2$=CHSnBu$_3$ (0.265 g, 0.835 mmol) in toluene was added to a mixture of iPr$_3$P (0.0054 g, 0.033 mmol) and Ni(COD)$_2$ (0.0046 g, 0.017 mmol). The solution was heated at 80 ºC for 12 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (99 % yield by NMR spectroscopy).

Synthesis of tributyl(2,3,4,5-tetrafluorophenyl)stannane (3.6). To a solution of 1,2,3,4-C$_6$F$_4$H$_2$ (0.417 g, 2.776 mmol) and CH$_2$=CHSnBu$_3$ (0.176 g, 0.55 mmol) in 0.6 g of C$_6$D$_6$ was added MeNC$_5$H$_4$NiPr (0.005 g, 0.033 mmol) and Ni(COD)$_2$ (0.004 g, 0.017 mmol). The solution was heated to 45 ºC for 12 h, filtered through silica and the solvent was removed, leaving a colourless oil. (38 % yield by NMR spectroscopy). $^1$H NMR (C$_6$D$_6$, 25 ºC, 300.13 MHz): $\delta$ 0.90 (t, 9H, CH$_3$, $^3J_{HH} = 7.4$ Hz); 1.10 (m with Sn satellites, 6H, SnCH$_2$, $^2J_{HSn} = 48.1$ Hz, $^3J_{HH} = 8.4$ Hz); 1.31 (qt, 6H, SnCH$_2$CH$_2$CH$_2$, $^3J_{HH} = 7.4$ Hz, $^3J_{HH} = 7.7$ Hz); 1.52 (tt, 6H, SnCH$_2$CH$_2$, $^3J_{HH} = 8.5$ Hz, $^3J_{HH} = 7.7$ Hz); 6.70 (dddd with Sn satellites, 1H, 6–Ar–H, $^3J_{HSn} = 21.0$ Hz, $^3J_{HF} = 2.3$ Hz, $^4J_{HF} = 2.3$ Hz, $^5J_{HF} = 8.1$ Hz). $^{19}$F{${^1}$H} NMR (C$_6$D$_6$, 25 ºC, 282.40 MHz): $\delta$ –120.6 (ddd, 1F, 2–Ar–F, $^3J_{FF} = 27.5$ Hz, $^5J_{FF} = 16.0$ Hz, $^4J_{FF} = 3.0$ Hz, $^3J_{SnF} = 14.3$ Hz); –139.4 (ddd, 1F, 5–Ar–F, $^3J_{FF} = 19.5$ Hz, $^4J_{FF} = 16.0$ Hz $^5J_{FF} = 1.8$ Hz); –155.5 (ddd, 1F, 3–Ar–F, $^3J_{FF} = 27.5$ Hz, $^2J_{FF} = 19.5$ Hz, $^4J_{FF} = 1.8$ Hz); –155.8 (ddd, 1F, 4–Ar–F, $^3J_{FF} = 19.5$ Hz, $^3J_{FF} = 19.5$ Hz, $^4J_{FF} = 3.0$ Hz). $^{13}$C{${^1}$H} NMR (C$_6$D$_6$, 25 ºC, 75.47 MHz): $\delta$ 10.4 (s with Sn satellites, SnCH$_2$, $^1J_{SnC(119)} = 356$ Hz, $^1J_{SnC(117)} = 339$ Hz); 13.8 (s,
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Alternate synthesis of tributyl(2,3,4,5-tetrafluorophenyl)stannane (3.6). A solution of 1,2,3,4-C₆F₄H₂ (0.252 g, 1.67 mmol) and CH₂=CHSnBu₃ (0.106 g, 0.335 mmol) in toluene was added to a mixture of ³Pr₃P (0.0054 g, 0.033 mmol) and Ni(COD)₂ (0.0046 g, 0.017 mmol). The solution was heated at 80 °C for 4 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (95 % yield by NMR spectroscopy).

Synthesis of tributyl(2,3,6-trifluorophenyl)stannane (3.7). To a solution of 1,2,4-C₆F₃H₃ (0.220 g, 1.67 mmol) and CH₂=CHSnBu₃ (0.176 g, 0.55 mmol) in 0.6 g of C₆D₆ was added MeNC₅H₄N°Pr (0.005 g, 0.033 mmol) and Ni(COD)₂ (0.004 g, 0.017 mmol). The solution was heated to 35 °C for 7 h, filtered through silica and the solvent was removed, leaving a colourless oil. (98 % yield by NMR spectroscopy).
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Alternate synthesis of tributyl(2,3,6-trifluorophenyl)stannane (3.7). A solution of 1,2,4-C₆F₃H₃ (0.192 g, 1.456 mmol) and CH₂=CHSnBu₃ (0.115 g, 0.36 mmol) in toluene was added to a mixture of iPr₃P (0.0058 g, 0.036 mmol) and Ni(COD)₂ (0.005 g, 0.018 mmol). The solution was heated at 80 °C for 1 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (98 % yield by NMR spectroscopy).

Synthesis of 2,3,6-trifluorophenyl-1,4-bis(tributylstannane) (3.8). A solution of 1,2,4-C₆F₃H₃ (0.048 g, 0.364 mmol) and CH₂=CHSnBu₃ (0.288 g, 0.910 mmol) in toluene was added to a mixture of iPr₃P (0.0058 g, 0.036 mmol) and Ni(COD)₂ (0.005 g, 0.018 mmol). The solution was heated at 80 °C for 48 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (50 % yield by NMR spectroscopy, 40 % of 3.7 and Sn₂Bu₆, 5 % of 2,4,5-trifluorophenyl-1,3-bis(tributylstannane), 3.9).

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NMR (C₆D₆, 25 ºC, 186.49 MHz): δ –30.5 (virtual quartet, 1Sn, 3J_{SnF} = 9.3 Hz, 3J_{SnF} = 8.6); –31.2 (m, 1Sn, 3J_{SnF} = 21.32 Hz, 3J_{SnF} = 11.44). Calcd for C₃₀H₅₅F₃Sn₂: [M+ – C₄H₉], 655.1596. Found: m/z 655.1594.

2,4,5-trifluorophenyl-1,3-bis(tributylstannane) (3.9). ¹H NMR (C₆D₆, 25 ºC, 300.13 MHz): δ 6.32 (m, 1H, 6–Ar–F). ¹⁹F{¹H} NMR (C₆D₆, 25 ºC, 282.40 MHz): δ –78.9 (dd with Sn satellites, 1F, 2–Ar–F, 3J_{FF} = 19.8 Hz, 5J_{FF} = 3.6 Hz, 3J_{SnF} = 14.7 Hz); –116.7 (dd with Sn satellites, 1F, 4–Ar–F, 3J_{FF} = 24.4 Hz, 5J_{FF} = 19.5 Hz); –143.5 (dd with Sn satellites, 1F, 5–Ar–F, 3J_{FF} = 24.4 Hz, 5J_{FF} = 19.8 Hz, 4J_{SnF} = 3.6 Hz). ¹¹⁹Sn{¹H} NMR (C₆D₆, 25 ºC, 186.49 MHz): δ –29.9 (m, 1Sn, 3–Ar–Sn, 3J_{SnF} = 9.7 Hz, 3J_{SnF} = 7.3); –34.3 (m, 1Sn, 1–Ar–Sn). Calcd for C₃₀H₅₅F₃Sn₂: [M+ – C₄H₉], 655.1596. Found: m/z 655.1594.

Synthesis of tributyl(2,4,6-trifluorophenyl)stannane (3.10). To a solution of 1,3,5-C₆F₃H₃ (0.147 g, 1.11 mmol) and CH₂=CHSnBu₃ (0.176 g, 0.55 mmol) in 0.6 g of C₆D₆ was added MeNC₅H₄N°Pr (0.005 g, 0.033 mmol) and Ni(COD)₂ (0.004 g, 0.017 mmol). The solution was heated to 40 ºC for 4 h, filtered through silica and the solvent was removed, leaving a colourless oil. (91 % yield by NMR spectroscopy; isolated 0.167 g, 83 % yield). ¹H NMR (C₆D₆, 25 ºC, 300.13 MHz): δ 0.87 (t, 9H, C₃H₃, 3J_{HH} = 7.3 Hz); 1.18 (m with Sn satellites, 6H, SnCH₂, 3J_{HH} = 8.7 Hz); 1.13 (qt, 6H, SnCH₂CH₂C₃H₂, 3J_{HH} = 7.6 Hz, 3J_{HH} = 7.3 Hz); 1.54 (tt, 6H, SnCH₂CH₂, 3J_{HH} = 8.9 Hz, 3J_{HH} = 7.5 Hz); 6.34 (AA'XYY' second order, 2H, 3,5–Ar–H, 3J_{HF} = 9.1, 3J_{HF} = 5.9 Hz). ¹⁹F{¹H} NMR (C₆D₆, 25 ºC, 282.40 MHz): δ –90.3 (d, 2F, 2,6–Ar–F, 3J_{FF} = 8.2 Hz, 4J_{FF} = 0.3 Hz); –108.7 (t with Sn satellites, 1F, 4–Ar–F, 3J_{FF} = 8.2 Hz, 5J_{FF} = 3.1 Hz). ¹³C{¹H} NMR (C₆D₆, 25 ºC, 75.47 MHz): δ 11.2 (t with Sn satellites, SnCH₂, ¹JC_{Sn(119)} = 361 Hz, ¹JC_{Sn(117)} = 349 Hz ¹JC = 1.7 Hz); 13.8 (s, C₃H₃); 27.6 (s with Sn satellites, SnCH₂CH₂, ²JC_{Sn(119)} = 64 Hz, ²JC_{Sn(117)} = 62 Hz); 29.4 (s with Sn satellites, SnCH₂CH₂CH₂, ³JC = 20.7 Hz); 9.97 (dd, 1–Ar–C, ²JC = 33.6 Hz, ²JC = 24.6 Hz, ³JC = 5.0 Hz); 109.1 (td, 1–Ar–C, ²JC = 51.0 Hz, ³JC = 4.2 Hz, ¹JC = 239.3 Hz); 164.9 (dt, 4–Ar–C, ¹JC = 248.2 Hz, ³JC = 14.6 Hz); 168.1 (dd, 2,6–Ar–C, ¹JC = 237.7 Hz, ³JC = 23.7 Hz, ³JC = 14.7 Hz). ¹¹⁹Sn{¹H} NMR (C₆D₆, 25 ºC, 111.96 MHz): δ –31.0 (td, 3J_{SnF} = 8.9 Hz, ⁵J_{SnF} = 3.1 Hz). Calcd for C₁₈H₂₉F₃Sn: [M+ – C₄H₉], 365.0539. Found: m/z 365.0519.
Alternate synthesis of tributyl(2,4,6-trifluorophenyl)stannane (3.10). A solution of 1,3,5-
C₆F₃H₃ (0.144 g, 1.092 mmol) and CH₂=CHSnBu₃ (0.106 g, 0.364 mmol) in toluene was
added to a mixture of iPr₃P (0.0058 g, 0.036 mmol) and Ni(COD)₂ (0.005 g, 0.018 mmol).
The solution was heated at 80 °C for 30 min. The reaction mixture was filtered through silica
and the solvent was removed, leaving a colourless oil. (83 % yield by NMR spectroscopy,
17 % of 3.11).

Synthesis of 2,4,6-trifluorophenyl-1,3-bis(tributylstannane) (3.11). To a solution of 1,3,5-
C₆F₃H₃ (0.061 g, 0.47 mmol) and CH₂=CHSnBu₃ (0.296 g, 0.93 mmol) in 0.6 g of C₆D₆ was
added MeNC₅H₄NPr (0.007 g, 0.047 mmol) and Ni(COD)₂ (0.006 g, 0.023 mmol). The
solution was heated to 40 °C for 18 h, filtered through silica and the solvent was removed,
leaving a colourless oil. (38 % yield by NMR spectroscopy, 55 % of 3.10). ¹H NMR (C₆D₆,
25 °C, 300.13 MHz): δ 0.90 (t, 18H, C₃H₃, 3JHH = 7.2 Hz); 1.27 (m with Sn satellites, 12H,
SnCH₂, 3JHH = 8.4 Hz); 1.36 (qt, 6H, SnCH₂CH₂CH₂, 3JHH = 7.8 Hz, 3JHH = 7.2 Hz); 1.62 (tt,
6H, SnCH₂CH₂, 3JHH = 7.6 Hz, 3JHH = 7.3 Hz); 6.50 (td with Sn satellites, 1H, 5–Ar–H, 3JHF
= 8.6, 5JHF = 2.8 Hz, 4JSnF = 6.9 Hz). ¹⁹F{¹H} NMR (C₆D₆, 25 °C, 282.40 MHz): δ –71.0 (t
with Sn satellites, 1F, 2–Ar–F, 4JFF = 2.5 Hz, 3JFSn = 5 Hz); –90.7 (d with Sn satellites, 2F,
4,6–Ar–F, 4JFF = 2.4 Hz, 3JSnF = 8 Hz). ¹³C{¹H} NMR (C₆D₆, 25 °C, 75.47 MHz): δ 11.3 (br s
with Sn satellites, SnCH₂, 1JCSn(119) = 367 Hz, 1JCSn(117) = 348 Hz); 13.8 (s, CH₃); 27.5 (s with
Sn satellites, SnCH₂, 2JCSn = 64 Hz); 29.4 (s with Sn satellites, SnCH₂CH₂, 3JCSn =
21 Hz); 99.5 (td, 5–Ar–C, 2JCF = 31.7 Hz, 4JCF = 5.7 Hz); 108.3 (dd, 1,3–Ar–C, 2JCF = 60.0
Hz, 2JCF = 53.3 Hz); 169.5 (ddd, 4,6–Ar–C, 1JCF = 238.3 Hz, 3JCF = 22.2 Hz, 3JCF = 14.6 Hz);
172.5 (dt, 2–Ar–C, 1JCF = 228.5 Hz, 3JCF = 23.2 Hz). ¹¹⁹Sn{¹H} NMR (C₆D₆, 25 °C, 111.96
MHz): δ –31.5 (virtual quartet, 3JSnF = 6.4 Hz, 2JSnF = 5.8 Hz).

Alternate synthesis of 2,4,6-trifluorophenyl-1,3-bis(tributylstannane) (3.11). A solution
of 1,3,5-C₆F₃H₃ (0.048 g, 0.364 mmol) and CH₂=CHSnBu₃ (0.288 g, 0.910 mmol) in toluene
was added to a mixture of iPr₃P (0.0058 g, 0.036 mmol) and Ni(COD)₂ (0.005 g, 0.018
mmol). The solution was heated at 80 °C for 12 h. The reaction mixture was filtered through
silica and the solvent was removed, leaving a colourless oil. (45 % yield by NMR spectroscopy, 50 % yield 3.12, 2 % yield 3.10).
Synthesis of 2,4,6-trifluorophenyl-1,3,5-tris(tributylstannane) (3.12). A solution of 1,3,5-C₆F₃H₃ (0.048 g, 0.364 mmol) and CH₂=CHSnBu₃ (0.404 g, 1.27 mmol) in toluene was added to a mixture of iPr₃P (0.0058 g, 0.036 mmol) and Ni(COD)₂ (0.005 g, 0.018 mmol). The solution was heated at 80 °C for 18 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (95 % yield by NMR spectroscopy, 5 % of 3.11). ¹H NMR (C₆D₆, 25 °C, 300.13 MHz): δ 0.93 (t, 9H, SnCH₂CH₂CH₂C₃H₃, ³JHH = 6.5 Hz); 1.26 (m, 6H, SnCH₂, ³JHH = 8.1 Hz); 1.38 (qt, 6H, SnCH₂CH₂CH₂, ³JHH = 7.7 Hz, ⁴JHH = 6.5 Hz); 1.65 (m, 6H, SnCH₂CH₂, ³JHH = 7.7 Hz). ¹⁹F{¹H} NMR (C₆D₆, 25 °C, 282.40 MHz): δ –73.0 (s with Sn satellites, 3F, ⁴JFSn = 44.2 Hz). ¹³C{¹H} NMR (C₆D₆, 25 °C, 75.47 MHz): δ 11.4 (s with Sn satellites, SnCH₂, ¹JCsn(119) = 360.9 Hz, ¹JCsn(117) = 341.3 Hz); 13.9 (s, SnCH₂CH₂CH₂CH₂); 27.6 (s with Sn satellites, SnCH₂CH₂, ²JCsn = 64 Hz); 29.4 (s with Sn satellites, SnCH₂CH₂CH₂, ³JCsn = 22 Hz); 107.4 (td with Sn satellites, 1,3,5–Ar–C, ²JC = ²JCsn = 57.75 Hz, ⁴JC = 3.17 Hz, ¹JCsn = 252 Hz); 174.2 (d with Sn satellites, 2,4,6–Ar–C, ¹JC = 228.08 Hz, ²JCsn = 22.92 Hz). ¹¹⁹Sn{¹H} NMR (C₆D₆, 25 °C, 111.96 MHz): δ –32.2 (m, ⁴JSnF = 7.28 Hz, ⁵JSnF = 1.4 Hz).

Synthesis of tributyl(2,3,5,6-tetrafluoropyridyl)stannane (3.13). A solution of 2,3,5,6-C₅F₄HN (0.101 g, 0.67 mmol) and CH₂=CHSnBu₃ (0.106 g, 0.33 mmol) in 0.6 g of C₆D₆ was added to MeNC₅H₄N+iPr (0.005 g, 0.033 mmol) and Ni(COD)₂ (0.004 g, 0.017 mmol). The solution was heated at 40 °C for 14 h. The reaction mixture was filtered through silica and the solvent was removed, leaving clear oil. (91 % yield by NMR spectroscopy; isolated 0.104 g, 72 %). ¹H NMR (C₆D₆, 25 °C, 300.13 MHz): δ 0.89 (t, 9H, SnCH₂CH₂CH₂CH₃, ³JHH = 6.6 Hz); 1.17 (m, 6H, SnCH₂, ³JHH = 7.7 Hz); 1.29 (qt, 6H, SnCH₂CH₂CH₂, ³JHH = 6.9 Hz, ³JHH = 6.6 Hz); 1.49 (tt, 6H, SnCH₂CH₂, ³JHH = 7.7 Hz, ³JHH = 6.6 Hz). ¹⁹F{¹H} NMR (C₆D₆, 25 °C, 282.40 MHz): δ –93.5 (AA'MM' second order, 2F, 2,6–Ar–F); -125.4 (AA'MM' second order, 2F, 2,6–Ar–F). ¹³C{¹H} NMR (C₆D₆, 25 °C, 75.47 MHz): δ 11.6 (t with Sn satellites, SnCH₂, ¹JCsn(119) = 359.7 Hz, ¹JCsn(117) = 341.6 Hz, ⁴JC = 1.8 Hz); 13.7 (s with Sn satellites, SnCH₂CH₂CH₂CH₃, ⁴JCsn = 2.7 Hz); 27.4 (s with Sn satellites, SnCH₂CH₂, ²JCsn(119) = 66.8 Hz, ²JCsn(117) = 63.3 Hz); 29.0 (s with Sn satellites, SnCH₂CH₂CH₂, ³JCsn = 21.1 Hz); 118.4 (tm, 1–Ar–C, ²JC = 21.1 Hz); 143.7 (ddddd second order, 2,6–Ar–C, ¹JC = 234.5 Hz, J = 24.1, 10.3, 1.7 Hz); 145.3 (dm second order, 3,5–Ar–C, ¹JC = 244.8 Hz).
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$^{119}\text{Sn}^1\text{H}$ NMR (C$_6$D$_6$, 25 °C, 111.95 MHz): $\delta$ –19.3 (tt, $^3J_{\text{SnF}}$ = 11.26 Hz, $^4J_{\text{SnF}}$ = 7.0 Hz). Calcd for C$_{17}$H$_{27}$F$_4$NSn: [M+ – C$_4$H$_9$], 384.0397. Found: m/z 384.0387.

Alternate Synthesis tributyl(2,3,5,6-tetrafluoropyridyl)stannane (3.13). A solution of 2,3,5,6-C$_3$F$_4$HN (0.110 g, 0.73 mmol) in toluene was added to a mixture of CH$_2$=CHSnBu$_3$ (0.231 g, 0.73 mmol), iPr$_3$P (0.0116 g, 0.073 mmol), and Ni(COD)$_2$ (0.01 g, 0.036 mmol). The solution was heated at 80 °C for 2 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a pale orange oil. (98 % yield by NMR spectroscopy; isolated 0.277 g, 87 %).

Synthesis of 2,3,5-trifluoro-4-(tributylstannyl)pyridine (3.14). A solution of 2,3,5-C$_5$F$_3$H$_2$N (0.044 g, 0.33 mmol) and CH$_2$=CHSnBu$_3$ (0.106 g, 0.33 mmol) in 0.6 g of C$_6$D$_6$ was added to MeNC$_5$H$_4$N$i$Pr (0.005 g, 0.033 mmol) and Ni(COD)$_2$ (0.004 g, 0.017 mmol). The solution was heated at 45 °C for 1 h. The reaction mixture was filtered through silica and the solvent was removed, leaving clear oil. (85 % yield by NMR spectroscopy; isolated 0.086 g, 62 %). $^1$H NMR (C$_6$D$_6$, 25 °C, 300.13 MHz): $\delta$ 0.86 (t, 9H, SnCH$_2$CH$_2$CH$_2$CH$_3$, $^3J_{\text{HH}}$ = 7.3 Hz); 1.15 (m, 6H, SnCH$_2$, $^3J_{\text{HH}}$ = 7.8 Hz); 1.28 (qt, 6H, SnCH$_2$CH$_2$CH$_2$, $^3J_{\text{HH}}$ = 7.5 Hz, $^3J_{\text{HH}}$ = 7.3 Hz); 1.47 (tt, 6H, SnCH$_2$CH$_2$, $^3J_{\text{HH}}$ = 7.7 Hz, $^3J_{\text{HH}}$ = 7.5 Hz); 7.49 (t with Sn satellites, 1H, py–H, $^3J_{\text{HF}}$ = 2.3 Hz, $^4J_{\text{HFSn}}$ = 9.0 Hz. $^{19}$F$^1$H NMR (C$_6$D$_6$, 25 °C, 282.40 MHz): $\delta$ –92.1 (dd with Sn satellites, 1F, Ar–F, $^3J_{\text{FF}}$ = 32.4 Hz, $^4J_{\text{FF}}$ = 30.6 Hz, $^3J_{\text{FSn}}$ = 10.2 Hz); –112.7 (d, 1F, Ar–F, $^3J_{\text{FF}}$ = 32.5 Hz); –118.8 (d with Sn satellites, 1F, Ar–F, $^4J_{\text{FF}}$ = 30.6 Hz, $^3J_{\text{FSn}}$ = 5.2 Hz). $^{13}$C$^1$H NMR (C$_6$D$_6$, 25 °C, 75.47 MHz): $\delta$ 11.4 (t with Sn satellites, SnCH$_2$, $^1J_{\text{Csn(119)}}$ = 359.0 Hz, $^1J_{\text{Csn(117)}}$ = 342.4 Hz, $^4J_{\text{CF}}$ = 1.8 Hz); 13.7 (s, SnCH$_2$CH$_2$CH$_2$CH$_3$); 27.4 (s with Sn satellites, SnCH$_2$CH$_2$, $^2J_{\text{Csn(119)}}$ = 66.8 Hz, $^2J_{\text{Csn(117)}}$ = 65.7 Hz); 29.1 (s with Sn satellites, SnCH$_2$CH$_2$CH$_2$, $^3J_{\text{Csn}}$ = 20.4 Hz); 129.7 (dd, py–C, $^2J_{\text{CF}}$ = 49.7 Hz, $^2J_{\text{CF}}$ = 43.0 Hz); 148.3 (dm, py–C, $^1J_{\text{CF}}$ = 234.2 Hz); 148.8 (dm, py–C, $^1J_{\text{CF}}$ = 252.2 Hz); 161.2 (dm, py–C, $^1J_{\text{CF}}$ = 243.4 Hz). $^{119}$Sn$^1$H NMR (C$_6$D$_6$, 25 °C, 111.95 MHz): $\delta$ –19.3 (ddd, $^3J_{\text{SnF}}$ = 10.4 Hz, $^3J_{\text{SnF}}$ = 5.0 Hz, $^4J_{\text{SnF}}$ = 2.3 Hz).

Alternate Synthesis 2,3,5-trifluoro-4-(tributylstannyl)pyridine (3.14). A solution of 2,3,5-C$_5$F$_3$H$_2$N (0.121 g, 0.91 mmol) in toluene was added to a mixture of CH$_2$=CHSnBu$_3$ (0.115 g, 0.36 mmol), iPr$_3$P (0.0058 g, 0.036 mmol), and Ni(COD)$_2$ (0.005 g, 0.018 mmol).
The solution was heated at 80 °C for 24 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (97% yield by NMR spectroscopy).

**Synthesis of 2,4,6-trifluoro-3-(tributylstannyl)pyridine (3.15).** A solution of 2,4,6-C₅F₃H₂N (0.044 g, 0.33 mmol) and CH₂=CHSnBu₃ (0.106 g, 0.33 mmol) in 0.6 g of C₆D₆ was added to MeNC₅H₄N³Pr (0.005 g, 0.033 mmol) and Ni(COD)₂ (0.004 g, 0.017 mmol). The solution was allowed to react at 40 °C for 2 h. (96% yield by NMR spectroscopy). **1H NMR** (CDCl₃, 25 °C, 300.13 MHz): δ 0.91 (t, 9H, SnCH₂CH₂CH₂C₃H₃, 3J_HH = 7.4 Hz); 1.22 (m with Sn satellites, 6H, SnCH₂, 3J_HH = 7.5 Hz, 3J_HSn = 8.2 Hz, 3J_HF = 5.9 Hz, 4J_HSn = 1.5 Hz, 4J_HF = 16.0 Hz, 4J_FF = 12.4 Hz); 1.35 (qt, 6H, SnCH₂CH₂H₂, 3J_HH = 8.2 Hz, 3J_HH = 7.5 Hz, 3J_HSn = 7.2 Hz); 1.55 (tt, 6H, SnCH₂CH₂H₂, 3J_HH = 8.2 Hz, 3J_HH = 7.5 Hz); 6.50 (dd, 1H, py–H, 3J_HF = 5.9 Hz, 4J_HF = 12.4 Hz); –67.5 (dd, 1F, Ar–F, 4J_FF = 16.0 Hz, 4J_FF = 12.4 Hz); –76.8 (d, 1F, Ar–F, 4J_FF = 12.6 Hz). **13C{1H} NMR** (CDCl₃, 25 °C, 75.47 MHz): δ 11.1 (s with Sn satellites, SnCH₂, 1J_CSn(119) = 362.1 Hz, 1J_CSn(117) = 347.2 Hz); 13.7 (s, SnCH₂CH₂CH₂CH₃); 27.3 (s with Sn satellites, SnCH₂CH₂CH₂, 2J_CSn = 64.1 Hz); 29.0 (s with Sn satellites, SnCH₂CH₂CH₂, 3J_CSn = 21.2 Hz); 94.5 (ddd, py–C, 2J_CF = 38.0 Hz, 2J_CF = 30.9 Hz, 4J_CF = 7.2 Hz); 104.1 (m, py–C); 164.3 (dm, py–C, 1J_CF = 243.5 Hz); 167.1 (dm, py–C, 1J_CF = 234.5 Hz); 178.6 (dm, py–C, 1J_CF = 252.6 Hz). **119Sn{1H} NMR** (C₆D₆, 25 °C, 111.95 MHz): δ –28.8 (m, Sn, 3J_SnF = 17.6 Hz).

**Alternate Synthesis 2,4,6-trifluoro-3-(tributylstannyl)pyridine (3.15).** A solution of 2,4,6-C₅F₃H₂N (0.121 g, 0.91 mmol) in toluene was added to a mixture of CH₂=CHSnBu₃ (0.115 g, 0.36 mmol), iPr₃P (0.0058 g, 0.036 mmol), and Ni(COD)₂ (0.005 g, 0.018 mmol). The solution was heated at 80 °C for 12 h. The reaction mixture was filtered through silica and the solvent was removed, leaving pale orange oil. (96% yield by NMR spectroscopy, 4% 3.16).

**2,4,6-trifluoro-3,5-bis(tributylstannyl)pyridine (3.16).** **1H NMR** (CDCl₃, 25 °C, 300.13 MHz): δ 0.91 (t, 18H, SnCH₂CH₂CH₂CH₂, 3J_HH = 7.5 Hz); 1.21 (m with Sn satellites, 12H, SnCH₂, 3J_HH = 8.0 Hz, 3J_HH = 8.4 Hz, 3J_HSn = 51.0 Hz); 1.35 (qt, 12H, SnCH₂CH₂CH₂H₂, 3J_HH = 7.5 Hz, 3J_HH = 7.9 Hz); 1.55 (tt, 12H, SnCH₂CH₂, 3J_HH = 8.3 Hz, 3J_HH = 7.9 Hz). **19F{1H}**
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NMR (CDCl₃, 25 °C, 282.40 MHz): δ –52.9 (d, 2F, Ar–F, ⁴J₉F = 19.0 Hz); –60.2 (t, 1F, Ar–F, ⁴J₉F = 19.1 Hz). ¹³C{¹H} NMR (CDCl₃, 25 °C, 75.47 MHz): δ 9.5 (s with Sn satellites, SnCH₂, ¹¹JCSn(119) = 334.3 Hz, ¹¹JCSn(117) = 328.1 Hz); 13.9 (s, SnCH₂CH₂CH₂CH₃); 27.5 (s with Sn satellites, SnCH₂CH₂, ²JCSn = 53.7 Hz); 29.3 (s with Sn satellites, SnCH₂CH₂CH₂, ³JCSn = 21.1 Hz); 102.6 (ddd, py–C, ²JC₉F = 64.3 Hz, ²JC₉F = 58.1 Hz, ⁴JC₉F = 3.6 Hz); 168.9 (dm, py–C, ¹JC₉F = 247.5 Hz). ¹¹⁹Sn{¹H} NMR (C₆D₆, 25 °C, 111.95 MHz): δ –29.7 (m, Sn, ³JSnF = 20.7 Hz, ³JSnF = 15.1 Hz, ⁴JSnF = 9.2 Hz).

Alternate Synthesis 2,4,6-trifluoro-3,5-bis(tributylstannyl)pyridine (3.16). A solution of 2,4,6-C₅F₃H₂N (0.0484 g, 0.36 mmol) in toluene was added to a mixture of CH₂=CHSnBu₃ (0.288 g, 0.91 mmol), ²Pr₃P (0.0058 g, 0.036 mmol), and Ni(COD)₂ (0.005 g, 0.018 mmol). The solution was heated at 80 °C for 24 h. The reaction mixture was filtered through silica and the solvent was removed, leaving pale orange oil. (99 % yield by NMR spectroscopy, 1 % 3.15).

Synthesis of tributyl(2,3,4-trifluorophenyl)stannane (3.17). A solution of 1,2,3-C₆F₃H₃ (0.192 g, 1.456 mmol) and CH₂=CHSnBu₃ (0.115 g, 0.36 mmol) in toluene was added to a mixture of ²Pr₃P (0.0058 g, 0.036 mmol) and Ni(COD)₂ (0.005 g, 0.018 mmol). The solution was heated at 80 °C for 48 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (50 % yield by NMR spectroscopy, 30 % of 3.18). ¹H NMR (C₆D₆, 25 °C, 300.13 MHz): δ 0.86 (t, 9H, SnCH₂CH₂CH₂C₃H₃, ³JHH = 7.5 Hz); 1.06 (m with Sn satellites, 6H, SnCH₂, ³JHH = 7.8 Hz, ³JHSn = 51.6 Hz); 1.31 (qt, 6H, SnCH₂CH₂CH₂, ³JHH = 11.4 Hz, ³JHH = 7.1 Hz); 1.52 (tt, 6H, SnCH₂CH₂, ³JHH = 11.4 Hz, ³JHH = 7.8 Hz); 6.58 (m, 1H, 6–Ar–H, ⁴JHF = 2.1, ³JHH = 7.0 Hz); 6.75 (m, 1H, 5–Ar–H, ³JHH = 7.0 Hz). ¹⁹F{¹H} NMR (C₆D₆, 25 °C, 282.40 MHz): δ –117.1 (dd with Sn satellites, 1F, 2–Ar–F, ³J₉F = 27.48, ⁴J₉F = 8.1 Hz, ³J₉Sn = 27.8 Hz); –135.9 (dd, 1F, 4–Ar–F, ³J₉F = 19.51, ⁴J₉F = 8.1 Hz); –161.7 (dd with Sn satellites, 1F, 3–Ar–F, ³J₉F = 27.48, ⁴J₉F = 8.1 Hz, ³J₉Sn = 12.2 Hz). ¹³C{¹H} NMR (C₆D₆, 25 °C, 75.47 MHz): δ 10.3 (s with Sn satellites, SnCH₂, ¹¹JCSn(119) = 354.4 Hz, ¹¹JCSn(117) = 338.3 Hz); 13.9 (s, SnCH₂CH₂CH₂CH₃); 27.6 (s with Sn satellites, SnCH₂CH₂, ²JCSn = 65.7 Hz); 29.3 (s with Sn satellites, SnCH₂CH₂CH₂, ³JCSn = 20 Hz); 113.4 (d with Sn satellites, 1–Ar–C, ²JC₉F = 16 Hz, ²JC₉Sn = 12.2 Hz).
53.7 Hz); 124.2 (dm, 5–Ar–C, $^2J_{CF} = 44.5$ Hz, $^3J_{CF} = 5.6$ Hz); 130.3 (dm, 6–Ar–C, $^3J_{CF} = 17.6$ Hz, $^4J_{CF} = 6.4$ Hz); 140.1 (ddd, 3–Ar–C, $^1J_{CF} = 242.2$ Hz, $^2J_{CF} = 12.0$ Hz, $^2J_{CF} = 7.2$ Hz); 152.2 (ddd, 2–Ar–C, $^1J_{CF} = 242.9$ Hz, $^2J_{CF} = 13.6$ Hz, $^3J_{CF} = 4$ Hz); 155.4 (dm, 4–Ar–C, $^1J_{CF} = 227.7$ Hz, $^3J_{CF} = 5.6$ Hz). $^{119}$Sn$^1{^1}$H NMR (C$_6$D$_6$, 25 °C, 186.49 MHz): $\delta$ –31.8 (ddd, $^3J_{SnF} = 20.72$ Hz, $^4J_{SnF} = 12.24$ Hz, $^5J_{SnF} = 3.59$ Hz). Calcd for C$_{18}$H$_{29}$F$_3$Sn: [M+ – C$_4$H$_9$], 365.0539. Found: m/z 365.0534.

**Synthesis of 2,3,4-trifluorophenyl-1,5-bis(tributylstannane) (3.18).** A solution of 1,2,3-C$_6$F$_3$H$_3$ (0.048 g, 0.364 mmol) and CH$_2$=CHSnBu$_3$ (0.288 g, 0.910 mmol) in toluene was added to a mixture of iPr$_3$P (0.0058 g, 0.036 mmol) and Ni(COD)$_2$ (0.005 g, 0.018 mmol). The solution was heated at 80 °C for 72 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (30 % yield by NMR spectroscopy, 40 % of 3.17 and Sn$_2$Bu$_6$). $^1$H NMR (C$_6$D$_6$, 25 °C, 300.13 MHz): $\delta$ 0.91 (t, 9H, SnCH$_2$CH$_2$CH$_2$CH$_3$, $^3J_{HH} = 7.3$ Hz); 1.18 (m, 6H, SnCH$_2$H$_2$, $^3J_{HH} = 8.1$ Hz); 1.36 (m, 6H, SnCH$_2$CH$_2$CH$_2$H$_2$); 1.59 (m, 6H, 6–Ar–H, $^4J_{HF} = 2.6$, $^3J_{HSn} = 32.9$ Hz). $^{19}$F$^1{^1}$H NMR (C$_6$D$_6$, 25 °C, 282.40 MHz): $\delta$ –118.0 (d with Sn satellites, 2F, 2,4–Ar–F, $^3J_{FF} = 25.9$, $^3J_{FSn} = 17.4$ Hz); –161.6 (t with Sn satellites, 1F, 3–Ar–F, $^3J_{FF} = 25.9$, $^3J_{FSn} = 9.93$ Hz). $^{13}$C$^1{^1}$H NMR (C$_6$D$_6$, 25 °C, 75.47 MHz): $\delta$ 10.4 (s with Sn satellites, SnC$_2$, $^1J_{Sn(119)} = 353.1$ Hz, $^1J_{Sn(117)} = 335.2$ Hz); 13.8 (s, SnCH$_2$CH$_2$CH$_2$CH$_3$); 27.7 (s with Sn satellites, SnCH$_2$CH$_2$, $^2J_{CSn} = 60.2$ Hz); 29.4 (s with Sn satellites, SnCH$_2$CH$_2$CH$_3$, $^3J_{CSn} = 22$ Hz); 125.0 (dd with Sn satellites, 6–Ar–C, $^3J_{CF} = 4.6$ Hz, $^2J_{CSn} = 44.2$ Hz); 137.3 (td with Sn satellites, 1,5–Ar–C, $^2J_{CF} = 16.1$ Hz, $^3J_{CF} = 8.4$ Hz, $^2J_{CSn} = 131.1$ Hz); 152.2 (ddd, 2,4–Ar–C, $^1J_{CF} = 244.5$ Hz, $^2J_{CF} = 12.3$ Hz, $^3J_{CF} = 8.2$ Hz); 156.0 (ddd, 3–Ar–C, $^1J_{CF} = 236.5$ Hz, $^2J_{CF} = 11.6$ Hz, $^3J_{CF} = 7.5$ Hz). $^{119}$Sn$^1{^1}$H NMR (C$_6$D$_6$, 25 °C, 186.49 MHz): $\delta$ –33.4 (m AA'XX'Y second order, $^3J_{CF} = 10.64$ Hz, $^4J_{SnSn} = 5.7$ Hz).

**Synthesis of tributyl(2,6-difluorophenyl)stannane (3.19).** To a solution of 1,3-C$_6$F$_2$H$_4$ (0.180 g, 1.58 mmol) and CH$_2$=CHSnBu$_3$ (0.500 g, 1.58 mmol) in 1 mL of C$_6$D$_6$ was added MeNC$_5$H$_4$N$i$Pr (0.010 g, 0.063 mmol) and Ni(COD)$_2$ (0.009 g, 0.0315 mmol). The solution was allowed to react for 12 h at 37 °C, filtered through silica and the solvent was removed, leaving a colourless oil. (30 % yield by NMR spectroscopy, 30 % Sn$_2$Bu$_6$). $^1$H NMR (C$_6$D$_6$, 25 °C, 300.13 MHz): $\delta$ 0.91 (t, 9H, SnCH$_2$CH$_2$CH$_2$CH$_3$, $^3J_{HH} = 7.3$ Hz); 1.18 (m, 6H, SnCH$_2$H$_2$, $^3J_{HH} = 8.1$ Hz); 1.36 (m, 6H, SnCH$_2$CH$_2$CH$_2$H$_2$); 1.59 (m, 6H, 6–Ar–H, $^4J_{HF} = 2.6$, $^3J_{HSn} = 32.9$ Hz). $^{19}$F$^1{^1}$H NMR (C$_6$D$_6$, 25 °C, 282.40 MHz): $\delta$ –118.0 (d with Sn satellites, 2F, 2,4–Ar–F, $^3J_{FF} = 25.9$, $^3J_{FSn} = 17.4$ Hz); –161.6 (t with Sn satellites, 1F, 3–Ar–F, $^3J_{FF} = 25.9$, $^3J_{FSn} = 9.93$ Hz). $^{13}$C$^1{^1}$H NMR (C$_6$D$_6$, 25 °C, 75.47 MHz): $\delta$ 10.4 (s with Sn satellites, SnC$_2$, $^1J_{Sn(119)} = 353.1$ Hz, $^1J_{Sn(117)} = 335.2$ Hz); 13.8 (s, SnCH$_2$CH$_2$CH$_2$CH$_3$); 27.7 (s with Sn satellites, SnCH$_2$CH$_2$, $^2J_{CSn} = 60.2$ Hz); 29.4 (s with Sn satellites, SnCH$_2$CH$_2$CH$_3$, $^3J_{CSn} = 22$ Hz); 125.0 (dd with Sn satellites, 6–Ar–C, $^3J_{CF} = 4.6$ Hz, $^2J_{CSn} = 44.2$ Hz); 137.3 (td with Sn satellites, 1,5–Ar–C, $^2J_{CF} = 16.1$ Hz, $^3J_{CF} = 8.4$ Hz, $^2J_{CSn} = 131.1$ Hz); 152.2 (ddd, 2,4–Ar–C, $^1J_{CF} = 244.5$ Hz, $^2J_{CF} = 12.3$ Hz, $^3J_{CF} = 8.2$ Hz); 156.0 (ddd, 3–Ar–C, $^1J_{CF} = 236.5$ Hz, $^2J_{CF} = 11.6$ Hz, $^3J_{CF} = 7.5$ Hz). $^{119}$Sn$^1{^1}$H NMR (C$_6$D$_6$, 25 °C, 186.49 MHz): $\delta$ –33.4 (m AA'XX'Y second order, $^3J_{CF} = 10.64$ Hz, $^4J_{SnSn} = 5.7$ Hz).
Chapter 3 – Catalytic C–H Bond Stannylation: A New Regioselective Pathway to C–Sn Bonds via C–H Bond Functionalization

Alternate synthesis of tributyl(2,6-difluorophenyl)stannane (3.19). A solution of 1,3-C₆F₂H₄ (0.100 g, 0.88 mmol) and CH₂=CHSnBu₃ (0.231 g, 0.73 mmol) in toluene was added to a mixture of ³Pr₃P (0.012 g, 0.073 mmol) and Ni(COD)₂ (0.01 g, 0.036 mmol). The solution was heated at 80 °C for 18 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (90 % yield by NMR spectroscopy).

Synthesis of tributyl(2,3-difluorophenyl)stannane (3.20). A solution of 1,2-C₆F₂H₄ (0.381 g, 3.34 mmol) and CH₂=CHSnBu₃ (0.106 g, 0.335 mmol) in toluene was added to a mixture of ³Pr₃P (0.0054 g, 0.033 mmol) and Ni(COD)₂ (0.0046 g, 0.017 mmol). The solution was heated at 80 °C for 18 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (92 % yield by NMR spectroscopy, 2 % of 3.21). ¹H NMR (C₆D₆, 25 °C, 300.13 MHz): δ 0.84 (t, 9H, CH₃, ³J_HH = 7.2 Hz); 1.20 (m with Sn satellites, 6H, SnCH₂, ²J_HSn = 53.5 Hz, ³J_HH = 8.7 Hz); 1.32 (qt, 6H, SnCH₂CH₂CH₂, ³J_HH = 7.5 Hz, ³J_HH = 7.2 Hz); 1.55 (tt, 6H, SnCH₂CH₂, ³J_HH = 8.6 Hz, ³J_HH = 7.6 Hz); 6.57 (dd, 2H, 3,5–Ar–H, ³J_HF = 6.3, ³J_HH = 8.0 Hz); 6.78 (tt, 1H, 4–Ar–H, ³J_HH = 8.0, ³J_HF = 7.1 Hz). ¹⁹F{¹H} NMR (C₆D₆, 25 °C, 282.40 MHz): δ –92.1 (s with Sn satellites, 2F, 2,6–Ar–F, ³J_FSn = 14.5 Hz).
with Sn satellites, 1F, 3–Ar–F, \(^3J_{CF} = 28.5\) Hz, \(^4J_{FSn} = 17.5\) Hz). \(^{13}C\) \({}^1H\) NMR (C\(_6\)D\(_6\), 25 °C, 75.47 MHz): \(\delta\) 10.3 (s, SnCH\(_2\), \(^1J_{CSn(119)} = 353.5\) Hz, \(^1J_{CSn(117)} = 335.9\) Hz); 13.8 (s, SnCH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)); 27.6 (s with Sn satellites, SnCH\(_2\)CH\(_2\), \(^3J_{CSn} = 22.9\) Hz); 117.78 (d, 6–Ar–C, \(^3J_{CF} = 17.56\) Hz); 123.3 (s, 5–Ar–C); 130.2 (d, 4–Ar–C, \(^2J_{CF} = 41.7\) Hz); 131.7 (d, 1–Ar–C, \(^3J_{CF} = 13.17\) Hz); 150.7 (dd, 3–Ar–C, \(^1J_{CF} = 254.68\) Hz, \(^2J_{CF} = 21.96\) Hz); 154.7 (dd, 2–Ar–C, \(^1J_{CF} = 234.92\) Hz, \(^2J_{CF} = 21.96\) Hz). \(^{119}Sn\) \({}^1H\) NMR (C\(_6\)D\(_6\), 25 °C, 186.49 MHz): \(\delta\) –34.2 (dd, \(^3J_{SnF} = 30.6\) Hz, \(^4J_{SnF} = 18.1\) Hz). Calcd for C\(_{18}\)H\(_{30}\)F\(_2\)Sn: [M+ – C\(_4\)H\(_9\)], 347.0633. Found: m/z 347.0641.

**Synthesis of 2,3-difluorophenyl-1,4-bis(tributylstannane) (3.21).** A solution of 1,2-C\(_6\)F\(_2\)H\(_4\) (0.042 g, 0.364 mmol) and CH\(_2\)=CHSnBu\(_3\) (0.288 g, 0.910 mmol) in toluene was added to a mixture of \(^4\)Pr\(_3\)P (0.0058 g, 0.036 mmol) and Ni(COD)\(_2\) (0.005 g, 0.018 mmol). The solution was heated at 80 °C for 72 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (25 % yield by NMR spectroscopy, 50 % of 3.20 and Sn\(_2\)Bu\(_6\)). \(^1H\) NMR (C\(_6\)D\(_6\), 25 °C, 300.13 MHz): \(\delta\) 0.87 (t, 9H, SnCH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\), \(^3J_{HH} = 7.2\) Hz); 1.15 (m with satellites, 6H, SnCH\(_2\), \(^2J_{HSn} = 57.2\) Hz, \(^3J_{HH} = 8.5\) Hz); 1.33 (m, 6H, SnCH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)); 1.58 (m, 6H, SnCH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)); 2.73 (s with Sn satellites, 5,6–Ar–H, \(^3J_{HSn} = 12.7\) Hz). \(^19F\) \({}^1H\) NMR (C\(_6\)D\(_6\), 25 °C, 282.40 MHz): \(\delta\) –118.8 (s with Sn satellites, 2F, \(^1J_{FSn} = 28.3\) Hz). \(^{13}C\) \({}^1H\) NMR (C\(_6\)D\(_6\), 25 °C, 75.47 MHz): \(\delta\) 10.5 (s, SnCH\(_2\), \(^1J_{CSn(119)} = 352\) Hz, \(^1J_{CSn(117)} = 336\) Hz); 13.8 (s, SnCH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)); 27.6 (s with Sn satellites, SnCH\(_2\)CH\(_2\), \(^3J_{CSn} = 22.9\) Hz); 117.78 (d, 6–Ar–C, \(^3J_{CF} = 8.29\) Hz, \(^4J_{CF} = 7.3\) Hz); 125.3 (m, 1,4–Ar–C); 132.3 (dd, 5,6–Ar–C, \(^3J_{CF} = 19.25\) Hz). \(^{119}Sn\) \({}^1H\) NMR (C\(_6\)D\(_6\), 25 °C, 186.49 MHz): \(\delta\) –35.1 (t, \(^3J_{SnF} = 29.2\) Hz). C\(_{30}\)H\(_{56}\)F\(_2\)Sn\(_2\): [M+ – C\(_4\)H\(_9\)]. Found: m/z.

**Synthesis of tributyl(2,5-difluorophenyl)stannane (3.22).** A solution of 1,4-C\(_6\)F\(_2\)H\(_4\) (0.381 g, 3.34 mmol) and CH\(_2\)=CHSnBu\(_3\) (0.106 g, 0.335 mmol) in toluene was added to a mixture of \(^4\)Pr\(_3\)P (0.0054 g, 0.033 mmol) and Ni(COD)\(_2\) (0.0046 g, 0.017 mmol). The solution was heated at 80 °C for 18 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (90 % yield by NMR spectroscopy, 10 % of 3.23). \(^1H\) NMR (C\(_6\)D\(_6\), 25 °C, 300.13 MHz): \(\delta\) 0.85 (t, 9H, SnCH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\), \(^3J_{HH} = 7.1\) Hz); 1.07
(m with satellites, 6H, SnCH₂, ²J_HSn = 50.6 Hz, ³J_HH = 8.0 Hz); 1.31 (qt, 6H, SnCH₂CH₂H₂, ³J_HH = 6.6 Hz, ²J_HH = 6.6 Hz); 1.53 (tt, 6H, SnCH₂CH₂H₂, ³J_HH = 8.0 Hz, ²J_HH = 7.1 Hz); 6.64 (m, 3,4–Ar–H, ²J_HF = 8.1 Hz, ³J_HH = 6.6 Hz, ³J_HF = 4.7 Hz); 7.1 (dddd, 6–Ar–H, ³J_HH = 8 Hz, ³J_HF = 7.2 Hz, ²J_HH = 4.7 Hz, ²J_HF = 1.9 Hz). ¹⁹F{¹H} NMR (C₆D₆, 25 ºC, 282.40 MHz): δ – 101.3 (d with Sn satellites, 1F, 2–Ar–F, ³J_FF = 20.7 Hz, ³J_FSn = 8.7 Hz), –120.7 (d with Sn satellites, 1F, 5–Ar–F, ³J_FF = 20.7 Hz, ³J_FSn = 8.7 Hz). ¹³C{¹H} NMR (C₆D₆, 25 ºC, 75.47 MHz): δ 10.2 (s with Sn satellites, SnCH₂, ¹J_CSn(119) = 354 Hz, ¹J_CSn(117) = 340 Hz); 13.8 (s, SnCH₂CH₂CH₂CH₃); 27.7 (s with Sn satellites, SnCH₂CH₂H₂, ²J_CSn = 50.3 Hz); 29.3 (s with Sn satellites, SnCH₂CH₂CH₂H₂, ³J_CSn = 21.6 Hz); 115.5 (dd with Sn satellites, 4–Ar–C, ²J_CF = 32.3 Hz, ³J_CF = 7.9 Hz, ³J_CSn = 27.1 Hz); 117.0 (dd, 1–Ar–C, ²J_CF = 24.3 Hz, ³J_CSn = 9.4 Hz); 123.1 (dd with Sn satellites, 6–Ar–C, ²J_CF = 20.8 Hz, ³J_CSn = 16.1 Hz, ²J_CSn = 16.9 Hz); 129.5 (dd, 3–Ar–C, ²J_CF = 50.6 Hz, ³J_CSn = 4.7 Hz); 159.7 (d, 5–Ar–C, ²J_CF = 247.3 Hz); 163.5 (d, 2–Ar–C, ²J_CF = 229.7 Hz). ¹¹⁹Sn{¹H} NMR (C₆D₆, 25 ºC, 186.49 MHz): δ – 35.0 (dd, ³J_SnF = 26.98 Hz, ³J_SnF = 9.0 Hz). Calcd for C₁₈H₃₀F₂Sn: [M+ – C₄H₉], 347.0633. Found: m/z 347.0633.

Synthesis of 2,5-difluorophenyl-1,4-bis(tributylstannane) (3.23). A solution of 1,4-C₆F₄H₄ (0.042 g, 0.364 mmol) and CH₂=CHSnBu₃ (0.288 g, 0.910 mmol) in toluene was added to a mixture of iPr₃P (0.0058 g, 0.036 mmol) and Ni(COD)₂ (0.005 g, 0.018 mmol). The solution was heated at 80 ºC for 72 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (10 % yield by NMR spectroscopy, 70 % of 3.22 and Sn₂Bu₆, 10 % of 2,5-difluorophenyl-1,3-bis(tributylstannane), 3.24). ¹H NMR (C₆D₆, 25 ºC, 300.13 MHz): δ 0.85 (t, 9H, SnCH₂CH₂CH₂CH₃, ³J_HH = 6.8 Hz); 1.09 (m, 6H, SnCH₂, ³J_HH = 8.5 Hz); 1.3 (m, 6H, SnCH₂CH₂CH₂H₂); 1.55 (m, 6H, SnCH₂CH₂H₂); 6.95 (dd, 2H, 3,6–Ar–H, ³J_HF = 5.7 Hz, ³J_HF = 3.4 Hz, ³J_HSn = 17.8 Hz). ¹⁹F{¹H} NMR (C₆D₆, 25 ºC, 282.40 MHz): δ – 102.2 (s with Sn satellites, 2F, 2,5–Ar–F, ³J_FSn = 19.4 Hz). ¹³C{¹H} NMR (C₆D₆, 25 ºC, 186.49 MHz): δ 10.2 (s with Sn satellites, SnCH₂, ¹J_CSn(119) = 356 Hz, ¹J_CSn(117) = 336 Hz); 13.8 (s, SnCH₂CH₂CH₂CH₃); 27.6 (s with Sn satellites, SnCH₂CH₂, ²J_CSn = 61.5 Hz); 29.4 (s, SnCH₂CH₂CH₂H₂); 117.0 (dd, 1–Ar–C, ²J_CF = 24.2 Hz, ³J_CF = 8.8 Hz); 123.4 (dd, 3,6–Ar–C, ²J_CF = 21.96 Hz, ³J_CF = 17.56 Hz); 159.7 (d, 2,5–Ar–C, ²J_CF = 245.9 Hz). ¹¹⁹Sn{¹H} NMR (C₆D₆, 25 ºC, 186.49 MHz): δ – 35.9 (t, ³J_SnF = 20.0 Hz).
2,5-difluorophenyl-1,3-bis(tributylstannane) (3.24). $^1$H NMR (C$_6$D$_6$, 25 °C, 300.13 MHz): δ 0.85 (t, 9H, SnCH$_2$CH$_2$CH$_2$CH$_3$, $^3$J$_{HH}$ = 6.8 Hz); 1.11 (m, 6H, SnCH$_2$H, $^3$J$_{HH}$ = 8.5 Hz); 1.2 (m, 6H, SnCH$_2$CH$_2$CH$_2$); 1.55 (m, 6H, SnCH$_2$CH$_2$H); 7.21 (dd with Sn satellites, 2H, 4,6–Ar–H, $^3$J$_{HF}$ = 6.5 Hz, $^4$J$_{HF}$ = 3.4 Hz, $^3$J$_{H}$ = 31.0 Hz). $^{19}$F{$^1$H} NMR (C$_6$D$_6$, 25 °C, 282.40 MHz): δ –82.3 (d with Sn satellites, 1F, 2–Ar–F, $^5$J$_{FF}$ = 24.2 Hz, $^3$J$_{FSn}$ = 7.9 Hz). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 25 °C, 75.47 MHz): δ 11.6 (s with Sn satellites, SnCH$_2$, $^1$J$_{CSn}$ = 357.9 Hz); 14.3 (s, SnCH$_2$CH$_2$CH$_2$CH$_3$); 27.7 (s with Sn satellites, SnCH$_2$CH$_2$, $^2$J$_{CSn}$ = 63.7 Hz); 29.5 (s, SnCH$_2$CH$_2$CH$_2$); 115.5 (dd, 1–Ar–C, $^2$J$_{CF}$ = 32.9 Hz, $^3$J$_{CF}$ = 8.8 Hz); 122.1 (dd, 3,6–Ar–C, $^2$J$_{CF}$ = 21.96 Hz, $^3$J$_{CF}$ = 19.8 Hz); 161.0 (d, 2–Ar–C, $^1$J$_{CF}$ = 241.4 Hz); 163.5 (d, 2–Ar–C, $^1$J$_{CF}$ = 228.2 Hz). $^{119}$Sn{$^1$H} NMR (C$_6$D$_6$, 25 °C, 186.49 MHz): δ –35.6 (d, $^3$J$_{SfF}$ = 17.8 Hz, $^4$J$_{SfF}$ = 7.2 Hz).

**Synthesis of tributyl(2-fluorophenyl)stannane (3.25).** A solution of C$_6$FH$_5$ (0.321 g, 3.34 mmol) and CH$_2$=CHSnBu$_3$ (0.106 g, 0.334 mmol) in toluene was added to a mixture of iPr$_3$P (0.0054 g, 0.033 mmol) and Ni(COD)$_2$ (0.0046 g, 0.017 mmol). The solution was heated at 80 °C for 72 h. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (15 % yield by NMR spectroscopy). $^1$H NMR (C$_6$D$_6$, 25 °C, 300.13 MHz): δ 0.92 (t, 9H, SnCH$_2$CH$_2$CH$_2$CH$_3$, $^3$J$_{HH}$ = 7.7 Hz); 1.15 (m with satellites, 6H, SnCH$_2$H, $^3$J$_{HH}$ = 8.2 Hz); 1.35 (m, 6H, SnCH$_2$CH$_2$CH$_2$H); 1.6 (m, 6H, SnCH$_2$CH$_2$, $^3$J$_{HH}$ = 7.3 Hz, $^3$J$_{HH}$ = 8.2 Hz); 6.89 (dd, 1H, 3–Ar–H, $^3$J$_{HH}$ = 7.3, $^3$J$_{HH}$ = 8.2 Hz); 7.28 (m, 1H, 6–Ar–H, $^3$J$_{HH}$ = 7.3, $^4$J$_{HH}$ = 6.8 Hz); 7.37 and 7.39 (dd, 2H, 4,5–Ar–H, $^3$J$_{HH}$ = 7.8, $^4$J$_{HH}$ = 4.5 Hz, $^5$J$_{HH}$ = 2.1 Hz). $^{19}$F{$^1$H} NMR (C$_6$D$_6$, 25 °C, 282.40 MHz): δ –93.7 (s with Sn satellites, $^3$J$_{FSn}$ = 36 Hz). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 25 °C, 75.47 MHz): δ 10.2 (s with Sn satellites, SnCH$_2$, $^1$J$_{CSn}$(119) = 353 Hz, $^1$J$_{CSn}$(117) = 337 Hz); 13.9 (s, SnCH$_2$CH$_2$CH$_2$CH$_3$); 27.7 (s with Sn satellites, SnCH$_2$CH$_2$, $^2$J$_{CSn}$ = 53.4 Hz); 29.5 (s with Sn satellites, SnCH$_2$CH$_2$CH$_2$, $^3$J$_{CSn}$ = 21.1 Hz); 114.6 (d, 1–Ar–C, $^2$J$_{CF}$ = 27.8 Hz); 124.5 (d with Sn satellites, 6–Ar–C, $^3$J$_{CF}$ = 2.4 Hz, $^2$J$_{CSn}$ = 34.5 Hz); 128.8 (s, 4–Ar–C); 130.67 (d, 5–Ar–C, $^4$J$_{CF}$ = 7.7 Hz); 137.5 (d, 3–Ar–C, $^2$J$_{CF}$ = 15.1 Hz); 167.9 (d, 2–Ar–C, $^1$J$_{CF}$ = 234.5 Hz). $^{119}$Sn{$^1$H} NMR (C$_6$D$_6$, 25 °C, 186.49 MHz): δ –37.4 (d, $^3$J$_{SfF}$ = 36.35 Hz). Calcd for C$_{18}$H$_{31}$FSn: [M+ – C$_4$H$_9$], 329.0728. Found: m/z 329.0742.
Reaction of MeNC₅H₄N⁺Pr and CH₂=CHSnBu₃. A colourless solution of CH₂=CHSnBu₃ (0.010 g, 0.033 mmol) and MeNC₅H₄N⁺Pr (0.005 g, 0.033 mmol) in 1 mL of C₆D₆ was allowed to react overnight at room temperature. The reaction mixture was analyzed by ¹H NMR spectroscopy, and only starting materials were observed.

Reaction of C₆F₅H and CH₂=CHSnBu₃. A colourless solution of CH₂=CHSnBu₃ (0.010 g, 0.031 mmol) and C₆F₅H (0.005 g, 0.031 mmol) in 1 mL of C₆D₆ was allowed to react overnight at 100 °C. The reaction mixture was analyzed by ¹H and ¹⁹F{¹H} NMR spectroscopy, and only starting materials were observed.

Reaction of MeNC₅H₄N⁺Pr, C₆F₅H, and CH₂=CHSnBu₃. A colourless solution of CH₂=CHSnBu₃ (0.021 g, 0.067 mmol), C₆F₅H (0.011 g, 0.067 mmol) and MeNC₅H₄N⁺Pr (0.010 g, 0.067 mmol) in 1 mL of C₆D₆ was allowed to react overnight at 100 °C. The reaction mixture was analyzed by ¹H and ¹⁹F{¹H} NMR spectroscopy, and only starting materials were observed.

Reaction of Ni(COD)₂, C₆F₅H, and CH₂=CHSnBu₃. A bright orange solution of CH₂=CHSnBu₃ (0.115 g, 0.364 mmol), C₆F₅H (0.061 mg, 0.364 mmol), and Ni(COD)₂ (0.005 g, 0.018 mmol) in 1 mL of C₆D₆ was allowed to react overnight at 50 °C. The reaction mixture was analyzed by ¹H and ¹¹⁹Sn{¹H} NMR spectroscopy, there was free COD present at δ 2.10 and 5.50 and no remaining Ni(COD)₂. There was also a small amount of remaining tributyl(vinyl)tin, however, the major product was hexabutylditin with a 3 % impurity of the conversion to 3.1.

Reaction of C₆F₅H, CH₂=CHSnBu₃, Hg, and 10 % catalyst loading of Ni(COD)₂ and MeNC₅H₄N⁺Pr. A dark golden yellow solution of CH₂=CHSnBu₃ (0.053 g, 0.167 mmol), C₆F₅H (0.028 g, 0.167 mmol), Hg (0.500 g, 2.49 mmol), Ni(COD)₂ (0.004 g, 0.0167 mmol), and MeNC₅H₄N⁺Pr (0.005 mg, 0.033 mmol) in 1 mL of C₆D₆ was allowed to react for 30 min. ¹⁹F{¹H} NMR (C₆D₆, 25 °C, 282.40 MHz): –121.3 (AA'MM'N second order with satellites, 2F, 1,5–Ar–F, ³J_FSn = 7.7 Hz); –153.0 (tt with satellites, 1F, 3–Ar–F, ³J_FF = 19.9 Hz, ⁴J_FF = 1.8 Hz, ⁵J_FSn = 7.4 Hz); –160.7 (AA'MM'N second order, 2F, 2,4–Ar–F). After 30 min the desired product is formed, which indicates that MeNC₅H₄N⁺Pr and nickel are directly involved in the reaction, but nickel metal is not.
Chapter 3 – Catalytic C–H Bond Stannylation: A New Regioselective Pathway to C–Sn Bonds via C–H Bond Functionalization

Reaction of C₆F₅H, HSnBu₃, and 5 % catalyst loading of Ni(COD)₂ and MeNC₅H₄N⁴Pr.
A solution of C₆F₅H (0.056 g, 0.33 mmol), HSnBu₃ (0.097 g, 0.33 mmol) in 1 mL of C₆D₆ was mixed with Ni(COD)₂ (0.005 g, 0.0167 mmol) and MeNC₅H₄N⁴Pr (0.005 g, 0.033 mmol). Upon addition of all components, H₂ was vigorously released forming Sn₂Bu₆ and a precipitate. The precipitate was dissolved in CD₂Cl₂ and confirmed by ¹H and ¹⁹F{¹H} NMR spectroscopy to be trans–(MeNC₅H₄N⁴Pr)₂NiF(2,2',3,3'–C₆F₄H)²⁷ which is the expected C–F activation complex. This reaction was also performed analogously with Ni(COD)₂ and iPr₃P as the ligand and provided Sn₂Bu₆ and various activation products.

Reaction of C₆F₅H, SnBu₄, and 10 % catalyst loading of Ni(COD)₂ and MeNC₅H₄N⁴Pr.
A solution of C₆F₅H (0.028 g, 0.167 mmol), SnBu₄ (0.058 g, 0.167 mmol) in 1 mL of C₆D₆ was mixed with Ni(COD)₂ (0.004 g, 0.0167 mmol) and MeNC₅H₄N⁴Pr (0.005 g, 0.033 mmol) and allowed to react for 1 day at 60 °C. No significant reaction was observed by ¹H and ¹⁹F{¹H} NMR spectroscopy. This reaction was also performed stoichiometrically at room temperature with Ni(COD)₂ and iPr₃P as the ligand and provided the same results.

Reaction of C₆F₅H, SnPh₄, and 10 % catalyst loading of Ni(COD)₂ and MeNC₅H₄N⁴Pr.
A solution of C₆F₅H (0.028 g, 0.167 mmol), SnPh₄ (0.071 g, 0.167 mmol) in 1 mL of C₆D₆ was mixed with Ni(COD)₂ (0.004 g, 0.0167 mmol) and MeNC₅H₄N⁴Pr (0.005 g, 0.033 mmol) and allowed to react for 1 day at 60 °C. No significant reaction was observed by ¹H and ¹⁹F{¹H} NMR spectroscopy. This reaction was also performed stoichiometrically at room temperature with Ni(COD)₂ and iPr₃P as the ligand and provided the same results.

Reaction of C₆F₅H, PhSnBu₃, and 10 % catalyst loading of Ni(COD)₂ and MeNC₅H₄N⁴Pr.
A solution of C₆F₅H (0.028 g, 0.167 mmol), PhSnBu₃ (0.061 g, 0.167 mmol) in 1 mL of C₆D₆ was mixed with Ni(COD)₂ (0.004 g, 0.0167 mmol) and MeNC₅H₄N⁴Pr (0.005 g, 0.033 mmol) and allowed to react for 1 day at 60 °C. No significant reaction was observed by ¹H and ¹⁹F{¹H} NMR spectroscopy.

Reaction of 5 % catalyst loading of MeNC₅H₄N⁴Pr and Ni(COD)₂ with Sn₂Me₆.
A solution of Sn₂Me₆ (0.109 g, 0.333 mmol) in 1 mL of C₆D₆ was mixed with Ni(COD)₂ (0.004 g, 0.0167 mmol) and MeNC₅H₄N⁴Pr (0.005 g, 0.033 mmol) and allowed to react for 1 h at
room temperature. The reaction mixture was analyzed by $^1$H NMR spectroscopy, only starting materials were observed.

**Reaction of 5 % catalyst loading of MeNC$_5$H$_4$N$i$Pr and Ni(COD)$_2$ with Sn$_2$Me$_6$ and C$_6$F$_5$H.** A solution of Sn$_2$Me$_6$ (0.109 g, 0.333 mmol) and C$_6$F$_5$H (0.060 g, 0.333 mmol) in 1 mL of C$_6$D$_6$ was mixed with Ni(COD)$_2$ (0.004 g, 0.0167 mmol) and MeNC$_5$H$_4$N$i$Pr (0.005 g, 0.033 mmol) and allowed to react for 1 h at room temperature. The reaction mixture was analyzed by $^1$H and $^{19}$F{$^1$H} NMR spectroscopy, there was no observed reaction.

**Reaction of 5 % catalyst loading of MeNC$_5$H$_4$N$i$Pr and Ni(COD)$_2$ with C$_6$F$_5$H and CH$_2$=CHSnMe$_3$.** A solution of C$_6$F$_5$H (0.169 g, 1.00 mmol) and CH$_2$=CHSnMe$_3$ (0.250 g, 1.00 mmol) in 1 mL of C$_6$D$_6$ was mixed with Ni(COD)$_2$ (0.014 g, 0.050 mmol) and MeNC$_5$H$_4$N$i$Pr (0.015 g, 0.101 mmol) and allowed to react for 48 h at 50 ºC. The reaction mixture was analyzed by $^1$H and $^{19}$F{$^1$H} NMR spectroscopy, which indicated a 90 % conversion to the desired product by NMR spectroscopy, trimethyl(2,3,4,5,6–pentfluorophenyl)tin, with respect to C$_6$F$_5$H. This reaction was also performed analogously with Ni(COD)$_2$ and $^i$Pr$_3$P as the ligand yielding the same results after heating at 50 ºC for 24 h. $^1$H NMR (C$_6$D$_6$, 25 ºC, 300.13 MHz): $\delta$ 0.35 (s with satellites, 9H, $CH_3$, $^2J_{Hsn}=58.6$ Hz). $^{19}$F{$^1$H} NMR (C$_6$D$_6$, 25 ºC, 282.40 MHz): $-122.5$ (AA' MM' X second order, 2F, 2,6–Ar–F, $^3J_{FF}=15.8$ Hz); $-153.9$ (t, 1F, 4–Ar–F, $^3J_{FF}=19.6$ Hz); $-161.5$ (AA' MM' X second order, 2F, 3,5–Ar–F, $^3J_{FF}=15.8$ Hz, $^3J_{FF}=19.6$ Hz).

**Reaction of 3 % catalyst loading of $^t$Bu$_3$P and Ni(COD)$_2$ with 1,2,4,5–C$_6$F$_4$H$_2$ and CH$_2$=CHSnBu$_3$.** A solution of 1,2,4,5–C$_6$F$_4$H$_2$ (0.250 g, 1.67 mmol) and CH$_2$=CHSnBu$_3$ (0.176 g, 0.555 mmol) in 1 mL of C$_6$D$_6$ was mixed with Ni(COD)$_2$ (0.004 g, 0.0167 mmol) and $^t$Bu$_3$P (0.005 g, 0.033 mmol) and allowed to react overnight at 60 ºC. The reaction mixture was analyzed by $^1$H, $^{31}$P{$^1$H}, and $^{19}$F{$^1$H} NMR spectroscopy, which indicated a 42 % conversion to the desired product 3.2, with respect to remaining 1,2,4,5–C$_6$F$_4$H$_2$.

**Reaction of 3 % catalyst loading of Pt(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr with C$_6$F$_5$H and CH$_2$=CHSnBu$_3$.** A solution of C$_6$F$_5$H (0.094 g, 0.555 mmol) and CH$_2$=CHSnBu$_3$ (0.176 g, 0.555 mmol) in 1 mL of C$_6$D$_6$ was mixed with Pt(COD)$_2$ (0.007 g, 0.0167 mmol) and MeNC$_5$H$_4$N$i$Pr (0.005 g, 0.033 mmol) and allowed to react overnight at 90 ºC. The reaction
mixture was analyzed by $^1$H and $^{19}$F{$^1$H} NMR spectroscopy, the desired activation product was not observed.

**Reaction of 3 % catalyst loading of Pt(COD)$_2$ and $^3$Pr$_3$P with 1,2,3,4–C$_6$F$_4$H$_2$ and CH$_2$=CHSnBu$_3$.** A solution of 1,2,3,4–C$_6$F$_4$H$_2$ (0.083 g, 0.555 mmol) and CH$_2$=CHSnBu$_3$ (0.176 g, 0.555 mmol) in 1 mL of C$_6$D$_6$ was mixed with Pt(COD)$_2$ (0.007 g, 0.0167 mmol) and $^3$Pr$_3$P (0.005 g, 0.033 mmol) and allowed to react overnight at 90 °C. The reaction mixture was analyzed by $^1$H, $^{31}$P{$^1$H}, and $^{19}$F{$^1$H} NMR spectroscopy, the desired activation product was not observed.

**Reaction of 3 % catalyst loading of Pt(PCy$_3$)$_2$ with C$_6$F$_5$H and CH$_2$=CHSnBu$_3$.** A solution of C$_6$F$_5$H (0.056 g, 0.333 mmol) and CH$_2$=CHSnBu$_3$ (0.176 g, 0.333 mmol) in 1 mL of C$_6$D$_6$ was mixed with Pt(Cy$_3$P)$_2$ (0.013 g, 0.0167 mmol) and allowed to react overnight at 90 °C. The reaction mixture was analyzed by $^1$H, $^{31}$P{$^1$H}, and $^{19}$F{$^1$H} NMR spectroscopy, only about 3 % conversion to the desired product 3.1 was observed by NMR with respect to remaining C$_6$F$_5$H.

**Deuterium Labelling Studies**

**Reaction of 1,2,4,5–C$_6$F$_4$HD, CH$_2$=CHSnBu$_3$, and 5 % catalyst loading of Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr.** A solution of 1,2,4,5–C$_6$F$_4$HD (0.050 g, 0.33 mmol), CH$_2$=CHSnBu$_3$ (0.106 g, 0.33 mmol) in 1 mL of C$_6$D$_6$ was mixed with Ni(COD)$_2$ (0.005 g, 0.0167 mmol) and 3.1 (0.005 g, 0.033 mmol). The $^{19}$F{$^1$H} NMR spectra of the reaction mixture was recorded within 5 min of the initiation of the reaction in order to determine the initial deuterium isotope effect for C–H vs. C–D activation. Activation of hydrogen over deuterium can be confirmed by a ~0.3 ppm shift of any ortho fluorine adjacent to the remaining deuterium in the product and the isotope effect can be determined through integration. Oxidative addition is favored for C–H over C–D bonds, and the integrals of the peaks were found to be in a 2.1:1 at 298 K. $^{19}$F{$^1$H} NMR (C$_6$D$_6$, 25 °C, 282.40 MHz): –122.2 (AA'BB' second order, 2,4–Ar–F); –138.1 (AA'BB' second order, 1,4–Ar–F); –138.4 (AA'BB' second order, 1,4–Ar–F).
Section: Catalytic C–H Bond Stannylation: A New Regioselective Pathway to C–Sn Bonds via C–H Bond Functionalization

**Reaction of C₆F₅D, cis-(propene)SnBu₃, and 5 % catalyst loadings of Ni(COD)₂ and MeNC₅H₄NᵢPr.** A solution of C₆F₅D (0.056 g, 0.33 mmol), cis–(propene)SnBu₃ (0.110 g, 0.33 mmol) in 1 mL of C₆D₆ was mixed with Ni(COD)₂ (0.005 g, 0.0167 mmol) and MeNC₅H₄NᵢPr (0.005 g, 0.033 mmol). The reaction mixture was allowed to react overnight at room temperature. The resultant propene-d₁ was vacuum transferred to an NMR tube equipped with a Teflon valve, containing CDCl₃ and analyzed by ¹H NMR spectroscopy. This reaction was also performed analogously with iPr₃P in lieu of the MeNC₅H₄NᵢPr ligand at 10 mol % catalyst loading.

**Experimental chemical shifts and coupling constants of trans-propene-d₁ CDCl₃.** ¹H NMR (CDCl₃, 25 ºC, 300.13 MHz): δ 1.79 (dd, CH₃, ³J_HH = 6.78 Hz, ⁴J_HH = 1.5 Hz); 5.08 (second order, H, ³J_HH = 16.72 Hz, ⁴J_HH = 2.05 Hz); 5.90 (dqt, H, ³J_HH = 17.1 Hz, ³J_HH = 6.50 Hz, ³J_HD = 1.6 Hz).

**Reaction of C₆F₅D, (cis,trans–propenyl)SnBu₃, and 5 % catalyst loading Ni(COD)₂ and MeNC₅H₄NᵢPr.** A solution of C₆F₅D (0.056 g, 0.33 mmol), cis,trans–(propene)SnBu₃ (0.110 g, 0.33 mmol) in 1 mL of C₆D₆ was mixed with Ni(COD)₂ (0.005 g, 0.0167 mmol) and MeNC₅H₄NᵢPr (0.005 g, 0.033 mmol). After 20 min the ¹H NMR spectrum was used to confirm that both cis-propene-d₁ and trans-propene-d₁ are produced in equal amounts.
3.5 References


(20) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* 2010, 110, 890-931.


Chapter 3 – Catalytic C–H Bond Stannylation: A New Regioselective Pathway to C–Sn Bonds via C–H Bond Functionalization

(33) Perutz, R. N.; Sabo-Etienne, S. Angew. Chem., Int. Ed. 2007, 46, 2578-2592.
Chapter 4 – A Mechanistic Investigation of C–H Bond Stannylation: Synthesis and Characterization of Nickel Catalysts

4.1 Introduction

Over the past decades, catalytic C–H bond functionalization has undergone significant developments as a practical, economical and green synthetic approach.\textsuperscript{1-18} Our research has targeted methods to utilize available and cost effective Ni complexes for C–H activation in place of more expensive noble metal complexes (e.g. Pt, Ir, Rh, Au) that are commonly used in catalytic C–H functionalization reactions. Although Ni complexes have been suggested as better suited for selective C–F activation\textsuperscript{19-30} for thermodynamic reasons,\textsuperscript{31} Ni complexes are finding increasing use in the catalytic transformation of C–H bonds.\textsuperscript{32-37} We have found that partially fluorinated arenes and pyridines can undergo oxidative addition of their C–H bonds to Ni(0) phosphine complexes, which suggests that
these complexes should be capable of catalytic C–H bond functionalization.$^{38-43}$ We have previously shown that the reaction of partially fluorinated arenes with CH$_2$=CHSnBu$_3$ resulted in catalytic C–H bond stannylation with the loss of ethylene gas (Chapter 3), as shown in Scheme 4.1.$^{44}$ The reaction was catalyzed by a combination of Ni(COD)$_2$ and either the nitrogen donor MeNC$_5$H$_4$N$_i$Pr$_19$ or $^i$Pr$_3$P.

![Scheme 4.1](image)

**Scheme 4.1.** General reaction scheme for C–H bond stannylation.

To the best of our knowledge this is the first example of catalytic C–H bond stannylation. Equally intriguing is the mechanism of the conversion. The transformation of the Sn–C bond in Scheme 4.1 to form a new Sn–C in the product with the loss of ethylene bond provides a unique mechanism of C–H bond functionalization. Although this reaction is currently limited to activated aromatics, for example fluorobenzene has been found to react but not benzene, insight into the mechanism may allow for the design of catalysts capable of stannylation of a broader scope of substrates. Similarly, knowledge of the reaction mechanism may allow for the design of catalysts capable of converting C–H bonds to other carbon-heteroatom bonds, such as C–Si bonds. In this chapter, isolable species that perform catalytic C–H bond stannylation will be described, and the mechanism of this reaction will be investigated in greater detail. It should be noted that $^i$Pr$_3$P was chosen as the ancillary ligand for the mechanistic studies rather than MeNC$_5$H$_4$N$_i$Pr. More controlled studies could be provided with $^i$Pr$_3$P since C–H bond stannylation does not occur appreciably at room temperature and additional insight could be provided by $^{31}$P{$^1$H} NMR spectroscopy.
4.2 Results and Discussion

4.2.1 The Resting State of Nickel C–H Bond Stannylation Catalysts

Note: The compound \((\text{iPr}_3\text{P})\text{Ni}(\eta^2-\text{CH}_2=\text{CHSnPh}_3)_2\) \(\text{(4.1}^{\text{Ph}}\text{)}\) was synthesized and characterized by Jacob Matthews under my supervision.

The reaction of Ni(COD)_2 with one equivalent of triisopropylphosphine and two equivalents of CH_2=CHSnBu_3 provided the species \((\text{iPr}_3\text{P})\text{Ni}(\eta^2-\text{CH}_2=\text{CHSnBu}_3)_2\) \(\text{(4.1}^{\text{Bu}}\text{)}\), as shown in Scheme 4.2. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays a resonance at $\delta$ 50.2 with $^{119}\text{Sn}/^{117}\text{Sn}$ satellite peaks ($^3J_{\text{SnP}} = 29.7$ Hz) of appropriate intensities for two coordinated CH_2=CHSnBu_3 moieties ($^{117}\text{Sn}$, 7.7 %, and $^{119}\text{Sn}$, 8.6 % abundant, both I = $\frac{1}{2}$). The different couplings to $^{117}\text{Sn}$ and $^{119}\text{Sn}$ were not resolved owing to the line-widths and modest difference in gyromagnetic ratios between these isotopes. The $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum displayed the expected doublet from coupling to a single phosphorus nucleus. The intensities in the $^1\text{H}$ NMR spectrum were consistent with the proposed formulation, and featured the chemical shifts for the coordinated vinyl moieties shifted several ppm upfield relative to free CH_2=CHSnBu_3.

![Scheme 4.2](image-url)

**Scheme 4.2.** General reaction scheme for a variety of catalysts capable of C–H bond stannylation.
Although 4.1Bu was an isolable air-sensitive oil, it proved impossible to crystallize, so characterization was limited to multinuclear NMR spectroscopy. We chose to investigate CH$_2$=CHSnPh$_3$ as a reagent that could provide a crystalline and easily handled stannylation catalyst that was more amenable to mechanistic studies. The reaction of Ni(COD)$_2$ with one equivalent of $^i$Pr$_3$P and two equivalents of CH$_2$=CHSnPh$_3$ provided the complex ($^i$Pr$_3$P)Ni(η$_2$-CH$_2$=CHSnPh$_3$)$_2$ (4.1$^{\text{Ph}}$). Single crystals of 4.1$^{\text{Ph}}$, suitable for characterization by X-ray crystallography, were obtained from slow evaporation of a toluene solution at –40 °C; an ORTEP of the solid-state molecular structure is shown in Figure 4.1. The structure is as expected, with η$_2$-coordinated CH$_2$=CHSnPh$_3$ groups. The two SnPh$_3$ substituents arrange themselves so that they are far away from the bulky $^i$Pr$_3$P donor, and on opposite sides of the Ni coordination plane to best avoid each other, which gives a complex with pseudo-C$_2$ symmetry.

![Figure 4.1. ORTEP of complex 4.1$^{\text{Ph}}$, shown with 50 % thermal ellipsoid parameters. Hydrogen atoms are omitted, and only the ipso carbons of the aromatic rings are shown for clarity. Selected bond distances (Å) and angles (°): Ni(1)–C(2), 1.984(7); Ni(1)–C(4), 1.986(7); Ni(1)–C(1), 1.989(7); Ni(1)–C(3), 1.998(8); Ni(1)–P(1), 2.203(2); C(1)–C(2), 1.387(11); C(3)–C(4), 1.369(12); C(2)–Ni(1)–C(4), 171.0(4); C(2)–Ni(1)–C(3), 131.4(4); C(2)–Ni(1)–P(1), 94.7(2); C(4)–Ni(1)–P(1), 94.0(3); C(1)–Ni(1)–P(1), 135.2(2); C(3)–Ni(1)–P(1), 133.8(3).]
The NMR spectra of $\text{4.1}_{\text{Ph}}$ in $\text{C}_6\text{D}_6$ displayed resonances consistent with the solid-state structure. The $\text{31P}\{\text{1H}\}$ NMR spectrum displayed a signal at $\delta$ 49.8 with satellites separated by 32.3 Hz due to coupling to two equivalent Sn nuclei, and the $^{119}\text{Sn}$ NMR spectrum displayed a doublet at $\delta$ –122.0 with the same coupling constant. The $^1\text{H}$ NMR spectrum displayed diastereotopic methyl groups on the $^3\text{Pr}_3\text{P}$ donor, consistent with the lack of a mirror plane of symmetry in $\text{4.1}_{\text{Ph}}$, and featured coordinated vinyl moieties environments at $\delta$ 3.00, 3.09 and 4.11. The NMR parameters are all comparable to those for $\text{4.1}_{\text{Bu}}$ suggesting that the structure is isostructural to $\text{4.1}_{\text{Ph}}$.

### 4.2.2 Stoichiometric Stannlyation Using $\text{4.1}_{\text{Ph}}$

The addition of $\text{C}_6\text{F}_5\text{H}$ to solutions of $\text{4.1}_{\text{Ph}}$ in $\text{C}_6\text{D}_6$, shown in Scheme 4.3, provided conversion to the C–H activation product $\text{C}_6\text{F}_5\text{SnPh}_3$, as monitored by $^{19}\text{F}$ and $^{119}\text{Sn}\{\text{1H}\}$ NMR spectroscopy. The reaction proceeds slowly at room temperature under the conditions used. Two additional nickel-containing products were readily identified from a combination of $\text{31P}\{\text{1H}\}$, $^1\text{H}$ and $^{119}\text{Sn}\{\text{1H}\}$ NMR spectroscopy. Early in the reaction with $\text{4.1}_{\text{Ph}}$, a product assigned as ($^3\text{Pr}_3\text{P})\text{Ni}($$^\eta^2$-CH$_2$=CH$_2$SnPh$_3$)($^\eta^2$-C$_2$H$_4$) ($\text{4.2}_{\text{Ph}}$) was observed, with a $\text{31P}\{\text{1H}\}$ shift of $\delta$ 50.9 and satellites with a 25.2 Hz separation and intensities consistent with coupling to a single Sn environment. The $^{119}\text{Sn}\{\text{1H}\}$ NMR spectrum of $\text{4.2}_{\text{Ph}}$ features a doublet at –109.2, with a $^3J_{\text{PSn}}$ of 25.2 Hz, which confirms a single phosphine is coordinated to the metal centre. The $^1\text{H}$ NMR spectrum features diastereotopic Me groups from the $^3\text{Pr}_3\text{P}$ moiety and three distinctive multiplets from the coordinated vinyl moiety at $\delta$ 3.22, 3.03 and 2.78 that integrate to 1H each. A pair of second-order multiplets at $\delta$ 2.94 and 2.66 assigned as the coordinated ethylene moiety integrate to 2H environments each, consistent with rapid rotation about the Ni–($^\eta^2$-C$_2$H$_4$) bond at room temperature, which exchanges only the trans-disposed hydrogen environments. Before $\text{4.1}_{\text{Ph}}$ is fully consumed to form $\text{4.2}_{\text{Ph}}$, the reaction of $\text{4.1}_{\text{Ph}}$ with $\text{C}_6\text{F}_5\text{H}$ also generates ($^3\text{Pr}_3\text{P})\text{Ni}($$^\eta^2$-C$_2$H$_4$)$_2$ ($\text{4.3}$), presumably either by reaction of $\text{4.2}_{\text{Ph}}$ with $\text{C}_6\text{F}_5\text{H}$ or from ligand redistribution between two equivalents of $\text{4.2}_{\text{Ph}}$. This known$^{45,46}$ complex was identified by its distinctive $^1\text{H}$ NMR spectrum, which features a single $^3\text{Pr}_3\text{P}$ methyl environment, a singlet at $\delta$ 2.73 for the coordinated C$_2$H$_4$ moiety, and a singlet in the $\text{31P}\{\text{1H}\}$ NMR spectrum at $\delta$ 52.5. Unfortunately, no further intermediates
were observed to provide insight into the mechanism of C–Sn bond formation. The compositions of 4.2\textsuperscript{Ph} and 4.3, which could not be isolated from these reaction mixtures, were further confirmed by an alternate synthesis. Ethylene was added to a C\textsubscript{6}D\textsubscript{6} solution of 4.1\textsuperscript{Ph} in an NMR tube, followed by warming the sealed tube to 50 °C in an NMR probe, as shown on the bottom of Scheme 4.3. This reaction provided equilibrium amounts of 4.2\textsuperscript{Ph} and 4.3, as analysed by multinuclear NMR spectroscopy. The reverse reaction, the replacement of coordinated ethylene in 4.2\textsuperscript{Ph} and 4.3 by CH\textsubscript{2}=CHSnPh\textsubscript{3}, regenerated 4.1\textsuperscript{Ph} from 4.2\textsuperscript{Ph} and 4.3, and thus allows the catalytic stannylation of C–H bonds with vinyltin reagents.

![Scheme 4.3](image)

**Scheme 4.3.** Stoichiometric C–H bond stannylation with 4.1\textsuperscript{Ph}.

### 4.2.3 Rate Law and Mechanism of Catalytic Stannylation.

The failure to observe any additional intermediates in the stoichiometric reactions of 4.1\textsuperscript{Ph} with C\textsubscript{6}F\textsubscript{5}H provides little additional insight into the mechanism of this unusual C–H functionalization reaction. The effect of the concentration of nickel catalyst, C\textsubscript{6}F\textsubscript{5}H, and CH\textsubscript{2}=CHSnPh\textsubscript{3} was examined in an attempt to determine the rate law. The determination of exact rate constants in these systems was complicated by small amounts of Ni metal precipitating over the course of reactions, and the multiple components sometimes observed in solution (e.g. 4.1\textsuperscript{Ph} and 4.2\textsuperscript{Ph}); however, experimentally it proved possible to generate reproducible and informative rate data.

Given the fact that Ni complexes sometimes undergo reactions to form dinuclear complexes that perform transformations involving both C–C bond formation\textsuperscript{47-49} and C–H activation\textsuperscript{42,50} we chose to initially verify that the active catalyst remains mononuclear
during the rate determining steps of the reaction. By using a stock solution of 0.172 M CH$_2$=CHSnPh$_3$ and 0.177 M C$_6$F$_5$H with both a $^{19}$F and $^1$H NMR internal standard, different masses of the catalyst ($^{i}$Pr$_3$P)Ni($^\eta^2$-CH$_2$=CHSnPh$_3$)$_2$ 4.1$^{\text{Ph}}$ were added to 0.6 mL aliquots to give approximate catalyst concentrations of 0.005 M, 0.01 M, 0.02 M, 0.04 M and 0.08 M, respectively. These solutions do not react appreciably at room temperature, and transferring to an NMR probe preheated to 338 K provided a convenient means to monitor the initial reaction rates, which remained constant for several minutes under these conditions. The results clearly show a linear correlation between reaction rate and catalyst concentration, as shown in Figure 4.2. This supports a mononuclear nickel complex as the active species during the rate determining steps of catalytic stannylation, since the graph displays a first-order system. This data also suggests that metallic nickel or nickel nanoparticles are not the active species, since the same data was reproducible after multiple trials.

![Figure 4.2](image_url)

**Figure 4.2.** Rate of formation of C$_6$F$_5$SnPh$_3$ versus the concentration of the catalyst ($^{i}$Pr$_3$P)Ni($^\eta^2$-CH$_2$=CHSnPh$_3$)$_2$ (4.1$^{\text{Ph}}$) in the catalytic stannylation of C$_6$F$_5$H with CH$_2$=CHSnPh$_3$.

Similar experiments were performed to determine the effect the concentration of
C₆F₅H and CH₂=CHSnPh₃ have on the reaction rate. A stock solution in toluene with concentrations of 0.0052 M of catalyst 4.₁Ph₄, and 0.212 M CH₂=CHSnPh₃, was used to make five solutions with concentrations of C₆F₅H ranging from 0.123 to 1.97 M. These were transferred to an NMR probe preheated to 338 K and the initial catalytic reaction rates were monitored. The reaction rate was found to be linearly proportional to the C₆F₅H concentration. A similar experiment where a stock solution with constant catalyst 4.₁Ph₄ concentration (0.0052 M) and C₆F₅H concentration (0.476 M) was used to make five solutions with different CH₂=CHSnPh₃ concentrations (0.053, 0.094, 0.218, 0.507, and 1.13 M) showed that reaction rate is inversely proportional to the concentration of CH₂=CHSnPh₃. With the lowest concentration of CH₂=CHSnPh₃ used (0.053 M) the initial reaction rate did not remain constant over the course of minutes, but instead slowed rapidly until the reaction was complete after only 20 min. The precipitation of a visibly large amount of nickel suggests that the catalyst is not stable with low CH₂=CHSnPh₃ concentrations at the temperature used.

The reaction kinetics are suggestive of the mechanism shown in Scheme 4.4. The initial step is a reversible dissociation of one of the two CH₂=CHSnPh₃ moieties from 4.₁Ph₄ to generate the unobserved species ((Pr₃P)Ni(η²-CH₂=CHSnPh₃)) 4.₄Ph₄ with forward rate constant $k₁$ and reverse rate constant $k₋₁$. This step is consistent with the reduction in reaction rate upon increased CH₂=CHSnPh₃ concentration. The rate-determining step is a reaction between 4.₄Ph₄ and C₆F₅H, with rate constant $k₂$. Though more than one step may be required to reach 4.₅Ph₄ from 4.₄Ph₄, little insight into these steps is provided from the rate data. Complex 4.₅Ph₄ should readily associate CH₂=CHSnPh₃ to generate 4.₂Ph₄, which can then lose ethylene to form 4.₄Ph₄, and is in equilibrium with 4.₁Ph₄, but 4.₅Ph₄ is a speculative intermediate, and alternate pathways where the ethylene moiety is lost prior to C–Sn bond formation are viable. An alternate mechanism where arene coordination precedes vinyl dissociation also cannot be discounted.
The rate law given in eq 4.1 can be derived using a steady-state approximation for the concentration of intermediate $4.4^\text{Ph}$. Under catalytic conditions, a simpler rate law can be derived providing that $k_2[C_6F_5H]$ is much less than $k_{-1}[\text{CH}_2=\text{CHSnPh}_3]$, and is shown in equation 4.2. A plot of reaction rate versus $[4.1^\text{Ph}][C_6F_5H]/[\text{CH}_2=\text{CHSnPh}_3]$ for the catalytic data provided a linear plot as shown in Figure 4.3. The observed rate constant, $(k_1/k_{-1}) \times k_2$, can be estimated as $0.0016(2) \text{ s}^{-1}$ at 338 K from these data. Therefore, the rate law is consistent with a rapid pre-equilibrium formation of $4.4^\text{Ph}$, followed by rate determining reaction with $C_6F_5H$. 

**Scheme 4.4.** Proposed mechanism for C–H bond stannylation.
Steady-state rate law:

\[
\frac{d[\text{C}_6\text{F}_5\text{SnPh}_3]}{dt} = \frac{k_1k_2[4.1^{\text{Ph}}][\text{C}_6\text{F}_5\text{H}]}{k_{-1}[\text{CH}_2=\text{CHSnPh}_3] + k_2[\text{C}_6\text{F}_5\text{H}]} \tag{4.1}
\]

Under catalytic conditions, where \(k_2[\text{C}_6\text{F}_5\text{H}] \ll k_{-1}[\text{CH}_2=\text{CHSnPh}_3]\)

\[
\frac{d[\text{C}_6\text{F}_5\text{SnPh}_3]}{dt} = \frac{k_1k_2[4.1^{\text{Ph}}][\text{C}_6\text{F}_5\text{H}]}{k_{-1}[\text{CH}_2=\text{CHSnPh}_3]} \tag{4.2}
\]

**Figure 4.3.** Rate of \(\text{C}_6\text{F}_5\text{SnPh}_3\) formation versus \([4.1^{\text{Ph}}][\text{C}_6\text{F}_5\text{H}]/[\text{CH}_2=\text{CHSnPh}_3]\) at 338 K for the catalytic stannylation of \(\text{C}_6\text{F}_5\text{H}\) with \(\text{CH}_2=\text{CHSnPh}_3\), shown for nine different sets of concentrations for the reagents but identical catalyst concentration, \([4.1^{\text{Ph}}]\). The solid line is a least squares linear fit.
Insight into the Arene C–H Bond Cleavage Step

4.2.4.1 Deuterium Labeling Study

Various studies were performed to gain insight into the nature of the step that cleaves the arene C–H bond in the catalytic stannylation reaction. The catalytic reaction of 4.1Ph with 1,2,4,5-tetrafluorobenzene-$d_1$ provided an intramolecular kinetic isotope effect (KIE) of 2.0 for the catalytic conversion to 2,3,5,6-C$_6$F$_4$D-SnPh$_3$ and to 2,3,5,6-C$_6$F$_4$H-SnPh$_3$, as shown in Scheme 4.5. This is similar to the equilibrium isotope effect we previously reported for the reversible C–H/D activation of 1,2,4,5-tetrafluorobenzene-$d_1$ to a $(Et_3P)_2Ni$ synthon. In contrast, the seemingly closely related alkenylation of the C–H bond in para-MeOC$_6$F$_4$H using a 3 % loading of a catalyst obtained from Ni(COD)$_2$ and P(Cyp)$_3$ has been reported to have a KIE of 1.0. From DFT calculations, it was hypothesized that this is due to a mechanism where C–H activation and insertion occur in one step, although this analysis does not explain the similarly low KIE that was reported for the oxidative addition of 1,2,4,5-tetrafluorobenzene-$d_1$ to an $(i$Pr$_3P)_2Ni$ synthon at 298 K. The KIE of 2.0 that we report here supports a typical oxidative addition process, though ligand assistance of this process by a barrierless insertion into the vinyl group step cannot be discounted.

**Scheme 4.5.** Deuterium labelling study to determine the kinetic isotope effect of the C–H cleavage step.
4.2.4.2 Competition for C–H Stannylation Between Different Fluorinate Arenes

Note: The competition studies presented in this section were performed by Manar Shoshani under my supervision.

Further support for significant metal-carbon bond formation in the C–H bond cleaving step was obtained from a comparison of reaction rate with different fluorinated arenes containing two ortho-F substituents. The rates of reaction relative to pentafluorobenzene are shown for the substrates 1,2,4,5-tetrafluorobenzene, 1,2,3,5-tetrafluorobenzene, 1,2,4-trifluorobenzene, 1,3,5-trifluorobenzene and 1,3-difluorobenzene in Table 4.1. The relative rates were obtained by competition studies between these substrates at 338 K. The ratio of initial products can be used to generate a difference in Gibbs free energy of activation, $\Delta\Delta G^\ddagger$, for these substrates relative to pentafluorobenzene. An estimated difference in enthalpy of activation, $\Delta\Delta H^\ddagger$, can be obtained by correcting for the statistical increase in activation that occurs due to the presence of multiple identical sites of activation. Previous computational studies allow for an estimate of aryl–H and aryl–Ni bond dissociation energies.52 The $\Delta\Delta H^\ddagger$ values correlate well with the difference between aryl–H and aryl–Ni bond strengths, as shown in Figure 4.4. Both the relative enthalpies and relative bond dissociation energy differences are with respect to pentafluorobenzene, the most reactive fluorinated benzene. There are several interesting trends observed from this plot. The first is that there is a clear correlation between the $\Delta\Delta H^\ddagger$ and the difference between predicted C–H and C–Ni bond strengths for these substrates. Secondly, there is a clear effect of meta-substitution, where the substrates with more meta-fluorine substituents react faster than similar substrates with para-fluorine substituents, and this correlates with the greater importance of meta-F substituents towards Ni–C bond strength than C–H bond strength. Interestingly, the plot has an initial slope of ~1 for the substrates 1,2,4,5- and 1,2,3,5-tetrafluorobenzene, suggestive of a transition state where Ni–C bond formation and C–H bond cleavage is substantial. For the less fluorinated substrates the $\Delta\Delta H^\ddagger$ values increase faster than the difference in dissociation energies between the C–H and Ni–C bonds, perhaps indicative of an earlier transition state, with less Ni–C bond formation.
Table 4.1. Relative reaction rates compared to pentafluorobenzene in competition experiments with stannylation using CH$_2$=CHSnPh$_3$ using catalyst 4.1$^{Ph}$. $\Delta \Delta G^\ddagger$ values were calculated by $\Delta \Delta G^\ddagger = -RT \ln(k_1/k_2)$, where $k_1$ and $k_2$ are the relative rates of product formation. $\Delta \Delta H^\ddagger$ values were adjusted to consider equivalent hydrogen environments using the following equation $\Delta \Delta H^\ddagger = \Delta \Delta G^\ddagger + RT \ln(H_1/H_2)$.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Relative Rate</th>
<th>$\Delta \Delta G^\ddagger$ kcal·mol$^{-1}$</th>
<th>Equiv H</th>
<th>$\Delta \Delta H^\ddagger$ kcal·mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$F$_5$H</td>
<td>1.00</td>
<td>0.00</td>
<td>1</td>
<td>0.00</td>
</tr>
<tr>
<td>1,2,4,5-C$_6$F$_4$H$_2$</td>
<td>0.93</td>
<td>0.05</td>
<td>2</td>
<td>0.51</td>
</tr>
<tr>
<td>1,2,3,5-C$_6$F$_4$H$_2$</td>
<td>0.32</td>
<td>0.77</td>
<td>2</td>
<td>1.24</td>
</tr>
<tr>
<td>1,2,4-C$_6$F$_3$H$_3$</td>
<td>0.047</td>
<td>2.05</td>
<td>1</td>
<td>2.05</td>
</tr>
<tr>
<td>1,3,5-C$_6$F$_3$H$_3$</td>
<td>0.039</td>
<td>2.18</td>
<td>3</td>
<td>2.92</td>
</tr>
<tr>
<td>1,3-C$_6$F$_2$H$_4$</td>
<td>0.0021</td>
<td>4.13</td>
<td>1</td>
<td>4.13</td>
</tr>
</tbody>
</table>

Figure 4.4. Plot of the estimated difference in relative Ni–aryl vs H–aryl bond dissociation energies, $\Delta D_{C-H} - \Delta D_{Ni-C}$, versus the difference in enthalpy of activation for catalytic stannylation, $\Delta \Delta H^\ddagger$, determined from competition reactions between a series of fluorinated substrates. The relative $\Delta D$ value and $\Delta \Delta H^\ddagger$ values are both with respect to C$_6$F$_5$H.
The relative reaction rates of the different fluorinated substrates, as well as the observed KIE with 1,2,4,5-C₆F₄HD, are consistent with a mechanism where the stannylation reaction has a step where both aryl–H bond breaking and Ni–C bond formation to the fluoroaryl moiety occur in a concerted manner, leading to oxidative addition. The reaction of pentafluorobenzene-₄H and cis-1-propenyl-tributyltin catalysed by 4.1Ph produced primarily trans-propene-₄H, consistent with the data obtained in section 3.2.2, which is suggestive of an insertion pathway, as illustrated in Scheme 4.6. The first step proceeding from the binding of the pentafluorobenzene may involve distinct oxidative addition and insertion step, or this may be ligand assisted, with no barrier to insertion upon C–H bond breaking. Either β-elimination or β-abstraction could conceivably lead to the product. Future computational studies may provide greater detail to the exact mechanism of this reaction during and after the rate-determining step.

**Scheme 4.6.** Plausible mechanism of aryl–H bond breaking and Ni–C bond formation to the fluoroaryl moiety.
4.3 Conclusions

Experimental evidence shows that monophosphine nickel complexes such as \((\text{Pr}_3\text{P})\text{Ni}(\eta^2\text{-CH}_2\text{-CHSnBu}_3)_2\) (4.1Bu) and \((\text{Pr}_3\text{P})\text{Ni}(\eta^2\text{-CH}_2\text{-CHSnPh}_3)_2\) (4.1Ph) are the active precatalysts for the catalytic stannylation of partially fluorinated aromatics such as pentafluorobenzene. Complex 4.1Ph is a solid, which allowed for facile handling and thus was amenable to mechanistic studies. The observed kinetic data is consistent with a mononuclear nickel complex throughout the key steps of the catalytic cycle, and with a dissociative step with the loss of a CH\(_2\text{-CHSnPh}_3\) moiety prior to reaction with C\(_6\text{F}_5\)H. The Sn–C bond forming step appears to occur via \(\beta\)-elimination or \(\beta\)-abstraction after hydrogen insertion into the vinyltin moiety. Competition studies suggest that the rate determining step occurs with significant metal-aryl bond formation with highly fluorinated aromatics. Further studies are needed to better understand the importance of stannylic substituents and ancillary donor choice on both catalyst thermal stability and reaction rate.

4.4 Experimental

4.4.1 General Procedures

Unless otherwise stated, all manipulations were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or an MBraun glovebox. Benzene–\(d_6\) was dried by refluxing with Na/K and was then vacuum transferred and degassed by three freeze–pump–thaw cycles. All other solvents were purchased anhydrous from Aldrich and further purified using a Grubbs’ type column system supplied by Innovative Technology. \(^1\text{H}, \quad 13\text{C}\{^1\text{H}\}, \quad 19\text{F}\{^1\text{H}\}, \quad 31\text{P}\{^1\text{H}\}\) and \(^{119}\text{Sn}\{^1\text{H}\}\) were recorded on a Bruker AMX Spectrometer operating at 300 MHz or where stated at 500 MHz with respect to proton nuclei. \(^1\text{H}\) NMR spectra were referenced to residual protons (C\(_6\text{D}_6, \delta 7.15\)) with respect to tetramethylsilane at \(\delta 0.00\). \(^{13}\text{C}\{^1\text{H}\}\) spectra were referenced relative to solvent resonances (C\(_6\text{D}_6, \delta 128.0\)). \(^{19}\text{F}\{^1\text{H}\}\) NMR spectra were referenced to an external sample of 80 % CCl\(_3\)F in CDCl\(_3\) at \(\delta 0.0\). \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra were referenced to an external sample of phosphoric acid at \(\delta 0.0\). \(^{119}\text{Sn}\{^1\text{H}\}\) NMR spectra were referenced to an external sample of SnMe\(_4\) at \(\delta 0.0\). C\(_6\text{D}_6\) and toluene-\(d_8\)
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were purchased from Aldrich. The compounds pentafluorobenzene, \textsuperscript{1}Pr\textsubscript{3}P, CH\textsubscript{2}=CHSnBu\textsubscript{3}, and ClSnPh\textsubscript{3} were purchased from Aldrich. The compounds cis–(1–propenyl)SnBu\textsubscript{3}, cis–trans–(1–propenyl)SnBu\textsubscript{3}, bromo–2,3,4,5,6–pentafluorobenzene, and bromo–2,3,5,6–tetrafluorobenzene were purchased from Alfa Aesar. Ethylene was purchased from BOC gases. The compounds Ni(COD)\textsubscript{2},\textsuperscript{54} C\textsubscript{6}F\textsubscript{5}D,\textsuperscript{41} C\textsubscript{6}F\textsubscript{4}HD,\textsuperscript{39} CH\textsubscript{2}=CHSnPh\textsubscript{3},\textsuperscript{55} were prepared by literature procedures. Elemental analyses were conducted at the Centre for Catalysis and Materials Research at the University of Windsor by Dr. Samuel Johnson and Dr. Janeen Auld, Instrument Technician.

4.4.2 Synthesis, Characterization and Reactivity of Complexes

Synthesis of (\textsuperscript{1}Pr\textsubscript{3}P)Ni[\eta\textsuperscript{2}-CH\textsubscript{2}=CHSnBu\textsubscript{3}]\textsubscript{2} (4.1\textsubscript{Bu}). A toluene solution of Ni(COD)\textsubscript{2} (500 mg, 1.82 mmol), \textsuperscript{1}Pr\textsubscript{3}P (291.3 mg, 1.82 mmol), and CH\textsubscript{2}=CHSnBu\textsubscript{3} (1.15 g, 3.64 mmol, 2 equiv) were reacted immediately at room temperature. The solvent was removed under vacuum leaving an oil. The resultant oil was identified by multinuclear NMR spectroscopy to be (P\textsuperscript{1}Pr\textsubscript{3})Ni[\eta\textsuperscript{2}-CH\textsubscript{2}=CHSnBu\textsubscript{3}]\textsubscript{2}, 4.1\textsubscript{Bu}. \textsuperscript{1}H NMR (toluene-\textit{d}\textsubscript{8}, 25 °C, 300.13 MHz): \(\delta\) 0.93 (overlapping m, 30H, SnC\textsubscript{H}\textsubscript{3} and SnCH\textsubscript{2}CH\textsubscript{2}, \(3J\text{HH} = 7.3\) Hz); 0.97 and 0.99 (d, 18H, CH(CH\textsubscript{3})\textsubscript{2}, \(3J\text{HH} = 7\) Hz); 1.39 (m with Sn satellites, 12H, SnCH\textsubscript{2}), \(3J\text{HSn} = 60.4\) Hz, \(3J\text{HH} = 7.3\) Hz); 1.51 (m, 3H, CH(CH\textsubscript{3})\textsubscript{2}); 1.62 (m, 12H, SnCH\textsubscript{2}CH\textsubscript{2}); 2.80 (dd with Sn satellites, 2H, vinyl–CH, \(3J\text{HH} = 6.6\) Hz, \(3J\text{HH} = 2.3\) Hz, \(3J\text{HSn} = 62.1\) Hz); 2.86 (m, 2H, vinyl–CH); 3.35 (ddd with Sn satellites, 2H, vinyl–CH, \(2J\text{PH} = 15.3\) Hz, \(3J\text{HH} = 6.3\) Hz, \(3J\text{HH} = 4.3\) Hz, \(2J\text{HSn} = 67.8\) Hz). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (toluene-\textit{d}\textsubscript{8}, 25 °C, 121.5 MHz): \(\delta\) 50.2 (s with Sn satellites, 1P, \(4J\text{PSn} = 29.7\) Hz). \textsuperscript{119}Sn\{\textsuperscript{1}H\} (toluene-\textit{d}\textsubscript{8}, 25 °C, 111.96 MHz): \(\delta\) –35.7 (d, 1Sn, \(3J\text{SnP} = 30.3\) Hz).

Synthesis of (\textsuperscript{1}Pr\textsubscript{3}P)Ni[\eta\textsuperscript{2}-CH\textsubscript{2}=CHSnPh\textsubscript{3}]\textsubscript{2} (4.1\textsubscript{Ph}). To a solution of CH\textsubscript{2}=CHSnPh\textsubscript{3} (0.719 g, 1.90 mmol) in 15 mL of toluene was added \textsuperscript{1}Pr\textsubscript{3}P (0.262 g, 0.95 mmol) and Ni(COD)\textsubscript{2} (0.153 g, 0.95 mmol). The solution was stirred for 30 min and the solvent was removed, leaving a yellow solid. (0.898 g, 97 % yield). \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 25 °C, 500.13 MHz): \(\delta\) 0.64 (dd, 9H, CH(CH\textsubscript{3})\textsubscript{2}, \(3J\text{HH} = 7.1\) Hz, \(3J\text{HP} = 12.3\) Hz); 0.77 (dd, 9H, CH(CH\textsubscript{3})\textsubscript{2}, \(3J\text{HH} = 7.1\) Hz, \(3J\text{HP} = 12.3\) Hz); 1.90 (d septet, 3H, CH(CH\textsubscript{3})\textsubscript{2}, \(2J\text{HP} = 7.2\) Hz, \(3J\text{HH} = 6.9\) Hz); 3.00 (dd with Sn satellites, 2H, vinyl–CH, \(2J\text{HH} = 11.7\) Hz, \(3J\text{HH} = 4.1\) Hz,
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\[ 2J_{\text{HSn}} = 151 \text{ Hz}; \]  3.09 (dd, 2H, vinyl–CH, \[ 3J_{\text{HH}} = 14.8 \text{ Hz}, 2J_{\text{HH}} = 9.4 \text{ Hz}; \] 4.11 (dd with Sn satellites, 2H, vinyl–CH, \[ 2J_{\text{HH}} = 14.5 \text{ Hz}, 3J_{\text{HH}} = 12.0 \text{ Hz}, 3J_{\text{HH}} = 3.0 \text{ Hz}, 3J_{\text{HSn}} = 61.6 \text{ Hz}); 7.15 (m, 12H, Ar–H); 7.6 (m with Sn satellites, 12H, Ar–H, \[ 3J_{\text{HSn}} = 45.2 \text{ Hz}). \]

\[^{31}\text{P}\{^{1}\text{H}\} \text{NMR} (\text{C}_6\text{D}_6, 25 \text{ °C}, 202.46 \text{ MHz}): \delta 49.8 (\text{s with Sn satellites}, 1\text{P}, \[ 3J_{\text{PSn}} = 30.7 \text{ Hz}). \]

\[^{119}\text{Sn}\{^{1}\text{H}\} \text{NMR} (\text{toluene}, 25 \text{ °C}, 111.96 \text{ MHz}): \delta –122.0 (\text{d}, 1\text{Sn}, \[ 3J_{\text{SnP}} = 32.4 \text{ Hz}). \]

Stoichiometric Stannylation of C\textsubscript{6}F\textsubscript{5}H with 4.1\textsuperscript{Ph}. The addition of 40 mg C\textsubscript{6}F\textsubscript{5}H to 40 mg 4.1\textsuperscript{Ph} in benzene-\textit{d}\textsubscript{6} was monitored by \[^{1}\text{H}, {^{19}}\text{F} \text{ and } {^{119}}\text{Sn NMR spectroscopy. The product C}_{6}\text{F}_{5}\text{SnPh}_{3} \text{ and complexes 4.2}\textsuperscript{Ph} \text{ and 4.3 were the only species observed. The assignment was confirmed by consistency with the reaction products observed in the reaction of 4.1}\textsuperscript{Ph} \text{ and ethylene, provided below.} \]

Catalysis and Characterization of C\textsubscript{6}F\textsubscript{5}SnPh\textsubscript{3}. A solution of C\textsubscript{6}F\textsubscript{3}H (0.052 g, 0.309 mmol) in C\textsubscript{6}D\textsubscript{6} was added to a mixture of CH\textsubscript{2}=CHSnPh\textsubscript{3} (0.039 g, 0.103 mmol) and \((^3\text{Pr}_3\text{P})\text{Ni(}^{\eta^2-\text{CH}_2}=\text{CHSnPh}_3)\text{)}_2 \text{ (4.1}\textsuperscript{Ph}) \text{ (0.003 g, 0.0031 mmol). The solution was heated at 338 K for 0.5 h to allow the reaction to go to completion. (95 % yield by NMR spectroscopy).} \[^{1}\text{H}\text{NMR} (\text{C}_6\text{D}_6, 65 \text{ °C}, 300.13 \text{ MHz}): \delta 7.28 (\text{m}, 17\text{H}, \text{Ar–H}); 7.70 (\text{m with Sn satellites}, 8\text{H}, \text{Ar–H}, \[ 2J_{\text{HSn}} = 55.0 \text{ Hz}). \]

\[^{19}\text{F}\{^{1}\text{H}\} \text{NMR} (\text{C}_6\text{D}_6, 65 \text{ °C}, 282.40 \text{ MHz}): \delta –118.6 (\text{AA’MM’N second order with Sn satellites}, 2\text{F}, 2,6–\text{Ar–F}); –151.0 (\text{tt with Sn satellites}, 1\text{F}, 4–\text{Ar–F}, \[ 3J_{\text{FF}} = 19.6 \text{ Hz}, 4J_{\text{FF}} = 2.7 \text{ Hz}); –159.7 (\text{AA’MM’N second order}, 2\text{F}, 3,5–\text{Ar–F}). \]

\[^{119}\text{Sn}\{^{1}\text{H}\} \text{NMR} (\text{C}_6\text{D}_6, 25 \text{ °C}, 111.96 \text{ MHz}): \delta –137.9 (\text{m, Sn}). \]

Reaction of 4.1\textsuperscript{Ph} with ethylene. A solution of 4.1\textsuperscript{Ph} (40 mg) in benzene-\textit{d}\textsubscript{6} was transferred into an NMR tube equipped with a Teflon valve. The nitrogen atmosphere was removed by two freeze-pump-thaw cycles, and an atmosphere of ethylene was added. The sample was heated at 50 °C for 30 minutes. The probe was then cooled to 25 °C and spectra were collected consistent with 4.2\textsuperscript{Ph} and 3.

Characterization of \((^3\text{Pr}_3\text{P})\text{Ni(}^{\eta^2-\text{CH}_2}=\text{CHSnPh}_3\text{SnCH}=\text{CH}_2)(^{\eta^2-\text{C}_2\text{H}_4}) \text{ (4.2}\textsuperscript{Ph}). \[^{1}\text{H}\text{NMR} (\text{C}_6\text{D}_6, 25 \text{ °C}, 500.13 \text{ MHz}): \delta 0.85 (\text{dd}, 9\text{H}, \text{CH(CH}_3)_2, \[ 2J_{\text{HH}} = 7 \text{ Hz}, 3J_{\text{HP}} = 12.5 \text{ Hz}); 0.90 (\text{dd}, 9\text{H}, \text{CH(CH}_3)_2, \[ 2J_{\text{HH}} = 7 \text{ Hz}, 3J_{\text{HP}} = 12.5 \text{ Hz}); 2.00 (\text{m}, 3\text{H}, \text{CH(CH}_3)_2); 2.70 (\text{2nd order m}, 2\text{H}, \text{CHH on } \eta^2 \text{ ethylene}); 2.97 (\text{2nd order m}, 2\text{H}, \text{CHH on } \eta^2 \text{ ethylene}). \]
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Characterization of (iPr₃P)Ni(η²-C₂H₄)₂ (4.3). ¹H NMR (C₆D₆, 25 °C, 500.13MHz): δ 0.97 (dd, 18H, CH(CH₃)₂, 2J_HH = 7.5 Hz, 3J_HP = 12.5 Hz); 1.93 (m, 3H, CH(CH₃)₂); 2.76 (s, 4H, C₂H₄). ³¹P {¹H} NMR (C₆D₆, 25 °C, 121.54 MHz): δ 52.46 (s, 1P).

Catalytic Reaction Rate versus [Catalyst]. A stock solution of the reagent CH₂=CHSnPh₃ (232 mg, 0.62 mmol), the reagent C₆F₅H (107 mg, 0.64 mmol), the internal standard C₆H₅F (60 mg, 0.62 mmol) and the internal standard hexamethyldisiloxane (HMDSO) (100 mg, 0.62 mmol) were dissolved in toluene and the solution was diluted to 3.6 mL, to provide a solution that is 0.172 M of CH₂=CHSnPh₃, C₆H₅F and HMDSO and 0.177 M of C₆F₅H. Approximate masses of 3, 6, 12, 24 and 48 mg of the catalyst 4.1Ph were weighed into a vial and 0.6 mL of the stock solution was added to give approximate catalyst concentrations of 0.005 M, 0.01 M, 0.02 M, 0.04 M and 0.08 M respectively. The resulting solution was transferred to an NMR tube. The samples did not react appreciably at room temperature, and were introduced into an NMR spectrometer probe preheated to 338 K. The rate of reaction production was monitored via concentration of C₆F₅SnPh₃ formed versus time. The concentration of C₆F₅SnPh₃ formed was estimated from integration of the ¹⁹F NMR signals compared to the internal standard C₆H₅F. Plotting concentration of product formed versus time, the slope was found to be linear for extended periods of time and was recorded as the reaction rate. The observed reactions rates were found to be 1.347×10⁻⁵, 2.162×10⁻⁵, 3.961×10⁻⁵, 8.387×10⁻⁵ and 1.794×10⁻⁴ M·s⁻¹, respectively. Plotting catalyst concentration versus the respective reaction rates, yields a linear slope.

Catalytic Reaction Rate versus [C₆F₅H]. A stock solution of the reagent CH₂=CHSnPh₃ (400 mg, 1.06 mmol), the catalyst 4.1Ph (25 mg, 0.026 mmol) and the
internal standard C₆H₅F (100 mg, 1.04 mmol) was dissolved in 5 mL toluene, to provide a solution that was 0.212 M, 0.0052 M and 0.208 M in these three components, respectively. Approximate masses of 12, 25, 50, 100 and 200 mg of C₆F₅H were weighed directly into five 5 mm NMR tubes, and the stock solution was added to dilute the solution to a total volume of 0.64 mL. The samples did not react appreciably at room temperature. The samples were introduced into an NMR spectrometer probe preheated to 338 K, and the concentration of C₆F₅SnPh₃ was monitored versus time by ¹⁹F NMR spectroscopy. The slope of this plot was found to be linear for extended periods, and the slope was recorded as the reaction rate. The concentrations of C₆F₅H for the five separate samples were estimated from integration compared to the internal standard to be 0.123, 0.218, 0.480, 0.82 and 1.97 M, and the observed reaction rates were 3.64×10⁻⁶, 6.76×10⁻⁶, 1.68×10⁻⁵, 2.72×10⁻⁵, and 7.64×10⁻⁵ M·s⁻¹, respectively.

**Catalytic Reaction Rate versus [CH₂=CHSnPh₃].** A stock solution of the reagent CH₂=CHSnPh₃ (100 mg, 0.265 mmol), the reagent C₆F₅H (400 mg, 2.38 mmol) the catalyst 4.1Ph (25 mg, 0.026 mmol) and the internal standard C₆H₅F (100 mg, 1.04 mmol) was dissolved in 5 mL toluene, to provide a solution that was 0.053 M, 0.476 M 0.0052 M and 0.208 M in these four components, respectively. Five NMR tubes were loaded with 0, 10, 30, 70, 82, and 162 mg of CH₂=CHSnPh₃, and the stock solution was added to dilute the solution to a total volume of 0.64 mL. No reaction was observed at room temperature. The samples were introduced into an NMR spectrometer probe preheated to 338 K, and the rate of production of concentration of C₆F₅SnPh₃ was monitored versus time by ¹⁹F NMR spectroscopy. The slope of this plot was found to be linear for extended periods, and the slope was recorded as the reaction rate. The initial concentrations of CH₂=CHSnPh₃ for the five separate samples are calculated to be 0.053, 0.094, 0.218, 0.507, and 1.13 M, and the observed reaction rates were 1.18×10⁻⁴, 4.39×10⁻⁵, 1.80×10⁻⁵, 7.45×10⁻⁶, and 3.12×10⁻⁶ M·s⁻¹, respectively.

**Reaction of 1,2,4,5-C₆F₄HD, CH₂=CHSnPh₃, and 5 % catalyst loading (iPr₃P)Ni(η²-CH₂=CHSnPh₃).** A solution of 1,2,4,5-C₆F₄HD (0.015 g, 0.103 mmol), CH₂=CHSnPh₃ (0.039 g, 0.103 mmol) in 1 mL of C₆D₆ was mixed with 4.1Ph (0.005 g, 0.005 mmol) and placed in a preheated NMR probe at 338 K. The ¹⁹F NMR spectrum of the reaction
mixture was recorded after 5 min of initiation of the reaction in order to determine the initial deuterium isotope effect for C–H vs. C–D activation. Activation of hydrogen over deuterium can be confirmed by a ~0.3 ppm shift of any ortho fluorine adjacent to the remaining deuterium in the product and the isotope effect can be determined through integration. Oxidative addition is favoured for C–H over C–D bonds, and the ratio of integrals for the products (2,3,5,6–C₆F₄D)SnPh₃ and (2,3,5,6–C₆F₄H)SnPh₃ were found to be 2.0 : 1 at 338 K. ¹⁹F{¹H} NMR (C₆D₆, 65 °C, 282.40 MHz): −118.7 (AA'BB' second order, 3F, 2,6–Ar–F); −136.9 (AA'BB' second order, 1F, 3,5–Ar(H)–F); −137.2 (AA'BB' second order, 2F, 3,5–Ar(D)–F).

Fluorinated Aromatic Competition Reactions. A stock solution of CH₂=CHSnPh₃ (400 mg, 1.06 mmol), catalyst 4.1Ph (30 mg, 0.031 mmol) and the internal standard C₆FH₅ (100 mg, 1.04 mmol) were dissolved in 5 mL of toluene. Equimolar amounts of fluorinated aromatics were added. The following proportions were used with each competition: a) C₆F₅H (100 mg, 0.595 mmol) vs. 1,2,4,5- C₆F₄H₂ (89 mg, 0.595 mmol); b) 1,2,4,5-C₆F₄H₂ (100 mg, 0.666 mmol) vs. 1,2,3,5-C₆F₄H₂ (100 mg, 0.666 mmol); c) 1,2,3,5-C₆F₄H₂ (100 mg, 0.666 mmol) vs. 1,2,4-C₆F₃H₃ (88 mg, 0.666 mmol); d) 1,2,4-C₆F₃H₃ (100 mg, 0.757 mmol) vs. 1,3,5-C₆F₃H₃ (100 mg, 0.757 mmol); and e) 1,2,4-C₆F₃H₃ (100 mg, 0.757 mmol) vs. 1,3-C₆F₂H₄ (86 mg, 0.757 mmol). Soon after the reactants were mixed ¹⁹F NMR spectroscopy was used to analyze the sample at 338 K. At this point the conversion was minimal relative to the starting materials, which allowed integration of the products ¹⁹F NMR resonances to be used to determine relative rates. Using the relative rate constant, the change in Gibbs free energy of activation and change in enthalpy of activation versus pentafluorobenzene were also determined.

Reaction of C₆F₅D, (cis-propenyl)SnBu₃, and 5 % catalyst loading 4.1Ph. A solution of C₆F₅D (0.046 g, 0.2718 mmol), (cis-propenyl)SnBu₃ (0.090 g, 0.2718 mmol) in 1 mL of C₆D₆ was mixed with 4.1Ph (0.013 g, 0.0136 mmol) and placed in a preheated NMR probe at 338 K. After 20 min the ¹H NMR spectrum was used to confirm that trans-propene-d₁ is produced exclusively.
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**Reaction of C₆F₅D, (cis,trans-propenyl)SnBu₃, and 5 % catalyst loading 4.1ₚₜ.** A solution of C₆F₅D (0.046 g, 0.2718 mmol), (cis,trans-propenyl)SnBu₃ (0.090 g, 0.2718 mmol) in 1 mL of C₆D₆ was mixed with 4.1ₚₜ (0.013 g, 0.0136 mmol) and placed in a preheated NMR probe at 338 K. After 20 min the ¹H NMR spectrum was used to confirm that both cis-propene-d₁ and trans-propene-d₁ are produced in equal amounts.

### 4.5 X-ray Crystallography

#### 4.5.1 General Collection and Refinement Information

The X-ray structure of 4.1ₚₜ was obtained at −100 °C, with the crystal covered in Paratone and placed rapidly into the cold N₂ stream of the Kryo-Flex low-temperature device. The data was collected using the SMART⁵⁶ software on a Bruker APEX CCD diffractometer using a graphite monochromator with Mo Kα radiation (\(\lambda = 0.71073 \text{ Å}\)). A hemisphere of data was collected using a counting time of 10 s per frame. Data reductions were performed using the SAINT⁵⁷ software, and the data were corrected for absorption using SADABS.⁵⁸,⁵⁹ The structures were solved by direct methods using SIR97⁶⁰ and refined by full-matrix least-squares on \(F²\) with anisotropic displacement parameters for the non-H atoms using SHELX-97⁶¹,⁶² and the WinGX⁶³ software package, and thermal ellipsoid plots were produced using ORTEP32.⁶⁴ The hydrogen atoms on the coordinated carbon atoms of the vinyl moiety were located in the electron-density difference map and their positions were refined. The remaining hydrogen atoms were placed in idealized locations using the AFIX command in SHELX.

#### 4.5.2 Crystallographic Data

**Table 4.2. Crystallographic Data for \((\text{iPr₃P})\text{Ni}[\eta₂-\text{CH₂-CHSnPh₃}]₂, 4.1ₚₜ.**

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<td></td>
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4.6 References


136 References begin on page 136
Chapter 4 – A Mechanistic Investigation of C–H Bond Stannylation: Synthesis and Characterization of Nickel Catalysts


Chapter 4 – A Mechanistic Investigation of C–H Bond Stannylation: Synthesis and Characterization of Nickel Catalysts


(49) Lin, S.; Agapie, T. Synlett 2011, 1-5.


(56) SMART, Molecular analysis research tool; Bruker AXS Inc. Madison, WI.: 2001., .

(57) SAINTPlus, Data reduction and correction program; Bruker AXS Inc.: Madison, WI, 2001.


5.1 Introduction

Reactions that convert simple hydrocarbons into molecules that bear versatile functional groups are of great importance in organic and organometallic chemistry.\(^1\)-\(^9\) The addition of element-element or element-hydrogen bonds across a multiple bond has proven to be a useful methodology for forming new element-carbon bonds. Hydroboration\(^1\(^0\) and hydrosilylation\(^1\(^0\),\(^1\(^1\) of alkenes and alkynes are two well-known reactions of this type, which can be used to prepare a variety of organoboranes and organosilanes, as shown in Scheme 5.1. These hydroboration and hydrosilylation products can be used for further transformations such as Miyaura-Suzuki\(^1\(^2\) or Hiyama\(^1\(^3\) cross-coupling reactions. Hydrostannylation\(^1\(^0\),\(^1\(^4\) are also accessible; however, they typically involve alkynes and generally proceed by a radical mechanism. Hydrostannylation of alkenes is more difficult and usually requires the addition of a
Lewis acid\textsuperscript{15}, radical initiator\textsuperscript{16} or a strained alkene\textsuperscript{17} to overcome side reactions which produce H\textsubscript{2} and distannanes.

\begin{center}
\begin{tabular}{|c|c|c|}
\hline
E & E' & ref \\
\hline
H & SiR\textsubscript{3} & 10, 11 \\
H & BrR\textsubscript{2} & 10 \\
H & SnR\textsubscript{3} & 10, 14, 15 - 17 \\
\hline
\end{tabular}
\end{center}

\textbf{Scheme 5.1.} General reaction scheme for the addition of an element-hydrogen bond across an alkyne to form new element-carbon bonds.

Unlike hydrostannylations, carbostannylations provide an alternative for accessing a wide range of functionalized organostannane reagents without competing side reactions. Organostannanes are typically air and moisture stable and can be utilized for the Stille cross-coupling reaction,\textsuperscript{18-20} which offers functional-group tolerance. The carbostannylation\textsuperscript{21} of alkynes or 1,2-dienes for the synthesis of alkenylstannanes is limited to organostannane reagents containing alkynyl,\textsuperscript{22-29} alkenyl\textsuperscript{30}, allyl\textsuperscript{31-38} or acyl\textsuperscript{24,39-42} groups. There is one example of carbostannylation with an aryl organostannane, which undergoes a double insertion reaction with alkynes, but requires a methoxy group in the \textit{para} position of the aryl group.\textsuperscript{43} The carbostannylation of alkenes is more difficult and to the best of our knowledge has only being observed in systems that involve strained alkenes\textsuperscript{44} or radical chain mechanisms.\textsuperscript{31,45}

In Chapter 3 we showed that Ni(COD)\textsubscript{2} (COD = 1,5-cyclooctadiene) and an ancillary ligand (MeNC\textsubscript{5}H\textsubscript{4}N\textsubscript{i}Pr or \textit{i}Pr\textsubscript{3}P) catalyze the reaction of CH\textsubscript{2}=CHSnBu\textsubscript{3} and fluorinated aromatics, via selective C–H bond stannylation to give C\textsubscript{6}F\textsubscript{n}H\textsubscript{5-n}SnBu\textsubscript{3} (5.1\textsubscript{Bu}) and ethylene, as shown in Scheme 5.2 for the substrate C\textsubscript{6}F\textsubscript{5}H.\textsuperscript{46,47} We have shown in Chapter 4 that with \textit{i}Pr\textsubscript{3}P as the ancillary ligand, the resting state of the reaction is (\textit{i}Pr\textsubscript{3}P)Ni(\eta\textsubscript{2}-CH\textsubscript{2}=CHSnR\textsubscript{3})\textsubscript{2} (R = Bu or Ph).\textsuperscript{48} The proposed mechanism was shown to
Chapter 5 – C–H Alkylation of Fluorinated Aromatics and Carbostannylation of Ethylene with Fluorinated Organostannanes with Catalytic Amounts of Ni(0) and a Nitrogen Ancillary Ligand

involve the reversible dissociation of one of the CH$_2$=CHSnR$_3$ moieties from the catalyst to produce the unobserved intermediate (i$^3$Pr$_3$P)Ni($\eta^2$-CH$_2$=CHSnR$_3$), which reacts with C$_6$F$_5$H to produce 5.1$^\text{Bu}$ or 5.1$^\text{Ph}$. Little is known about the final C–Sn bond forming step, because it occurs after the rate determining step.

![Scheme 5.2. C–H bond stannylation of pentafluorobenzene with CH$_2$=CHSnBu$_3$ using catalytic amounts of Ni(COD)$_2$ and an ancillary ligand (MeNC$_5$H$_4$N$i^3$Pr or $i^3$Pr$_3$P).](image)

This chapter details a mechanistic study of the C–H bond alkylation reaction that occurs when the ancillary ligand is MeNC$_5$H$_4$N$i^3$Pr and the organostannane is CH$_2$=CHSnR$_3$ (R = Ph or Bn). Insight into the C–H bond stannylation mechanism is also provided from the carbostannylation reaction that occurs when the organostannane is C$_6$F$_5$SnR$_3$ (R = Bn or Ph) and the ancillary ligand is MeNC$_5$H$_4$N$i^3$Pr.

### 5.2 Results and Discussion

#### 5.2.1 Formation and Characterization of (MeNC$_5$H$_4$N$i^3$Pr)Ni($\eta^2$-CH$_2$=CHSnPh$_3$)$_2$

The reaction of Ni(COD)$_2$ with one equivalent of MeNC$_5$H$_4$N$i^3$Pr and two equivalents of CH$_2$=CHSnPh$_3$ in pentane provides the complex (MeNC$_5$H$_4$N$i^3$Pr)Ni($\eta^2$-CH$_2$=CHSnPh$_3$)$_2$ (5.2$^\text{Ph}$), which precipitates as a yellow powder in a 69 % isolated yield, as shown in Scheme 5.3. A similar reaction with CH$_2$=CHSnBn$_3$ in pentane did not yield the desired product (MeNC$_5$H$_4$N$i^3$Pr)Ni($\eta^2$-CH$_2$=CHSnBn$_3$)$_2$ (5.2$^\text{Bn}$). Repeating the reaction in toluene and monitoring by $^1$H NMR shows that 5.2$^\text{Bn}$ initially
forms; however, the complex proved to be unstable. The solution turned from a bright yellow to a dark green within 10 min, and the sample decomposed making isolation and further characterization impossible. Complex $5.2^\text{Ph}$ has $C_1$ symmetry from the $^1$H NMR spectrum, due to restricted rotation around the Ni–N bond and the SnPh$_3$ groups residing on opposite faces of the planar nickel coordination environment. A similar structure was observed for ($^i$Pr$_3$P)Ni($\eta^2$-CH$_2$=CHSnPh$_3$)$_2$. Complex $5.2^\text{Ph}$ contains six proton environments for the two coordinated vinyl moieties that are shifted several ppm upfield relative to free CH$_2$=CHSnPh$_3$. There are four proton environments for the nitrogen-containing ring of MeNC$_5$H$_4$N$i$Pr, which are also shifted several ppm upfield relative to free MeNC$_5$H$_4$N$i$Pr, and two diastereotopic methyl environments at $\delta$ 0.57 and 0.75 for the isopropyl group, which integrate to 3H each. The $^1$H NMR data confirms that $5.2^\text{Ph}$ contains one MeNC$_5$H$_4$N$i$Pr and two CH$_2$=CHSnPh$_3$ moieties, which are coordinated to the nickel metal center. The IR spectrum of $5.2^\text{Ph}$ displays a C=N stretching frequency at 1654.6 cm$^{-1}$. The C=N stretching frequency of free MeNC$_5$H$_4$N$i$Pr is 1661.6 cm$^{-1}$, thus by this measure the MeNC$_5$H$_4$N$i$Pr is $\sigma$-bound to the nickel metal center in complex $5.2^\text{Ph}$ not $\pi$-bound. Unfortunately, X-ray quality crystals of $5.2^\text{Ph}$ were not obtained due to twinning of the small needle shaped crystals.

![Scheme 5.3. General reaction scheme for the formation of $5.2^\text{Ph}$.](image-url)
Chapter 5 – C–H Alkylation of Fluorinated Aromatics and Carbostannylation of Ethylene with Fluorinated Organostannanes with Catalytic Amounts of Ni(0) and a Nitrogen Ancillary Ligand

5.2.2 C–H Bond Alkylation

The reaction of catalytic amounts of isolated complex \( \text{5.2}^{\text{Ph}} \) or Ni(COD)_2 and MeNC_5H_4N^iPr with \( \text{CH}_2=\text{CHSnPh}_3 \) and C_6F_5H provides the unexpected C–H bond alkylation\(^{49,50} \) product C_6F_5CH_2CH_2SnPh_3 (\( \text{5.3}^{\text{Ph}} \)), as shown in Scheme 5.4, with only minor amounts of the previously observed C–H bond stannylation product, \( \text{5.1}^{\text{Ph}} \). This reaction can be carried out at room temperature with as little as 5 mol % catalyst and goes to completion after 4–5 days. The rate of the reaction can be increased by heating to 315 K, though temperatures exceeding 315 K cause catalyst decomposition and decreased yields. Monitoring the reaction by \(^{19}\text{F}\{^1\text{H}\} \) NMR spectroscopy after 4 hours showed \( \text{5.3}^{\text{Ph}}, \text{5.1}^{\text{Ph}} \) and \( \text{cis}-(\text{MeNC}_5\text{H}_4\text{N}^\text{iPr})_2\text{Ni(C}_6\text{F}_5)(\text{SnPh}_3) \) (\( \text{5.4}^{\text{Ph}} \)) (\textit{vide infra}) in a ratio of 1:0.13:0.86, respectively. After 5 days, less than 5 % of the \( \text{CH}_2=\text{CHSnPh}_3 \) starting material remains and the mixture of products contains 73 % of \( \text{5.3}^{\text{Ph}} \), 24 % of \( \text{5.1}^{\text{Ph}} \) and 3 % of \( \text{5.4}^{\text{Ph}} \) by \(^{19}\text{F}\{^1\text{H}\} \) NMR spectroscopy. Over the course of a few weeks \( \text{5.4}^{\text{Ph}} \) disappears and \( \text{5.1}^{\text{Ph}} \) is slowly converted to \( \text{5.3}^{\text{Ph}} \), with three \(^{19}\text{F} \) environments at \( \delta \) –144.7, –158.4 and –162.7. Catalysts \( \text{5.2}^{\text{Ph}} \) and \( \text{5.4}^{\text{Ph}} \) were observed in the \(^1\text{H} \) NMR spectra after 4 hours. The \(^1\text{H} \) NMR spectrum indicates \( \text{5.3}^{\text{Ph}} \) has two distinct CH\(_2\) environments that are multiplets with Sn satellites at \( \delta \) 1.66 and 2.96 that integrate to 2H each. When the reaction was complete the \(^{19}\text{Sn}\{^1\text{H}\} \) NMR spectrum had a single environment for \( \text{5.3}^{\text{Ph}} \) at \( \delta \) –103.7, which is shifted downfield from \( \text{CH}_2=\text{CHSnPh}_3 \) at \( \delta \) –134.4.
Scheme 5.4. General reaction for the formation of $5.3^\text{Ph}$ including intermediate $5.4^\text{Ph}$ and the minor product $5.1^\text{Ph}$.

5.2.3 Synthesis of cis-(MeNC$_5$H$_4$N$i^\text{Pr})_2$Ni(C$_6$F$_5$)(SnR$_3$) Complexes $5.4^\text{Ph}$ and $5.4^\text{Bn}$

To better understand catalytic C–H bond stannylation and C–H bond alkylation, attempts were made to isolate intermediate $5.4^\text{R}$. Reacting two equivalents of MeNC$_5$H$_4$N$i^\text{Pr}$, Ni(COD)$_2$ and isolated Ph$_3$SnC$_6$F$_5$ ($5.1^\text{Ph}$) or Bn$_3$SnC$_6$F$_5$ ($5.1^\text{Bn}$) provided an alternate route to cis-(MeNC$_5$H$_4$N$i^\text{Pr})_2$Ni(C$_6$F$_5$)(SnR$_3$), where $R = \text{Ph}$ ($5.4^\text{Ph}$) or Bn ($5.4^\text{Bn}$), as shown in Scheme 5.5. Activation of the C–Sn bond of $5.1$ to form $5.4$ is the microscopic reverse of the C–Sn bond forming step in the catalytic C–H bond stannylation reaction.
Scheme 5.5. The formation of $5.4^R$ from the reaction of $5.1^R$ with Ni(COD)$_2$ and MeNC$_5$H$_4$NiPr.

The solid-state structure of $5.4^\text{Bn}$ was determined by X-ray crystallography and despite the low quality data, shows the connectivity of the structure and confirms that product $5.4^\text{Bn}$ is square planar with the ancillary ligands cis-disposed, as shown in the ORTEP depiction of the solid-state structure in Figure 5.1. The nitrogen-containing and pentafluorophenyl rings lie out of the coordination plane and the isopropyl substituents of the ancillary ligands are situated on opposite faces of the square plane. The Ni(1)–Sn(1), Ni–C(1) bond lengths were 2.470(5) and 1.976(13) Å, respectively. The Ni(1)–N(1) and Ni(1)–N(3) bond lengths were 1.93(2) and 2.01(2) Å, respectively. The N(1)–Ni(1)–C(1), N(1)–Ni(1)–N(3), C(1)–Ni(1)–N(3), N(1)–Ni(1)–Sn(1), C(1)–Ni(1)–Sn(1), N(3)–Ni(1)–Sn(1), bond angles indicate that the structure is slightly distorted from square planar, with angles of 174.2(9), 93.8(9), 90.0(8), 91.2(7), 84.6(5), 172.6(6)$^\circ$, respectively.
Figure 5.1. Solid-state molecular structure of $5.4^{\text{Bn}}$ as determined by X-ray crystallography. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Ni(1), 1.976(13); N(1)–Ni(1), 1.91(2); N(3)–Ni(1), 2.01(2); Ni(1)–Sn(1), 2.470(5); N(1)–Ni(1)–C(1), 174.2(9); N(1)–Ni(1)–N(3), 93.8(9); C(1)–Ni(1)–N(3), 90.0(8); N(1)–Ni(1)–Sn(1), 91.2(7); C(1)–Ni(1)–Sn(1), 84.6(5); N(3)–Ni(1)–Sn(1), 172.6(6).

Complex $5.4^{\text{Ph}}$ and $5.4^{\text{Bn}}$ were characterized by $^1\text{H}$, $^{19}\text{F}$$\{^1\text{H}\}$, $^{13}\text{C}$$\{^1\text{H}\}$ and $^{119}\text{Sn}$$\{^1\text{H}\}$ NMR spectroscopy. Broad resonances were observed in both the $^1\text{H}$ and $^{19}\text{F}$$\{^1\text{H}\}$ NMR spectra. Variable-temperature NMR spectroscopy was used to determine if the broadening was due to a fluxional process. The $^{19}\text{F}$$\{^1\text{H}\}$ NMR spectra of $5.4^{\text{Ph}}$ and $5.4^{\text{Bn}}$ indicate that there is hindered rotation either about the Ni–C$_6$F$_5$ bond of the pentafluorophenyl ring, or about the Ni–N bonds. At 293 K both the ortho and meta fluorine environments are near coalescence, with broad peaks at $\delta$ –110 and –165, respectively. At 323 K the ortho fluorine resonance for complex $5.4^{\text{Bn}}$ sharpens into a doublet with a coupling constant of 34 Hz, and the meta fluorine resonance resolves into
a complex multiplet. The fast-exchange limit $^{19}$F NMR spectrum of $5.4^\text{Ph}$ could not be obtained. Complex $5.4^\text{Ph}$ has much lower solubility in $d_8$-toluene than $5.4^\text{Bn}$ and thus the variable-temperature NMR was obtained in CD$_2$Cl$_2$. Upon heating this sample or leaving for more than 30 min at room temperature the sample reacted with CD$_2$Cl$_2$ to cleanly form a complex identified as trans-(MeNC$_5$H$_4$N‘Pr)$_2$NiCl(C$_6$F$_5$) (5.5).

Below the coalescence temperature for complex $5.4^\text{Bn}$ and $5.4^\text{Ph}$ the ortho-fluorines at $\delta$ –110 begin to separate and sharpen and the meta-fluorines at $\delta$ –165 sharpen into two complex multiplets. The $^{19}$F{$^1$H} variable-temperature NMR spectra of $5.4^\text{Ph}$ and $5.4^\text{Bn}$ were modeled using WinDNMR$^{51}$ to estimate the rate constant for the fluxional process, the Arrhenius equation was then used to estimate the activation energy to be 25 and 26 kcal·mol$^{-1}$ for $5.4^\text{Ph}$ and $5.4^\text{Bn}$, respectively. The low-temperature limit for hindered rotation was reached at 273 K, however, there was still some broadening of the ortho- and meta-fluorines that is not due to hindered rotation. Figure 5.2 displays the $^{19}$F{$^1$H} NMR experimental and modeled spectra for the ortho region of $5.4^\text{Bn}$ between 223 K and 273 K. The 273 K $^{19}$F{$^1$H} NMR spectrum has two ortho resonances for the fluorinated aromatic at $\delta$ –109.2 and –110.9 with significantly different linewidths. Below 273 K the two resonances sharpen into two doublets with $3^J_{FF}$ values of approximately 35 Hz, and a second set of smaller peaks, approximately 7 % in intensity, begin to separate. The model displayed in Figure 5.2 was used to confirm that the second set of smaller peaks are exchanging with the larger peaks. The most likely identity of this minor species is a rotamer of $5.4^\text{Bn}$ where the isopropyl groups of MeNC$_5$H$_4$N‘Pr lie on the same side of the coordination plane, rather than on opposite faces. The variable-temperature NMR spectra were modeled using WinDNMR$^{51}$ and the Arrhenius equation was used to estimate an activation energy of 5.5 kcal·mol$^{-1}$ for the exchange between the two isomers of $5.4^\text{Bn}$. A similar exchange process between two isomers of $5.4^\text{Ph}$ was also observed for the variable-temperature $^{19}$F{$^1$H} NMR spectra between 223 K and 273 K.
Figure 5.2. a) Simulated and b) experimental, variable-temperature $^{19}$F{$^1$H} NMR spectra for the ortho fluorines of compound $5.4_{Bn}$ obtained at 282.4 MHz in $d_8$-toluene.

At 298 K, the $^1$H NMR spectra for the SnR$_3$ moiety of $5.4_{Ph}$ and $5.4_{Bn}$ displayed three and four resonances, respectively, as expected. There were fourteen resolved resonances for the two MeNC$_5$H$_4$N$i$Pr ancillary ligands in $5.4_{Ph}$ and $5.4_{Bn}$, with two broad resonances integrating to 6H each, which indicated that two pairs of isopropyl methyl environments were in exchange. At 253 K, the isopropyl methyl group resonances at $\delta$ 0.82 and 0.84 for $5.4_{Ph}$ and 1.23 and 1.27 for $5.4_{Bn}$ were both resolved into two sets of doublets, however, the resonances at $\delta$ 1.08 in $5.4_{Ph}$ and 1.60 in $5.4_{Bn}$ were not resolved. The isopropyl CH protons at 298 K were observed as an unresolved multiplet and a septet at $\delta$ 1.98 and 3.29 for $5.4_{Ph}$ and at $\delta$ 4.91 and 3.31 for $5.4_{Bn}$, respectively. The protons associated with C(1) and C(14) of the nitrogen containing rings are shifted downfield, due to their close proximity to the nickel center, and are observed as a broad multiplet and as a doublet at $\delta$ 8.65 and 9.69 respectively for $5.4_{Ph}$ and at $\delta$ 8.70 and 9.71 respectively for $5.4_{Bn}$ at 298 K. The observation of one set of broad and one set of sharp ligand resonances was suggestive of an exchange process. Attempts to resolve the one set of broad ligand resonances were unsuccessful even upon cooling the samples to 223 K.

To determine if ligand dissociation was the source of line-broadening for the one set of ligand peaks, the $^1$H NMR spectra of $5.4_{Bn}$ when 0.5, 1 and 2 equivalents of MeNC$_5$H$_4$N$i$Pr were added at 293 K were compared. The broad set of ligand resonances
were no longer visible and there was broadening of the free ligand peaks in the $^1$H NMR spectra. The results suggest that the broadening of the one set of MeNC$_5$H$_4$N$i$Pr resonances was due to a dissociative process where only one of the MeNC$_5$H$_4$N$i$Pr ligands exchanged with free ligand. The relative large trans effect of the SnR$_3$ (R= Ph or Bn) moiety versus the pentafluorophenyl ring presumably dissociates the ancillary ligand trans to the SnR$_3$ (R= Ph or Bn) moiety. The results also suggest that if a dissociative process was involved that a T-shape structure must have been maintained throughout the exchange process since the two MeNC$_5$H$_4$N$i$Pr environments of 5.4$_{\text{Bn}}$ were not exchanged with each other, and one set of MeNC$_5$H$_4$N$i$Pr resonances remained sharp and were not exchanged with free ligand.

5.2.4 Carbostannylation of Ethylene

To determine if ethylene can be inserted into the Ni–Sn bond of 5.4$_{\text{Bn}}$, and if the intermediate with ethylene inserted into the Ni–Sn bond before reductive elimination can be isolated, 5.4$_{\text{Bn}}$ was reacted with an atmosphere of ethylene and the reaction was tracked by $^{19}$F{$_1$H} NMR. Conversion to 5.3$_{\text{Bn}}$ was observed by $^{19}$F NMR spectroscopy at 303 K; however, the desired intermediate where ethylene was inserted into the Ni–Sn bond was not isolated. There were unidentified peaks at $\delta$ –115, –164 and –165 throughout the reaction; however it remains unclear if these are resonances of the desired nickel complex. However, the results indicate that 5.4$_{\text{Bn}}$ is an intermediate in both the carbostannylation and C–H stannylation reactions.

To further confirm the C–Sn bond of 5.1$_{\text{Ph}}$ was added across ethylene via a carbostannylation reaction, independently synthesized 5.1$_{\text{Ph}}$ was reacted with ethylene and catalytic amounts of MeNC$_5$H$_4$N$i$Pr and Ni(COD)$_2$ and the reaction mixture was monitored by $^{19}$F NMR spectroscopy. The results indicated that 5.1$_{\text{Ph}}$ was converted to 5.3$_{\text{Ph}}$ via carbostannylation, as shown in Scheme 5.6. The formation of 5.3$_{\text{Ph}}$ via carbostannylation was slower than C–H alkylation with CH$_2$=CHSnPh$_3$ and C$_6$F$_5$H, which indicates either inhibition by ethylene or that CH$_2$=CHSnPh$_3$ or C$_6$F$_5$H are required to accelerate the reactivity. The carbostannylation reaction was repeated with the addition
of CH$_2$=CHSnPh$_3$ to the reaction mixture and this decreased the rate of the reaction even further. The addition of C$_6$F$_5$H under identical reaction conditions had no affect on the rate of carbostannylation. The addition of ethylene to a mixture of MeNC$_5$H$_4$N$i$Pr and Ni(COD)$_2$ provided an equilibrium amount of the ethylene complex (MeNC$_5$H$_4$N$i$Pr)Ni($\eta^2$-C$_2$H$_4$)$_2$ (5.8) as observed by $^1$H NMR spectroscopy. Complex 5.8 is present throughout the carbostannylation reaction but was only present in equilibrium amounts and thus was not isolable for further characterization. A large excess of ethylene should accelerate the insertion of ethylene, however, this reaction proved to be quite complex due to the formation of 5.8 hindering the rate of the carbostannylation reaction. However, the results do confirm that 5.1$^\text{Ph}$ can be converted to 5.3$^\text{Ph}$ via activation of the C–Sn bond, insertion of ethylene and reductive elimination. To the best of our knowledge this is the first example where an aryl stannane was added across an unactivated alkene double bond.

It should also be noted that before the addition of ethylene complex 5.4$^\text{Ph}$ was present in minor amounts, approximately 20 % of the sample, while after the addition of ethylene the concentration of 5.4$^\text{Ph}$ was increased and made up approximately 85 % of the sample, which suggests that dissociation of ethylene from 5.8 to form 5.4$^\text{Ph}$ is kinetically more facile than dissociation of COD from Ni(COD)$_2$.

Similar reactions with ethylene, Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr were carried out with Bn$_3$SnC$_6$F$_5$ and Bu$_3$SnC$_6$F$_5$. Over time Bn$_3$SnC$_6$F$_5$ produced 5.3$^\text{Bn}$ while Bu$_3$SnC$_6$F$_5$ yielded a complex mixture of products.

Scheme 5.6. Carbostannylation of ethylene with a fluorinated organostannane using catalytic amounts of Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr.
A plausible mechanistic manifold that includes intermediates $5.2^{\text{Ph}}$ and $5.4^{\text{Ph}}$ and is capable of catalytic C–H alkylation, C–H bond stannylation and ethylene carbostannylation to form $5.1^{\text{Ph}}$ and $5.3^{\text{Ph}}$, respectively, is shown in Scheme 5.7. The mechanism involves the reaction of Ni(COD)$_2$ with two equivalents of CH$_2$=CHSnR$_3$ (R = Bu, Ph or Bn) and one equivalent of L (L = P$_3$Pr$_3$ or MeNC$_5$H$_4$N$_i$Pr) to form $5.2^R$, as has been demonstrated. We have previously proposed for L = P$_3$Pr$_3$ that this step is followed by reversible dissociation of one of the two CH$_2$=CHSnR$_3$ moieties to generate the unobservable species (L)Ni(η-CH$_2$=CHSnR$_3$), which then reacts with C$_6$F$_5$H either by oxidative addition of the C–H bond and insertion of R$_3$SnCH=CH$_2$ or by a one step H transfer to give the unobserved species $5.6$. The C–H bond stannylation product $5.1^{\text{Ph}}$ may be formed from $5.6$ by β-elimination of the SnR$_3$ group to form intermediate $5.7$ followed by ligand substitution with the loss of ethylene to form $5.4^{\text{Ph}}$ and then reductive elimination. Product $5.3^{\text{Ph}}$ can be formed by C–H bond alkylation via reductive elimination from $5.6$ or carbostannylation via C–Sn bond activation of $5.1^{\text{Ph}}$ to the nickel metal center followed by coordination of ethylene to the metal center and insertion into the Ni–Sn bond and reductive elimination.
5.7. Proposed mechanism for C–H alkylation, C–H stannylation and carbostannylation of ethylene with Ni(COD)₂ and MeNC₅H₄N’Pr.

There are two plausible steps that 5.6 can undergo in the mechanistic pathway proposed, reductive elimination associated with $k_4$ and $\beta$-elimination associated with $k_1$. A deuterium labeling study was performed by reacting C₆F₅D with CH₂=CHSnPh₃ to distinguish between these manifolds. If the rate of reductive elimination is much faster than $\beta$-elimination from 5.6 ($k_4 \gg k_1$), the product 5.3Ph-$d_1$ will have a single isotopomer with the deuterium located in the CH₂ group adjacent to the SnPh₃ group, due to the
preference to insert CH₂=CHSnPh₃ into the Ni–D bond with the Ph₃Sn moiety away from the nickel center, as shown in Scheme 5.8. If the rate of β-elimination is much faster than reductive elimination from 5.6 ($k_1 >> k_4$), then product $5.3^{Ph-d_1}$ will be an equal molar mixture of the two isotopomers, since C₂HD will have no preference when it inserts into the Ni–Sn bond, as shown in Scheme 5.7. To confirm ethylene inserts into the Ni–SnR₃ bond rather than Ni–C₆F₅ bond, a variety of alkynes and alkenes were added to trans-(MeNC₅H₄N′Pr)NiF(C₆F₅),⁵² where no insertion was observed into the Ni–C₆F₅ bond.

Scheme 5.8. Deuterium labeling study to distinguish between two potential reaction pathways.

Experimentally, the functionalization of C₆F₅D with CH₂=CHSnPh₃ was found to produce a 1:1 mixture of C₆F₅CH₂CHDSnPh₃ and C₆F₅CHDCH₂SnPh₃ as observed by both $^1$H and $^2$H NMR spectroscopy. This result indicates that β-elimination of the SnR₃
group is much faster than reductive elimination from \(5.6\) \(k_1 \gg k_4\) and that \(5.3^{\text{Ph}}\) forms from the reinsertion of ethylene and reductive elimination rather than directly from \(5.6\).

After \(\beta\)-elimination the unobservable species \(5.7\) has two possible pathways it can undergo, 1,2–insertion of ethylene to reform \(5.6\), or ethylene can be displaced by a second \(\text{L}\) donor to form intermediate \(5.4\). If the rate of ethylene displacement associated with \(k_2\), is faster than the rate of re-insertion of ethylene associated with \(k_{-1}\), then removing ethylene from the reaction mixture, either by stirring in an open flask, sparging with \(\text{N}_2\) or under reduced pressure, should drive the formation of \(5.1\) and stop the formation of \(5.3\). Experimentally, equimolar amounts of the reaction mixture containing \(\text{CH}_2=\text{CHSnPh}_3\), \(\text{C}_6\text{F}_5\text{H}\) and catalytic amounts of \(\text{Ni(COD)}_2\) and \(\text{MeNC}_5\text{H}_4\text{NiPr}\) were stirred simultaneously in an open and closed reaction vessel. After 3 days the reaction mixture was analyzed by \(^{19}\text{F}\{^1\text{H}\}\) NMR spectroscopy and the product distribution was found to be 83 % \(5.3^{\text{Ph}}\) and 17 % \(5.1^{\text{Ph}}\) in the open vessel and > 99 % \(5.3^{\text{Ph}}\) in the closed vessel. The formation of compound \(5.3^{\text{Ph}}\) was only slightly hindered, which suggests that the re-insertion of ethylene must occur faster than displacement of ethylene by \(\text{L}\) \((k_{-1}\gg k_2)\) under these conditions.

### 5.2.6 The Influence of \(R\) in \(\text{CH}_2=\text{CHSnPh}_3\)

The relative reactivity of \(\text{CH}_2=\text{CHSnBu}_3\), \(\text{CH}_2=\text{CHSnBn}_3\) and \(\text{CH}_2=\text{CHSnPh}_3\) were next examined to compare the influence of electron-withdrawing and electron-donating groups on the kinetics and thermodynamics of the \(\text{C–H}\) bond stannylation and \(\text{C–H}\) bond alkylation reactions. Catalytic amounts of \(\text{MeNC}_5\text{H}_4\text{NiPr}\) (40 mol %) and \(\text{Ni(COD)}_2\) (20 mol %), were reacted with \(\text{C}_6\text{F}_5\text{H}\) and \(\text{CH}_2=\text{CHSnR}_3\) \((R = \text{Bu, Bn or Ph})\) as shown in Scheme 5.9. The progress of the reaction was tracked by \(^{19}\text{F}\) NMR spectroscopy every 30 min for 120 min to get the initial product ratios. After 120 min the reaction with \(\text{CH}_2=\text{CHSnBu}_3\) is almost completely converted to \(5.1^{\text{Bu}}\) (87.1 %) with minor amounts of \(\text{C}_6\text{F}_5\text{H}\) (8.2 %), \(5.4^{\text{Bu}}\) (0.7 %) and \(5.3^{\text{Bu}}\) (4.0 %) present in solution. This result suggests that electron-donating groups favor the formation of \(5.1^{\text{Bu}}\), indicating that the rate of displacement of ethylene from \(5.7^{\text{Bu}}\) associated with \(k_2\) is faster than the 1,2-
insertion of ethylene associated with $k_1$. It also suggests that the rate of reductive elimination from $5.4_{\text{Bu}}$ to form $5.1_{\text{Bu}}$ associated with $k_3$ is faster than the displacement of L and the coordination of ethylene associated with $k_2$, and faster than the reverse process of activating the C–Sn bond of $5.1_{\text{Bu}}$ to form $5.4_{\text{Bu}}$ associated with $k_3$. After 120 min the reaction with CH$_2$=CHSnBn$_3$ produced a mixture with $5.1_{\text{Bn}}$ (23.3 %), C$_6$F$_5$H (48.0 %), $5.4_{\text{Bn}}$ (24.7 %) and $5.3_{\text{Bn}}$ (4.0 %) present in solution. This result suggests that with slightly less electron-donating groups such as benzyl the rate of displacement of ethylene from $5.7_{\text{Bn}}$ associated with $k_2$ is faster than the 1,2-insertion of ethylene associated with $k_1$. It also suggests that the rate of reductive elimination from $5.4_{\text{Bn}}$ to form $5.1_{\text{Bn}}$ associated with $k_3$ is faster than the re-insertion of ethylene associated with $k_2$, and the rate of C–Sn activation of $5.1_{\text{Bn}}$ to form $5.4_{\text{Bn}}$ associated with $k_3$ is similar. After 120 min the reaction with CH$_2$=CHSnPh$_3$ produced a mixture of products with $5.1_{\text{Ph}}$ (1.5 %), C$_6$F$_5$H (51.2 %), $5.4_{\text{Ph}}$ (17.5 %) and $5.3_{\text{Ph}}$ (29.8 %) present in solution. This result suggests that with electron-withdrawing groups such as phenyl, the rate of 1,2-insertion of ethylene from $5.7_{\text{Ph}}$ associated with $k_1$ is faster than the displacement of ethylene to form $5.4_{\text{Ph}}$ associated with $k_2$. With MeNC$_5$H$_4$N$_2$iPr as the ancillary ligand, the choice of R substituent can thus be used to control how favorable the equilibrium processes are and thus the products that are preferred, $5.1$ versus $5.3$.

Scheme 5.9. Product distribution for the reaction of C$_6$F$_5$H and CH$_2$=CHSnR$_3$ with catalytic amounts of Ni(COD)$_2$ and MeNC$_5$H$_4$N$_2$iPr, after 120 min.
The influence of the ancillary ligands, \textit{i}Pr$_3$P versus MeNC$_5$H$_4$N\textit{i}Pr, on the product distribution was also studied. By using a stock solution of 0.10 M C$_6$F$_5$H with a $^{19}$F internal standard, equimolar amounts of (L)Ni(\(\eta^2\)-CH$_2$=CHSnPh$_3$)$_2$ (L = \textit{i}Pr$_3$P$_4$ or MeNC$_5$H$_4$N\textit{i}Pr) were added to 0.6 mL aliquots. The solutions were immediately transferred to an NMR probe preheated to 315 K and were tracked every minute for the first 6 min to get the initial product ratios. After 6 min the reaction with \textit{i}Pr$_3$P produced 5.1$^{Ph}$ exclusively with a concentration of 0.017 M. This suggests that with \textit{i}Pr$_3$P as the ancillary ligand, the rate of displacement of ethylene from 5.7$^{Bu}$ associated with $k_2$ is faster than the 1,2-insertion of ethylene associated with $k_1$, also the rate of reductive elimination from 5.4$^{Bu}$ to form 5.1$^{Bu}$ associated with $k_3$ is faster than the reinsertion of ethylene associated with $k_{-2}$, and faster than the reverse process of activating the C–Sn bond of 5.1$^{Bu}$ to form 5.4$^{Bu}$ associated with $k_{-3}$. After 6 min the reaction with MeNC$_5$H$_4$N\textit{i}Pr produced a mixture containing 5.1$^{Ph}$ (0.0034 M), 5.3$^{Ph}$ (0.016 M) and 5.4$^{Ph}$ (0.0025 M), which suggests that with MeNC$_5$H$_4$N\textit{i}Pr as the ancillary ligand the rate of 1,2-insertion of ethylene from 5.7$^{Ph}$ associated with $k_{-1}$ is faster than the displacement of ethylene to form 5.4$^{Ph}$ associated with $k_2$. Thus hard nitrogen donors favor the formation of 5.3$^{Ph}$ and soft phosphine donors favor the formation of 5.1$^{Ph}$. With CH$_2$=CHSnPh$_3$ as the substrate, the ancillary ligand can be used to control the preferred product 5.1$^{Ph}$ versus 5.3$^{Ph}$ depending on if a soft or hard donor ligand is utilized.

5.2.8 Concentration Effects

The effect of changing the concentration of MeNC$_5$H$_4$N\textit{i}Pr on the rate of products formed was next examined to further confirm the proposed mechanism. Using two stock solutions, the first containing 0.37 M of CH$_2$=CHSnBn$_3$ and C$_6$F$_5$H and the second containing 0.167 M of Ni(COD)$_2$ and a $^{19}$F internal standard, different masses of MeNC$_5$H$_4$N\textit{i}Pr were added to 0.45 mL aliquots of the first stock solution and 0.2 mL aliquots of the second, to give approximate ligand concentrations of 0.05 M, 0.1 M, 0.2 M and 0.8 M, respectively. These solutions were then frozen in liquid N$_2$ until they were
transferred to an NMR probe where the initial product ratios were monitored every 20 min for 80 min. It was found that as the concentration of MeNC$_5$H$_4$N$i$Pr was increased, the equilibrium amount of 5.1$^Bn$ in solution was decreased with concentrations of 0.071 M, 0.041 M, 0.0069 M and 0 M at 80 min for 1, 2, 4 and 16 equivalents respectively. The rate of formation of 5.4$^Bn$ is increased with increasing amounts of MeNC$_5$H$_4$N$i$Pr with initial relative rates of 1, 9.9, 19 and 31 M·s$^{-1}$ for the addition of 1, 2, 4 and 16 equivalents of MeNC$_5$H$_4$N$i$Pr respectively. This result suggests that additional MeNC$_5$H$_4$N$i$Pr in solution favors the equilibrium formation of 5.4$^Bn$ from both 5.1$^Bn$ and from 5.7$^Bn$, which also supports the decrease in equilibrium amounts of 5.1$^Bn$ in solution. The rate of formation of 5.3$^Bn$ was unaffected with the addition of excess MeNC$_5$H$_4$N$i$Pr with an average rate of formation of 1.09×10$^{-6}$ M·s$^{-1}$.

The effect of changing the concentration of CH$_2$=CHSnBn$_3$ on the rates of the products and intermediates formed were also determined. Using two stock solutions the first 0.11 M of MeNC$_5$H$_4$N$i$Pr and 0.28 M C$_6$F$_5$H and the second 0.167 M of Ni(COD)$_2$ with a $^{19}$F internal standard, different masses of CH$_2$=CHSnBn$_3$ were added to give approximate CH$_2$=CHSnBn$_3$ concentrations of 0.1 M, 0.2 M, 0.4 M and 0.8 M, respectively. These solutions were then frozen in liquid N$_2$ until they were transferred to an NMR probe where the initial product ratios were monitored every 20 min for 80 min. It was found that as the concentration of CH$_2$=CHSnBn$_3$ increases the rate of formation of 5.1$^Bn$ decreases with relative rates of 1, 0.99, 0.82 and 0.083 M·s$^{-1}$ for the addition of 2.5, 5, 10 and 20 equivalents respectively. This is the same result that was previously obtained with $^i$Pr$_3$P$_{48}$ as the ancillary ligand and was attributed to the reversible dissociation of CH$_2$=CHSnBn$_3$ from 5.2$^Bn$, which explains why the rates of formation of 5.4$^Bn$ and 5.3$^Bn$ were also decreased with increasing concentration of CH$_2$=CHSnBn$_3$.

5.2.9 Scope of C–H Alkylation

To investigate the generality of catalytic C–H alkylation we examined the scope of fluorinated aromatics that undergo this type of reaction. Catalytic amounts of 10 mol % MeNC$_5$H$_4$N$i$Pr and 5 mol % Ni(COD)$_2$ were reacted with CH$_2$=CHSnPh$_3$ and a variety
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of fluorinated aromatics at room temperature and the reaction progress was tracked by $^{19}$F NMR spectroscopy. Aromatic substrates with C–H bonds ortho- to two fluorines, such as C$_6$F$_5$H, 1,2,4,5-C$_6$F$_4$H$_2$, 1,2,3,5-C$_6$F$_4$H$_2$ and 1,2,4-C$_6$F$_3$H$_3$ proved to be the most reactive, with the yields and rate dropping off as the degree of fluorination decreased. The reaction with 1,2,4,5-C$_6$F$_4$H$_2$ after 3 days produced 65 % of expected C–H bond alkylation product 2,3,5,6-(C$_6$F$_4$H)-1-CH$_2$CH$_2$SnPh$_3$ (5.9) by NMR, 18 % of the doubly functionalized product 2,3,5,6-(C$_6$F$_4$)-1,4-(CH$_2$CH$_2$SnPh$_3$)$_2$ (5.10), 2.3 % C–H stannylation of 1,2,4,5-C$_6$F$_4$H$_2$, 1.7 % C–H stannylation of 5.9 and 10 % remaining 1,2,4,5-C$_6$F$_4$H$_2$, as shown in Scheme 10. Similar reactivity and products were observed for 1,2,3,5-C$_6$F$_4$H$_2$ after 3 days while the reaction with 1,2,4-C$_6$F$_3$H$_3$ showed only a 14 % conversion to 2,3,6-C$_6$F$_3$H$_2$-1-SnPh$_3$. Similar reactions with 1,2,3,4-C$_6$F$_4$H$_2$ and 1,2,3-C$_6$F$_3$H$_3$ showed less than a 1 % conversion after 3 days at room temperature and after heating the reaction at 60 °C overnight.

![Scheme 5.10](image)

**Scheme 5.10.** C–H alkylation products formed with 1,2,4,5-C$_6$F$_4$H$_2$ and CH$_2$=CHSnPh$_3$.

5.2.10 Scope of Carbostannylation

To determine if this system can carbostannylate other alkenes trimethylvinylsilane, styrene, ethyl acrylate, ethyl crotonate, cyclohexene, norborne and 1-hexene were reacted with complexes 5.4$^\text{Ph}$ and 5.4$^\text{Bn}$. The progress of the reaction was
monitored by $^{19}$F NMR spectroscopy. Most of the alkenes promoted reductive elimination to form C$_6$F$_5$SnR$_3$ (R = Bn or Ph) or C$_6$F$_5$H. Norbornene formed a new complex with three fluorine environments at $\delta$ −118.2 (m), −152.2 (t) and −159.9 (m) and 1-hexene formed mostly the desired carbostannylation product though it was not regioselective. Neither of these substrates provided good yields.

5.3 Conclusions

Experimental evidence shows that nickel complexes such as (MeNC$_5$H$_4$N$i$Pr)Ni($\eta^2$-CH$_2$=CHSnPh$_3$)$_2$ (5.2$^{Ph}$) are precatalysts for the catalytic C–H bond alkylation of fluorinated aromatics and CH$_2$=CHSnR$_3$ (R = Ph or Bn) to form products of the type C$_6$F$_5$CH$_2$CH$_2$SnR$_3$ (5.3$^R$) (R = Ph or Bn). Isolated intermediates of the type cis-(MeNC$_5$H$_4$N$i$Pr)$_2$Ni(C$_6$F$_5$)(SnR$_3$), where R = Ph (5.4$^{Ph}$) or Bn (5.4$^{Bn}$) show that the C–Sn bond of the organostannane reagents 5.1$^R$ (R = Ph or Bn) can be activated by Ni(0) and MeNC$_5$H$_4$N$i$Pr, and that they can react with ethylene to provide C$_6$F$_5$CH$_2$CH$_2$SnR$_3$ (5.3$^R$) where R is Ph or Bn. The reaction of 5.1$^R$ (R = Ph or Bn) with an atmosphere of ethylene and catalytic amounts of MeNC$_5$H$_4$N$i$Pr and Ni(COD)$_2$ underwent the first example of carbostannylation with an aryl organostannane and an unactivated alkene. Although the scope of carbostannylation is currently limited, this reactivity may provide an alternative method for preparing new organostannane reagents for the Stille coupling reaction directly from the C–Sn bond of organostannane reagents.

5.4 Experimental Section

5.4.1 General Procedures

All reactions were performed under an atmosphere of dry oxygen-free dinitrogen by means of standard Schlenk or glovebox techniques. Benzene-$d_6$ was dried by refluxing with Na/K and was then vacuum transferred and degassed by three freeze-pump-thaw cycles. Toluene-$d_8$ and CD$_2$Cl$_2$ were dried in an analogous manner by refluxing over Na and CaH$_2$ respectively. All other solvents were purchased anhydrous from Aldrich and further purified using a Grubbs’ type column system,$^{53}$ produced by
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Innovative Technology. $^1$H, $^{13}$C$\{^1$H$\}$, $^{19}$F$\{^1$H$\}$, and $^{119}$Sn$\{^1$H$\}$ NMR spectra were recorded on a Bruker AMX Spectrometer operating at 300 MHz or where stated at 500 MHz with respect to proton nuclei. All chemical shifts are reported in parts per million (ppm) and all coupling constants are in hertz (Hz). $^1$H NMR spectra were referenced to residual protons ($C_6D_5H$, δ 7.15; CDHCl$_2$, δ 5.32; $C_7D_7H$, δ 2.09; CHCl$_3$, δ 7.26) with respect to tetramethylsilane at δ 0.00. $^{13}$C$\{^1$H$\}$ spectra were referenced relative to solvent resonances ($C_6D_6$, δ 128.0, CDCl$_3$, δ 77.0, $C_7D_8$, δ 20.4). $^{19}$F$\{^1$H$\}$ NMR spectra were referenced to an external sample of 80% CCl$_3$F in CDCl$_3$ at δ 0.0. $^{119}$Sn$\{^1$H$\}$ NMR spectra were referenced to an external sample of SnMe$_4$ at δ 0.0. $C_6D_6$, $C_7D_8$, CDCl$_3$ and CD$_2$Cl$_2$ were purchased from Aldrich. The compounds pentafluorobenzene, 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-tetrafluorobenzene, 1,3,5-, 1,2,4-, and 1,2,3-trifluorobenzene, CH$_2$=CHSnBu$_3$, ClSnPh$_3$ and ClSnBn$_3$ were purchased from Aldrich. The reagent $P^\Pr_3$ was purchased from Strem Chemicals. Ethylene was purchased from BOC gases. The compounds MeNC$_5$H$_4$N$^\Pr$, Ni(COD)$_2$, $C_6F_5D$, $C_6F_5SnBn_3$ and $C_6F_5SnPh_3$ were purchased by literature procedures. The compounds CH$_2$=CHSnBn$_3$ and $C_6F_5SnPh_3$ were prepared by analogous procedures to that of CH$_2$=CHSnPh$_3$ and $C_6F_5SnBn_3$ respectively. Elemental Analysis and Mass Spectroscopy was performed at the University of Windsor, Windsor, Ontario Canada by Dr. Janeen Auld, Instrument Technician.

5.4.2 Synthesis, Characterization and Reactivity of Complexes

Synthesis of (MeNC$_5$H$_4$N$^\Pr$)Ni[η$^2$-CH$_2$=CHSnPh$_3$]$_2$, (5.2). To a solution of triphenyl(vinyl)tin (0.100 g, 0.265 mmol) in 10 mL of pentane was added MeNC$_5$H$_4$N$^\Pr$ (0.020 g, 0.133 mmol) and Ni(COD)$_2$ (0.036 g, 0.133 mmol). The solution was left undisturbed for 2 h, which yielded a yellow solid. The solid was filtered, rinsed with pentane and then dried. (0.128 g, 69% yield). $^1$H NMR ($C_6D_6$, 25 ºC, 500.13 MHz): δ 0.57 (d, 3H, CH(C$_3$H$_3$)$_2$, $^3$J$_{HH}$ = 6.4 Hz); 0.75 (d, 3H, CH(C$_3$H$_3$)$_2$, $^3$J$_{HH}$ = 6.3 Hz); 1.53 (s, 3H, NCH$_3$); 2.72 (d with Sn satellites, 1H, vinyl–CH, $^2$J$_{HH}$ = 15.1 Hz, $^2$J$_{HN}$ = 91 Hz); 2.81 (d, 1H, vinyl–CH, $^2$J$_{HH}$ = 15.1 Hz); 2.97 (overlapping m, 3H, vinyl–CH, vinyl–CH and CH(CH$_3$)$_2$); 3.45 (dd with Sn satellites, 1H, vinyl–CH, $^3$J$_{HH}$ = 15.2 Hz, $^2$J$_{HH}$ = 11.4 Hz, $^3$J$_{HN}$ = 60 Hz); 3.59 (dd with Sn satellites, 1H, vinyl–CH, $^3$J$_{HH}$ = 15.1 Hz, $^2$J$_{HH}$ =
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Reaction of tribenzyl(vinyl)tin, Ni(COD)\textsubscript{2} and MeNC\textsubscript{5}H\textsubscript{4}N\textsubscript{Pr}. To a solution of tribenzyl(vinyl)tin (0.020 g, 0.048 mmol) in 1 mL of C\textsubscript{6}D\textsubscript{6} was added MeNC\textsubscript{5}H\textsubscript{4}N\textsubscript{Pr} (0.004 g, 0.024 mmol) and Ni(COD)\textsubscript{2} (0.006 g, 0.024 mmol). The solution was characterized by \textsuperscript{1}H NMR spectroscopy at room temperature after 20 min. \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 25 ºC, 500.13 MHz): δ 1.24 (d, 3H, CH(C\textsubscript{3})\textsubscript{2}), 1.27 (d, 3H, CH(C\textsubscript{3})\textsubscript{2}), 2.00 (s, 3H, NC\textsubscript{3}H\textsubscript{3}); 2.20 (s, 12H, C\textsubscript{6}H\textsubscript{2}Ph); 2.6 – 3.4 (m, 6H, vinyl–C\textsubscript{H}); 5.5 – 6.7 (m, 4H, C\textsubscript{5}H\textsubscript{4}N); 6.7 – 7.2 (m, 30H, Ph–H). \textsuperscript{119}Sn\textsubscript{1}{\textsuperscript{1}H} (C\textsubscript{6}D\textsubscript{6}, 25 ºC, 111.96 MHz): δ –136.3 (s, 1Sn).

Synthesis of C\textsubscript{6}F\textsubscript{5}CH\textsubscript{2}CH\textsubscript{2}SnPh\textsubscript{3} (5.3\textsubscript{ph}). A solution of pentafluorobenzene (0.225 g, 1.32 mmol) and triphenyl(vinyl)tin (0.500 g, 1.32 mmol) in 10 mL of toluene was added to MeNC\textsubscript{5}H\textsubscript{4}N\textsubscript{Pr} (0.020 g, 0.132 mmol) and Ni(COD)\textsubscript{2} (0.018 g, 0.067 mmol). The solution was stirred at room temperature for 5 days. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless powder. (74% yield by NMR spectroscopy). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 25 ºC, 300.13 MHz): δ 1.66 (m with Sn satellites, 2H, SnCH\textsubscript{2}), 2.96 (m with Sn satellites, 2H, SnCH\textsubscript{2}CH\textsubscript{2}), \textsuperscript{3}J\textsubscript{HSn} = 45.6 Hz); 7.25–7.32 (m, 9H, m–Ar–H and p–Ar–H); 7.44 (m with Sn satellites, 6H, o–Ar–H, \textsuperscript{3}J\textsubscript{HSn} = 46.4 Hz). \textsuperscript{19}F\textsubscript{1}{\textsuperscript{1}H} NMR (CDCl\textsubscript{3}, 25 ºC, 282.40 MHz): δ –144.7 (AA'MM' second order m, 2F, 2,6–Ar–F); –158.4 (t, 1F, 4–Ar–F, \textsuperscript{3}J\textsubscript{FF} = 20.9 Hz); –162.7 (AA'MM'X second order m, 2F, 3,5–Ar–F). \textsuperscript{13}C\textsubscript{1}{\textsuperscript{1}H} NMR (CDCl\textsubscript{3}, 25 ºC, 75.47 MHz): δ 10.3 (s with Sn satellites, SnCH\textsubscript{2}, \textsuperscript{1}J\textsubscript{CSn(119)} = 367 Hz, \textsuperscript{1}J\textsubscript{CSn(117)} = 349 Hz); 19.6 (s, SnCH\textsubscript{2}CH\textsubscript{2}); 117.5 (tm, ipso–Ar–C, \textsuperscript{2}J\textsubscript{CF} = 18.9 Hz); 128.6 (s, Ph–C); 136.8 (s, Ph–C); 137.3 (dm, Ar–C, \textsuperscript{1}J\textsubscript{CF} = 249.1 Hz); 137.7 (s, Ph–C); 139.1 (s, ipso–Ph–C); 139.2 (dm, Ar–C, \textsuperscript{1}J\textsubscript{CF} = 267.9 Hz); 144.7 (dm, Ar–C, \textsuperscript{1}J\textsubscript{CF} = 244.3 Hz). \textsuperscript{119}Sn\textsubscript{1}{\textsuperscript{1}H} NMR (C\textsubscript{6}D\textsubscript{6}, 25
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ºC, 111.96 MHz): δ –103.7 (s, Sn). Calcd for C26H19F5Sn: [M+–C6H5], 469.0038. Found: m/z 469.0076.

Synthesis of C₆F₅CH₂CH₂SnBn₃ (5.3). A solution of pentafluorobenzene (0.200 g, 1.19 mmol) and tribenzyl(vinyl)tin (0.500 g, 1.19 mmol) in 10 mL of toluene was added to MeNC₅H₄N′Pr (0.036 g, 0.24 mmol) and Ni(COD)₂ (0.033 g, 0.012 mmol). The solution was stirred at room temperature for 2 weeks. The reaction mixture was filtered through silica and the solvent was removed, leaving a colourless oil. (81 % yield by NMR spectroscopy). ¹H NMR (CDCl₃, 25 ºC, 300.13 MHz): δ 0.89 (m with Sn satellites, 2H, SnCH₂CH₂, ²J_HSn = 46.8 Hz); 2.35 (s with Sn satellites, 6H, SnCH₂Ph, ²J_HSn = 58.5 Hz); 2.47 (m, 2H, SnCH₂CH₂); 6.88 (d, 6H, o–Ar–H, ³J_HH = 7.4 Hz); 7.04 (t, 3H, p–Ar–H, ³J_HH = 7.2 Hz); and 7.19 (m, 6H, m–Ar–H). ¹⁹F{¹H} NMR (CDCl₃, 25 ºC, 282.40 MHz): δ –145.1 (AA′MM′ second order m, 2F, 2,6–Ar–F); –158.3 (t, 1F, 4–Ar–F, ³J_FF = 20.8 Hz); –162.8 (AA′MM′X second order m, 2F, 3,5–Ar–F). ¹³C{¹H} NMR (CDCl₃, 25 ºC, 75.47 MHz): δ 10.2 (s with Sn satellites, SnCH₂CH₂, ¹J_CSn(119) = 265.1 Hz, ¹J_CSn(117) = 253.3 Hz ); 19.2 (s with Sn satellites, SnCH₂CH₂, ²J_CSn = 36.5 Hz); 118.2 (t, ipso–Ar F–C, ²J_CF = 20.5 Hz); 123.9 (s with Sn satellites, Ph–C, ³J_CSn = 15.4 Hz); 127.4 (s with Sn satellites, Ph–C, ³J_CSn = 23.5 Hz); 128.8 (s with Sn satellites, Ph–C, ³J_CSn = 12.6 Hz); 137.7 (dm, Ar F–C, ¹J_CF = 250.8 Hz); 141.2 (dm, Ar F–C, ¹J_CF = 280.6 Hz); 141.6 (s, ipso–Ph–C); 144.8 (dm, Ar F–C, ¹J_CF = 247.5 Hz). ¹¹⁹Sn{¹H} NMR (C₆D₆, 25 ºC, 111.96 MHz): δ –43.0 (s, Sn). Calcd for C₂₉H₂₅F₅Sn: [M+–CH₂C₆H₅], 497.04. Found: m/z 497.10.

Synthesis of cis-(MeNC₅H₄N′Pr)₂Ni(SnPh₃)(C₆F₅), (5.4). To a solution of MeNC₅H₄N′Pr (0.290 g, 1.94 mmol) and Ni(COD)₂ (0.266 g, 0.97 mmol) in 20 mL of toluene was added C₆F₅SnPh₃ (0.500 g, 0.97 mmol). The solution was stirred for 2 h, the solvent was removed, washed with pentane and dried to yield an orange solid. (0.690 g, 79 % yield). ¹H NMR (CD₂Cl₂, –20 ºC, 500.13 MHz): δ 0.83 (d, 3H, CH(CH₃)₂, ³J_HH = 7.4 Hz); 0.86 (d, 3H, CH(CH₃)₂, ³J_HH = 6.6 Hz); 1.08 (br, 6H, CH(CH₃)₂); 1.98 (br, 1H, CH(CH₃)₂); 2.31 (s, 3H, NCH₃); 3.29 (m, 1H, CH(CH₃)₂); 3.38 (s, 3H, NCH₃); 5.81 (d, 1H, C₃H₄N, ³J_HH = 7.3 Hz); 6.04 (d, 1H, C₃H₄N, ³J_HH = 7.3 Hz); 6.60 (d, 1H, C₃H₄N,
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3 HH = 7.6 Hz); 6.64 (d, 1H, C5H4N, 3 J HH = 6.7 Hz); 6.88 (d, 1H, C5H4N, 3 J HH = 7.0 Hz); 7.01 (m, 6H, Ph–H); 7.18 (m, 3H, Ph–p–H); 7.23 (m, 6H, Ph–H); 7.58 (d, 1H, C5H4N, 3 J HH = 6.8 Hz); 8.65 (br, 1H, C5H4N); 9.69 (br, 1H, C5H4N). 19F NMR (CD2Cl2, –20 ºC, 282.40 MHz): –109.9 (br d, 1F, o–F, 3 J FF = 36 Hz); –112.6 (br, 1F, o–F); –166.2 (br, 1F, m–F); –166.6 (br t, 1F, p–F, 3 J FF = 34 Hz); –167.5 (br, 1F, m–F). 13C{1H} NMR (CD2Cl2, –20 ºC, 125.77 MHz): δ 14.1 (s, CH(C5H3)2); 21.3 (s, CH(CH3)2); 22.9 (s, CH(CH3)2); 28.2 (s, CH(CH3)2); 34.4 (s, CH(CH3)2 or NCH3); 43.7 (s, CH(CH3)2 or NCH3); 43.8 (s, CH(CH3)2 or NCH3); 50.9 (s, CH(CH3)2 or NCH3); 125.4 (s, C5H4N); 126.2 (s, Ph–C); 126.9 (s with Sn satellites, Ph–C, 3 J CSn = 27.6 Hz); 128.4 (s, C5H4N); 129.2 (s, C5H4N); 137.2 (s with Sn satellites, Ph–C, 3 J CSn = 30.3 Hz); 147.2 (s, Ph–C); 157.7 (s, C5H4N). 119Sn{1H} (CD2Cl2, –20 ºC, 186.50 MHz): δ –334 (br, 1Sn, 1–Sn). Anal. Calcd. C, 57.57; H, 4.95; N, 6.39. Found C, 53.92; H, 5.48; N, 6.14.

Synthesis of cis-(MeNC5H4N^iPr)2Ni(SnBn3)(C6F5), (5.4Bn). To a solution of MeNC5H4N^iPr (0.268 g, 1.79 mmol) and Ni(COD)2 (0.246 g, 0.89 mmol) in 20 mL of toluene was added C6F5SnBn3 (0.500 g, 0.89 mmol). The solution was stirred for 2 h, the solvent was removed, washed with pentane and dried to yield an orange solid (0.735 g, 80 % yield). The solid was recrystallized in toluene at –40 ºC to yield X-ray quality crystals. 1H NMR (C6D6, 25 ºC, 300.13 MHz): δ 1.25 (br, 6H, CHCH3 ); 1.60 (br, 6H, CHCH3 ); 1.98 (s, 3H, CH3); 2.17 (s, 3H, CH3); 2.36 (s with Sn satillites, 6H, CH22, JHH = 33.0 Hz); 3.31 (septet, 1H, CH, 3 J HH = 6.6 Hz); 4.91 (br, 1H, CHF); 5.43 (dd, 1H, C5H4N, JHH = 8.1 Hz, JHH = 2.4 Hz); 6.03 (dd, 1H, C5H4N, JHH = 7.5 Hz); 6.41 (d, 1H, C5H4N, JHH = 7.8 Hz); 6.91 (m, 6H, Ph–H); 7.02 (m, 3H, Ph–p–H); 7.15 (m, 6H, Ph–H); 8.70 (br, 1H, C5H4N); 9.71 (dd, 1H, C5H4N, JHH = 6.6 Hz, JHH = 2.5 Hz). 19F NMR (C6D6, 25 ºC, 282.40 MHz): –109.5 (br, 2F, 2,6–Ar–F); –164.3 (t, 1F, 4–Ar–F, JFF = 19.3 Hz); –165.1 (br, 2F, 3,5–Ar–F). 13C{1H} NMR (C6D6, 25 ºC, 125.77 MHz): δ 21.1 (s, SnCH2); 24.2 (s, CH(CH3)2); 28.1 (s, CH(CH3)2); 40.4 (s, NCH3); 41.0 (s, NCH3); 50.9 (s, CH(CH3)2); 106.9 (s, C5H4N); 117.0 (s, C5H4N); 122.2 (s, s, Ph–C); 135.1 (s, C5H4N); 136.0 (s, C5H4N); 146.3 (s, Ph–C); 156.7 (s, C5H4N). 119Sn{1H} (C6D6, 25 ºC, 186.47 MHz): δ
Synthesis of trans-(MeNC_5H_4N^iPr)_2NiCl(C_6F_5) (5.5). A solution of 5.4^Ph (0.030 g, 0.034 mol) in 0.6 mL of CD_2Cl_2 decomposes after 30–40 min at room temperature or 15 min at 313 K to form complex 5.5 and a tin byproduct. \(^1\)H NMR (CD_2Cl_2, 25 °C, 500.13 MHz): δ 0.24 (3H, NCH(CH_3)_2); δ 2.56 (3H, NCH(CH_3)_2); 3.13 (1H, NCH); 3.50 (s, 3H, NCH_3); 5.92 (1H, C_5H_4N); 6.78 (1H, C_5H_4N); 7.79 (1H, C_5H_4N); 9.78 (br, 1H, C_5H_4N). \(^{19}\)F{^1\}H} NMR (CD_2Cl_2, 25 °C, 470.54 MHz): –115.7 (AA'BB' apparent d, 2H, ortho–F, \(^3\)J_F_F = 28.1 Hz); –163.5 (t, 1H, para–F, \(^3\)J_F_F = 19.6 Hz); –166.6 (AA'BB'C apparent t, 2H, meta–F, \(^3\)J_F_F = 23.5 Hz). \(^{13}\)C{^1\}H} NMR (CD_2Cl_2, 25 °C, 125.77 MHz): δ 19.8 and 24.9 (s, (NCH\_C\_H_3)_2); 43.0 and 51.1 (s, NCH_3 and CH); 107.4 (s, C_5H_4N); 118.6 (s, C_5H_4N); 134.8 (s, C_2H_4N); 137.4 (s, C_2H_4N); 158.1 (s, C_3H_4N).

Synthesis of 2,3,5,6-(C_6F_4H)-1-CH_2CH_2SnPh_3 (5.9) and 2,3,5,6-(C_6F_4)-1,4-(CH_2CH_2SnPh_3)_2 (5.10). A solution of CH_2=CHSnPh_3 (0.126 g, 0.33 mmol) and 1,2,4,5-tetrafluorobenzene (0.050 g, 0.33 mmol) in 0.6 mL of C_6D_6 was added to MeNC_5H_4N^iPr (0.005 g, 0.033 mmol) and Ni(COD)_2 (0.005 g, 0.017 mmol). The reaction mixture was allowed to sit at room temperature for 3 days. (65 % yield of 5.9 and 18 % yield of 5.10 by NMR spectroscopy). Spectroscopic data for 5.9: \(^1\)H NMR (CDCl_3, 25 °C, 300.13 MHz): δ 1.48 (m, 2H, SnC_2H_2); 2.81 (m with Sn satellites, 2H, SnCH_2CH_2), \(^3\)J_HSn = 43.2 Hz); 6.15 (tt, 1H, C_6F_4H, \(^3\)J_HF = 10.1 Hz, \(^4\)J_HF = 7.2 Hz); 7.13–7.18 (m, 9H, Ar–m–H and Ar–p–H); 7.48 (m, 6H, Ar–o–H). \(^{19}\)F{^1\}H} NMR (CDCl_3, 25 °C, 282.40 MHz): δ –139.6 (dd with Sn satellites, 2F, 2,6–Ar–F, \(^3\)J_F_F = 22.4 Hz, \(^4\)J_F_F = 12.9 Hz, \(^3\)J_FSn = 20 Hz); –145.2 (dd, 2F, 3,5–Ar–F, \(^3\)J_F_F = 22.6, \(^4\)J_F_F = 13.1 Hz). Spectroscopic data for 5.10: \(^1\)H NMR (CDCl_3, 25 °C, 300.13 MHz): δ 1.59 (m, 2H, SnCH_2); 2.90 (m with Sn satellites, 2H, SnCH_2CH_2), \(^3\)J_HSn = 43.8 Hz); 7.13–7.18 (m, 9H, Ar–m–H and Ar–p–H); 7.48 (m, 6H, Ar–o–H). \(^{19}\)F{^1\}H} NMR (CDCl_3, 25 °C, 282.40 MHz): δ –151.1 (s, 4F, C_6F_4).

Ethylene reactions with C_6F_5SnR_3 (R = Bu, Ph or Bn). A solution of Bu_3SnC_6F_5 (0.015 g, 0.033 mmol), C_6F_5SnPh_3 (0.017 g, 0.033 mmol) or C_6F_4SnBn_3 (0.019 g, 0.033 mmol),
MeNC₃H₄N′Pr (0.010 g, 0.067 mmol), Ni(COD)₂ (0.009 g, 0.033 mmol) in 0.6 mL of C₆D₆ was transferred to an NMR tube equipped with a Teflon valve. The reaction mixture was allowed to react for 1 h to form complexes 5.₄¹Ph and 5.₄¹Bn in situ. The nitrogen atmosphere was then removed by two freeze-pump-thaw cycles and an atmosphere of ethylene was added. The sample was then placed in the NMR probe and the reaction progress was monitored by ¹⁹F{¹H} NMR spectroscopy. Slow conversion to 5.₃¹Ph or 5.₃¹Bn was observed for the reactions with CH₂=CHSnPh₃ and CH₂=CHBn₃ respectively, however other reactivity was observed for CH₂=CHSnBu₃.

**Ethylene reaction with 5.₄¹Bn.** A solution of 5.₄¹Bn (0.020 g, 0.022 mmol) in 0.6 mL of d₈-toluene was transferred to an NMR tube equipped with a Teflon valve. The nitrogen atmosphere was then removed by two freeze-pump-thaw cycles and an atmosphere of ethylene was added. The sample was then placed in the NMR probe and the reaction progress was monitored by ¹⁹F{¹H} NMR spectroscopy as the temperature was increased from 273–313 K. Slow conversion to 5.₃¹Bn was observed once the temperature reached 298 K, upon heating further to 303 K an increase in the rate of conversion was observed while temperatures at or above 313 K caused the catalyst to decompose.

**Reaction of CH₂=CHSnR₃ (R = Bu, Ph or Bn) and C₆F₅H to determine if C–H stannylation or C–Sn insertion is preferred.** The reagents MeNC₃H₄N′Pr (0.010 g, 0.067 mmol), Ni(COD)₂ (0.009 g, 0.033 mmol) and either CH₂=CHSnPh₃ (0.063 g, 0.167 mmol), CH₂=CHSnBn₃ (0.070 g, 0.167 mmol) or CH₂=CHSnBu₃ (0.053 g, 0.167 mmol) were weighed into a vial and 0.6 mL of a 0.278 M stock solution of C₆F₅H diluted with C₆D₆ was added and the components were placed into an NMR tube. The reaction was tracked by ¹⁹F{¹H} NMR spectroscopy every 30 min for 120 min at room temperature to determine the initial product ratios. The reaction with CH₂=CHSnBu₃ best promoted the formation of 5.₁¹Bu with only trace amounts of 5.₃¹Bu, approximately 22:1 by integration, CH₂=CHSnBn₃ had a slight preference for 5.₁¹Bn over 5.₃¹Bn, approximately 6:1 by integration and CH₂=CHSnPh₃ best promoted the formation of 5.₃¹Ph with only minor amounts of 5.₁¹Ph approximately 0.05:1 by integration.
Effect of Increasing Concentration of MeNC₅H₄NᵢPr. Various amounts of MeNC₅H₄NᵢPr were weighed into vials (0.005 g, 0.033 mmol), (0.010 g, 0.067 mmol), (0.020 g, 0.133 mmol) and (0.080 g, 0.533 mmol). To each vial was added 0.45 mL of a 0.37 M stock solution containing equal molar amounts of CH₂=CHSnBn₃ and C₆F₅H, 0.2 mL of a second stock solution containing 0.167 M of Ni(COD)₂ and 0.333 M of C₆H₃F as an internal standard. Each mixture was placed into an NMR tube and the concentration of 5.₁Bn, 5.₃Bn and 5.₄Bn, by integration compared to the internal standard C₆H₃F, was monitored every 20 min for 80 min by ¹⁹F NMR spectroscopy. After 80 min the equilibrium amount of 5.₁Bn in solution was found to be 0.071 M, 0.041 M, 0.0069 M and 0 M after the addition of 1, 2, 4 and 16 equivalents of MeNC₅H₄NᵢPr respectively. The rate of formation of 5.₄Bn was increased with increasing amounts of MeNC₅H₄NᵢPr with initial relative rates of 1, 9.9, 19 and 31 M⋅s⁻¹ for the addition of 1, 2, 4 and 16 equivalents of MeNC₅H₄NᵢPr respectively. The rate of formation of 5.₃Bn was unaffected with the addition of excess MeNC₅H₄NᵢPr with an average rate of formation of 1.09×10⁻⁶ M⋅s⁻¹.

Catalytic Reaction Rate versus [CH₂=CHSnBn₃]. Various amounts of CH₂=CHSnBn₃ were weighed into vials (0.035 g, 0.083 mmol), (0.070 g, 0.167 mmol), (0.140 g, 0.333 mmol) and (0.279 g, 0.666 mmol). To each vial was added 0.6 mL of a stock solution containing 0.11 M of MeNC₅H₄NᵢPr and 0.28 M C₆F₅H, 0.2 mL of a second stock solution containing 0.167 M of Ni(COD)₂ and 0.333 M of C₆H₃F as an internal standard. Each mixture was placed into an NMR tube and concentration of 5.₁Bn, 5.₃Bn and 5.₄Bn, by integration compared to the internal standard C₆H₃F, was monitored every 20 min of 80 min by ¹⁹F NMR spectroscopy. It was found that as the concentration of CH₂=CHSnBn₃ increases the rate of formation of 5.₁Bn decreases with relative rates of 1, 0.99, 0.82 and 0.083 M⋅s⁻¹ for the addition of 2.5, 5, 10 and 20 equivalents respectively. The rate of formation 5.₄Bn is decreased with relative initial rates of 1, 0.43, 0.098 and 0 M⋅s⁻¹ with the addition of 2.5, 5, 10 and 20 equivalents of CH₂=CHSnBn₃ respectively. The rate of formation 5.₃Bn is also decreased with relative initial rates of 1, 0.94, 0.77 and
0.36 M·s⁻¹ with the addition of 2.5, 5, 10 and 20 equivalents of CH₂=CHSnBn₃ respectively.

5.5 Mass Spectrometry

The methods used were positive-ion electron impact (EI) to analyze \(5.3^{\text{Bn}}\), this is a high impact method and the loss of a benzyl group can be expected as EI often brings about the loss of \(R\) from \(R_3\text{SnR}'\).⁵⁸,⁵⁹ However, when \(5.3^{\text{Ph}}\) was analyzed by EI the loss of \(\text{SnR}'\) made it impossible to identify if the product was formed, therefore Matrix-Assisted Laser Desorption/Ionization (MALDI) was used to analyze \(5.3^{\text{Ph}}\), which is a “soft ionization” method used for molecules that are prone to fragmentation with higher impact methods thus the loss of \(\text{SnR}'\) is not expected.⁶⁰-⁶²

5.6 Elemental Analysis

Products \(5.2^R\) \((R = \text{Ph or Bn})\) and \(5.4^R\) were dried overnight under vacuum, \(^1\)H NMR spectroscopy was used to confirm that no water or solvents remained co-crystallized within the lattice. Combustion of \(5.2^{\text{Ph}}\) and \(5.4^R\) gave accurate % values for N and H, however the % C values were found to be consistently low after multiple trials. The inconsistent % C values are expected for \(5.4^R\), because combustion of fluorocarbon compounds often results in incompatible % C values for elemental analysis.⁶³,⁶⁴

5.7 X-ray Crystallography

5.7.1 General Collection and Refinement Information

The X-ray structure of \(5.4^{\text{Bn}}\) was obtained at low temperature, with the crystal covered in Paratone and placed rapidly into a cold \(\text{N}_2\) stream of the Kryo-Flex low-temperature device. The data was collected using SMART⁶⁵ software on a Bruker APEX CCD diffractometer using a graphite monochromator with Mo Kα radiation (\(\lambda = 0.71073\) Å). A hemisphere of data was collected using a counting time of 10 s per frame. Data reductions were performed using SAINT⁶⁶ software and the data was corrected for absorption using SADABS.⁶⁷ The structure was solved by direct methods using SIR97⁶⁸.
and refined by full-matrix least squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELX-97 and WinGX software package, and thermal ellipsoid plots were produced using ORTEP32.

5.7.2 Crystallographic Data

**Table 5.1. Crystallographic Data for cis-(MeNC₅H₄NiPr₂Ni(SnBn₃)(C₆F₅), 5.4Bn.**

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<td></td>
<td>c = 32.881(19) Å, ( \gamma = 90^\circ )</td>
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Chapter 5 – C–H Alkylation of Fluorinated Aromatics and Carbostannylation of Ethylene with Fluorinated Organostannanes with Catalytic Amounts of Ni(0) and a Nitrogen Ancillary Ligand

Goodness-of-fit on F²            0.883
Final R indices [I>2sigma(I)]    R₁ = 0.0990, wR₂ = 0.1776
R indices (all data)             R₁ = 0.3332, wR₂ = 0.2790
Largest diff. peak and hole      0.738 and –0.764 e.A⁻³
Chapter 5 – C–H Alkylation of Fluorinated Aromatics and Carbostannylation of Ethylene with Fluorinated Organostannanes with Catalytic Amounts of Ni(0) and a Nitrogen Ancillary Ligand

5.8 References

(2) Lyons, T. W.; Sanford, M. S. Chem. Rev. 2012, 110, 1147-1169.
Chapter 5 – C–H Alkylation of Fluorinated Aromatics and Carbostannylation of Ethylene with Fluorinated Organostannanes with Catalytic Amounts of Ni(0) and a Nitrogen Ancillary Ligand


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Chapter 5 – C–H Alkylation of Fluorinated Aromatics and Carbostannylation of Ethylene with Fluorinated Organostannanes with Catalytic Amounts of Ni(0) and a Nitrogen Ancillary Ligand


(64) Banks, R. E.; MacDonald and Company: London, 1970.

(65) SMART; Bruker AXS Inc.: Madison, WI, 2001.


6.1 Introduction

Fluorinated organics have found widespread applications in pharmaceuticals and agrochemicals. Substituting hydrogen atoms or methyl substituents for fluorine atoms or trifluoromethyl (CF₃) groups in the aromatic ring system of pharmaceutical drugs and agrochemicals creates strong polar interactions that affect the properties and reactivity of these molecules. In pharmaceuticals the introduction of fluorine or CF₃ moieties can drastically affect the lipophilicity, bioavailability, metabolic stability and interactions with target proteins. One approach traditionally utilized for introducing fluorine atoms involves fluorination with fluorinating agents; however, these methods are restricted to molecules with a limited range of functional groups or multiple positions and the fluorination of specific positions in more complex molecules is difficult. The most common methods for introducing CF₃ groups involve cross-coupling reactions, but are limited in generality, due to both the cost and lack of commercially available reagents.
Chapter 6 – C–F Bond Activation and Catalytic C–H Bond Stannylation of Trifluoromethyl Fluorinated Benzene Derivatives with Ni(0) and a Nitrogen Ancillary Ligand and Reactivity

The development of alternative methods for synthesizing fluorinated organics that include the following criteria would be highly beneficial: cost effective; easy to handle; controllable selectivity; and effective with a wide variety of substrates. Selective functionalizations of fluorinated aromatics via C–H or C–F bond oxidative addition to transition metals has been proposed as a viable alternative route to synthesizing fluorinated organics. The C–F and C–H bond activation and functionalization of fluorinated aromatics is well known, though expansion to substrates containing CF3 substituents on the fluorinated aromatic is not as well established and has been limited to mostly perfluorinated substrates with activation para to the site of the CF3 moiety. This is surprising given the frequency with which CF3 and aromatic C–F functionalities appear in modern pharmaceuticals and agrochemicals. Further expansion of this chemistry to less fluorinated CF3 containing aromatics is crucial to the development of alternative synthetic pathways for introducing CF3 moieties to fluorinated organics. It is well known that C–H bond oxidative addition is thermodynamically favored ortho to fluorine substituents. However, little is known about the affect of other substituents and thus a more in-depth understanding of the influence of substituents such as CF3 have on C–F and C–H bond activation would be beneficial to developing optimal catalysts for these systems.

We have previously shown in Chapter 2 that a variety of fluorinated aromatics such as C6F5H react with stoichiometric amounts of Ni(COD)2 (1,5-cyclooctadiene) and the strong N-donor ligand MeNC5H4NiPr at room temperature to give the thermodynamically favorable C–F bond activation complex trans-(MeNC5H4NiPr)2NiF(C6F5) as shown in Scheme 6.1. Chapter 3 demonstrated that the C–H bond of partially fluorinated aromatics such as C6F5H can be functionalized with the addition of CH2=CHSnBu3 and catalytic amounts of Ni(COD)2 and an ancillary ligand (MeNC5H4NiPr or PPr3), via C–H bond stannylation, as shown in Scheme 6.2. We were later able to demonstrate in Chapter 4 that with PPr3 as the ancillary ligand the active catalyst of this reaction is (PPr3)Ni(η2-CH2=CHSnPh3)2. This chapter describes the details of C–F bond activation and C–H bond stannylation of a variety trifluoromethyl fluorinated benzene derivatives, the reactivity of these species, and evidence that the CF3...
moieties meta and para to the site of activation increase the reaction rates of C–H bond activation relative to a variety of fluorinated aromatic derivatives.

![Scheme 6.1](image)

**Scheme 6.1.** C–F bond activation of fluorinated aromatics as demonstrated in Chapter 2.

![Scheme 6.2](image)

**Scheme 6.2.** C–H bond stannylation of fluorinated aromatics as demonstrated in Chapter 3 and 4.

### 6.2 Results and Discussion

#### 6.2.1 The Synthesis and Characterization of C–H Bond Stannylation Products

To expand the range of fluorinated substrates that can undergo C–H bond stannylation, the scope of cheap and readily available trifluoromethyl fluorinated benzene derivatives, ranging in price from $1.62/g – $53.00/g, were investigated and the influence of a CF$_3$ functional group on the reactivity was determined. Catalytic amounts of Ni(COD)$_2$ and MeNC$_5$H$_4$N/iPr were added to CH$_2$=CHSnBu$_3$ and a variety of trifluoromethyl fluorinated benzene substrates including 2,3,5,6-tetrafluorobenzotrifluoride, 2,3,4,5-tetrafluorobenzotrifluoride, 2,4,6-trifluorobenzotrifluoride, 2,3-difluorobenzotrifluoride, 3,4-difluorobenzotrifluoride, 2-fluorobenzotrifluoride, 3-fluorobenzotrifluoride and 4-fluorobenzotrifluoride. The
reaction mixtures were allowed to react at 40 °C for 0.5–3 h, as shown in Scheme 6.3. Upon completion the products were isolated by passing the crude reaction mixture (in toluene) through a silica plug to remove any nickel-containing compounds and the solvent was removed in vacuo yielding colorless oils. The reaction with 2,3,5,6-tetrafluorobenzotrifluoride produced 6.1 in a 90 % yield by $^{19}$F{$^1$H} NMR spectroscopy. The reaction with 2,4,6-trifluorobenzotrifluoride produced the monostannylated product 6.2 in a 94 % by $^{19}$F{$^1$H} NMR spectroscopy, using a modest excess of 2,4,6-trifluorobenzotrifluoride. The only significant impurity for the reaction with 2,4,6-trifluorobenzotrifluoride was the distannylated product 6.3 which was readily separated from 6.2 through further purification by a reverse-phase silica column. The distannylated compound 6.3 could be obtained with good selectively by using three equivalents of CH$_2$=CHSnBu$_3$, to give 98 % of 6.3 by $^{19}$F{$^1$H} NMR spectroscopy, after 12 h. The rate of the reaction is significantly decreased by the addition of excess of CH$_2$=CHSnBu$_3$.68

![Scheme 6.3](image)

**Scheme 6.3.** C–H bond stannylation of trifluoromethyl fluorinated benzenes with CH$_2$=CHSnBu$_3$ and catalytic amounts of Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr.

The reactions of substrates where only one fluorine is *ortho* disposed to the C–H bond did not undergo any significant reactivity. For example the reaction with 2,3-difluorobenzotrifluoride underwent less than one catalytic turnover, approximately a 3 % yield of (2,3-difluoro-4-(trifluoromethyl)phenyl)tributylstannane by $^{19}$F{$^1$H} spectroscopy, while the reactions with 3,4-difluorobenzotrifluoride,
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2-fluorobenzotrifluoride, 3-fluorobenzotrifluoride and 4-fluorobenzotrifluoride had no observable product formation even after 24 h heating at 50 °C. The reaction with 2,3,4,5-tetrafluorobenzotrifluoride did not form any of the C–H bond stannylated product, but, it readily formed a mixture of C–F bond activation products. The major site of activation was the fluorine para to the CF₃ moiety and two isomers of the complex trans-(MeNC₅H₄N′Pr)₂NiF(2,3,6-C₆F₃H-1-CF₃) (6.4) vide infra, were formed in a 1.5:1 ratio. These result indicate that activation of a C–H bond ortho to the CF₃ moiety or ortho to only one fluorine are not possible at 40 °C with catalytic amounts of MeNC₅H₄N′Pr and Ni(COD)₂. The observation of some product formation in the reaction with 2,3-difluorobenzotrifluoride, implies CF₃ is para activating relative to H, since difluorobenzene was not activated under similar conditions.⁶⁷

The ¹H NMR spectra of products 6.1–6.3 have very similar butyl resonances at approximately δ 0.87, 1.17, 1.29 and 1.49. Compound 6.2 has an additional resonance for the proton on the fluorinated arene at δ 6.10. The ¹¹⁹Sn{¹H} NMR spectra for 6.1–6.3 have resonances at δ –17.2, –26.2 and –27.7 respectively, which indicates that the presence/absence of meta fluorines and the location of the CF₃ moiety have a strong influence on the ¹¹⁹Sn chemical shift. The ¹⁹F{¹H} NMR spectra of compounds 6.1–6.3 have CF₃ resonances at δ –56.3, –56.0 and –55.5 respectively. The ¹⁹F{¹H} NMR spectra has aromatic fluorine resonances at δ –119.4 and –139.7 for 6.1, δ –83.1, –89.2 and –108.3 for 6.2 and δ –64.2 and –90.2 for 6.3, compared to 2,3,5,6-tetrafluorobenzotrifluoride starting material which has aromatic fluorine resonances at δ –101.2 and –108.0 and 2,4,6-trifluorobenzotrifluoride starting material which has resonances at δ –141.3 and –137.1. The ¹⁹F{¹H} NMR spectra indicate that the presence of a SnBu₃ moiety has a strong influence on the chemical shift of fluorines ortho to an Sn metal center with a shift of approximately 20 ppm downfield and a weak effect over fluorines meta to the Sn metal center with a shift of less than 3 ppm downfield, compared to the respective starting materials.
6.2.2 The Reactivity of the C–Sn Bond

If compounds 6.1–6.3 are not isolated from the crude reaction mixture upon completion of the reaction, the C–Sn bond of the products will react with the remaining catalytic amounts of Ni(COD)$_2$ and MeNC$_3$H$_4$N$^i$Pr in solution to form a mixture of three products. This reaction was studied using isolated 6.1. The reaction of three equivalents of 6.1 with one equivalent of Ni(COD)$_2$ and two equivalents of MeNC$_3$H$_4$N$^i$Pr in toluene for 4 days at room temperature, produced cis-(MeNC$_3$H$_4$N$^i$Pr)$_2$Ni(2,3,5,6-C$_6$F$_4$-4-CF$_3$)$_2$ (6.5), (2,4,5-trifluoro-6-(trifluoromethyl)-1,3-phenylene)bis(tributylstannane) (6.6) and FSnBu$_3$, as shown in Scheme 6.4. The $^{19}$F{$^1$H} NMR spectrum after 4 days indicates that the mixture consisted of approximately 33.7 % of 6.5, 33.7 % of 6.6, 15 % of FSnBu$_3$ and 17.6 % of 6.1. However, FSnBu$_3$ has low solubility in toluene and some precipitated from the crude reaction mixture as a white crystalline solid, which was isolated by filtration and was identified as FSnBu$_3$ by MS, IR and $^{19}$F NMR spectroscopy, thus the products were formed in an approximate 1:1:1 ratio. The remaining solution was cooled to –40 °C to obtain 6.5 as a yellow crystalline solid, the toluene was removed and 6.6 was extracted into pentane. After removing the solvent, 6.6 was obtained as a colorless oil.
Scheme 6.4. The reaction of 6.1 with Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr.

The solid-state molecular structure of 6.5 was determined by X-ray crystallography and an ORTEP depiction is shown in Figure 6.1. Product 6.5 is square planar, with the ancillary ligands cis disposed, though it remains unclear why the cis conformation is preferred over the trans. The nitrogen-containing and perfluorinated toluene rings of the ancillary ligands lie out of the coordination plane with the isopropyl groups situated on opposite faces of the square plane. The Ni(1)–N(1) and Ni(1)–N(3) bond lengths are 1.982(4) Å and 1.974(3) Å respectively and the Ni(1)–C(1) and Ni(1)–C(8) bond lengths are 1.893(4) Å and 1.923(4) Å respectively. The N(1)–C(15) bond length is 1.299(6) Å, which is similar to that observed for MeNC$_5$H$_4$N$i$Pr.$^{66}$ The bond lengths for the nitrogen containing ring are also comparable to those observed in free MeNC$_5$H$_4$N$i$Pr. The C(15)–C(16), C(16)–C(17) and C(17)–N(2) bonds had bond lengths of 1.443(6) Å, 1.332(7) Å and 1.358(7) Å respectively.
The solid-state molecular structure of complex 6.5 was maintained in solution, as confirmed by $^1$H and $^{19}$F-$^1$H NMR spectroscopy. The room temperature $^{19}$F-$^1$H NMR spectrum in $d_8$-toluene revealed four resolved resonances at $\delta$ -55.5, -115.0, -145.2 and -147.5 corresponding to the CF$_3$ fluorines, two overlapping ortho-fluorine environments and the two meta-fluorine environments respectively. The overlapping resonances associated with the ortho-fluorine environments are second order multiplets, the two meta-fluorines are complex multiplets, quartets of second order multiplets, while the para-CF$_3$ fluorines are a triplet, with coupling to the two meta-fluorine environments with a $^4J_{FF}$ value of 20.9 Hz. The data confirms that the ortho and meta-fluorines are not exchanged by rotation within the same ring due to hindered rotation but the two opposite rings are equivalent by the $C_2$ symmetry of the molecule.
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The $^1$H NMR spectrum of 6.5 is consistent with the $C_2$ symmetry observed in the solid-state, with eight proton resonances, which indicates that there is a single ancillary ligand environment. It should be noted that the protons closest to the nickel center for compound 6.5 have very different chemical shifts compared to similar nickel complexes previously published, such as trans-(MeNC$_5$H$_4$N$i$Pr)$_2$NiF(C$_6$F$_5$), which have the nitrogen donor ligands trans disposed.$^{66}$ The isopropyl CH resonance is shifted downfield to $\delta$ 4.60 compared to both free MeNC$_5$H$_4$N$i$Pr at $\delta$ 3.69 and trans-(MeNC$_5$H$_4$N$i$Pr)$_2$NiF(C$_6$F$_5$) at $\delta$ 3.07. The isopropyl CH$_3$ groups are diasterotopic since they are not exchanged by a mirror plane, with resonances at $\delta$ 1.0 and 1.54, compared to compound trans-(MeNC$_5$H$_4$N$i$Pr)$_2$NiF(C$_6$F$_5$) which has resonances at $\delta$ 0.2 and 2.60. The NCH$_3$ and the four protons in the nitrogen contain ring have resonances at $\delta$ 3.48, 6.10, 6.75, 7.22 and 9.70 respectively and are comparable to those observed for trans-(MeNC$_5$H$_4$N$i$Pr)$_2$NiF(C$_6$F$_5$).

Compound 6.6 was isolated as a clear oil upon extraction into pentane, and was analyzed by $^1$H, $^{19}$F$\{^1$H$\}$, $^{13}$C$\{^1$H$\}$ and $^{119}$Sn$\{^1$H$\}$ NMR spectroscopy. There are two sets of butyl resonances in the $^1$H NMR spectrum, with each environment separated by less than 0.05 ppm and integrating 1:1, which indicates that there are two SnBu$_3$ moieties in 6.6. The $^{19}$F$\{^1$H$\}$ NMR spectrum shows that there are four fluorine environments with resonances at $\delta$ –56.9, –70.8, –114.8 and –142.1. The resonance for the CF$_3$ moiety was observed at $\delta$ –56.9 as a doublet with tin satellites, this coupling pattern is consistent with coupling to one adjacent fluorine and tin, with $^4$J$_{FF}$ and $^4$J$_{FSn}$ values of 21.5 and 3.7 Hz respectively. The fluorine ortho to the CF$_3$ moiety was observed at $\delta$ –142.1 as a quartet of doublet of doublets with tin satellites, with coupling to the adjacent CF$_3$ group, ortho- and para-fluorines and the two tin groups, with $^3$J$_{FF}$, $^4$J$_{FF}$, $^5$J$_{FF}$ and $^4$J$_{FSn}$ values of 24.4, 21.7, 18.1 and 5.2 Hz respectively. The fluorine resonance at $\delta$ –70.8 was observed as a doublet of doublets with tin satellites, this coupling pattern indicates that there is coupling to two fluorine atoms and tin, with $^4$J$_{FF}$, $^5$J$_{FF}$, $^3$J$_{SnF}$ and $^3$J$_{SnF}$ values of 1.6, 18.0, 23.6 and 5.6 Hz respectively, due to the large downfield shift this fluorine was assigned as the one with two adjacent tin moieties. The last fluorine resonance at $\delta$ –114.8 was observed as a doublet of doublets with tin satellites, with coupling to two fluorines and tin, with $^3$J$_{FF}$,
$^4J_{FF}$ and $^3J_{SnF}$ values of 24.1, 1.6 and 5.7 Hz, respectively, and was assigned as the fluorine adjacent to one tin and one fluorine. The $^{119}$Sn{¹H} spectrum confirms the presence of two tin moieties in 6.6 with resonances at $\delta$ –18.4 and –26.1 both as doublet of doublet of doublets, consistent with coupling to the three fluorine environments. All these spectra are consistent with the assigned structure of 6.6.

### 6.2.3 Plausible Mechanism

A plausible mechanistic manifold that can explain both C–Sn bond activation to form 6.5 and C–F bond activation to form 6.6 is shown in Scheme 6.5. The presence of broad unidentifiable resonances in the $^1$H NMR spectra at $\delta$ –7.7, 16.5, 28.3 and 75.6 and in the $^{19}$F NMR spectra at $\delta$ –180, throughout the reaction implies a radical mechanism is likely.

**Scheme 6.5.** Proposed mechanism for synthesis of 6.5, 6.6 and FSnBu$_3$ from 6.1, Ni(COD)$_2$ and MeNC$_5$H$_4$N/iPr.
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The first step of the proposed mechanism involves C–Sn bond activation of 6.1 to form complex 6.7. There is precedence for C–Sn bond activation by Pd and Pt in the literature\textsuperscript{69-74} which makes compound 6.7 a viable intermediate. The $^{19}$F NMR spectrum shows trace amounts of a nickel complex that could be identified as 6.7, with resonances at $\delta$ –54.7, –110.9, –145.9 and –148.7 as a triplet and three broad multiplets integrating to 3:2:1:1 respectively, attempts to isolate the complex were unsuccessful. The second step involves the ligand redistribution of two equivalents of 6.7 to form product 6.5 and intermediate 6.9. Reductive elimination of Sn$_2$Bu$_6$ from 6.9 regenerates Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr, which can undergo further reactivity. Trace amount of Sn$_2$Bu$_6$ were observed by $^{119}$Sn$^{1}$H NMR spectroscopy. There is no clear evidence of how compound 6.6 is formed, though a plausible intermediate is complex 6.8, which could be formed from the reaction of 6.1 and Sn$_2$Bu$_6$ with Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr, with the loss of FSnBu$_3$. There is also a nickel species present throughout the reaction which is consistent with the coupling pattern expected for 6.8 at $\delta$ –61.0, –95.1, –114.2 and –148.3, integrating to 3:1:1:1 as three doublets and a multiplet respectively, attempts to isolate the trace amounts of the unidentified compound were unsuccessful. Complex 6.6 could then potentially be formed from the cis/trans isomerization of 6.8 followed by reductive elimination, regenerating Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr. The reaction would then continue until all of the nickel and MeNC$_5$H$_4$N$i$Pr are consumed from the formation of 6.5.

It was confirmed that all three components Ni(COD)$_2$, MeNC$_5$H$_4$N$i$Pr and 6.1 are required to form 6.5 and 6.6, no reaction was observed in solutions of just 6.1, or Ni(COD)$_2$ with 6.1, or MeNC$_5$H$_4$N$i$Pr with 6.1, after reacting for one day at both room temperature and at 60 °C. The addition of ten equivalents of MeNC$_5$H$_4$N$i$Pr did not have any effect on the rate or the ratio of products formed.

The reaction of Ni(COD)$_2$, MeNC$_5$H$_4$N$i$Pr and 6.1 in C$_6$D$_6$ was monitored by $^{19}$F NMR spectroscopy with added Sn$_2$Bu$_6$. Initial spectra show an increase in the amount of intermediates 6.7 and 6.8 formed relative to the same reaction without the addition of
Sn$_2$Bu$_6$. The results suggest that the addition of Sn$_2$Bu$_6$ decreases the rate compound 6.5 is formed and that the addition of excess Sn$_2$Bu$_6$ increases the rate of formation of compound 6.6 and FSnBu$_3$.

**6.2.4 Consideration of Ni–C Bond Strength**

Further support that the Sn–C bond can undergo reversible oxidative addition to Ni was obtained from the reaction of Ni(COD)$_2$ and two equivalents of MeNC$_5$H$_4$N$i$Pr with 6.1 in the presence of added 1,2,4,5-C$_6$F$_4$H$_2$, which produced the C–H bond stannylation product 2,3,5,6-C$_6$F$_4$H-1-SnBu$_3$ and the C–F bond activation product trans-(MeNC$_5$H$_4$N$i$Pr)$_2$NiF(2,4,5-C$_6$F$_3$-3-CF$_3$) (6.10), as shown in Scheme 6.6. To gain some mechanistic insight, a reaction of 1,2,4,5-C$_6$F$_4$HD with 6.1 and stoichiometric amounts of Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr was utilized to determine the initial ratio of C–H functionalized product to C–D functionalized product, which was found to be 1:1 at 298 K by integration of the $^{19}$F{$_1$H} NMR resonances of the products. This isotope effect is not consistent with the kinetic isotope effect we previously observed for the ratio of C–H-functionalized product to the C–D-functionalized product in the reaction of 1,2,4,5-C$_6$F$_4$HD with CH$_2$=CHSnBu$_3$ using catalytic Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr, which was 2.1:1. A mechanism involving rapidly reversible C–H/D C–Sn scrambling, as shown in Scheme 6.6, seems likely, thus the thermodynamic (equilibrium) isotope effect is observed rather than the kinetic isotope effect. The theoretical Gibbs free energies of the reactants 1,2,4,5-C$_6$F$_4$H$_2$ and 2,3,5,6-C$_6$F$_4$-1-SnMe$_3$-4-CF$_3$ and the products 2,3,5,6-C$_6$F$_4$H-1-SnMe$_3$ and 2,3,5,6-C$_6$F$_4$H-1-CF$_3$ were calculated using DFT and the ΔG of reaction was found to be 1.35 kcal·mol$^{-1}$. Though this step of the reaction is slightly uphill, the C–F bond activation of 2,3,5,6-C$_6$F$_4$H-1-CF$_3$ to form complex 6.10 is much faster than the C–F bond activation of 1,2,4,5-C$_6$F$_4$H$_2$, confirmed by a competition study between the two substrates, which produced a product ratio of 5:1 for 6.10 and trans-(MeNC$_5$H$_4$N$i$Pr)$_2$NiF(2,4,5-C$_6$F$_3$H$_2$), respectively. This result indicates that 6.10 and 2,3,5,6-C$_6$F$_4$H-1-SnBu$_3$ will be formed exclusively, since these C–F bond activations are irreversible. The increased rate of C–F bond activation of more electron-deficient arenes is well documented.$^{26,75,76}$
Chapter 6 – C–F Bond Activation and Catalytic C–H Bond Stannylation of Trifluoromethyl Fluorinated Benzene Derivatives with Ni(0) and a Nitrogen Ancillary Ligand and Reactivity

![Chemical structure](image)

**Scheme 6.6.** The reaction of Ni(COD)$_2$ and two equivalents of MeNC$_5$H$_4$N$_2$Pr with 6.1 in the presence of added 1,2,4,5-C$_6$F$_4$H$_2$.

**6.2.5 Influence of Substituents in the Meta and Para Position on the Relative Rate of C–H Bond Stannylation**

*Note: The competition studies presented in this section were performed by Manar Shoshani under my supervision.*

Support that CF$_3$ substituents are meta directing and have a greater influence on the rate of C–H bond stannylation than para CF$_3$ substitutes was obtained from a comparison of reaction rates with different fluorinated substrates containing two ortho fluorines and a variety of substituents, as shown in Scheme 6.7. The reaction rates relative to 1,2,4,5-C$_6$F$_4$H$_2$ are shown in Table 6.1 for the para-substituted substrates, pentafluorobenzene, 2,3,5,6-tetrafluorobenzotrifluoride, 2,3,5,6-tetrafluoropyridine, 2,3,5,6-tetrafluorotoluene and 2,3,5,6-tetrafluoroanisole. The reaction rates relative to 1,3,5-C$_6$F$_3$H$_3$ are shown in Table 6.2 to compare the meta substituted substrates, 1,2,3,5-tetrafluorobenzene, 2,4,6-trifluorobenzotrifluoride, 2,4,6-trifluoropyridine and 2,4,6-trifluoroanisole.
Scheme 6.7. Competition for C–H stannylation between different fluorinated substrates containing two ortho fluorines and a variety of substituents.

**Table 6.1.** Comparison of the rate of C–H stannylation for a variety of substrates with substituents in the para position, as shown in Scheme 6.7. \( \Delta \Delta G^\ddagger \) values were calculated by \( \Delta \Delta G^\ddagger = -RT \ln (k_1/k_2) \), where \( k_1 \) and \( k_2 \) are the relative rates the products are formed with 1,2,4,5-C\(_6\)F\(_4\)H\(_2\) and the competing substrate, respectively. \( \Delta \Delta H^\ddagger \) values were adjusted for the second equivalent hydrogen in 1,2,4,5-C\(_6\)F\(_4\)H\(_2\) using the following equation \( \Delta \Delta H^\ddagger = \Delta \Delta G^\ddagger + RT \ln (2/1) \).

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<tr>
<td>H</td>
<td>1,2,4,5-C(_6)F(_4)H(_2)</td>
<td><strong>6.13</strong></td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>2,3,5,6-C(_6)F(_4)H-1-CH(_3)</td>
<td><strong>6.14</strong></td>
<td>0.36</td>
<td>-0.60</td>
<td>1</td>
<td>-0.19</td>
</tr>
<tr>
<td>OCH(_3)</td>
<td>2,3,5,6-C(_6)F(_4)H-1-OCH(_3)</td>
<td><strong>6.15</strong></td>
<td>0.31</td>
<td>-0.69</td>
<td>1</td>
<td>-0.28</td>
</tr>
</tbody>
</table>
Table 6.2. Comparison of the rate of C–H stannylation for a variety of substrates with substituents in the meta position. ΔΔG‡ values were calculated by ΔΔG‡ = −RTln(k1/k2), where k1 and k2 are the relative rates the products are formed with 1,2,4,5-C₆F₄H₂ and the competing substrate, respectively. ΔΔH‡ values were adjusted for the additional equivalent hydrogen in 1,3,5-C₆F₃H₃ using the following equation ΔΔH‡ = ΔΔG‡ + RTln(3/2).

<table>
<thead>
<tr>
<th>X = Substrate</th>
<th># Relative Rate</th>
<th>ΔΔG‡ kcal·mol⁻¹</th>
<th>Equivalent H</th>
<th>ΔΔH‡ kcal·mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃</td>
<td>2,4,6-C₆F₃H₂-1-CF₃</td>
<td>6.2</td>
<td>1.19</td>
<td>1.43</td>
</tr>
<tr>
<td>N</td>
<td>2,4,6-C₅F₃H₂N</td>
<td>6.16</td>
<td>1.49</td>
<td>1.73</td>
</tr>
<tr>
<td>F</td>
<td>1,2,3,5-C₆F₄H₂</td>
<td>6.17</td>
<td>0.94</td>
<td>1.18</td>
</tr>
<tr>
<td>H</td>
<td>1,3,5-C₆F₃H₃</td>
<td>6.18</td>
<td>0.95</td>
<td>0.21</td>
</tr>
<tr>
<td>OCH₃</td>
<td>2,4,6-C₆F₃H₂-1-OCH₃</td>
<td>6.19</td>
<td>−0.033</td>
<td>2</td>
</tr>
</tbody>
</table>

The relative rates were obtained by competition studies between these substrates at 298 K. The ratio of initial products can be used to generate a difference in Gibbs free energy of activation, ΔΔG‡, for these substrates relative to 1,2,4,5-tetrafluorobenzene for the para competition and 1,3,5-trifluorobenzene for the meta competition. An estimated difference in enthalpy of activation, ΔΔH‡, was obtained by correcting for the statistical increase in activation that arises from the presence of multiple equivalent sites of activation. From the ΔΔH‡ obtained the substrates with the lowest kinetic barrier for C–H activation with substituents para to the site of activation are CF₃ < N(pyridine) < F < H < CH₃ < OCH₃ and with substituents meta to the site of activation are N(pyridine) < CF₃ < F < H < OCH₃. The large range of ΔΔH‡ values obtained for the meta substituents indicates that substituents meta to the site of activation have a larger effect on the reaction rates than para substituents. This result suggests that substituents meta to the site of activation correlate to faster reaction rates and stronger Ni–C bonds than para substituents with the exception of the methoxy substituent, which led to slower rates. The results indicate that the presence of a CF₃ substituent meta or para to the site of activation is favorable for C–H stannylation, with a meta-CF₃ having a larger affect than a para-CF₃.
substituent, the only substituent that better promoted C–H activation in the meta position was the nitrogen containing pyridine substrate.

6.2.6 The Synthesis and Characterization of C–F Bond Activation Products

To better understand how a CF₃ substituent influences C–F bond activation, and to expand the scope of fluorinated aromatic substrates that undergo C–F bond activation, a variety of fluorinated toluene substrates were investigated. Stoichiometric amounts of pentafluorobenzotrifluoride, 2,3,5,6-tetrafluorobenzotrifluoride, 2,3,4,5-tetrafluorobenzotrifluoride, 2,4,6-trifluorobenzotrifluoride, 2,3-difluorobenzotrifluoride, 3,4-difluorobenzotrifluoride, 2-fluorobenzotrifluoride, 3-fluorobenzotrifluoride and 4-fluorobenzotrifluoride were reacted with one equivalent of Ni(COD)₂ and two equivalents of MeNC₅H₄NPr in toluene. The reaction mixtures were allowed to react for 5–15 hours at room temperature with no stirring. The reactions with pentafluorobenzotrifluoride, 2,3,5,6-tetrafluorobenzotrifluoride, 2,3,4,5-tetrafluorobenzotrifluoride and 2,4,6-trifluoro-1-(trifluoromethyl)benzene formed bright-orange crystalline solids which precipitated from solution in a 32–56% yield, as the desired C–F bond activation complexes 6.4ᵃ, 6.4ᵇ, 6.10, 6.20 and 6.21 as shown in Scheme 6.8. The reactions with 2,3-difluorobenzotrifluoride, 3,4-difluorobenzotrifluoride, 2-fluorobenzotrifluoride, 3-fluorobenzotrifluoride or 4-fluorobenzotrifluoride did not undergo the desired C–F bond activation reactions, this can be attributed to a decrease in reactivity from a decrease in the number of fluorines. Even upon heating the reaction mixtures no reaction was observed, and nickel precipitated from solution when the temperature was increased above 50 °C.
Chapter 6 – C–F Bond Activation and Catalytic C–H Bond Stannylation of Trifluoromethyl Fluorinated Benzene Derivatives with Ni(0) and a Nitrogen Ancillary Ligand and Reactivity

\[
\text{Ar}^R \text{F} + \text{Ni(COD)}_2 + 2 \text{L} \xrightarrow{\text{toluene}} \text{L} = \begin{array}{c}
\text{N} \\
\text{\textit{i}Pr}
\end{array}
\xrightarrow{\text{F or Ni}} \text{Ar}^R \text{L}
\]

\[\text{L} = \begin{array}{c}
\text{N} \\
\text{\textit{i}Pr}
\end{array}\]

\[\text{X} = \begin{array}{c}
\text{F} \\
\text{F}
\end{array}\]

\[\text{Ar}^R = \begin{array}{c}
\text{F} \\
\text{F}
\end{array}\]

\[\text{X} = \begin{array}{c}
\text{F} \\
\text{CF}_3
\end{array}\]

Scheme 6.8. C–F bond activation of trifluoromethyl fluorinated benzene derivatives with Ni(COD)\(_2\) and MeNC\(_5\)H\(_4\)N\textit{i}Pr.

Compounds \(6.4^a, 6.4^b, 6.10, 6.20\) and \(6.21\) were analyzed by both \(^1\text{H}\) and \(^{19}\text{F}\{^1\text{H}\}\) NMR spectroscopy in CD\(_2\)Cl\(_2\). The reactions with pentafluorobenzotrifluoride, 2,3,5,6-tetrafluorobenzotrifluoride and 2,4,6-trifluoro-1-(trifluoromethyl)benzene occurred regioselectively, with no detectable impurities or byproducts. The reaction with 2,3,4,5-tetrafluorobenzotrifluoride forms a mixture of products, and minor amounts of another isomer of each of these products, the ratio of products formed is concentration dependant. However, there is a preference for activating the fluorine para to the CF\(_3\) group over the fluorine para to the H. The \(^{19}\text{F}\{^1\text{H}\}\) NMR resonances for compounds \(6.4^a, 6.4^b, 6.10, 6.20\) and \(6.21\) are summarized in Table 6.3.
The $^{19}$F{$_1$H} NMR spectra indicate that the fluoride resonance is directly affected by the substitution pattern of the fluorinated aromatic and the degree of fluorination. The chemical shift of the CF$_3$ substituent was affected by the absence of an adjacent fluorine causing a shift of approximately 4 ppm upfield as in complex 6.4$^a$ and 6.4$^b$. The aromatic fluorine chemical shifts are most affected by the absence of an ortho or meta fluorine with shifts of up to 15 ppm downfield as in 6.4$^a$, 6.4$^b$, 6.10 and 6.21.

The $^1$H NMR spectra for the ancillary ligand resonances in 6.4$^a$, 6.4$^b$, 6.10, 6.20 and 6.21 suggests that these complexes are isostructural. The two methyl groups on each isopropyl moiety are diastereotopic and are not exchanged by rotation about the Ni–N bond on the NMR time scale, with resonances at $\delta$ 0.2 and 2.5. The isopropyl CH is shifted slightly upfield relative to free MeNC$_5$H$_4$N$i$Pr at $\delta$ 3.1 while the NMe group is shifted downfield at $\delta$ 3.5. The isopropyl groups in complexes 6.4$^a$, 6.4$^b$, 6.10, 6.20 and 6.21 have significantly different chemical shifts than the isopropyl resonances for MeNC$_5$H$_4$N$i$Pr in complex 6.5, which suggests that there is a large chemical shift difference for the isopropyl groups depending on if the ancillary ligands are cis or trans disposed to one another and to the fluorinated aromatic. There are four resonances for the nitrogen containing ring at approximately $\delta$ 6.0, 6.8, 7.4 and 10.2, which indicates

### Table 6.3.

Summary of the $^{19}$F{$_1$H} NMR resonances of 6.4$^a$, 6.4$^b$, 6.10, 6.20 and 6.21, where X = FNi(trans-(MeNC$_5$H$_4$N$i$Pr)$_2$).

<table>
<thead>
<tr>
<th></th>
<th>6.4$^a$</th>
<th>6.4$^b$</th>
<th>6.10</th>
<th>6.20</th>
<th>6.21</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$</td>
<td>-60.8</td>
<td>-61.6</td>
<td>-56.1</td>
<td>-56.1</td>
<td>-55.3</td>
</tr>
<tr>
<td>$\delta$</td>
<td>-91.0</td>
<td>-93.0</td>
<td>-95.4</td>
<td>-115.7</td>
<td>-122.3</td>
</tr>
<tr>
<td>$\delta$</td>
<td>-110.5</td>
<td>-105.5</td>
<td>-147.8</td>
<td>-148.5</td>
<td>-325.6</td>
</tr>
<tr>
<td>$\delta$</td>
<td>-151.9</td>
<td>-147.6</td>
<td>-340.1</td>
<td>-355.3</td>
<td></td>
</tr>
<tr>
<td>$\delta$</td>
<td>-349.7</td>
<td>-351.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
that the protons within the same ring are not exchanged by rotation around the N=C bond. The close proximity of the nickel metal center to one of the protons in the nitrogen-containing ring causes the large downfield shift in the \(^1\text{H}\) NMR spectra to 10.2 ppm.

### 6.2.7 C–F Bond Activation Competition Experiments

Support that a \textit{para} CF\(_3\) substituent has a greater influence on the rate of C–F bond activation was obtained from a comparison of similar substrates which contain a \textit{para} H or \textit{para} F and the ratio of products formed during competition reactions, as shown in Scheme 6.9. An excess of pentafluorobenzotrifluoride with an equal amount of either hexafluorobenzene or pentafluorobenzene were added to Ni(COD)\(_2\) and MeNC\(_5\)H\(_4\)N\(\text{\text{Pr}}\), and the reaction mixtures were left undisturbed for 1 day to allow precipitation of the C–F activated products. Upon isolation of the products, \(^{19}\text{F}\{^1\text{H}\}\) NMR spectroscopy was used to compare the ratio of products formed. For the competition between pentafluorobenzotrifluoride and hexafluorobenzene the ratio of C–F bond activation complexes was 8:1 respectively and the competition between pentafluorobenzotrifluoride and pentafluorobenzene formed complex 6.20 exclusively. The results indicate that substrates with the lowest kinetic barriers for C–F bond activation with substituents \textit{para} to the site of activation are CF\(_3\) < F < H. Attempts to obtain X-ray quality crystals were unsuccessful due to twinning and layering of crystals, which lead to disorder and low quality structures.

![Scheme 6.9. Competition for C–F bond activation between substrates with various substituents \textit{para} to the site of activation.](image-url)
6.3 Conclusions

Experimental evidence shows that trifluoromethyl fluorinated benzene substrates are capable of selective catalytic C–H bond stannylation 6.1–6.3 and fast regioselective C–F bond activation 6.4a, 6.4b, 6.10, 6.20 and 6.21 with MeNC5H4N\textsuperscript{i}Pr as the ancillary ligand and Ni(COD)\textsubscript{2}, which includes the first examples of selective activation and functionalization of non-perfluorinated toluene substrates. The reaction of compound 6.1 with MeNC5H4N\textsuperscript{i}Pr and Ni(COD)\textsubscript{2} produced the unexpected products 6.5, 6.6 and FSnBu\textsubscript{3}, which were isolated and characterized. The mechanism of this unexpected reaction appears too complicated and possibly radical mediated. Several competition studies were conducted to gain some insight into how the CF\textsubscript{3} substituents affect the kinetics of C–H and C–F bond activation reactions. A competition between 6.1 and 1,2,4,5-tetrafluorobenzene with MeNC5H4N\textsuperscript{i}Pr and Ni(COD)\textsubscript{2} produced 6.10 and 2,3,5,6-C\textsubscript{6}F\textsubscript{4}H-1-SnBu\textsubscript{3} exclusively. This reaction demonstrates that the C–Sn bond activation of 6.1 and the C–H bond stannylation of 1,2,4,5-C\textsubscript{6}F\textsubscript{4}H\textsubscript{2} are reversible processes and that the fluorinated aromatic containing a CF\textsubscript{3} substituent para to the site of activation undergoes irreversible C–F bond activation faster than when the para substituent is H. This result was further confirmed by a competition between CF\textsubscript{3}C\textsubscript{6}F\textsubscript{5}, C\textsubscript{6}F\textsubscript{6} and C\textsubscript{6}F\textsubscript{5}H, with MeNC5H4N\textsuperscript{i}Pr and Ni(COD)\textsubscript{2}, where the rate of C–F bond activation was found to be fastest for substrates with a para-CF\textsubscript{3} substituent. Support that meta substituents have an even greater affect on the reaction rate of C–H activation than para, with the exception of methoxy substituents, was gained by comparing the \( \Delta\Delta H^\ddagger \) values from a competition study between a variety of substrates with meta and para substituents. Most literature examples of C–F activation with trifluoromethyl fluorinated benzene substrates have a CF\textsubscript{3} group para to the site of activation. The results presented here indicate that a CF\textsubscript{3} group meta to the site of activation actually leads to even faster reaction rates, which suggests that harder to activate substrates, such as CF\textsubscript{3}C\textsubscript{6}F\textsubscript{2}H\textsubscript{3}, CF\textsubscript{3}C\textsubscript{6}FH\textsubscript{4} and even CF\textsubscript{3}C\textsubscript{6}H\textsubscript{5} can be activated, thus expanding the scope of fluorinated substrates that can be utilized for further reactivity.
6.4 Experimental

6.4.1 General Procedures

All reactions were performed under an atmosphere of dry oxygen-free dinitrogen by means of standard Schlenk or glovebox techniques. Benzene-$d_6$ was dried by refluxing with Na/K and was then vacuum transferred and degassed by three freeze-pump-thaw cycles. Toluene-$d_8$ and CD$_2$Cl$_2$ were dried in an analogous manner by refluxing over Na and CaH$_2$ respectively. All other solvents were purchased anhydrous from Aldrich and further purified using a Grubbs’ type column system, 77 produced by Innovative Technology. $^1$H, $^{13}$C{$^1$H}, $^{19}$F{$^1$H} and $^{119}$Sn{$^1$H} NMR spectra were recorded on a Bruker AMX Spectrometer operating at 300 MHz or where stated at 500 MHz with respect to proton nuclei. All chemical shifts are reported in parts per million (ppm) and all coupling constants are in hertz (Hz). $^1$H NMR spectra were referenced to residual protons (C$_6$D$_5$H, δ 7.15; CDCl$_3$, δ 5.32; C$_7$D$_8$H δ 2.09; CHCl$_3$, δ 7.26) with respect to tetramethylsilane at δ 0.00. $^{13}$C{$^1$H} spectra were referenced relative to solvent resonances (C$_6$D$_6$, δ 128.0, CDCl$_3$, δ 77.0, C$_7$D$_8$, δ 20.4). $^{19}$F{$^1$H} NMR spectra were referenced to an external sample of 80 % CCl$_3$F in CDCl$_3$ at δ 0.0. $^{119}$Sn{$^1$H} NMR spectra were referenced to an external sample of SnMe$_4$ at δ 0.0. The substrates C$_6$D$_6$, C$_7$D$_8$, CDCl$_3$, CD$_2$Cl$_2$, C$_6$F$_5$H, 1,2,4,5-C$_6$F$_4$H$_2$, 1,2,3,5-tetrafluorobenzene, 1,3,5-C$_6$F$_3$H$_3$, 2,3,5,6-tetrafluorotoluene, CH$_2$=CHSnBu$_3$ and Bu$_6$Sn$_2$ were purchased from Aldrich. The compounds pentfluorobenzotrifluoride, 2,3,5,6-tetrafluorobenzotrifluoride, 2,3,4,5-tetrafluorobenzotrifluoride, 2,4,6-trifluorobenzotrifluoride, 2,3-difluorobenzotrifluoride, 3,4-difluorobenzotrifluoride, 2-fluorobenzotrifluoride, 3-fluorobenzotrifluoride, 4-fluorobenzotrifluoride, 2,3,5,6-tetrafluoropyridine, 2,3,5,6-tetrafluoroanisole, 2,4,6-trifluoropyridine and 2,4,6-trifluoroanisole were purchased from Alfa Aesar. The compounds MeNC$_5$H$_4$N$i$Pr$_6$, Ni(COD)$_2$ and 1,2,4,5-C$_6$F$_4$HD were prepared by literature procedures.
6.4.2 Synthesis, Characterization and Reactivity of Complexes

Synthesis of C–H stannylation products (6.1–6.3 and 6.11–6.19). A solution of fluorinated aromatic (0.67 mmol) and tributyl(vinyl)tin (0.211 g, 0.67 mmol) in 0.6 g of C₆D₆ was added to MeNC₅H₄NPr (0.010 g, 0.067 mmol) and Ni(COD)₂ (0.009 g, 0.033 mmol). The solutions were at heated at 40 °C for 0.5 – 12 h or were left at room temperature for 2–4 days. The reaction mixtures were filtered through silica and the solvent was removed, leaving colourless oils. Compounds 6.12, 6.13, 6.17 and 6.18 have been previous characterized.⁶⁷

Characterization of (2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)tributylstannane (6.1). (90 % yield by NMR spectroscopy). ¹H NMR (C₆D₆, 25 ºC, 300.13 MHz): δ 0.87 (t, 9H, CH₃, ³J_HH = 7.3 Hz); 1.17 (m with Sn satellites, 6H, SnCH₂, ²J_HSn = 52.5 Hz); 1.29 (qt, 6H, SnCH₂CH₂CH₂, ³J_HH = 7.3 Hz, ³J_HH = 7.4 Hz); 1.49 (m, 6H, SnCH₂CH₂).

¹⁹F{¹H} NMR (C₆D₆, 25 ºC, 282.40 MHz): δ –56.3 (t, 3F, C₃F₃, ³J_FF = 21.5 Hz); –119.4 (AA’MM’N₃ second order with Sn satellites, 2F, 2,6–Ar–F, ³J_FSn = 8.4 Hz); –139.7 (AA’MM’N₃ second order, 2F, 3,5–Ar–F). ¹³C{¹H} NMR (C₆D₆, 25 ºC, 75.47 MHz): δ 11.8 (t with Sn satellites, SnCH₂, ¹J_CSn(119) = 358 Hz, ¹J_CSn(117) = 341 Hz, ⁴J_CF = 1.8 Hz); 13.7 (s, CH₃); 27.5 (s with Sn satellites, SnCH₂CH₂CH₂, ³J_CSn = 20.2 Hz); 110.9 (m, 4–Ar–C); 121.7 (q, CF₃, ¹J_CF = 274.0 Hz); 124.0 (t, 1–Ar–C, ²J_CF = 49.5 Hz); 143.6 (dm, Ar–C, ¹J_CF = 263.3 Hz); 149.4 (dm, Ar–C, ¹J_CF = 253.9 Hz). ¹¹⁹Sn{¹H} NMR (C₆D₆, 25 ºC, 111.96 MHz): δ –17.2 (ttq, Sn, ³J_SnF = 8.3 Hz, ⁴J_SnF = 3.1 Hz, ⁵J_SnF = 2.3 Hz).

Characterization of (2,4,6-trifluoro-3-trifluoromethyl)phenyl)tributylstannane (6.2). (94 % yield by NMR spectroscopy; isolated 0.123 g, 76 % yield). ¹H NMR (C₆D₆, 25°C, 300.13 MHz): δ 0.86 (t, 9H, CH₃, ³J_HH = 7.5 Hz); 1.18 (m, with Sn satellites, 6H, SnCH₂, ³J_HSn = 50.6 Hz); 1.30 (qd, 6H, SnCH₂CH₂CH₂, ³J_HH = 7.2 Hz, ³J_HH = 7.5 Hz); 1.52 (m, 6H, SnCH₂CH₂); 6.10 (dddq, 1H, ³J_HF = 10.8 Hz, ³J_HF = 6.5 Hz, ⁵J_HF = 1.8 Hz, ⁵J_HF = 0.8 Hz). ¹⁹F{¹H} NMR (C₆D₆, 25°C, 282.40 MHz) δ –56.0 (dddd, 3F, CF₃, ⁴J_FF = 23.5 Hz, ⁴J_FF = 21.9 Hz, ⁶J_FF = 1.7 Hz); –83.1 (dddq, 1F, 4–Ar–F, ⁴J_FF = 11.7 Hz, ⁴J_FF = 3.5 Hz).
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Characterization of (2,4,6-trifluoro-5-trifluoromethyl)phenyl)-1,3-bistributylstannane (6.3). (98 % yield by NMR spectroscopy; isolated 0.178 g, 68 % yield). $^1$H NMR (C$_6$D$_6$, 25°C, 300.13 MHz): $\delta$ 0.97 (t, 18H, C$_3$H$_3$, $^3$J$_{HH}$ = 7.5 Hz); 1.17 (m, with Sn satellites, 12H, SnCH$_2$, $^2$J$_{HSn}$ = 54.0 Hz); 1.30 (qd, 12H, SnCH$_2$CH$_2$CH$_2$, $^3$J$_{HH}$ = 7.49 Hz, $^3$J$_{HH}$ = 7.2 Hz); 1.51 (m, 12H, SnCH$_2$C$_2$). $^{19}$F$^1$H NMR (C$_6$D$_6$, 25°C, 282.40 MHz) $\delta$ –55.5 (td, 1F, C$_3$F$_3$, $^4$J$_{FF}$ = 22.9 Hz, $^6$J$_{FF}$ = 1.5 Hz); –64.2 (qt, 2F, 2–Ar–F, $^4$J$_{FF}$ = 5.7 Hz, $^6$J$_{FF}$ = 1.7 Hz); –90.2 (qd with Sn satellites, 1F, 4,6–Ar–F, $^4$J$_{FF}$ = 23.1 Hz, $^4$J$_{FF}$ = 5.9 Hz, $^3$J$_{FF}$ = 7.1 Hz). $^{13}$C$^1$H NMR (C$_6$D$_6$, 25°C, 75.47 MHz): $\delta$ 11.5 (s with Sn satellites, SnCH$_2$, $^1$J$_{CSn}$ = 358.4 Hz); 13.8 (s, SnCH$_2$CH$_2$CH$_2$CH$_3$); 27.6 (s with Sn satellites, SnCH$_2$CH$_2$, $^2$J$_{CSn(19)}$ = 64.8 Hz, $^2$J$_{CSn(17)}$ = 61.6 Hz); 29.3 (s with Sn satellites, SnCH$_2$CH$_2$, $^3$J$_{CSn}$ = 6.1 Hz); 110.2 (dd, 2C, 1,3–Ar–C, $^2$J$_{CF}$ = 33.5 Hz, $^2$J$_{CF}$ = 28.1 Hz, $^4$J$_{CF}$ = 4.0 Hz); 123.1 (qt, 1C, CF$_3$, $^1$J$_{CF}$ = 274.3 Hz, $^3$J$_{CF}$ = 3.3 Hz); 166.4 (dd, 2C, 4,6–Ar–C, $^1$J$_{CF}$ = 246.0 Hz, $^3$J$_{CF}$ = 24.2 Hz, $^2$J$_{CF}$ = 6.8 Hz, $^3$J$_{CF}$ = 1.6 Hz); 174.3 (dt, 1C, $^1$J$_{CF}$ = 232.7 Hz $^3$J$_{CF}$ = 24.7 Hz). $^{119}$Sn$^1$H NMR (C$_6$D$_6$, 25°C, 111.96MHz): $\delta$ –27.7 (dd, Sn, $^4$J$_{SnF}$ = 4.65 Hz, $^5$J$_{SnF}$ = 1.72 Hz). Calcd for C$_{31}$H$_{54}$F$_6$Sn$_2$: [M$^+$– C$_4$H$_9$], 723.1469. Found: m/z 723.1509.
Characterization of (2,3,5,6-tetrafluoropyridyl)tributylstannane (6.11). (91 % yield by NMR spectroscopy; isolated 0.104 g, 72 %). $^1$H NMR (C$_6$D$_6$, 25 ºC, 300.13 MHz): δ 0.87 (t, 9H, SnCH$_2$CH$_2$CH$_2$CH$_3$, $^3$J$_{HH}$ = 7.3 Hz); 1.3 (m, 6H, SnCH$_2$, $^3$J$_{HH}$ = 7.7 Hz); 1.27 (qt, 6H, SnCH$_2$CH$_2$CH$_2$, $^3$J$_{HH}$ = 7.7 Hz, $^3$J$_{HH}$ = 6.9 Hz); 1.45 (tt, 6H, SnCH$_2$CH$_2$, $^3$J$_{HH}$ = 7.5 Hz, $^3$J$_{HH}$ = 6.6 Hz). $^{19}$F{1H} NMR (C$_6$D$_6$, 25 ºC, 282.40 MHz): δ –93.5 (AA’MM’ second order with satillites, 2F, 3,5–Ar–F, $^4$J$_{FSn}$ = 6.6 Hz); –125.4 (AA’MM’ second order with satillites, 2F, 2,6–Ar–F, $^3$J$_{FSn}$ = 11.2 Hz). $^{13}$C{1H} NMR (C$_6$D$_6$, 25 ºC, 75.47 MHz): δ 11.6 (t with Sn satellites, SnCH$_2$, $^1$J$_{CSn(119)}$ = 357.4 Hz, $^1$J$_{CSn(117)}$ = 340.2 Hz, $^4$J$_{CF}$ = 3.5 Hz); 13.7 (s with Sn satellites, SnCH$_2$CH$_2$CH$_2$CH$_3$, $^4$J$_{CSn}$ = 2.7 Hz); 27.4 (s with Sn satellites, SnCH$_2$CH$_2$, $^2$J$_{CSn(119)}$ = 66.8 Hz, $^2$J$_{CSn(117)}$ = 63.3 Hz); 29.0 (s with Sn satellites, SnCH$_2$CH$_2$CH$_2$, $^3$J$_{CSn}$ = 21.3 Hz); 135.2 (t, 1–Ar–C, $^2$J$_{CF}$ = 47.7 Hz); 143.4 (dddd second order, 2,6–Ar–C, $^1$J$_{CF}$ = 249.0 Hz, $J$ = 24.1, 10.3, 1.7 Hz); 145.1 (dm second order, 3,5–Ar–C, $^1$J$_{CF}$ = 252.4 Hz). $^{119}$Sn{1H} NMR (C$_6$D$_6$, 25 ºC, 111.95 MHz): δ –19.3 (tt, $^3$J$_{SnF}$ = 11.3 Hz, $^4$J$_{SnF}$ = 6.7 Hz).

Characterization of (2,3,5,6-tetrafluoro-1-methyl)phenyl)tributylstannane (6.14). (93 % yield by NMR spectroscopy). $^1$H NMR (C$_6$D$_6$, 25 ºC, 300.13 MHz): δ 0.89 (t, 9H, CH$_3$, $^3$J$_{HH}$ = 7.3 Hz); 1.24 (m, with Sn satellites, 6H, SnCH$_2$, $^3$J$_{HH}$ = 8.3 Hz, $^3$J$_{HH}$ = 8.0 Hz); 1.33 (qd, 6H, SnCH$_2$CH$_2$CH$_2$, $^3$J$_{HH}$ = 7.3 Hz, $^3$J$_{HH}$ = 7.5 Hz); 1.58 (tt, 6H SnCH$_2$CH$_2$, $^3$J$_{HH}$ = 7.4 Hz, $^3$J$_{HH}$ = 8.1 Hz); 1.7 (t, 3H, CH$_3$, $^3$J$_{HH}$ = 2.1 Hz). $^{19}$F{1H} NMR (C$_6$D$_6$, 25 ºC, 282.40 MHz): δ –123.3 (AA’MM’ second, 2F, 2,6–Ar–F); –142.8 (AA’MM’ second order with Sn satellites, 2F, 3,5–Ar–F, $^4$J$_{FSn}$ = 5.9Hz). $^{13}$C{1H} NMR (C$_6$D$_6$, 25 ºC, 75.47 MHz): δ 11.2 (t with Sn satellites, SnCH$_2$, $^4$J$_{CF}$ = 1.90 Hz, $^1$J$_{CSn(119)}$ = 359 Hz, $^1$J$_{CSn(117)}$ = 341 Hz); 13.4 (s, SnCH$_2$CH$_2$CH$_2$CH$_3$); 27.2 (s with Sn satellites, SnCH$_2$CH$_2$, $^2$J$_{CSn}$ = 64.0 Hz); 28.9 (s with Sn satellites, SnCH$_2$CH$_2$CH$_2$, $^3$J$_{CSn}$ = 21.4 Hz); 102.9 (t, CH$_3$, $^2$J$_{CF}$ = 30 Hz) 114.0 (tt, 1C, 1–Ar–C, $^2$J$_{CF}$ = 48.5 Hz, $^3$J$_{CF}$ = 3.9 Hz); 117.0 (t, 1C, 4–Ar–C, $^2$J$_{CF}$=19.3 Hz) 144.7 (dm, 2C, Ar–C, $^1$J$_{CF}$ = 251.9 Hz); 145.5 (dm, 2C, Ar–C, $^1$J$_{CF}$ = 233.3 Hz). $^{119}$Sn{1H} NMR (C$_6$D$_6$, 25 ºC, 111.96 MHz): δ –22.5 (m, Sn). Calcd for C$_{19}$H$_{30}$F$_4$Sn: [M$^+$–C$_4$H$_9$], 397.0640. Found: m/z 397.0626.
Characterization of (2,3,5,6-tetrafluoro-4-methoxy)phenyl)tributylstannane (6.15). (97 % yield by NMR spectroscopy). $^1$H NMR (CD$_6$D$_6$, 25 °C, 300.13 MHz): δ 0.90 (t, 9H, CH$_3$, $^3$J$_{HH}$ = 7.3 Hz); 1.23 (m with Sn satellites, 6H, SnCH$_2$, $^2$J$_{HSn}$ = 53.0 Hz); 1.34 (qt, 6H, SnCH$_2$CH$_2$CH$_2$, $^3$J$_{HH}$ = 7.3 Hz, $^3$J$_{HH}$ = 7.4 Hz); 1.58 (m, 6H, SnCH$_2$CH$_2$); 3.54 (t, 3H, OCH$_3$, $^5$J$_{HF}$ = 1.4). $^{19}$F{$_1$H} NMR (CD$_6$D$_6$, 25 °C, 282.40 MHz): δ –122.3 (AA’MM’ second order, 2F, 2,6–Ar–F); –155.8 (AA’MM’ second order, 2F, 3,5–Ar–F). $^{13}$C{$_1$H} NMR (CD$_6$D$_6$, 25 ºC, 75.47 MHz): δ 11.2 (t with Sn satellites, SnCH$_2$, $^1$J$_{CSn(119)}$ = 360.4 Hz, $^1$J$_{CSn(117)}$ = 344.0 Hz, $^4$J$_{CF}$ = 1.8 Hz); 13.4 (s, CH$_3$); 27.2 (s with Sn satellites, SnCH$_2$CH$_2$, $^2$J$_{CSn}$ = 65.0 Hz); 28.9 (s with Sn satellites, SnCH$_2$CH$_2$CH$_2$, $^3$J$_{CSn}$ = 21.2 Hz); 61.1 (t, OCH$_3$, $^4$J$_{CF}$ = 3.5 Hz); 98.4 (t, 4–Ar–C, $^2$J$_{CF}$ = 23.1 Hz); 108.8 (tt, 1–Ar–C, $^2$J$_{CF}$ = 49.6 Hz, $^3$J$_{CF}$ = 4.9 Hz); 140.6 (dm, Ar–C, $^1$J$_{CF}$ = 251.9 Hz); 149.2 (dm, Ar–C, $^1$J$_{CF}$ = 233.4 Hz). $^{119}$Sn{$_1$H} NMR (CD$_6$D$_6$, 25 ºC, 111.96 MHz): δ –21.5 (tt, Sn, $^3$J$_{SnF}$ = 4.6 Hz, $^4$J$_{SnF}$ = 2.4 Hz). Calcd for C$_{19}$H$_{30}$F$_4$OSn: [M+–C$_4$H$_9$], 413.0551. Found: m/z 413.0544.

Characterization of (2,4,6-trifluoropyridyl)tributylstannane (6.16). (82 % yield by NMR spectroscopy). $^1$H NMR (CD$_6$D$_6$, 25 ºC, 300.13 MHz): δ 0.87 (t, 9H, SnCH$_2$CH$_2$CH$_2$CH$_3$, $^3$J$_{HH}$ = 7.2 Hz); 1.14 (m, 6H, SnCH$_2$, $^3$J$_{HH}$ = 7.7 Hz); 1.29 (qt, 6H, SnCH$_2$CH$_2$CH$_2$, $^3$J$_{HH}$ = 7.4 Hz, $^3$J$_{HH}$ = 7.2 Hz); 1.50 (tt, 6H, SnCH$_2$CH$_2$, $^3$J$_{HH}$ = 7.8 Hz, $^3$J$_{HH}$ = 7.6 Hz). $^{19}$F{$_1$H} NMR (CD$_6$D$_6$, 25 ºC, 282.40 MHz): δ –50.5 (dd, 1F, 2–Ar–F, $^4$J$_{FF}$ = 12.4 Hz, $^4$J$_{FF}$ = 16.1 Hz); –67.0 (dd, 1F, 6–Ar–F, $^4$J$_{FF}$ = 22.6 Hz, $^4$J$_{FF}$ = 12.8 Hz); –76.9 (dd, 1F, 4–Ar–F, $^4$J$_{FF}$ = 22.9 Hz, $^4$J$_{FF}$ = 16.2 Hz). Calcd for C$_{17}$H$_{28}$F$_3$NSn: [M+–C$_4$H$_9$], 366.0492. Found: m/z 366.0493.

Characterization of (2,4,6-trifluoro-3-methoxy)phenyl)tributylstannane (6.19). (56 % yield by NMR spectroscopy). $^1$H NMR (CD$_6$D$_6$, 25 ºC, 300.13 MHz): δ 0.90 (t, 9H, CH$_3$, $^3$J$_{HH}$ = 7.9 Hz); 1.17 (m with Sn satellites, 6H, SnCH$_2$, $^2$J$_{HSn}$ = 52.5 Hz); 1.33 (qt, 6H, SnCH$_2$CH$_2$CH$_2$, $^3$J$_{HH}$ = 7.4 Hz, $^3$J$_{HH}$ = 7.4 Hz); 1.52 (m, 6H, SnCH$_2$CH$_2$); 3.94 (s, 3H, OCH$_3$); 6.61 (ddd, 1H, Ar–H, $^3$J$_{HF}$ = 10.6 Hz, $^3$J$_{HF}$ = 6.1 Hz, $^4$J$_{HF}$ = 2.1 Hz). $^{19}$F{$_1$H} NMR (CD$_6$D$_6$, 25 ºC, 282.40 MHz): δ –96.8 (dd with Sn satellites, 1F, Ar–F, $^4$J$_{FF}$ = 4.2 Hz, $^4$J$_{FF}$ = 2.9 Hz, $^3$J$_{FSn}$ = 5.9 Hz); –108.4 (dd with Sn satellites, 1F, Ar–F, $^4$J$_{FF}$ = 8.8 Hz, $^4$J$_{FF}$ = 2.9 Hz, $^3$J$_{FSn}$ = 8.3 Hz). –126.4 (dd with Sn satellites, 1F, Ar–F, $^4$J$_{FF}$ = 8.8 Hz, $^4$J$_{FF}$
= 4.2 Hz, $^5J_{FSn} = 4.7$ Hz). $^{13}$C $^{1}$H NMR (C$_6$D$_6$, 25 °C, 75.47 MHz): δ 11.0 (s with Sn satellites, SnCH$_2$); $^1J_{C_{Sn}(119)} = 359.8$ Hz, $^1J_{C_{Sn}(117)} = 345.1$ Hz); 13.7 (s, CH$_3$); 27.3 (s with Sn satellites, SnCH$_2$CH$_2$); $^2J_{C_{Sn}} = 68.2$ Hz); 29.1 (s with Sn satellites, SnCH$_2$CH$_2$CH$_2$); $^3J_{C_{Sn}} = 21.5$ Hz); 62.1 (s, OCH$_3$); 100.1 (dd, 5–Ar–C, $^2J_{CF} = 35.1$ Hz, $^2J_{CF} = 22.6$ Hz, $^4J_{CF} = 3.9$ Hz); 156 (dm, Ar–C, $^1J_{CF} = 243.2$ Hz); 159 (dm, Ar–C, $^1J_{CF} = 241.3$ Hz); 161 (dm, Ar–C, $^1J_{CF} = 233.1$ Hz). $^{119}$Sn $^{1}$H NMR (C$_6$D$_6$, 25 °C, 111.96 MHz): δ –28.5 (ddd, Sn, $^3J_{SnF} = 8.3$ Hz, $^3J_{SnF} = 6.0$ Hz, $^5J_{SnF} = 4.7$ Hz). Calcd for C$_{19}$H$_{31}$F$_3$OSn: [M$^+$–C$_4$H$_9$], 395.0645. Found: m/z 395.0635.

Synthesis of cis-(MeNC$_5$H$_4$N$i$Pr)$_2$(2,3,5,6-C$_6$F$_4$-4-CF$_3$)$_2$Ni (6.5). A solution of (2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)tributylstannane (1) (0.075 g, 0.148 mmol) in 0.6 g of $d_8$-toluene was added to MeNC$_5$H$_4$N$i$Pr (0.015 g, 0.098 mmol) and Ni(COD)$_2$ (0.014 g, 0.049 mmol). The solution was allowed to react for 4 days at room temperature. The desired product was then separated by recrystallization of the reaction mixture at –40 °C and isolated by vacuum filtration to yield a yellow crystalline solid. (33 % yield by $^{19}$F $^{1}$H NMR). $^1$H NMR ($d_8$-toluene, 25 °C, 300.13 MHz): δ 1.0 (d, 6H, NCH(CH$_3$)$_2$, $^3J_{HH} = 6.8$ Hz); δ 1.54 (d, 6H, NCH(CH$_3$)$_2$, $^3J_{HH} = 6.5$ Hz); 1.93 (s, 6H, NCH$_3$); 4.60 (br m, 2H, NCH$_2$); 5.50 (dd, 2H, C$_5$H$_4$N, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.7$ Hz); 5.69 (dd, 2H, C$_5$H$_4$N, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.9$ Hz); 6.17 (dd, 2H, C$_5$H$_4$N, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.9$ Hz); 10.03 (br, 2H, C$_5$H$_4$N). $^{19}$F $^{1}$H NMR ($d_8$-toluene, 25 °C, 282.40 MHz): δ –55.4 (t, 6F, $CF_3$, $^3J_{FF} = 20.9$ Hz); –115.3 (m, 2F, Ar–F); –145.5 (m, 1F, Ar–F); –147.7 (m, 1F, Ar–F). $^{13}$C $^{1}$H NMR (CD$_2$Cl$_2$, 25 °C, 75.47 MHz): δ 21.0 (s, (NCH(CH$_3$)$_2$); 21.5 (s, (NCH(CH$_3$)$_2$); 42.8 (s, (NCH$_3$); 52.3 (s, (NCH(CH$_3$)$_2$); 109.2 (s, C$_5$H$_4$N); 128.5 (s, C$_5$H$_4$N); 129.3 (s, C$_5$H$_4$N); 136.0 (s, C$_5$H$_4$N); 137.8 (s, C$_5$H$_4$N); 141.3 (dm, Ar–C, $^1J_{CF} = 256.6$ Hz); 149.5 (dm, Ar–C, $^1J_{CF} = 226.4$ Hz); 158.0 (s, C$_5$H$_4$N).

Synthesis of (2,4,5-trifluoro-6-(trifluoromethyl)-1,3-phenylene)bis(tributylstannane) (6.6). A solution of (2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)tributylstannane (0.075 g, 0.148 mmol) in 0.6 g of $d_8$-toluene was added to MeNC$_5$H$_4$N$i$Pr (0.015 g, 0.098 mmol) and Ni(COD)$_2$ (0.014 g, 0.049 mmol). The solution was allowed to react for 1 day at room temperature. The solvent was removed and the desired product was extracted into
pentane, filtered and the solvent was removed to yield colourless oil. (33 % yield by $^{19}$F{¹H} NMR spectroscopy). $^1$H NMR (C₆D₆, 25 ºC, 300.13 MHz): $\delta$ 0.88 (t, 9H, $CH_3$, $^3J_{HH} = 7.3$ Hz); $\delta$ 0.92 (t, 9H, $CH_3$, $^3J_{HH} = 7.1$ Hz); 1.21 (m with Sn satellites, 6H, $SnCH_2$, $^2J_{HSn} = 24.9$ Hz); 1.25 (m with Sn satellites, 6H, $SnCH_2$, $^2J_{HSn} = 24.0$ Hz); 1.35 (m, 6H, $SnCH_2CH_2CH_2$); 1.37 (m, 6H, $SnCH_2CH_2CH_2$); 1.57 (m, 6H, $SnCH_2CH_2$); 1.58 (m, 6H, $SnCH_2CH_2$). $^{19}$F{¹H} NMR (C₆D₆, 25 ºC, 282.40 MHz): $\delta$ -56.9 (d with Sn satellites, 3F, $CF_3$, $^3J_{FF} = 21.5$ Hz, $^4J_{FSn} = 3.7$ Hz); -70.8 (dd with Sn satellites, 1F, 2–Ar–F, $^5J_{FF} = 18.1$ Hz, $^4J_{FF} = 1.6$ Hz, $^3J_{FSn} = 23.6$ Hz, $^3J_{FSn} = 5.6$ Hz); -114.8 (dd with Sn satellites, 1F, 4–Ar–F, $^3J_{FF} = 24.1$ Hz, $^4J_{FF} = 1.6$ Hz, $^3J_{FSn} = 5.7$ Hz); -142.1 (ddq with Sn satellites, 1F, 5–Ar–F, $^3J_{FF} = 24.4$ Hz, $^4J_{FF} = 21.7$ Hz, $^5J_{FF} = 18.1$ Hz, $^4J_{FSn} = 5.2$ Hz).

$^{13}$C{¹H} NMR (C₆D₆, 25 ºC, 75.47 MHz): $\delta$ 11.6 (s with Sn satellites, $SnCH_2$, $^1J_{CSn} = 358.9$ Hz); 13.0 (s with Sn satellites, $SnCH_2$, $^1J_{CSn} = 338.1$ Hz); 13.8 (s, $SnCH_2CH_2CH_2$); 13.9 (s, $SnCH_2CH_2CH_2$); 27.5 (s with Sn satellites, $SnCH_2$, $^2J_{CSn} = 65.2$ Hz); 27.6 (s with Sn satellites, $SnCH_2$, $^2J_{CSn} = 65.2$ Hz); 29.3 (s with Sn satellites, $SnCH_2CH_2$, $^3J_{CSn} = 21.0$ Hz); 29.4 (s with Sn satellites, $SnCH_2CH_2$, $^3J_{CSn} = 21.7$ Hz); 120.6 (dd, Ar–C, $^2J_{CF} = 66.6$ Hz, $^2J_{CF} = 44.4$ Hz); 123.7 (q, $CF_3$, $^1J_{CF} = 273.3$ Hz); 146.8 (dm, Ar–C, $^1J_{CF} = 262.8$ Hz); 154.2 (dm, Ar–C, $^1J_{CF} = 287.3$ Hz); 154.8 (dm, Ar–C, $^1J_{CF} = 239.8$ Hz); 167.6 (d, Ar–C, $^2J_{CF} = 17.0$ Hz). $^{119}$Sn{¹H} NMR (C₆D₆, 25 ºC, 111.96 MHz): $\delta$ -18.4 (d, Sn, $^3J_{SnF} = 20.1$ Hz); -26.1 (m, Sn).

**Reaction of (6.1) and 1,2,4,5-tetrafluorobenzene with Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr.**

A solution of (2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)tributylstannane (0.050 g, 0.098 mmol) and 1,2,4,5-tetrafluorobenzene (0.015 g, 0.098 mmol) in 1 mL of C₆D₆ was mixed with Ni(COD)$_2$ (0.027 g, 0.098 mmol) and MeNC$_5$H$_4$N$i$Pr (0.030 g, 0.197 mmol) and allowed to react at room temperature for 24 h to provide an orange crystalline precipitate. The reaction mixture was analyzed by $^1$H, $^{19}$F{¹H}, and $^{119}$Sn{¹H} NMR spectroscopy, which indicated that tributyl(2,3,5,6-tetrafluorophenyl)tributylstannane was formed and trace amounts of (2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)tributylstannane remain in solution. The orange crystalline solid...
was redissolved in CD$_2$Cl$_2$ and analyzed by $^1$H, $^{19}$F$\{^1$H$\}$, and $^{119}$Sn$\{^1$H$\}$ NMR spectroscopy and identified as compound (6.2).

**Reaction of Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr with (2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyltributylstannane and 1,2,4,5–C$_6$F$_4$HD.** A solution of (2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyltributylstannane (0.043 g, 0.083 mmol) and 1,2,4,5-C$_6$F$_4$HD (0.013 g, 0.083 mmol) in 1 mL of C$_6$D$_6$ was mixed with Ni(COD)$_2$ (0.023 g, 0.083 mmol) and MeNC$_5$H$_4$N$i$Pr (0.025 g, 0.167 mmol). The $^{19}$F$\{^1$H$\}$ NMR spectra of the reaction mixture was recorded within 5 min of the initiation of the reaction in order to determine the initial deuterium isotope effect for C–H vs. C–D activation. Activation of hydrogen over deuterium can be confirmed by a ~0.3 ppm shift in the $^{19}$F$\{^1$H$\}$ NMR spectrum of any fluorine coupled to deuterium in the products and the isotope effect can be determined through integration.$^{66}$ The integrals of the peaks were found to be in a 1:1 ratio at 298 K. $^{19}$F$\{^1$H$\}$ NMR (C$_6$D$_6$, 25 ºC, 282.40 MHz): –122.2 (AA'BB' second order, 2F, 2,4–C$_6$F$_4$HSnBu$_3$); –122.2 (AA'BB' second order, 2F, 2,4–C$_6$F$_4$DSnBu$_3$); –138.3 (AA'BB' second order, 2F, 1,3–C$_6$F$_4$HSnBu$_3$); –138.6 (AA'BB' second order, 2F, 1,3–C$_6$F$_4$DSnBu$_3$).

**C–H bond stannylation competitions with para substituted substrates.** To a solution of MeNC$_5$H$_4$N$i$Pr (0.005 g, 0.033 mmol) and Ni(COD)$_2$ (0.004 g, 0.033 mmol) was added 1,2,4,5-C$_6$F$_4$H$_2$ (0.055 g, 0.367 mmol) and 0.367 mmol of pentafluorobenzene, 2,3,5,6-tetrafluorobenzotri fluoride, 2,3,5,6-tetrafluoropyridine, 2,3,5,6-tetrafluorotoluene or 2,3,5,6-tetrafluoroanisole. The reaction mixtures were then analyzed by $^{19}$F$\{^1$H$\}$ NMR spectroscopy (within 10–20 min so the starting material reagents did not deplete) and the integrals of the product peaks were used to determine the relative rates of reaction.

**C–H bond stannylation competitions with meta substituted substrates.** To a solution of MeNC$_5$H$_4$N$i$Pr (0.005 g, 0.033 mmol) and Ni(COD)$_2$ (0.004 g, 0.033 mmol) was added 1,3,5-C$_6$F$_3$H$_3$ (0.050 g, 0.25 mmol) and 0.25 mmol of 1,2,3,5-tetrafluorobenzene, 2,4,6-trifluorobenzotri fluoride, 2,4,6-trifluoropyridine or 2,4,6-trifluoroanisole. The reaction mixtures were then analyzed by $^{19}$F$\{^1$H$\}$ NMR spectroscopy (within 10–20 min so the
starting material reagents did not deplete) and the integrals of the product peaks were used to determine the relative rates of reaction.

**Synthesis of C–F activation products (6.4a, 6.4b, 6.10, 6.20 and 6.21).** A solution of pentafluorobenzotrifluoride (0.118 g, 0.50 mmol), 2,3,5,6-tetrafluorobenzotrifluoride (0.109 g, 0.50 mmol), 2,3,4,5-tetrafluorobenzotrifluoride (0.109 g, 0.50 mmol), 2,4,6-trifluorobenzotrifluoride (0.100 g, 0.50 mmol) or 2,3,5,6-tetrafluorotoluene (0.082 g, 0.5 mmol) in 15 mL of toluene was added to MeNC$_5$H$_4$N$i$Pr (0.150 g, 1.0 mmol) and Ni(COD)$_2$ (0.137 g, 0.50 mmol). The solutions were left undisturbed for 5–12 h, which yielded bright-orange crystalline solids. The solids were filtered, rinsed with toluene and pentane, then evacuated to dryness.

**Characterization of trans-(MeNC$_5$H$_4$N$i$Pr)$_2$NiF(2,3,6-C$_6$F$_4$-4-CF$_3$) (6.4a).** (0.115 g, 40% yield). $^1$H NMR (CD$_2$Cl$_2$, 25 °C, 300.13 MHz): δ 0.14 (d, 6H, NCH(CH$_3$)$_2$, $^3$J$_{HH}$ = 6.5 Hz); δ 2.59 (d, 6H, NCH(CH$_3$)$_2$, $^3$J$_{HH}$ = 6.3 Hz); 3.08 (septet, 2H, $^3$J$_{HH}$ = 6.3 Hz); 3.53 (s, 6H, NCH$_3$); 5.83 (dd, 2H, C$_5$H$_4$N, $^3$J$_{HH}$ = 7.9 Hz, $^4$J$_{HH}$ = 3.1 Hz); 6.82 (d, 2H, C$_5$H$_4$N, $^3$J$_{HH}$ = 7.5 Hz); 7.22 (d, 2H, C$_5$H$_4$N, $^3$J$_{HH}$ = 6.5 Hz); 10.06 (br, 2H, C$_5$H$_4$N). $^{19}$F{$_1^H$} NMR (CD$_2$Cl$_2$, 25 °C, 282.40 MHz): δ –60.8 (d, 3F, CF$_3$, $^3$J$_{FF}$ = 12.2 Hz); –91.0 (dm, 1F, Ar–F, $^3$J$_{FF}$ = 15.4 Hz); –110.5 (d, 1F, Ar–F, $^3$J$_{FF}$ = 29.6 Hz); –151.9 (ddq, 1F, Ar–F, $^3$J$_{FF}$ = 29.3 Hz, $^3$J$_{FF}$ = 15.5 Hz, $^3$J$_{FF}$ = 12.5 Hz); –349.7 (s, 1F, Ni–F).

**Characterization of trans-(MeNC$_5$H$_4$N$i$Pr)$_2$NiF(2,3,4-C$_6$F$_4$-5-CF$_3$) (6.4b).** $^{19}$F{$_1^H$} NMR (CD$_2$Cl$_2$, 25 °C, 282.40 MHz): δ –61.6 (d, 3F, CF$_3$, $^3$J$_{FF}$ = 13.2 Hz); –93.0 (m, 1F, Ar–F); –105.4 (d, F, Ar–F, $^3$J$_{FF}$ = 31.2 Hz); –147.5 (dd, F, Ar–F, $^3$J$_{FF}$ = 30.6 Hz, $^4$J$_{FF}$ = 16.8 Hz); –351.8 (s, 1F, Ni–F).

**Characterization of trans-(MeNC$_5$H$_4$N$i$Pr)$_2$NiF(2,4,5-C$_6$F$_3$-3-CF$_3$) (6.10).** (0.125 g, 43% yield). $^1$H NMR (CD$_2$Cl$_2$, 25 °C, 300.13 MHz): δ 0.20 (d, 6H, NCH(CH$_3$)$_2$, $^3$J$_{HH}$ = 6.4 Hz); δ 2.52 (d, 6H, NCH(CH$_3$)$_2$, $^3$J$_{HH}$ = 6.4 Hz); 3.12 (septet, 2H, $^3$J$_{HH}$ = 6.4 Hz); 3.53 (s, 6H, NCH$_3$); 5.98 (d, 2H, C$_5$H$_4$N, $^3$J$_{HH}$ = 7.7 Hz); 6.82 (d, 2H, C$_5$H$_4$N, $^3$J$_{HH}$ = 7.7 Hz); 7.30 (d, 2H, C$_5$H$_4$N, $^3$J$_{HH}$ = 7.6 Hz); 10.18 (d, 2H, C$_5$H$_4$N, $^3$J$_{HH}$ = 7.4 Hz). $^{19}$F{$_1^H$} NMR (CD$_2$Cl$_2$, 25 °C, 282.40 MHz): δ –56.1 (dd, 3F, CF$_3$, $^3$J$_{FF}$ = 20.3 Hz, $^3$J$_{FF}$ = 24.8 Hz); –
Chapter 6 – C–F Bond Activation and Catalytic C–H Bond Stannylation of Trifluoromethyl Fluorinated Benzene Derivatives with Ni(0) and a Nitrogen Ancillary Ligand and Reactivity

95.4 (qd, 2F, Ar–F, $^3J_{FF} = 20.3$ Hz, $^3J_{FF} = 17.5$ Hz); −147.8 (qd, 2F, Ar–F, $^3J_{FF} = 24.8$ Hz, $^3J_{FF} = 19.3$ Hz); −340.1 (s, 1F, Ni–F). $^{13}$C{H} NMR (CD$_2$Cl$_2$, 25 ºC, 75.47 MHz): δ 19.1 and 24.9 (s, (NCH$_3$)$_2$); 42.1 and 50.0 (s, NCH$_3$ and CH); 106.7 (s, C$_5$H$_4$N); 116.2 (s, C$_5$H$_4$N); 130.1 (dd, Ar–C, $^2J_{CF} = 27$ Hz, $^3J_{CF} = 14$ Hz); 135.3 (s, C$_5$H$_4$N); 136.9 (s, C$_5$H$_4$N); 157.1 (s, C$_5$H$_4$N).

Characterization of trans-(MeNC$_5$H$_4$N$i$Pr)$_2$NiF(2,3,5,6-C$_6$F$_4$-4-CF$_3$) (6.20). (0.165 g, 56 % yield). $^1$H NMR (CD$_2$Cl$_2$, 25 ºC, 300.13 MHz): δ 0.20 (d, 6H, NCH($CH_3$)$_2$, $^3J_{HH} = 6.3$ Hz); δ 2.60 (d, 6H, NCH($CH_3$)$_2$, $^3J_{HH} = 6.3$ Hz); 3.07 (septet, 2H, $^3J_{HH} = 6.3$ Hz); 3.55 (s, 6H, NCH$_3$); 5.98 (dd, 2H, C$_5$H$_4$N, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 2.6$ Hz); 6.82 (d, 2H, C$_5$H$_4$N, $^3J_{HH} = 7.7$ Hz); 7.26 (d, 2H, C$_5$H$_4$N, $^3J_{HH} = 7.7$ Hz); 10.05 (br, 2H, C$_5$H$_4$N). $^{19}$F{H} NMR (CD$_2$Cl$_2$, 25 ºC, 282.40 MHz): δ −56.1 (t, 3F, CF$_3$, $^3J_{FF} = 21.0$ Hz); −115.7 (m, 2F, Ar–F); −148.5 (m, 2F, Ar–F); −355.3 (s, 1F, Ni–F). $^{13}$C{H} NMR (CD$_2$Cl$_2$, 25 ºC, 75.47 MHz): δ 19.9 and 25.6 (s, (NCH$_3$)$_2$); 43.0 and 50.8 (s, NCH$_3$ and CH); 107.2 (s, C$_5$H$_4$N); 118.3 (s, C$_5$H$_4$N); 129.1 (t, Ar–C, $^2J_{CF} = 47.6$ Hz); 135.7 (s, C$_5$H$_4$N); 137.9 (s, C$_5$H$_4$N); 158.9 (s, C$_5$H$_4$N).

Characterization of trans-(MeNC$_5$H$_4$N$i$Pr)$_2$NiF(3,5-C$_6$F$_4$-4-CF$_3$) (6.21). (0.090 g, 32 % yield). $^1$H NMR (CD$_2$Cl$_2$, 25 ºC, 300.13 MHz): δ 0.51 (d, 6H, NCH($CH_3$)$_2$, $^3J_{HH} = 6.6$ Hz); δ 2.31 (d, 6H, NCH($CH_3$)$_2$, $^3J_{HH} = 6.4$ Hz); 3.22 (septet, 2H, $^3J_{HH} = 6.4$ Hz); 3.54 (s, 6H, NCH$_3$); 6.01 (dd, 2H, C$_5$H$_4$N, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 3.0$ Hz); 6.84 (d, 2H, C$_5$H$_4$N, $^3J_{HH} = 6.2$ Hz); 7.30 (d, 2H, C$_5$H$_4$N, $^3J_{HH} = 7.7$ Hz); 10.10 (br, 2H, C$_5$H$_4$N). $^{19}$F{H} NMR (CD$_2$Cl$_2$, 25 ºC, 282.40 MHz): δ −55.3 (t, 3F, CF$_3$, $^3J_{FF} = 21.2$ Hz); −122.3 (q, 2F, Ar–F, $^3J_{FF} = 21.3$ Hz); −325.6 (s, 1F, Ni–F).

C–F bond activation competition between CF$_3$C$_6$F$_5$, C$_6$F$_6$ and C$_6$F$_5$H with Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr. A solution of CF$_3$C$_6$F$_5$ (0.157 g, 0.66 mmol) and C$_6$F$_6$ (0.124 g, 0.66 mmol) or C$_5$F$_6$H (0.111 g, 0.66 mmol) in 10 mL of toluene were mixed with Ni(COD)$_2$ (0.018 g, 0.066 mmol) and MeNC$_5$H$_4$N$i$Pr (0.020 g, 0.133 mmol). The solution was left undisturbed for 5 h, which yielded a crystalline orange solid. The solid was filtered, rinsed with toluene and pentane, then dried. The crystalline orange solid was
dissolved in CD$_2$Cl$_2$ and analyzed $^1$H and $^{19}$F-$^1$H NMR and the ratio of the C–F bond activation complexes was determined by integration.

6.5 X-ray Crystallography

6.5.1 General Collection and Refinement Information

The X-ray structure of 6.5 was obtained at $-100$ °C, with the crystal covered in Paratone and placed rapidly into the cold N$_2$ stream of the Kryo-Flex low-temperature device. The data was collected using the SMART$^{79}$ software on a Bruker APEX CCD diffractometer using a graphite monochromator with Mo Ka radiation ($\lambda = 0.71073$ Å). A hemisphere of data was collected using a counting time of 10 s per frame. Data reductions were performed using the SAINT$^{80}$ software, and the data were corrected for absorption using SADABS.$^{81,82}$ The structures were solved by direct methods using SIR97$^{83}$ and refined by full-matrix least-squares on $F^2$ with anisotropic displacement parameters for the non-H atoms using SHELX-$97^{84,85}$ and the WinGX$^{86}$ software package, and thermal ellipsoid plots were produced using ORTEP32.$^{87}$

6.5.2 Crystallographic Data

Table 6.4. Crystallographic Data for cis-(MeNC$_5$H$_4$N$i$Pr)$_2$Ni(2,3,5,6-C$_6$F$_4$-4-CF$_3$)$_2$ (6.5).

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<tr>
<td>Space group</td>
<td>P2(1)2(1)2(1)</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 13.7012(18) Å</td>
</tr>
<tr>
<td></td>
<td>b = 16.500(2) Å</td>
</tr>
<tr>
<td></td>
<td>c = 16.514(2) Å</td>
</tr>
<tr>
<td></td>
<td>$\alpha = 90^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\beta = 90^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\gamma = 90^\circ$</td>
</tr>
</tbody>
</table>

References begin on page 206
Volume \(3733.3(8) \text{\AA}^3\)

Z \(4\)

Density (calculated) \(1.550 \text{Mg/m}^3\)

Absorption coefficient \(0.624 \text{mm}^{-1}\)

\(F(000)\) \(1776\)

Crystal size \(0.35 \times 0.25 \times 0.18 \text{mm}^3\)

Theta range for data collection 2.47 to 27.50°

Index ranges \(-17 \leq h \leq 17, -21 \leq k \leq 21, -21 \leq l \leq 20\)

Reflections collected 40791

Independent reflections 8451 \([R(\text{int}) = 0.0703]\)

Completeness to theta = 27.50° 99.0%

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.8959 and 0.8111

Refinement method Full-matrix least-squares on \(F^2\)

Data / restraints / parameters 8451 / 6 / 507

Goodness-of-fit on \(F^2\) 1.059

Final R indices \([I>2\sigma(I)]\) R1 = 0.0644, wR2 = 0.1447

R indices (all data) R1 = 0.0892, wR2 = 0.1566

Absolute structure parameter 0.346(18)

Largest diff. peak and hole 1.353 and \(-0.652 \text{e.\AA}^{-3}\)
6.6 References

(15) Tomashenko, O. A.; Grushin, V. V. Chem. Rev., 111, 4475-4521.
Chapter 6 – C–F Bond Activation and Catalytic C–H Bond Stannylation of Trifluoromethyl Fluorinated Benzene Derivatives with Ni(0) and a Nitrogen Ancillary Ligand and Reactivity


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Chapter 6 – C–F Bond Activation and Catalytic C–H Bond Stannylation of Trifluoromethyl Fluorinated Benzene Derivatives with Ni(0) and a Nitrogen Ancillary Ligand and Reactivity


(64) Slattery, J.; Thatcher, R. J.; Shi, Q.; Douthwaite, R. E. *Pure Appl. Chem.*, **82**, 1663-1671.


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(80) SAINTPlus, Data reduction and correction program; Bruker AXS Inc.: Madison, WI, 2001.


Chapter 7 - Future Work and Conclusions

7.1 Future Work

The neutral amido donor ligand, MeNC$_5$H$_4$N$^i$Pr, discussed in Chapter 2 was designed to promote oxidative addition reactions. The addition of MeNC$_5$H$_4$N$^i$Pr to Ni(COD)$_2$, has proven to be a successful system for promoting regioselective C–F bond activation$^1$ (Chapter 2), catalytic C–H bond stannylation$^2$ (Chapter 3) and catalytic C–H bond alkylation (Chapter 5) of a variety of fluorinated aromatics. It was also shown that catalytic carbostannylation of unactivated alkenes was possible (Chapter 5). Further studies need to be conducted to better understand the mechanism of these catalytic processes for the development of improved catalysts.
This Chapter will discuss how substituents on the stannyl substrates influence the rate of C–H bond stannylation and the thermal stability of the catalyst. The mechanistic studies were conducted with \(^{i} \text{Pr}_3 \text{P}\) rather than MeNC\(_5\)H\(_4\)N\(^{i} \text{Pr}\). The C–H bond stannylation reaction rates with \(^{i} \text{Pr}_3 \text{P}\) are much slower, which allow for more controlled experiments than with MeNC\(_5\)H\(_4\)N\(^{i} \text{Pr}\). The catalyst with \(^{i} \text{Pr}_3 \text{P}\) as the ancillary ligand has a much greater thermal stability than with MeNC\(_5\)H\(_4\)N\(^{i} \text{Pr}\), therefore the affect of temperature over a much wider range can be studied.

Chapters 2, 3, 5 and 6 discussed the reactivity of MeNC\(_5\)H\(_4\)N\(^{i} \text{Pr}\) with nickel and a variety of fluorinated substrates, these reactions included both C–F bond activation, and catalytic C–H bond functionalization. This Chapter will expand the catalytic reactions possible with MeNC\(_5\)H\(_4\)N\(^{i} \text{Pr}\) and nickel to include both C–H bond alkenylation and cyclotrimerization. This chapter will also discuss the reactivity of MeNC\(_5\)H\(_4\)NH\(^{i} \text{Pr}\)I with yttrium, and the complexes formed. Expanding the scope of functionalization reactions possible with nickel and studying the reactivity of MeNC\(_5\)H\(_4\)N\(^{i} \text{Pr}\) with other transition metals will be crucial for determining the full potential of this new neutral amido donor ligand.

7.2 Importance of Stannyl Substituents on the C–H Bond Stannylation Reaction

A better understanding of the C–H bond stannylation reaction is required to design improved catalysts capable of functionalizing a wider substrate scope, and to provide insight for developing catalysts that can convert C–H bonds to other carbon–heteroatom bonds, such as C–Si bonds. To determine the importance of stannyl substituents on catalyst thermal stability and reaction rate, a variety of catalysts of the type \((^{i} \text{Pr}_3 \text{P}) \text{Ni} (\eta^2-\text{CH}_2=\text{CHSnR}_3)_2\)\(^{3}\), were synthesized and the reactivity was studied. The reaction of Ni(COD)\(_2\) with one equivalent of \(^{i} \text{Pr}_3 \text{P}\) and two equivalents of CH\(_2=\text{CHSnR}_3\) (where R = Bu\(^3\), Ph\(^3\), Bn, p-C\(_6\)H\(_4\)Me, p-C\(_6\)H\(_4\)OMe or p-C\(_6\)H\(_4\)CF\(_3\)) provided the complexes \((^{i} \text{Pr}_3 \text{P}) \text{Ni} (\eta^2-\text{CH}_2=\text{CHSnR}_3)_2\) (7.1\(^{R'}\)) (R' = Bu, Bn, Ph, p–Me, p–OMe or p–CF\(_3\)), as shown in Scheme 7.1.
Scheme 7.1. General synthesis of \((\text{Pr}_3\text{P})\text{Ni}(\eta^2-\text{CH}_2=\text{CHSnR}_3)_2\) \(7.1^{\text{R}}\).

The NMR spectra of \(7.1^{\text{R}}\) in C\(_6\)D\(_6\) displayed resonances consistent with the solid-state structure of \((\text{Pr}_3\text{P})\text{Ni}(\eta^2-\text{CH}_2=\text{CHSnPh}_3)_2\) \(7.1^{\text{Ph}}\), discussed in section 4.2.1, and are summarized in Table 7.1. The \(^1\text{H}\) vinyl and \(^{31}\text{P}\) chemical shifts are similar for all of the complexes and are not significantly influenced by the substituents bound to Sn. The \(^{119}\text{Sn}\) chemical shift was influenced by the substituents bound to Sn. Alkyl and phenyl substituents bound to Sn had significantly different \(^{119}\text{Sn}\) chemical shifts, however only minuscule differences for the chemical shift was observed for the different aryl substituents bound to Sn.

Table 7.1. Summary of the \(^1\text{H}\), \(^{31}\text{P}\{^1\text{H}\}\) and \(^{119}\text{Sn}\{^1\text{H}\}\) NMR chemical shifts of \(7.1^{\text{R}}\).

<table>
<thead>
<tr>
<th>(7.1^{\text{Bu}})</th>
<th>(7.1^{\text{Bn}})</th>
<th>(7.1^{\text{Ph}})</th>
<th>(7.1^{\text{p-Me}})</th>
<th>(7.1^{\text{p-OMe}})</th>
<th>(7.1^{\text{p-CF}_3})</th>
</tr>
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<tbody>
<tr>
<td>(^1\text{H}) (vinyl)</td>
<td>2.80, 2.86,</td>
<td>2.92, 2.92,</td>
<td>3.00, 3.09,</td>
<td>3.08, 3.17,</td>
<td>3.11, 3.20,</td>
</tr>
<tr>
<td>(\delta)</td>
<td>3.35</td>
<td>3.61</td>
<td>4.11</td>
<td>4.22</td>
<td>4.26</td>
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<tr>
<td>(^{31}\text{P}) (\delta)</td>
<td>50.2</td>
<td>50.9</td>
<td>49.8</td>
<td>50.8</td>
<td>50.1</td>
</tr>
<tr>
<td>(^{119}\text{Sn}) (\delta)</td>
<td>2.80</td>
<td>2.86</td>
<td>2.92</td>
<td>2.92</td>
<td>3.00</td>
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<tr>
<td>(^{31}\text{P}) (\delta)</td>
<td>50.2</td>
<td>50.9</td>
<td>49.8</td>
<td>50.8</td>
<td>50.1</td>
</tr>
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</table>
7.2.1 Stoichiometric Stannylation with 7.1\textsuperscript{R'} (R' = Bu, Bn, Ph, p–Me, p–OMe or p–CF\textsubscript{3})

A stock solution in C\textsubscript{6}D\textsubscript{6} with a concentration of 0.1004 M of C\textsubscript{6}F\textsubscript{5}H, was used to make six solutions with concentrations of 0.0464 M of 7.1\textsuperscript{R'} (R' = Bu, Bn, Ph, p–Me, p–OMe and CF\textsubscript{3}). These solutions were transferred to an NMR probe preheated to 315 K and the initial catalytic reaction rates, for conversion to C\textsubscript{6}F\textsubscript{5}SnR\textsubscript{3}, (R = Bu, Ph, Bn, p–C\textsubscript{6}H\textsubscript{4}Me, p–C\textsubscript{6}H\textsubscript{4}OMe and p–C\textsubscript{6}H\textsubscript{4}CF\textsubscript{3}) were monitored, the reaction is shown in Scheme 7.2. The initial reaction rates were all found to remain constant for several minutes under these conditions. The initial reaction rates were found to be significantly affected by the stannylation substituents: the substituents with the lowest kinetic barrier for C–H activation were found to be Bu < Bn < Ph < p–C\textsubscript{6}H\textsubscript{4}Me < p–C\textsubscript{6}H\textsubscript{4}OMe < p–C\textsubscript{6}H\textsubscript{4}CF\textsubscript{3}, with respective relative reaction rates of 2.7, 2.2, 1, 0.9, 0.8 and 0.3 M/s, under the conditions used. The results suggest that alkyl substituents, such as butyl, have a much lower kinetic barrier to C–H bond stannylation than aryl substituents, such as phenyl. The results also indicate that the addition of electron-withdrawing or electron-donating groups to the phenyl substituent does not decrease the kinetic barrier to C–H bond stannylation.

![Scheme 7.2. Stoichiometric stannylation of C\textsubscript{6}F\textsubscript{5}H with 7.1\textsuperscript{R'}](image)

<table>
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<tr>
<th>R</th>
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<td>Bu</td>
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<td>0.93</td>
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<tr>
<td>0.88</td>
</tr>
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<td>0.56</td>
</tr>
</tbody>
</table>

*no reaction observed*
To determine how temperature affects the initial rate of C–H bond stannylation when \(7.1^{R'}\) contains the aryl stannyl substituents, a stock solution in \(C_6D_6\) with a concentration of 0.1004 M of \(C_6F_5H\), was used to make twelve solutions with concentrations of 0.0464 M of \(7.1^{R'}\) (\(R' = \text{Ph, Me, MeO and CF}_3\)). These solutions were transferred to an NMR probe preheated to 305, 310 or 315 K and the initial catalytic reaction rates, for conversion to \(C_6F_5SnR_3\), (\(R = \text{Ph, } p-C_6H_4Me, p-C_6H_4OMe\) or \(p-C_6H_4CF_3\)) were monitored. The reaction rates were found to increase linearly with temperature, thus the order of stannyl substituents with the lowest kinetic barrier for C–H stannylation was unchanged \(\text{Ph} < p-C_6H_4Me < p-C_6H_4OMe < p-C_6H_4CF_3\) under these conditions. The change in Gibbs energy of activation for C–H stannylation, between the four stannyl substituents, was found to be less than 1 kcal·mol\(^{-1}\). The enthalpies of activation of C–H stannylation were calculated using the Eyring equation and were found to be 33.2, 32.9, 29.4 and 37.5 kcal·mol\(^{-1}\) with \(\text{Ph, } p-C_6H_4Me, p-C_6H_4OMe\) and \(p-C_6H_4CF_3\) stannyl substituents respectively.

Similar stoichiometric stannylation studies with \(7.1^{R'}\) (\(R' = \text{Bu, Bn, Ph, } p-Me, p-\text{OMe and } p-\text{CF}_3\)) were also conducted with 1,3-\(C_6F_2H_4\) as the substrate at both 315 K and 338 K, as shown in Scheme 7.3. The C–H stannylation reaction with 1,3-\(C_6F_2H_4\) was significantly slower than with \(C_6F_5H\) at 305 and 310 K, thus temperatures of 315 and 338 K were chosen. The stannyl substituents at 315 K with the lowest kinetic barrier for C–H stannylation were found to be the same as those observed for \(C_6F_5H\) at 315 K, \(\text{Bu} < \text{Bn} < \text{Ph} < p-C_6H_4Me < p-C_6H_4OMe < p-C_6H_4CF_3\), with respective relative reaction rates of 18.14, 12.0, 1, 0.92, 0.23 and 0.06 M/s, under the conditions used. However, the order of stannyl substituents with the lowest kinetic barrier for C–H stannylation was changed when the temperature was increased to 338 K for 1,3-\(C_6F_2H_2\), \(\text{Bu} < \text{Bn} < p-C_6H_4CF_3 < \text{Ph} < p-C_6H_4Me < p-C_6H_4OMe\), with respective relative rates of 40.2, 15.3, 2.6, 1.0, 0.89 and 0.55 M/s, under the conditions used. The results suggest that the rate determining step in the mechanism present in Section 4.2.4 may change as temperature is increased, thus the activation of unactivated substrates such as \(C_6H_6\) may become possible if even higher temperatures can be reached without decomposition of the catalyst. Further studies need to be conducted that compare how the kinetic barrier of C–
H stannylation is affected at various temperatures between 315–350 K for C₆F₅H and 1,3-C₆F₂H₄, unfortunately previous temperature studies conducted with C₆F₅H were all below 315 K and no change in the rate determining step was observed. It remains unclear which step of the mechanism presented in Section 4.2.4 is rate determining and further studies still need to be conducted.

\[
\text{Scheme 7.3. Stoichiometric stannylation of 1,3-C₆F₂H₄ with 7.1R'} \text{ at 315 and 338 K.}
\]

### 7.2.2 Exchange of the CH₂=CHSnR₃ Moieties from Nickel: Associative versus Dissociative Pathway

To confirm that the vinyl moieties are dissociated from the nickel center as proposed in the mechanism in Section 4.2.4, increasing amounts of CH₂=CHSnBu₃ (4, 8 and 16 equivalents) were added to three solutions containing equal molar amounts of 7.1Ph, and the initial rate of exchange was monitored by \textsuperscript{31}P\text{\textsuperscript{1}H} NMR at 305 K. There are two plausible mechanisms that can exchange the two vinyl moieties, the first is a dissociative mechanism, which involves the loss of CH₂=CHSnPh₃ followed by the association of CH₂=CHSnBu₃ to form (\textit{i}Pr₃P)Ni(\textit{η}²-CH₂=CHSnPh₃)(\textit{η}²-CH₂=CHSnBu₃) and the second is an associative mechanism, which involves the association of a CH₂=CHSnBu₃ moiety followed by the loss of CH₂=CHSnPh₃ to form (\textit{i}Pr₃P)Ni(\textit{η}²-CH₂=CHSnPh₃)(\textit{η}²-CH₂=CHSnBu₃), as shown in Scheme 7.4. If exchange occurs via a dissociative mechanism then the rate of exchange is controlled by the rate CH₂=CHSnPh₃
dissociates from the nickel metal center, since this is the slow step, therefore increasing concentrations of CH$_2$=CHSnBu$_3$ will have no affect on the rate of exchange. If exchange occurs via an associative mechanism then the rate of exchange is controlled by the rate CH$_2$=CHSnBu$_3$ associates to the nickel metal center, since this is the slow step, therefore increasing concentrations of CH$_2$=CHSnBu$_3$ will increase the rate of exchange. Experimentally, there was no observable change in the rate of exchange, even with the addition of 16 equivalents of CH$_2$=CHSnBu$_3$. This result confirmed that the rate of exchange was controlled by the dissociation of CH$_2$=CHSnPh$_3$ moiety from nickel rather than the association of CH$_2$=CHSnBu$_3$.

\[
\text{Dissociative Mechanism:} \quad \begin{align*}
\text{SnPh}_3 & \rightarrow \text{SnBu}_3 + \text{CH}_2=\text{CHSnBu}_3 \\
\text{Ni} & \rightarrow \text{Ni} + \text{CH}_2=\text{CHSnBu}_3
\end{align*}
\]

\[
\text{Associative Mechanism:} \quad \begin{align*}
\text{SnBu}_3 & \rightarrow \text{SnPh}_3 + \text{CH}_2=\text{CHSnBu}_3 \\
\text{Ni} & \rightarrow \text{Ni} + \text{CH}_2=\text{CHSnBu}_3
\end{align*}
\]

**Scheme 7.4.** Dissociative and associative pathways for the exchange of two vinyl moieties.

To determine how the rate of exchange was affected by increasing temperature, CH$_2$=CHSnBu$_3$ was added to three solutions containing equal molar amounts of 7.1$^{\text{Ph}}$ and the initial rate of exchange was monitored by $^{31}\text{P}$$\{^1\text{H}\}$ NMR at 305, 310 and 315 K. The rate of exchange was found to increase linearly with increasing temperature, with relative rates of 1, 1.9 and 3.8 M/s for 305, 310 and 315 K, respectively. This result indicates that the rate of dissociation of CH$_2$=CHSnPh$_3$ from the nickel metal center increases with temperature.
7.2.3 Determination of the Equilibrium Constants for Exchange of 7.1<sub>Ph</sub> and 7.1<sub>R'</sub> and Gibbs Free Energy for Exchange

Gibbs free energy for exchange can be determined from the equilibrium constants for exchange between two different CH<sub>2</sub>=CHSnR<sub>3</sub> moieties, and can be used to estimate the difference in energy between 7.1<sub>R'</sub>. A stock solution containing one equivalent of Ni(COD)<sub>2</sub>, one equivalent of iPr<sub>3</sub>P, and ten equivalents of CH<sub>2</sub>=CHSnPh<sub>3</sub> was added to five solutions containing ten equivalents of CH<sub>2</sub>=CHSnR<sub>3</sub> (R = Bu, Bn, p-C<sub>6</sub>H<sub>4</sub>Me, p-C<sub>6</sub>H<sub>4</sub>OMe or p-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>), to provide an equilibrium mixture of the three plausible products 7.1<sub>Ph</sub>, 7.1<sub>Ph,R'</sub> or 7.1<sub>R'</sub>, as shown in Scheme 7.5, after 10 min at 338 K. The concentration of each product was determined by integration of the resonances in the 31P<sup>1</sup>H NMR spectra relative to an internal standard, and used to determine the first equilibrium constant $K_1$ for exchange between 7.1<sub>R'</sub> and 7.1<sub>Ph,R'</sub>, and the second equilibrium constant $K_2$ for exchange between 7.1<sub>Ph,R'</sub> 7.1<sub>Ph</sub>, shown in Table 7.2. The equilibrium constants were converted to the Gibbs free energy for exchange, and used to establish the energy differences between the different catalysts, relative to 7.1<sub>Ph</sub>.

Scheme 7.5. General reaction and equilibrium that is formed between CH<sub>2</sub>=CHSnPh<sub>3</sub> and CH<sub>2</sub>=CHSnR<sub>3</sub>.
Table 7.2. Equilibrium constants and relative ground state energies between CH$_2$=CHSnPh$_3$ and CH$_2$=CHSnR$_3$.

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>$K_1$</th>
<th>$\Delta G_1$ (kcal·mol$^{-1}$)</th>
<th>$\Delta H_1$ (kcal·mol$^{-1}$)</th>
<th>$K_2$</th>
<th>$\Delta G_2$ (kcal·mol$^{-1}$)</th>
<th>$\Delta H_2$ (kcal·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1$^{Ph}$ &amp; 7.1$^{Bu}$</td>
<td>13.906</td>
<td>-1.637</td>
<td>-1.206</td>
<td>3.425</td>
<td>-0.766</td>
<td>-1.197</td>
</tr>
<tr>
<td>7.1$^{Ph}$ &amp; 7.1$^{Bn}$</td>
<td>7.587</td>
<td>-1.260</td>
<td>-0.829</td>
<td>1.403</td>
<td>-0.221</td>
<td>-0.642</td>
</tr>
<tr>
<td>7.1$^{Ph}$ &amp; 7.1$^{p}$-Me</td>
<td>2.221</td>
<td>-0.496</td>
<td>-0.065</td>
<td>0.636</td>
<td>0.281</td>
<td>-0.150</td>
</tr>
<tr>
<td>7.1$^{Ph}$ &amp; 7.1$^{p}$-Ome</td>
<td>2.399</td>
<td>-0.544</td>
<td>-0.113</td>
<td>0.672</td>
<td>0.247</td>
<td>-0.184</td>
</tr>
<tr>
<td>7.1$^{Ph}$ &amp; 7.1$^{p}$-CF$_3$</td>
<td>1.334</td>
<td>-0.180</td>
<td>0.251</td>
<td>0.101</td>
<td>1.428</td>
<td>0.996</td>
</tr>
</tbody>
</table>

Figure 7.1. Relative ground state energies in kcal of 7.1$^{R'}$ with respect to 7.1$^{Ph}$.

7.2.4 Determination of Relative $\Delta \Delta G^\ddagger$

The product distribution of a C–H bond stannylation competition between two different CH$_2$=CHSnR$_3$ moieties can be used to determine the relative $\Delta \Delta G^\ddagger$ for C–H bond stannylation of the different 7.1$^{R'}$ (R' = Bu, Bn, Ph, p–Me, p–Ome and p–CF$_3$) catalysts. A stock solution containing one equivalent of Ni(COD)$_2$, one equivalent of iPr$_3$P, and ten equivalents of CH$_2$=CHSnPh$_3$ was added to five solutions containing ten equivalents of CH$_2$=CHSnR$_3$ (R = Bu, Bn, p–C$_6$H$_4$Me, p–C$_6$H$_4$Ome or p–C$_6$H$_4$CF$_3$), the
reaction mixtures were reacted for 10 min at 338 K to establish equilibrium between the three plausible catalysts $7.1^{\text{Ph}}$, $7.1^{\text{Ph,R'}}$ and $7.1^{\text{R'}}$. Once equilibrium was established C$_6$F$_5$H was added to the reaction mixtures, shown in Scheme 7.6, and the mixtures were placed in an NMR probe preheated to 338 K. The initial product ratios were determined by integration and were used to determine the $\Delta \Delta G^\ddagger$ for C–H bond stannylation, shown in Table 7.3.

Scheme 7.6. Competition to determine the ratio of products formed when catalysts $7.1^{\text{Ph}}$, $7.1^{\text{Ph,R'}}$ and $7.1^{\text{R'}}$ are in equilibrium.

Table 7.3. Product distribution and relative $\Delta \Delta G^\ddagger$ for C–H bond stannylation, determined by the competition between CH$_2$=CHSnPh$_3$ and CH$_2$=CHSnR$_3$.

<table>
<thead>
<tr>
<th>Competition with CH$_2$=CHSnPh$_3$ &amp; CH$_2$=CHSnR$_3$</th>
<th>C$_6$F$_5$SnPh$_3$ (%)</th>
<th>C$_6$F$_5$SnR$_3$ (%)</th>
<th>$\Delta \Delta G$ (kcal·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$=CHSnBu$_3$</td>
<td>0.586</td>
<td>0.414</td>
<td>0.232</td>
</tr>
<tr>
<td>CH$_2$=CHSnBn$_3$</td>
<td>0.431</td>
<td>0.569</td>
<td>–0.187</td>
</tr>
<tr>
<td>CH$_2$=CHSn[p–(C$_6$H$_4$Me)]$_3$</td>
<td>0.480</td>
<td>0.520</td>
<td>–0.054</td>
</tr>
<tr>
<td>CH$_2$=CHSn[p–(C$_6$H$_4$OMe)]$_3$</td>
<td>0.405</td>
<td>0.595</td>
<td>–0.258</td>
</tr>
<tr>
<td>CH$_2$=CHSn[p–(C$_6$H$_4$CF$_3$)]$_3$</td>
<td>0.3535</td>
<td>0.646</td>
<td>–0.405</td>
</tr>
</tbody>
</table>
7.2.5 Mechanistic Insight

Reaction profiles can be determined by combining the data obtained from the relative ΔG values for each of the different 7.1\textsuperscript{R'} catalysts determined from the equilibrium constants and the ΔΔG\textsuperscript{‡} for C–H bond stannylation. The relative ΔG values for the 7.1\textsuperscript{R'} catalysts indicate that 7.1\textsuperscript{CF\textsubscript{3}} is the lowest in energy and that 7.1\textsuperscript{Bu} is the highest, with all of the other catalysts falling somewhere in between, as shown Figure 7.1. The ΔΔG\textsuperscript{‡} for C–H bond stannylation provides insight into the difference in energy between the transition states for the different 7.1\textsuperscript{R'} catalysts. The 7.1\textsuperscript{Bu} transition state for C–H bond stannylation was found to be the highest in energy and the transition state for 7.1\textsuperscript{p–CF\textsubscript{3}} was the lowest in energy. In-order to explain why the rate of C–H bond stannylation is the fastest for 7.1\textsuperscript{Bu} (Scheme 7.2) even though the transition state is the highest in energy (Table 7.3) and the slowest for 7.1\textsuperscript{p–CF\textsubscript{3}} even though the transition state is the lowest in energy, the difference in the relative energy between 7.1\textsuperscript{Bu} and 7.1\textsuperscript{p–CF\textsubscript{3}}, and the transition states must be considered. The difference in relative energy between 7.1\textsuperscript{Bu} and 7.1\textsuperscript{p–CF\textsubscript{3}} is much greater than the difference in energy between the transition states, thus the activation barrier for C–H bond stannylation is actually much smaller for 7.1\textsuperscript{Bu} than 7.1\textsuperscript{p–CF\textsubscript{3}}, as shown in Figure 7.2. Further studies need to be conducted to determine how temperature and choice of fluorinated aromatic substrate (i.e. C\textsubscript{6}F\textsubscript{5}H versus 1,3-C\textsubscript{6}F\textsubscript{2}H\textsubscript{4}) will affect the rate determining step in C–H bond stannylation and the ΔΔG\textsuperscript{‡} of the transition states. These studies will be crucial for understanding how the stannyl substituents influence the rate of C–H bond stannylation and for developing improved catalysts.
7.3 Catalytic Functionalizations

7.3.1 Cyclotrimerization of Alkynes

Nickel catalyst, such as Ni(COD)$_2$, are commonly used for the coupling of disubstituted alkynes. Unfortunately high temperatures are typically required for these reactions to occur,$^{4-7}$ but, the addition of MeNC$_5$H$_4$N$i$Pr to the reaction mixture in catalytic amounts allows the reaction to be conducted at room temperature in high yields. These mild conditions may be useful in improving the regio- and chemoselectivities of the final cyclotrimerized products,$^8$ which have found extensive use as building blocks for molecular materials.$^9$ Solutions of diphenylacetylene and catalytic amounts of Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr react over the course of 18 hours at 30 °C to form a white crystalline solid, identified as hexaphenylbenzene by $^1$H NMR spectroscopy and mass spectrometry. These reactions can be carried out with as little as 2.5 mol % Ni(COD)$_2$ and 5 mol % MeNC$_5$H$_4$N$i$Pr. The scope of this cyclotrimerization reaction was expanded to alkynes bearing a phenyl group and either a methyl group or fluorinated phenyl
substituent. The major products formed were the unsymmetrical cycloctrimeredized products, as shown in Scheme 7.7. Further studies need to be conducted on the mechanism of this reaction and how different conditions influence the rate and selectivity of the reaction.

![Scheme 7.7. Cyclotrimerization of alkynes with Ni(COD)_2 and MeNC_5H_4N^iPr.](image)

**7.3.2 Catalytic C–H Bond Alkenylation**

We were able to expand the nickel-mediated C–H bond functionalization methodology discussed to include the formal insertion of alkynes into the \( sp^2 \) C–H bond of fluorinated aromatics. The addition of diphenylacetylene and C_6F_5H to catalytic amounts of Ni(COD)_2 and MeNC_5H_4N^iPr resulted in catalytic conversion to a mixture of C–H bond functionalized products, which included mono-insertion product \((Z)-(1-(2,3,4,5,6-pentafluorophenyl)ethene-1,2-diyl)dibenzene (7.2)\) in minor amounts and double-insertion products \(((1Z,3Z)-1-(2,3,4,5,6-tetrafluorophenyl)buta-1,3-diene-1,2,3,4-tetrayl)tetrabenzene (7.3)\) and \(((1E,3Z)-1-(2,3,4,5,6-tetrafluorophenyl)buta-1,3-diene-1,2,3,4-tetrayl)tetrabenzene (7.4)\) as major products, after 12 hours at room temperature, as shown in Scheme 7.8. A similar reaction with 1,2,4,5-C_6F_4H_2 as the substrate produced the mono-insertion \((E)-(1-(2,3,5,6-tetrafluorophenyl)ethene-1,2-diyl)dibenzene (7.5)\) in minor amounts and the double-insertion products \(((1Z,3Z)-1-(2,3,5,6-tetrafluorophenyl)buta-1,3-diene-1,2,3,4-tetrayl)tetrabenzene (7.6)\) and \((1E,3Z)-1-
(2,3,5,6-tetrafluorophenyl)buta-1,3-diene-1,2,3,4-tetrayl)tetrabenzenes (7.7), after 12 hours at room temperature, as shown in Scheme 7.9. At the time this was the first example of a nickel-mediated C–H bond functionalization in the presence of C–F bonds. Another group published a very similar result at the same time, reacting partially fluorinated aromatics and a variety of alkynes with catalytic amounts of Ni(COD)$_2$ and PCyp$_3$ at 80 °C, to form the corresponding C–H bond alkenylation products after 3 – 15 hours.$^{10,11}$

\[
\text{N} \quad \text{Ni(COD)$_2$} \\
\text{2L} + \text{Ni(COD)$_2$} \\
\text{12 h} \\
\text{Room Temp}
\]

\[
\begin{align*}
\text{Ph} &\quad \equiv \quad \text{Ph} \\
F &\quad F &\quad F &\quad F \\
H &\quad F &\quad F &\quad F \\
\text{Ph} &\quad \equiv \quad \text{Ph} \\
\text{L} &\quad = \quad \text{N} \quad \equiv \quad \text{N} / \text{Pr} \\
\end{align*}
\]

**Scheme 7.8.** Catalytic C–H bond functionalization of C$_6$F$_5$H with diphenylacetylene.
Scheme 7.9. Catalytic C–H bond functionalization of 1,2,4,5-C₆F₄H₂ with diphenylacetylene.

Cyclotrimerized diphenylacetylene (hexaphenylbenzene), was observed as a byproduct and precipitated from solution as a white crystalline solid. With 1,2,4,5-C₆F₄H₂ as a substrate minor amounts of functionalization was also occurred at the second H–site forming several by-products shown in Scheme 7.9, ((1Z)-1-(4-((E)-1,2-diphenylvinyl)-2,3,5,6-tetrafluorophenyl)buta-1,3-diene-1,2,3,4-tetrayl)tetrabenzen (7.8), ((1E,3Z)-1-(4-((E)-1,2-diphenylvinyl)-2,3,5,6-tetrafluorophenyl)buta-1,3-diene-1,2,3,4-tetrayl)tetrabenzen (7.9), and two symmetric double-activation double-insertion products which could not be distinguished by ¹⁹F or ¹H NMR 7.10 and 7.11. The mixture of products was separated by silica-gel column chromatography. The isolated products
were characterized by $^1$H, $^{19}$F{$^1$H}, $^{19}$F NMR spectroscopy. Mass spectrometry and $^{13}$C{$^1$H} NMR spectroscopy were also obtained for the major products 7.3, 7.5 and 7.6.

Single crystals of 7.5 suitable for structural analysis by X-ray crystallography were obtained from slow evaporation of a hexane solution at room temperature. An ORTEP of the solid-state molecular structure is shown in Figure 7.3. The structure confirms that one of the C–H bonds in 1,2,4,5-C$_6$F$_4$H$_2$ was functionalized with diphenylacetylene and that the two phenyl groups are orientated on the same side of the double bond (cis insertion).

![Figure 7.3](image)

*Figure 7.3. ORTEP of the solid-state molecular structure of 7.5 as determined by X-ray crystallography.*

Single crystals of 7.3 and 7.7 suitable for structural analysis by X-ray crystallography were obtained from slow evaporation of a hexane solution at room temperature. The ORTEPs of the solid-state molecular structures are shown in Figure 7.4. The structure of 7.3 confirms that the C–H bond in C$_6$F$_5$H was functionalized with two diphenylacetylene molecules and that both inserted with the phenyl groups on the same side of the double bond (cis-, cis-product). The structure of 7.7 confirms that that one of the C–H bonds in 1,2,4,5-C$_6$F$_4$H$_2$ was functionalized with two diphenylacetylene molecules and that both molecules have the phenyl groups on opposite sides of the double bond (trans-, trans-product).
**Fig. 7.4.** ORTEP of the solid-state molecular structure of 7.3 and 7.7 as determined by X-ray crystallography.

### 7.3.2.1 Mechanistic Insight

The format of two double-insertion products was an unexpected result. It has previously been shown that the C–H bond of C₆F₅H or 1,2,4,5-C₆F₄H₂ can be functionalized by either a H-transfer\(^{12}\) or C–H bond activation and insertion of diphenylacetylene,\(^{13,14}\) followed by reductive elimination to produce the mono-inserted compounds 7.2 and 7.5. The formation of the double-insertion products as the major products indicates that the catalytic cycle involves a more complex mechanism. There are three plausible mechanisms proposed in Scheme 7.10 to address the insertion of a second equivalent of diphenylacetylene. Mechanism-A involves the insertion of one equivalent of diphenylacetylene into the Ni–H bond and a second equivalent into the Ni–C bond of the fluorinated aromatic, followed by reductive elimination to give the expected double-insertion products. Mechanism-B involves the successive insertion of diphenylacetylene into the Ni–H bond followed by reductive elimination to give the desired double-insertion products. Mechanism-C involves first the formation of a 1,3-diene complex with nickel,\(^{15,16}\) followed by a H-transfer and reductive elimination to give the desired double-insertion products. Mechanism-A,B and C would be expected to form the cis-, cis-insertion products where the phenyl groups are on the same side of the double bond in the products formed, the second isomer can be explained by a thermal conversion. The cis-,
cis- and trans-, trans-isomers of a butadiene can undergo a butadiene-cyclobutene interconversion, exchanging the two isomers through a conrotary transition state, as shown in Scheme 7.10.\textsuperscript{17} The HOMO orbitals of the butadiene control the stereochemistry and rotate in the same direction exchanging the cis and trans isomers through a cyclobutene intermediate.\textsuperscript{17}

**Scheme 7.10.** Proposed mechanism for the formation of the two observed double-insertion products.

To determine if the second equivalent of diphenylacetylene was inserted into the Ni–H or Ni–C bond of the fluorinated aromatic, diphenylacetylene was added to \textit{trans-}{(MeNC\textsubscript{5}H\textsubscript{4}N\textsuperscript{i}Pr)NiF(C\textsubscript{6}F\textsubscript{5})\textsubscript{1}} and the reaction was tracked by \textsuperscript{19}F{\textsuperscript{1}H} NMR spectroscopy. There was no observed reaction by NMR spectroscopy, thus this result suggests that the second equivalent of diphenylacetylene does not insert into the Ni–C bond and insertion into the Ni–H bond is likely.
To confirm that this reaction occurs by an intramolecular mechanism via oxidative addition of the C–H bond, rather than an intermolecular mechanism via deprotonation of the fluorinated aromatic, a deuterium labeling study was designed to distinguish between these two mechanisms. Diphenylacetylene was added to mono-deuterated 1,2,4,5-C₆F₄HD and stoichiometric amounts of Ni(COD)$_2$ and MeNC$_5$H$_4$N$_i$Pr, as shown in Scheme 7.11, the reaction was allowed to go to completion and the products were separated by column chromatography and characterized by mass spectrometry. If the C–H alkenylation reaction occurs via an intramolecular reaction the mass spectra of the products will have a specific pattern for the M$^+$ peak when one deuterium incorporated into the product, m/z 329.09 (100%), 330.10 (21.8 %), and 331.10 (2.2 %). If the C–H alkenylation reaction occurs by an intermolecular mechanism the hydrogen and deuterium will scramble and the mass spectrometry spectrum will have an overlapping 1:2:1 pattern for products containing H/H, H/D and D/D in the products, respectively. Compound $d_1$-7.5 was isolated by silica-gel column chromatography and the mass spectrum displayed a single pattern for the M$^+$, m/z 329.19 (100 %), 330.27 (21.9 %), and 331.29 (1.9 %). This result confirms that this C–H alkenylation reaction occurs by an intramolecular mechanism.

Scheme 7.11. C–H alkenylation products with 1,2,4,5-C₆F₄HD.

All four components (Ni(0) source, ligand, fluorinated substrate and alkyne) are necessary to observe the desired C–H bond alkenylation. No reaction was observed with solutions of diphenylacetylene and MeNC$_5$H$_4$N$_i$Pr, diphenylacetylene and C$_6$F$_5$H or diphenylacetylene, C$_6$F$_5$H and MeNC$_5$H$_4$N$_i$Pr. Catalytic cyclotrimerization of
diphenylacetylene was observed in solutions of diphenylacetylene, Ni(COD)$_2$ and MeNC$_5$H$_4$N$^i$Pr at room temperature, and diphenylacetylene and Ni(COD)$_2$ at 66 °C.

An intermediate present throughout the C–H alkenylation reaction in the $^{19}$F{$^1$H} NMR spectrum was observed at $\delta$ = −107.7 (br m, 1F, o–F); −112.6 (br m, 1F, o–F); −164.4 (t, 1F, $p$–F, $J_{FF}$ = 20.5 Hz); −165.3 (br m, 2F, m–F). The $^1$H NMR spectrum indicated that two MeNC$_5$H$_4$N$^i$Pr ancillary ligands were bound to the nickel metal center and that there were new phenyl environments; however, it remains unclear from the $^1$H NMR spectrum how the alkyne was bound to the nickel center. Attempts to obtain X-ray quality crystals were unsuccessful, isolation of the intermediate failed, because only catalytic amounts were present in the toluene solution and the reaction with stoichiometric amounts of Ni(COD)$_2$ and MeNC$_5$H$_4$N$^i$Pr did not provide the desired intermediate. Diphenylacetylene and C$_6$F$_5$H were also added to solutions of catalytic amounts of Ni(COD)$_2$ and MeNC$_5$H$_4$N$^i$Pr in pentane, a precipitate formed and was analyzed by $^{19}$F{$^1$H} NMR spectroscopy, which confirmed the presence of the desired intermediate. Attempts to recrystallize the isolated intermediate were unsuccessful due to low solubility in pentane and toluene, and low stability in CH$_2$Cl$_2$.

Attempts to form the unknown intermediate from an alternate route were undertaken. A dinuclear complex [(1,5-C$_8$H$_{12}$)Ni]$_2$(μ-$\eta^2$-$\eta^2$-PhC≡CPh) was synthesized by literature procedures$^{18}$ and was added to a solution of MeNC$_5$H$_4$N$^i$Pr, as shown in Scheme 7.12. After 2 days, no reaction was observed, which indicates that MeNC$_5$H$_4$N$^i$Pr was not incorporated into the dinuclear complex. The complex [(1,5-C$_8$H$_{12}$)Ni]$_2$(μ-$\eta^2$-$\eta^2$-PhC≡CPh) was also added to a solution of two equivalents of MeNC$_5$H$_4$N$^i$Pr and C$_6$F$_5$H, and the reaction progress was tracked by $^1$H and $^{19}$F{$^1$H} NMR spectroscopy. After 20 min a new complex began to form in the $^{19}$F{$^1$H} NMR spectrum at $\delta$ = −98.0 (br, 2F), −160.8 (br, 1F) and −166.2 (br, 2F), however, no C–H bond alkenylation products were observed even after two days, which indicates that the intermediate involved in C–H bond alkenylation is not formed from (diphenylacetylene)bis(Ni(COD)$_2$). Further investigation into the intermediates involved in C–H bond alkenylation reaction needs to be conducted in the future.
Further attempts to synthesize the unknown intermediate involved the reaction of \((\text{Cp})_2\text{ZrCl}(1\text{-CH}_3\text{-1-propenyl})\) with trans-\((\text{MeNC}_5\text{H}_4\text{NPr})_2\text{NiF}(2,3,5,6\text{-C}_6\text{F}_4\text{H})\) in hopes of forming \((\text{Cp})_2\text{ZrCl}(\text{F})\), and trans-\((\text{MeNC}_5\text{H}_4\text{NPr})_2\text{NiF}(1\text{-CH}_3\text{-1-propenyl})\) or the reductive elimination product \((E)\text{-3-(but-2-en-2-yl)-1,2,4,5-tetrafluorobenzene},\) as shown in Scheme 7.13. The reactants were allowed to react at 70 °C for 18 h, after which the reaction mixture was passed through Celite and analyzed by \(^1\text{H}\) and \(^{19}\text{F}\) NMR spectroscopy. The \(^1\text{H}\) NMR spectrum indicates that the majority of the sample contains MeNC\(_5\text{H}_4\text{NPr}\) and an unknown product. The \(^{19}\text{F}\{^1\text{H}\}\) and \(^{19}\text{F}\) NMR spectra indicate that there was an unknown organic product with fluorine resonances at \(\delta -140.4\) and \(-144.0\), which are coupled to one hydrogen atom. This product requires further characterization to confirm if it was \((E)\text{-3-(but-2-en-2-yl)-1,2,4,5-tetrafluorobenzene}\).

\[\text{Cp}_2\text{ZrCl}(\text{1-CH}_3\text{-1-propenyl}) + \text{trans-}(\text{MeNC}_5\text{H}_4\text{NPr})_2\text{NiF}(2,3,5,6\text{-C}_6\text{F}_4\text{H}) \rightarrow \text{Possible Products}\]

**Scheme 7.13.** The reaction of \((\text{Cp})_2\text{ZrCl}(1\text{-CH}_3\text{-1-propenyl})\) with trans-\((\text{MeNC}_5\text{H}_4\text{NPr})_2\text{NiF}(2,3,5,6\text{-C}_6\text{F}_4\text{H})\) and the plausible products.

### 7.3.2.2 Expansion of Scope

The addition of a variety of alkyynes including phenylacetylene, 1-phenyl-1-butyne, 2-pentyne, 4-octyne, 1-hexyne and ethynyltrimethylsilane to C\(_6\text{F}_5\text{H}\) and catalytic amounts of Ni(COD)\(_2\) and MeNC\(_5\text{H}_4\text{NPr}\) led to a complex mixture, which should be
analyzed further. The addition of 3-hexyne and 2-butyne, undergo approximately 50 %
conversion to the C–H bond alkenylation products, however, the products still need to be
isolated and the reaction conditions should be optimized to get the reactions to go to
completion.

Alkynes such as phenylethynylmesitylene, 1,2,3,4,5-pentafluoro-6-(phenylethynyl)benzene, 1-methyl-4-((4-trifluoromethyl)phenyl)ethynyl)benzene, N,N-dimethyl-4-trifluoromethyl)phenyl)ethylamide, and N,N-dimethyl-4-trifluoromethyl)phenyl)ethynylaniline were added to solutions of C₆F₅H and
catalytic amounts of Ni(COD)₂ and MeNC₅H₄N/Pr to determine if the selectivity of
insertion can be controlled by the steric and electronics of the substituents on the
aromatics rings. The reaction with phenylethynylmesitylene, was analyzed by ¹⁹F{¹H}
NMR spectroscopy after 1 day, approximately 60 % conversion to a single isomer of the
C–H bond alkenylation product was observed at δ –141.9, –156.7 and –163.2, catalytic
amounts of a nickel complex was also observed at δ –117.4, –146.6 and –156.1. These
results indicate that bulky groups such as mesitylene can control the direction of
insertion; however, isolation and further characterization is still needed to confirm the
selectivity of the insertion reaction. The reaction with 1,2,3,4,5-pentafluoro-6-(phenylethynyl)benzene, 1-methyl-4-((4-trifluoromethyl)phenyl)ethynyl)benzene and
N,N-dimethyl-4-trifluoromethyl)phenyl)ethylamide led to complex mixtures and it is
inconclusive how electronic effects influence the selectivity of these reactions.

7.4 Expanding Reactivity of MeNC₅H₄N/Pr to Other Transition Metals

7.4.1 Reactivity with Yttrium: Formation of (MeNC₅H₄N/Pr)₂YI₂[N(TMS)₂]
Complex

It was initially thought that lanthanides might be interesting because a formally
neutral amido donor would retain reactive sites for further reactivity of the structure yet it
would be more firmly attached than strictly neutral donors. Originally, it was believed
that three amido donors would be able to complex to the metal center, however the
reaction of 4-(isopropylamino)-1-methylpyridinium iodide, MeNC₅H₄N/PrI (2.1), with
Y[N(TMS)₂]₃ in a 3:1 ratio did not result in the expected product. The reaction was done
in a toluene solution in which MeNC₅H₄N/PrI is insoluble. The final product
precipitated from solution leaving a mixture of MeNC₅H₄NH⁺PrI and a new product. The product was easily isolated by filtration because MeNC₅H₄NH⁺PrI adhered to the bottom of the flask. The product was dissolved in THF and ^1^H NMR spectroscopy indicated it was a single product. The product was recrystallized from THF at −40 °C and the solid-state molecular structure was obtained by X-ray crystallography. An ORTEP depiction is shown in Figure 7.5. From the X-ray structure it was determined that only two ligands were attached to the metal center thus (MeNC₅H₄N^iPr)₂YI₂[N(TMS)₂] (7.12) was formed. The formation of **7.12** is shown below in Scheme 7.14.

\[
\begin{align*}
\text{2} & \text{N}^\ominus \text{NH} + \text{Y[N(TMS)₂]³} \\
\text{toluene} & \text{Me₃Si} \quad \text{N}^\ominus \text{N}^\ominus \text{Pr} \quad \text{Y} \quad \text{N}^\ominus \text{Pr} + 2 \text{HN(TMS)₂}
\end{align*}
\]

**Scheme 7.14.** Formation of (MeNC₅H₄N^iPr)₂YI₂[N(TMS)₂] complex 7.12.

**Figure 7.5.** ORTEP of (MeNC₅H₄N^iPr)₂YI₂[N(TMS)₂] complex 7.12. Hydrogen atoms have been removed for clarity.
The structure displays a $C_2$ symmetric arrangement of the ligands about yttrium. The N(1)–C(4) bond has a length of 1.323(6) Å. This bond length is equivalent to that observed in MeNC$_5$H$_4$NHPrI (Section 2.2.1), which indicates that there was little change in the amount of imine character. This is further supported by the bond lengths observed in the nitrogen containing ring, which are also comparable to those observed in MeNC$_5$H$_4$NHPrI. The C(4)–C(5) bond, C(5)–C(6) and C(6)–N(2) had bond lengths of 1.450(6) Å, 1.343(7) Å and 1.355(6) Å respectively. The Y(1)–N(3) bond had a length of 2.201(4) Å, which is significantly shorter than the Y(1)–N(1) bonds that had a length of 2.394(3) Å. The Y(1)–I(1) bond has a length of 3.0789(5) Å, which indicates that iodide binds to yttrium and is no longer a free ion. The N(1)–Y(1)–N(1) bond angle of 142.91(15) ° is greater than the N(3)–Y(1)–N(1) angle of 108.55(8) °. The $^1$H NMR spectrum of 7.12 confirmed that the solution structure was consistent with the solid-state structure.

The formation of complex 7.12 was unexpected. The failure to add a third ligand via replacement of the final bis(trimethylsilyl)amide may have been due to several possible reasons. The first possibility is that the complex may be too insoluble to form. The second possibility may be that the iodides inhibited any other ligands from interacting with the metal center due to steric interactions. To test if solubility was the problem, the reaction of 7.12 and MeNC$_5$H$_4$NHPrI was attempted in THF, however, no reaction was observed, which may be because the iodides blocked the approach of any additional ligands. A way to test this could be to use a weakly coordinating group, such as triflate, in the place of iodide.

Several reactions were conducted on 7.12 to determine its properties and reactivity. Initial attempts consisted of a reaction of 7.12 with LiAlH$_4$ in a ratio of 1:2, this reaction seemed promising from the $^1$H NMR spectra, which displayed a single product. The product was recrystallized from THF at −40 °C. Single crystals were obtained and X-ray crystallography was attempted, despite the low quality data of the structure, the isolated crystals were confirmed to be the salt (THF)$_3$LiI. The solution was redissolved in toluene but no crystals were obtained. The exact product formed is still unknown.
Another reaction conducted was 7.12 with two equivalents of NaH. The reaction was almost instantaneous and a single product was produced and confirmed by $^1$H NMR by the presence of a sharp singlet at $\delta$ 1.08 integrating to 2H, which indicates the presence of a hydride in the product. The solid-state molecular structure has yet to be obtained.

Several avenues for future applications of 7.12 have yet to be explored. Organometallic complexes are a promising area for further research. A Grignard reagent with an alkyl group could be added to 7.12 or MeNC$_5$H$_4$NH$^i$PrI could be added to an alkylated yttrium center to achieve a metal-carbon bond. Hydroamination is another potential application as this yttrium complex has similar properties to other catalysts used for hydroamination.\textsuperscript{19,20} It is logical to assume the complex may possess the same properties and be a useful catalyst in this area. Further investigation into this aspect needs to be conducted.

7.4.2 Reactivity with Yttrium: Formation of (MeNC$_5$H$_4$N$^i$Pr)YI[N(TMS)$_2$]$_2$ Complex

It was next attempted to add only one MeNC$_5$H$_4$NH$^i$PrI to the yttrium metal center by stopping the reaction process early. In pentane, MeNC$_5$H$_4$NH$^i$PrI was added to excess Y[N(TMS)$_2$], as shown in Scheme 7.15, the reaction progressed slowly, and the product precipitated as a white powder. Single crystals suitable for structural analysis by X-ray crystallography were obtained by slow evaporation of a THF solution at –40 $^\circ$C. An ORTEP of the solid-state molecular structure is shown in Figure 7.6. The solid-state molecular structure confirmed that one MeNC$_5$H$_4$NH$^i$PrI was added to the yttrium centre forming (MeNC$_5$H$_4$N$^i$Pr)YI[N(TMS)$_2$]$_2$ (7.13).
Scheme 7.15. Formation of (MeNC₅H₄NᵢPr)Y[1][N(TMS)₂]₂ 7.13.

Figure 7.6. ORTEP of (MeNC₅H₄NᵢPr)Y[1][N(TMS)₂]₂ complex 7.13. Hydrogen atoms have been removed for clarity.

The Y(1)–N(3), Y(1)–N(4) and Y(1)–N(1) bonds have lengths that range from 2.2–2.3 Å and are 2.201(6) Å, 2.216(6) Å and 2.352(7) Å respectively. The N(4)–Y(1)–N(1), N(3)–Y(1)–N(1) and N(4)–Y(1)–N(3) bonds all have similar angles of 110.26(12) °, 109.44(11) ° and 112.30(12) ° respectively. The bond angles show that the structure is approximately tetrahedral. The N(3)–Y(1)–I(1), N(4)–Y(1)–I(1) and N(1)–Y(1)–I(1) bonds have angles that all deviate slightly from tetrahedral angles and are
Chapter 7 – Future Work and Conclusions

111.60(8) °, 108.78(8) °, and 104.16(7) °, respectively. The N(1)–C(4) bond had a shorter bond length than the free MeNC₅H₄NHPrI and the bond length found in 7.12. The ¹H NMR spectrum of 7.13 confirmed that the solution structure was consistent with the solid-state structure and that the ancillary ligands, MeNC₅H₄NPr, contained partial imine character.

In the future, the reactivity of 7.13 should be studied. Reactions of 7.13 with LiAlH₄ and NaH should be conducted, as well as testing if 7.13 is capable of hydroamination, since it also closely resembles literature catalysts.²⁰

7.5 Conclusions

The original goal of this thesis was accomplished, a novel nitrogen donor ligand with strong donor properties capable of promoting oxidative addition reactions and a net neutral charge to maintain sufficient reactive sites for further catalysis, was successfully designed, synthesized and characterized. The nitrogen donor ligand, MeNC₅H₄NPr, promoted fast regioselective C–F bond activation of fluorinated aromatics with nickel(0), which included the first example with tetrafluorobenzenes. The addition of catalytic amounts of Ni(COD)₂ and MeNC₅H₄NPr to fluorinated aromatics and CH₂=CHSnBu₃, promoted selective C–H bond stannylation to form products of the type C₆F₆-nH₅SnBu₃. The addition of catalytic amounts of Ni(COD)₂ and MeNC₅H₄NPr to fluorinated aromatics and CH₂=CHSnPh₃ promoted selective C–H bond alkylation to form products of the type C₆F₆-nH₅SnPh₃. The addition of C₆F₆-nH₅SnPh₃ to Ni(COD)₂, MeNC₅H₄NPr and ethylene underwent a carbostannylation to form products of the type C₆F₆-nH₅SnPh₃. The complex (∈Pr₃P)Ni(η²-C₂H₂=CHSnBu₃)₂ was determined to be a resting state for C–H bond stannylation and was used to determine a plausible mechanism. Further studies on the effect of changing the ancillary ligand, metal center and stannyl substituents, will have to be conducted to improve future catalysts. The substrate scope for C–F bond activation and C–H bond stannylation was also expanded to include trifluoromethyl fluorinated benzene derivatives, and the reactivity of the C–H stannylation products was studied. Further reactivity of MeNC₅H₄NPr with nickel still needs to be conducted as several other functionalization reactions have already proved to
be successful and so many others have yet to be tested. It has been shown that stable complexes can be formed with MeNC₅H₄N⁺PrI and a variety of early and late transition metals, the reactivity of many of these complexes still needs to be conducted.

### 7.6 Experimental

#### 7.6.1 General Procedures

All reactions were performed under an atmosphere of dry oxygen-free dinitrogen by means of standard Schlenk or glovebox techniques. Benzene-$d_6$ was dried by refluxing with Na/K and was then vacuum transferred and degassed by three freeze-pump-thaw cycles. Toluene-$d_8$ and CD₂Cl₂ were dried in an analogous manner by refluxing over Na and CaH₂ respectively. All other solvents were purchased anhydrous from Aldrich and further purified using a Grubbs’ type column system,²¹ produced by Innovative Technology. ¹H, ¹³C{¹H}, and ¹⁹F{¹H} NMR spectra were recorded on a Bruker AMX Spectrometer operating at 300 MHz or where stated at 500 MHz with respect to proton nuclei. All chemical shifts are reported in parts per million (ppm) and all coupling constants are in hertz (Hz). ¹H NMR spectra were referenced to residual protons (C₆D₅H, δ 7.15; CDHCl₂, δ 5.32; C₇D₇H δ 2.09; CHCl₃, δ 7.26) with respect to tetramethylsilane at δ 0.00. ¹³C{¹H} spectra were referenced relative to solvent resonances (C₆D₆, δ 128.0, CDCl₃, δ 77.0, C₇D₈, δ 20.4). ¹⁹F{¹H} NMR spectra were referenced to an external sample of 80 % CCl₃F in CDCl₃ at δ 0.0. C₆D₆, C₇D₈, CDCl₃ and CD₂Cl₂ were purchased from Aldrich. The compounds diphenylacetylene, phenylacetylene, prop-1-ynylbenzene, 2-pentyne, 3-hexyne, 4-octyne, 1-phenyl-1-butyn, 1-hexyne, 2-butyne, ethynyltrimethylsilane pentafluorobenzene, and 1,2,4,5-tetrafluorobenzene, iPr₃P, CH₂=CHSnBu₃, ClSnPh₃, LiAlH₄, NaH, YCl₃, and Li[N(SiMe₃)₂]₂ were purchased from Aldrich. The compounds cis–tributyl(1–propenyl) tin, cis–trans– tributyl(1–propenyl) tin, bromo–2,3,4,5,6–pentafluorobenzene, bromo–2,3,5,6–tetrafluorobenzene and tribenzyltinchloride were purchased from Alfa Aesar. The compounds MeNC₅H₄NH⁺PrI, MeNC₅H₄N⁺Pr,¹ Ni(COD)₂,²² C₆F₅D,²³ 1,2,4,5-C₆F₄H,¹³ CH₂=CHSnPh₃,²⁴ ClSn(p–MeC₆H₄)₃,²⁵ ClSn(p–MeOC₆H₄)₃,²⁵,²⁶ ClSn(p–CF₃C₆H₄)₃,²⁶,²⁷-²⁸ trans–(MeNC₅H₄N⁺Pr)₂NiF(2,3,5,6-C₆F₄H),¹ (diphenylacetylene)bis(Ni(COD)₂),¹⁸ (Cp)₂ZrCl(1–
CH$_3$-1-propenyl),$^{29,30}$ phenylethynylmesitylene,$^{31}$ 1-methyl-4-((4-trifluoromethyl)phenyl)ethynyl)benzene,$^{32}$ N,N-dimethyl-4-trifluoromethyl)phenyl)ethynyl)aniline,$^{33}$ 1,6-bis(perfluorophenyl)hexa-1,5-diyne$^{34}$, 1,2,3,4,5-pentafluoro-6-(phenylethynyl)benzene,$^{35,36}$ and Y[N(SiMe$_3$)$_2$]$^{37}$ were prepared by literature procedures. High-resolution mass spectroscopy was performed at McMaster University, Hamilton, Ontario, Canada. Elemental analyses were conducted at the Centre for Catalysis and Materials Research at the University of Windsor by Dr. Samuel Johnson and Dr. Janeen Auld, Instrument Technician.

7.6.2 Synthesis, Characterization and Reactivity of Complexes

**Synthesis of CH$_2$=CHSnBn$_3$.** A 100 mL round bottom equipped with a reflux condenser and stirbar was charged with ClSnBn$_3$ (2.8 g, 0.0065 mol), and 10 mL of toluene. The reagent CH$_2$=CHMgCl (0.68 g, 0.0078 mol, 4.9 mL) was slowly added dropwise to the reaction mixture at room temperature. The reaction mixture was then heated at reflux for 1 h and cooled to room temperature. The reaction mixture was quenched with 15 mL of 10 % HCl in H$_2$O and the organic layer was decanted off, 10 mL of toluene was added to the aqueous layer, decanted off and added to the first organic fraction. The solvents were removed and the resulting solid was recrystallized from methanol and cooled to –20 °C to yield CH$_2$=CHSnBn$_3$ as a white solid (0.81 g, 30 %). $^1$H NMR (C$_6$D$_6$, 25 °C, 300.23 MHz): $\delta$ 2.22 (s with Sn satellites, 6H, CH$_2$, $^2$J$_{HSn}$ = 61.7 Hz); 5.41 (dd with Sn satellites, 1H, vinyl–CH, $^2$J$_{HH}$ = 3.1 Hz, $^3$J$_{HH}$ = 20.1 Hz, $^2$J$_{HSn}$ = 80.5 Hz); 5.99 (dd with Sn satellites, 1H, vinyl–CH, $^2$J$_{HH}$ = 3.0 Hz, $^3$J$_{HH}$ = 13.9 Hz, $^2$J$_{HSn}$ = 167.3 Hz); 6.16 (dd with Sn satellites, 1H, vinyl–CH, $^3$J$_{HH}$ = 20.5 Hz, $^3$J$_{HH}$ = 13.8 Hz, $^3$J$_{HSn}$ = 93.1 Hz); 6.80 (d, 6H, Ar–H, $^3$J$_{HH}$ = 7.6 Hz); 6.93 (t, 3H, p–Ar–H, $^3$J$_{HH}$ = 7.4 Hz); 7.60 (virtual t, 6H, Ar–H, $^3$J$_{HH}$ = 7.6 Hz). $^{13}$C{$_1$H} NMR (C$_6$D$_6$, 25 °C, 125.76 MHz): $\delta$ 19.4 (s with Sn satellites, CH$_2$, $^2$J$_{CSn(119)}$ = 288.3 Hz, $^2$J$_{CSn(117)}$ = 275.7 Hz); 124.4 (s with Sn satellites, Ar–CH, $^3$J$_{CSn}$ = 15.7 Hz); 129.2 (s with Sn satellites, Ar–CH, $^4$J$_{CSn}$ = 12.6 Hz); 136.0 (s, CH); 137.4 (s, CH); 142.1 (s with Sn satellites, CH, $^2$J$_{CSn}$ = 39.5 Hz). $^{119}$Sn {$_1$H} (C$_6$D$_6$, 25 °C, 186.50 MHz): $\delta$ –76.4 (s, 1Sn).
**Synthesis of CH$_2$=CHSn(p-C$_6$H$_4$Me)$_3$.** A 250 mL round bottom equipped with a reflux condenser and stirbar was charged with ClSn(p-C$_6$H$_4$Me)$_3$ (5 g, 0.012 mol), and 25 mL of toluene. The reagent CH$_2$=CHMgCl (1.2 g, 0.014 mol, 8.6 mL) was slowly added dropwise to the reaction mixture at room temperature. The reaction mixture was then heated at reflux for 1 h and cooled to room temperature. The reaction mixture was quenched with 30 mL of 10 % HCl in H$_2$O and the organic layer was decanted off, 10 mL of ether was added to the aqueous layer and decanted off and added to the first organic layer. The solvents were removed and the resulting solid was recrystallized from boiling methanol to yield CH$_2$=CHSn(p-MeC$_6$H$_4$)$_3$ as a white solid (3.56 g, 71 %). $^1$H NMR (C$_6$D$_6$, 25 ºC, 300.23 MHz): $\delta$ 2.20 (s, 9H, CH$_3$); 6.08 (dd with Sn satellites, 1H, vinyl–CH, $^2$J$_{HH}$ = 3.3 Hz, $^3$J$_{HH}$ = 20.5 Hz, $^3$J$_{HSn}$ = 86.9 Hz); 6.44 (dd with Sn satellites, 1H, vinyl–CH, $^2$J$_{HH}$ = 3.3 Hz, $^3$J$_{HH}$ = 13.9 Hz, $^2$J$_{HSn}$ = 177.4 Hz); 6.87 (dd with Sn satellites, 1H, vinyl–CH, $^3$J$_{HH}$ = 20.6 Hz, $^3$J$_{HH}$ = 13.8 Hz, $^3$J$_{HSn}$ = 96.8 Hz); 7.18 (dm with Sn satellites, 6H, Ar–H, $^3$J$_{HH}$ = 7.18 Hz, $^4$J$_{HSn}$ = 12.3 Hz); 7.71 (d with Sn satellites, 6H, Ar–H, $^3$J$_{HH}$ = 7.82 Hz, $^4$J$_{HSn}$ = 47.5 Hz). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 25 ºC, 125.76 MHz): $\delta$ 21.5 (s, CH$_3$); 129.4 (s with Sn satellites, Ar–CH, $^3$J$_{CSn}$ = 52.6 Hz); 134.4 (s, CH); 135.6 (s, CH); 136.8 (s, CH); 137.1 (s with Sn satellites, Ar–CH, $^4$J$_{CSn}$ = 38.3 Hz); 138.5 (s with satellites, CH). $^{119}$Sn {$^1$H} (C$_6$D$_6$, 25 ºC, 186.50 MHz): $\delta$ –130.4 (s, 1Sn).

**Synthesis of CH$_2$=CHSn(p-C$_6$H$_4$OMe)$_3$.** A 250 mL round bottom equipped with a reflux condenser and stirbar was charged with ClSn(p-C$_6$H$_4$OMe)$_3$ (11.3 g, 0.0236 mol), and 50 mL of toluene. The reagent CH$_2$=CHMgCl (2.4 g, 0.028 mol, 17.5 mL) was slowly added dropwise to the reaction mixture at room temperature. The reaction mixture was then heated at reflux for 1 h and cooled to room temperature. The reaction mixture was quenched with 60 mL of 10 % HCl in H$_2$O and the organic layer was decanted off, 20 mL of toluene was added to the aqueous layer, decanted off and added to the first organic fraction. The solvents were removed and the resulting solid was recrystallized from ethanol and then again from toluene and cooled to –20 ºC to yield CH$_2$=CHSn(p-C$_6$H$_4$OMe)$_3$ as a white solid (2.26 g, 21 %). $^1$H NMR (C$_6$D$_6$, 25 ºC, 300.23 MHz): $\delta$ 3.31 (s, 9H, CH$_3$); 5.99 (dd with Sn satellites, 1H, vinyl–CH, $^2$J$_{HH}$ = 3.4 Hz, $^3$J$_{HH}$ = 20.5 Hz, $^3$J$_{HSn}$ = 87.4 Hz); 6.36 (dd with Sn satellites, 1H, vinyl–CH, $^2$J$_{HH}$ = 3.4
Hz, \( ^3J_{HH} = 13.4 \text{ Hz}, \ 2J_{H_{Sn}} = 178.3 \text{ Hz} \); 6.78 (dd with Sn satellites, 1H, vinyl–CH, \( ^3J_{HH} = 20.5 \text{ Hz}, \ 3J_{HH} = 13.7 \text{ Hz}, \ 3J_{H_{Sn}} = 98.1 \text{ Hz} \)); 6.88 (d, 6H, Ar–H, \( ^3J_{HH} = 8.1 \text{ Hz}, \ 3J_{H_{Sn}} = 46.2 \text{ Hz} \)). \(^{13}\text{C}\{^{1}\text{H}\} \) NMR (C\(_6\)D\(_6\), 25 °C, 125.76 MHz): \( \delta \) 54.9 (s, C\(_{H_3}O\)); 115.3 (s with Sn satellites, Ar–CH, \( ^2J_{CSn} = 55.5 \text{ Hz} \)); 129.3 (s, CH); 136.8 (s, CH); 137.4 (s, CH); 138.9 (s with Sn satellites, CH, \( ^2J_{CSn} = 43.2 \text{ Hz} \)); 161.5 (s with Sn satellites, CH, \( ^4J_{CSn} = 12.0 \text{ Hz} \)). \(^{119}\text{Sn} \{^{1}\text{H}\} \) (C\(_6\)D\(_6\), 25 °C, 186.50 MHz): \( \delta \) –124.7 (s, 1Sn).

**Synthesis of CH\(_2\)=CHSn(p-C\(_6\)H\(_4\)CF\(_3\))\(_3\).** A 100 mL round bottom equipped with a reflux condenser and stirbar was charged with ClSn(p–C\(_6\)H\(_4\)CF\(_3\))\(_3\) (0.782 g, 0.0013 mol), and 5 mL of toluene. The reagent CH\(_2\)=CHMgCl (0.130 g, 0.0015 mol, 0.9 mL) was slowly added dropwise to the reaction mixture at room temperature. The reaction mixture was then heated at reflux for 24 h and cooled to room temperature. The reaction mixture was quenched with 6 mL of 10 % HCl in H\(_2\)O and the organic layer was decanted off, 1 mL of toluene was added to the aqueous layer, decanted off and added to the first organic fraction. The solvents were removed and the resulting solid was recrystallized from hexane and cooled to −20 °C to yield CH\(_2\)=CHSn(p–C\(_6\)H\(_4\)CF\(_3\))\(_3\) as a white solid (0.420 g, 56 %). \(^1\text{H}\) NMR (C\(_6\)D\(_6\), 25 °C, 300.23 MHz): \( \delta \) 5.94 (dd, 1H, vinyl–CH, \( ^2J_{HH} = 2.8 \text{ Hz}, \ 3J_{HH} = 20.4 \text{ Hz} \)); 6.52 (dd, 1H, vinyl–CH, \( ^2J_{HH} = 2.8 \text{ Hz}, \ 3J_{HH} = 13.8 \text{ Hz} \)); 6.74 (dd, 1H, vinyl–CH, \( ^3J_{HH} = 19.9 \text{ Hz}, \ 2J_{H_{Sn}} = 13.7 \text{ Hz} \)); 7.65 (m, 12H, Ar–H). \(^{19}\text{F}\{^{1}\text{H}\} \) NMR (toluene, 25 °C, 282.40 MHz): \( \delta \) –63.5 (s, 1F, CF\(_3\)). \(^{13}\text{C}\{^{1}\text{H}\} \) NMR (C\(_6\)D\(_6\), 25 °C, 125.76 MHz): \( \delta \) 124.4 (q, CF\(_3\), \( ^1J_{CF} = 273.0 \text{ Hz} \)); 125.1 (q with Sn satellites, Ar–CH, \( ^3J_{CF} = 3.7 \text{ Hz} \)); 131.5 (q, Ar–C, \( ^2J_{CF} = 31.1 \text{ Hz} \)); 132.2 (s, CH); 137.1 (s with Sn satellites, Ar–CH, \( ^3J_{CSn} = 39.1 \text{ Hz} \)); 139.6 (s, CH); 141.7 (s, CH). \(^{119}\text{Sn} \{^{1}\text{H}\} \) (C\(_6\)D\(_6\), 25 °C, 186.50 MHz): \( \delta \) –137.9 (s, 1Sn).

**Synthesis of (\textit{i}Pr\(_3\)P)Ni(\eta\(^2\)-CH\(_2\)=CHSnBn\(_3\))\(_2\), (7.1\(^{8n}\)).** To a solution of CH\(_2\)=CHSnBn\(_3\) (0.350 g, 0.83 mmol) in 15 mL of toluene was added \textit{i}Pr\(_3\)P (0.067 g, 0.42 mmol) and Ni(COD)\(_2\) (0.115 g, 0.42 mmol). The solution was stirred for 30 min and the solvent was removed, yielding a yellow solid upon washing with pentane. (0.371 g, 84 % yield). \(^1\text{H}\) NMR (C\(_6\)D\(_6\), 25 °C, 500.13 MHz): \( \delta \) 0.96 (m, 18H, CH(CH\(_3\))\(_2\)); 2.01 (d septet, 3H, CH(CH\(_3\))\(_2\), \( ^2J_{HP} = 7.0 \text{ Hz}, \ 3J_{HH} = 7.0 \text{ Hz} \)); 2.42 (s with Sn satellites, 12H, CH\(_2\), \( ^2J_{H_{Sn}} = \))
Synthesis of $\left(\text{iPr}_3\text{P}\right)\text{Ni}\left[\eta^2-\text{CH}_2=\text{CHSn}(p-\text{C}_6\text{H}_4\text{Me})_3\right]_2$ (7.1-p-Me). To a solution of $\text{CH}_2=\text{CHSn}(p-\text{C}_6\text{H}_4\text{Me})_3$ (1.0 g, 2.39 mmol) in 15 mL of toluene was added $\text{iPr}_3\text{P}$ (0.191 g, 1.19 mmol) and $\text{Ni(COD)}_2$ (0.328 g, 1.19 mmol). The solution was stirred for 30 min and the solvent was removed, leaving a yellow solid. (1.250 g, 99 % yield). $^1\text{H}$ NMR ($\text{C}_6\text{D}_6$, 25 ºC, 500.13 MHz): $\delta$ 0.72 (dd, 9H, $\text{CH(C}_3\text{H}_3)_2$, $^3J_{\text{HP}} = 12.3$ Hz, $^3J_{\text{HH}} = 7.3$ Hz); 0.83 (dd, 9H, $\text{CH(CH}_3)_2$), $^3J_{\text{HP}} = 12.3$ Hz, $^3J_{\text{HH}} = 7.3$ Hz); 1.97 (d septet, 3H, $\text{CH(CH}_3)_2$, $^2J_{\text{HP}} = 7.3$ Hz, $^3J_{\text{HH}} = 7.3$ Hz); 2.14 (s, 18H, Ar–$\text{C}_3$); 3.08 (dd with Sn satellites, 2H, vinyl–$\text{C}_2$, $^2J_{\text{HP}} = 11.5$ Hz, $^3J_{\text{HH}} = 4.7$ Hz, $^2J_{\text{HSn}} = 146$ Hz); 3.17 (dd with Sn satellites, 2H, vinyl–$\text{C}_2$, $^3J_{\text{HH}} = 16.7$ Hz, $^2J_{\text{HH}} = 10.5$ Hz, $^3J_{\text{HSn}} = 92$ Hz); 4.22 (dd with Sn satellites, 2H, vinyl–$\text{C}_2$, $^2J_{\text{HH}} = 14.9$ Hz, $^3J_{\text{HH}} = 11.8$ Hz, $^3J_{\text{HSn}} = 40$ Hz, $^3J_{\text{HSn}} = 61.3$ Hz); 7.05 (m with Sn satellites, 12H, Ar–$\text{H}$, $^3J_{\text{HSn}} = 44.5$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_6$, 25 ºC, 202.46 MHz): $\delta$ 50.8 (s with Sn satellites, 1P, $^3J_{\text{PSn}} = 3.19$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ (toluene, 25 ºC, 111.96 MHz): $\delta$ −118.1 (d, 1Sn, $^3J_{\text{SnP}} = 32.6$ Hz).

Synthesis of $\left(\text{iPr}_3\text{P}\right)\text{Ni}\left[\eta^2-\text{CH}_2=\text{CHSn}(p-\text{C}_6\text{H}_4\text{OMe})_3\right]_2$ (7.1-p-OMe). To a solution of $\text{CH}_2=\text{CHSn}(p-\text{C}_6\text{H}_4\text{OMe})_3$ (1.0 g, 2.14 mmol) in 15 mL of toluene was added $\text{iPr}_3\text{P}$ (0.172 g, 1.10 mmol) and $\text{Ni(COD)}_2$ (0.294 g, 1.10 mmol). The solution was stirred for 30 min and the solvent was removed, leaving a yellow solid. (1.152 g, 91 % yield). $^1\text{H}$ NMR ($\text{C}_6\text{D}_6$, 25 ºC, 500.13 MHz): $\delta$ 0.75 (dd, 9H, $\text{CH(CH}_3)_2$), $^3J_{\text{HP}} = 12.6$ Hz, $^3J_{\text{HH}} = 7.3$ Hz); 0.86 (dd, 9H, $\text{CH(CH}_3)_2$), $^3J_{\text{HP}} = 12.0$ Hz, $^3J_{\text{HH}} = 7.3$ Hz); 1.98 (d septet, 3H, $\text{CH(CH}_3)_2$, $^2J_{\text{HP}} = 7.0$ Hz, $^3J_{\text{HH}} = 7.0$ Hz); 3.11 (dd with Sn satellites, 2H, vinyl–$\text{C}_2$, $^2J_{\text{HP}} = 7.0$ Hz, $^3J_{\text{HH}} = 7.0$ Hz); 3.20 (dd, 2H, vinyl–$\text{C}_2$, $^3J_{\text{HH}} = 15.1$ Hz, $^2J_{\text{HH}} = 9.5$ Hz); 3.36 (s, 18H, $\text{CH}_3\text{O}$); 4.26 (m with Sn satellites, 2H, vinyl–$\text{C}_2$, $^2J_{\text{HH}} = 13.9$ Hz, $^3J_{\text{HSn}} = 61.2$ Hz); 6.90 (d, 12H, Ar–$\text{H}$, $^3J_{\text{HH}} = 7.9$ Hz); 7.67 (d with Sn satellites, 12H, Ar–$\text{H}$, $^3J_{\text{HH}} = 8.2$ Hz, $^3J_{\text{HSn}} = 43.2$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_6$, 25 ºC, 202.46 MHz): $\delta$ 50.1
(s with Sn satellites, 1P, $^3J_{\text{SnP}} = 30.4$ Hz). $^{119}\text{Sn}[^1\text{H}]$ (toluene, 25 °C, 111.96 MHz): δ − 113.1 (d, 1Sn, $^3J_{\text{SnP}} = 32.6$ Hz).

**Synthesis of $(\text{iPr}_3\text{P})\text{Ni}[\eta^2\text{CH}_2=\text{CHSn}(\rho–\text{C}_6\text{H}_4\text{CF}_3)_3]\_2$, $(7.1^p$-$\text{CF}_3$).** To a solution of CH$_2$=CHSn(ρ–C$_6$H$_4$CF$_3$)$_3$ (0.302 g, 0.52 mmol) in 15 mL of toluene was added iPr$_3$P (0.042 g, 0.26 mmol) and Ni(COD)$_2$ (0.071 g, 0.26 mmol). The solution was stirred for 50 min and the solvent was removed, yielding a yellow solid upon washing with pentane.

(0.335 g, 93 % yield). $^1\text{H}$ NMR (C$_6$D$_6$, 25 °C, 500.13 MHz): δ 0.58 (dd, 9H, CH(CH$_3$)$_2$, $^3J_{\text{HP}} = 12.6$ Hz, $^3J_{\text{HH}} = 7.2$ Hz); 0.71 (dd, 9H, CH(CH$_3$)$_2$, $^3J_{\text{HP}} = 12.8$ Hz, $^3J_{\text{HH}} = 7.4$ Hz); 2.93 (m, 2H, vinyl–CH); 2.97 (m, 2H, vinyl–CH); 3.80 (ddd with Sn satellites, 2H, vinyl–CH, $^3J_{\text{HH}} = 14.7$ Hz, $^3J_{\text{HH}} = 7.2$ Hz); 7.48 (m, 24H Ar–H, $^3J_{\text{HH}} = 9.0$ Hz). $^{31}\text{P}[^1\text{H}]$ NMR (C$_6$D$_6$, 25 °C, 202.46 MHz): δ 48.3 (s with Sn satellites, 1P, $^3J_{\text{SnP}} = 30.4$ Hz).

$^{19}\text{F}[^1\text{H}]$ NMR (C$_6$D$_6$, 25 °C, 282.48 MHz): δ −63.1 (s, 3F, C$_3$F$_3$). $^{119}\text{Sn}[^1\text{H}]$ (C$_6$D$_6$, 25 °C, 111.96 MHz): δ −127.7 (d, 1Sn, $^3J_{\text{SnP}} = 31.7$ Hz).

**Stoichiometric Stannylation of C$_6$F$_5$H with 7.1$^R$ (R = Bu, Bn, Ph, p–Me, p–OMe or p–CF$_3$).** A stock solution of the reagent C$_6$F$_5$H (422 mg, 2.50 mmol), the internal standard Me$_3$SiF (178 mg, 0.64 mmol) and the internal standard hexamethyldisiloxane (HMDSO) (108 mg, 0.62 mmol) were dissolved in C$_6$D$_6$ and the solution was diluted to 25 mL, to provide a solution that is 0.1004 M of C$_6$F$_5$H, 0.0256 M of Me$_3$SiF and 0.0266 M of HMDSO. Each catalyst was weighed into a vial, $(\text{iPr}_3\text{P})\text{Ni}[\eta^2\text{CH}_2=\text{CHSnBu}_3]$ (25 mg, 0.0297 mmol), $(\text{iPr}_3\text{P})\text{Ni}[\eta^2\text{CH}_2=\text{CHSnBn}_3]$ (31 mg, 0.0297 mmol), $(\text{iPr}_3\text{P})\text{Ni}[\eta^2\text{CH}_2=\text{CHSnPh}_3]$ (29 mg, 0.0297 mmol), $(\text{iPr}_3\text{P})\text{Ni}[\eta^2\text{CH}_2=\text{CHSn}(\rho–\text{MeC}_6\text{H}_4)_3]$ (31 mg, 0.0297 mmol), $(\text{iPr}_3\text{P})\text{Ni}[\eta^2\text{CH}_2=\text{CHSn}(\rho–\text{MeOC}_6\text{H}_4)_3]$ (34 mg, 0.0297 mmol), and $(\text{iPr}_3\text{P})\text{Ni}[\eta^2\text{CH}_2=\text{CHSn}(\rho–\text{CF}_3\text{C}_6\text{H}_4)_3]$ (41 mg, 0.0297 mmol), followed by the addition of 0.64 mL of the stock solution to give approximate catalyst concentrations of 0.0464 M. Each solution was transferred to a NMR tube equipped with a Teflon valve and placed in an NMR probe preheated to 315 K and the rate of the reaction was monitored by $^1\text{H}$, $^{19}\text{F}$ and $^{119}\text{Sn}$ NMR spectroscopy. The product C$_6$F$_5$SnR$_3$ (R = Bu, Bn, Ph, p–C$_6$H$_4$Me, p–C$_6$H$_4$OMe, or p–C$_6$H$_4$CF$_3$) was the only species observed. Plotting concentration of product formed versus time, the slope was found to be linear for extended periods of
Chapter 7 – Future Work and Conclusions

time. Each catalyst was tested in duplicate and the average observed reactions rates are recorded in the Table 7.4 below. The reaction rates relative to \((\text{iPr}_3\text{P})\text{Ni}(\eta^2-\text{CH}_2=\text{CHSnPh}_3)\) were also calculated and recorded in the Table 7.4 below.

**Table 7.4.** Summary of the initial rates of formation of C\(_6\)F\(_5\)SnR\(_3\) (R = Bu, Bn, Ph, p–C\(_6\)H\(_4\)Me, p–C\(_6\)H\(_4\)OMe, or p–C\(_6\)H\(_4\)CF\(_3\)).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Observed Initial Reaction Rates (M·s(^{-1}))</th>
<th>Relative Reaction Rates With Respect to R = Ph (M·s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{iPr}_3\text{P})\text{Ni}(\eta^2-\text{CH}_2=\text{CHSnBu}_3))</td>
<td>0.00018778</td>
<td>2.69</td>
</tr>
<tr>
<td>((\text{iPr}_3\text{P})\text{Ni}(\eta^2-\text{CH}_2=\text{CHSnBn}_3))</td>
<td>0.00015317</td>
<td>2.20</td>
</tr>
<tr>
<td>((\text{iPr}_3\text{P})\text{Ni}(\eta^2-\text{CH}_2=\text{CHSnPh}_3))</td>
<td>0.000069768</td>
<td>1</td>
</tr>
<tr>
<td>((\text{iPr}_3\text{P})\text{Ni}[\eta^2-\text{CH}_2=\text{CHSn}(\text{p–C}_6\text{H}_4\text{Me})_3])</td>
<td>0.000064558</td>
<td>0.93</td>
</tr>
<tr>
<td>((\text{iPr}_3\text{P})\text{Ni}[\eta^2-\text{CH}_2=\text{CHSn}(\text{p–C}_6\text{H}_4\text{OMe})_3])</td>
<td>0.000032798</td>
<td>0.47</td>
</tr>
<tr>
<td>((\text{iPr}_3\text{P})\text{Ni}[\eta^2-\text{CH}_2=\text{CHSn}(\text{p–C}_6\text{H}_4\text{CF}_3)_3])</td>
<td>0.000021895</td>
<td>0.31</td>
</tr>
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</table>

**Effect on Initial Rates with Varying Temperature.** A stock solution of the reagent C\(_6\)F\(_5\)H (422 mg, 2.50 mmol), the internal standard Me\(_3\)SiF (178 mg, 0.64 mmol) and the internal standard hexamethyldisiloxane (HMDSO) (108 mg, 0.62 mmol) were dissolved in C\(_6\)D\(_6\) and the solution was diluted to 25 mL, to provide a solution that is 0.1004 M of C\(_6\)F\(_5\)H, 0.0256 M of Me\(_3\)SiF and 0.0266 M of HMDSO. Each catalyst was weighed into a vial, 7.1\(\text{R}'\) (R\(\text{'}\) = Ph, p–Me, p–OMe or p–CF\(_3\)) (0.0297 mmol), followed by the addition of 0.64 mL of the stock solution to give approximate catalyst concentrations of 0.0464 M. Each solution was transferred to a J-young tube and placed in an NMR probe preheated to 305, 310, 315 or 320 K and the initial rate of the reaction was tracked by integration over the course of 5 min. Plotting concentration of product formed versus time, the slope was found to be linear for extended periods of time. Each catalyst was tested in duplicate and the average observed reactions rates are recorded in the table below. Using the reaction rates \(\Delta G\), \(\Delta H\) and \(\Delta S\) were calculated from the Eyring equation and are recorded in the Table 7.5.
Table 7.5. Observed initial rate, $\Delta G$, $\Delta H$ and $\Delta S$ of C–H bond stannylation reaction, as temperature is increased with $7.1^{R'}$.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp (K)</th>
<th>Observed Rate (M·s$^{-1}$)</th>
<th>$\Delta G$ (kcal·mol$^{-1}$)</th>
<th>$\Delta H$ (kcal·mol$^{-1}$)</th>
<th>$\Delta S$ (kcal·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$7.1^{Ph}$</td>
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<td>0.000001185</td>
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<tr>
<td></td>
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<td>24.46</td>
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<td></td>
</tr>
<tr>
<td>$7.1^{p-Me}$</td>
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<td>24.82</td>
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<tr>
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<tr>
<td>$7.1^{p-OMe}$</td>
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<td>25.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td>25.17</td>
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<td>$7.1^{p-CF_3}$</td>
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<td></td>
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<td>25.24</td>
<td>37.5</td>
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</tr>
<tr>
<td></td>
<td>320</td>
<td>0.000004169</td>
<td>25.19</td>
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</tbody>
</table>

Stoichiometric Stannylation of $1,3$-$C_6F_2H_4$ with $7.1^{R'}$ ($R'$ = Bu, Bn, Ph, $p$–Me, $p$–OMe or $p$–CF$_3$). A stock solution of the reagent $1,3$-$C_6F_2H_4$ (271 mg, 2.38 mmol), and the internal standard $C_6H_5F$ (61 mg, 0.63 mmol) were dissolved in toluene and the solution was diluted to 25.6 mL, to provide a solution that is 0.0928 M of $1,3$-$C_6F_2H_4$ and 0.0232 M of $C_6H_5F$. Each catalyst was weighed into a vial, $7.1^{R'}$ ($R'$ = Bu, Bn, Ph, $p$–Me, $p$–OMe or $p$–CF$_3$) (0.0297 mmol), followed by the addition of 0.64 mL of the stock solution to give approximate catalyst concentrations of 0.0464 M. Each solution was transferred to a $J$-young tube and placed in an NMR probe preheated to 315 or 338 K and the initial rate of the reaction was tracked by integration over the course of 5 min. Plotting concentration of product formed versus time, the slope was found to be linear for
extended periods of time. Each catalyst was tested in duplicate and the relative observed reactions rates are recorded in Scheme 7.3.

**Association versus Dissociation of CH\textsubscript{2}=CHSnR\textsubscript{3} Moieties from Nickel.** To three solutions of 7.1\textsuperscript{Ph} (41 mg, 0.0426 mol) was added increasing amounts of CH\textsubscript{2}=CHSnBu\textsubscript{3} (54 mg, 0.17 mmol, 0.05 mL) in solution 1, (108 mg, 0.342 mmol, 0.1 mL) in solution 2 and (217 mg, 0.684 mmol, 0.2 mL) in solution 3. Each reaction mixture was placed in an NMR probe preheated to 305 K and the rate of exchanged was determined from the integration of the \textsuperscript{31}P\{\textsuperscript{1}H\} NMR in 12 experiments over 15 min. It was found that the amount of CH\textsubscript{2}=CHSnBu\textsubscript{3} added has no effect on the rate of exchange and therefore depends on the rate of dissociation of CH\textsubscript{2}=CHSnPh\textsubscript{3} and not the association of CH\textsubscript{2}=CHSnBu\textsubscript{3}.

**Table 7.6. Observed rate of exchange with an increasing concentration of CH\textsubscript{2}=CHSnBu\textsubscript{3}.**

<table>
<thead>
<tr>
<th>Equivalents of CH\textsubscript{2}=CHSnBu\textsubscript{3}</th>
<th>Observed Rate (M·s\textsuperscript{−1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.0000299</td>
</tr>
<tr>
<td>8</td>
<td>0.0000296</td>
</tr>
<tr>
<td>16</td>
<td>0.0000334</td>
</tr>
</tbody>
</table>

**Effect of Temperature on the Rate of Dissociation.** To three solutions of 7.1\textsuperscript{Ph} (41 mg, 0.0426 mol) was added CH\textsubscript{2}=CHSnBu\textsubscript{3} (108 mg, 0.342 mmol, 0.1 mL) to each solution. Each reaction mixture was placed in an NMR probe preheated to 300, 305 or 310 K and the rate of exchange was estimated from the integration of the \textsuperscript{31}P\{\textsuperscript{1}H\} NMR in 12 experiments over 20 min as shown in the table below. The relative rate of exchange increased linearly with increasing in temperature.
Table 7.7. Observed rate of exchange with increasing temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Observed Rate (M·s⁻¹)</th>
<th>Relative Rate (M·s⁻¹)</th>
<th>∆G (kcal·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.0000136</td>
<td>1</td>
<td>24.25</td>
</tr>
<tr>
<td>305</td>
<td>0.0000257</td>
<td>1.89</td>
<td>24.27</td>
</tr>
<tr>
<td>310</td>
<td>0.0000514</td>
<td>3.78</td>
<td>24.26</td>
</tr>
</tbody>
</table>

Dissociation Competitions and Determination of Equilibrium Constants. To a solution of CH₂=CHSnPh₃ (68 mg, 0.18 mmol) and CH₂=CHSnR₃ (R = Bu, Bn, p-C₆H₄Me, p-C₆H₄OMe or p-C₆H₄CF₃) (0.18 mmol) in 0.6 mL of toluene was added ³Pr₃P (3 mg, 0.018 mmol) and Ni(COD)₂ (5 mg, 0.018 mmol). The reaction mixture was placed into a NMR probe preheated to 338 K and a ¹H and ³¹P{¹H} NMR was obtained after approximately 5 min and again after 10 min to confirm that equilibrium has been reached. The integrals of the produced products (³Pr₃P)Ni(η²-CH₂=CHSnR₃)₂ (7.1ₚ) and (³Pr₃P)Ni(η²-CH₂=CHSnPh₃)(η²-CH₂=CHSnR₃) (7.1ₚₚ) were used to estimate the concentration of the products, which were used to determine the equilibrium constants, Gibbs free energy, and the heats of formation, summarized in Table 7.2.

Determination of ΔΔG‡. A solution of CH₂=CHSnPh₃ (68 mg, 0.18 mol) and CH₂=CHSnR₃ (R = Bu, Bn, p-C₆H₄Me, p-C₆H₄OMe or p-C₆H₄CF₃) (0.18 mmol) in 0.6 mL of C₆D₆ was added to ³Pr₃P (3 mg, 0.018 mmol) and Ni(COD)₂ (5 mg, 0.018 mmol) and allowed to react at 338 K for 10 min to establish equilibrium between the two catalysts. Upon cooling to room temperature the reagent C₆F₅H (15 mg, 0.009 mol) was added to the reaction mixture under an inert atmosphere and then the reaction mixture was placed into an NMR probe preheated to 338 K. The initial product ratios (C₆F₅SnR₃) were determined by integration and used to estimate the ΔΔG‡ between the transition states, [ΔΔG = –RTLn(% C₆F₅SnR₃ / % C₆F₅SnR₃)], and are shown in the Table 7.3.

Reaction of diphenylacetylene and catalytic amounts of Ni(COD)₂ and MeNC₅H₄NPr. To a solution of diphenylacetylene (0.583 g, 3.27 mmol) was added Ni(COD)₂ (0.090 g, 0.327 mmol) and MeNC₅H₄NPr (0.098 g, 0.654 mmol) in 15 mL of
The reaction was allowed to react for 24 h, the product precipitated from solution as a white crystalline solid and was isolated by vacuum filtration. (0.416 g, 71 % yield). MS (EI) Calcd for \( \text{C}_{42}\text{H}_{30} \): M+, 534.23. Found: m/z 534.19.

**Reaction of prop-1-ynylbenzene and catalytic amounts of Ni(COD)\_2 and MeNC\_5H\_4N\^iPr.** To a solution of prop-1-ynylbenzene (0.040 g, 0.333 mmol) was added Ni(COD)\_2 (0.005 g, 0.033 mmol) and MeNC\_5H\_4N\^iPr (0.098 g, 0.0654 mmol) in 1 mL of \( \text{C}_6\text{D}_6 \). The solution was allowed to react for 24 h. \( ^1\text{H} \) NMR (\( \text{C}_6\text{D}_6 \), 27 °C, 300.13 MHz): \( \delta \) 2.00 (s, 3H, \( \text{CH}_3 \)); 2.06 (s, 3H, \( \text{CH}_3 \)); 2.09 (s, 3H, \( \text{CH}_3 \)); 6.89–7.50 (m, 27H, Ph–H).

**Reaction of 1,2,3,4,5-pentafluoro-6-(phenylethynyl)benzene and catalytic amounts of Ni(COD)\_2 and MeNC\_5H\_4N\^iPr.** To a solution of 1,2,3,4,5-pentafluoro-6-(phenylethynyl)benzene (0.090 g, 0.333 mmol) was added Ni(COD)\_2 (0.005 g, 0.017 mmol) and MeNC\_5H\_4N\^iPr (0.005 g, 0.030 mmol) in 1 mL of \( \text{C}_6\text{D}_6 \). The solution was allowed to react for 24 h. \( ^{19}\text{F} \{ ^1\text{H} \} \) NMR (\( \text{C}_6\text{D}_6 \), 27 °C, 282.40 MHz): \( \delta \) –61.5 (AA'BB' second order multiplet, 4F, \( \text{C}_6\text{F}_5 \)); –65.7 (AA'BB' second order multiplet, 2F, \( \text{C}_6\text{F}_5 \)); –79.7 (t, 1F, \( \text{C}_6\text{F}_5 \), \( \text{J}_{\text{FF}} = 22 \text{ Hz} \)); –81.1 (t, 2F, \( \text{C}_6\text{F}_5 \), \( \text{J}_{\text{FF}} = 22 \text{ Hz} \)); –85.7 (AA'BB' second order multiplet, 2F, \( \text{C}_6\text{F}_5 \)); –86.1 (AA'BB' second order multiplet, 4F, \( \text{C}_6\text{F}_5 \)).

**Reaction of \( \text{C}_6\text{F}_5\text{H} \), diphenylacetylene and catalytic amounts of Ni(COD)\_2 and MeNC\_5H\_4N\^iPr.** To a solution of \( \text{C}_6\text{F}_5\text{H} \) (0.750 g, 4.49 mmol) and diphenylacetylene (0.800 g, 4.49 mmol) was added Ni(COD)\_2 (0.123 g, 0.449 mmol) and MeNC\_5H\_4N\^iPr (0.135 g, 0.898 mmol) in 30 mL of toluene. The reaction was stirred for 2 days at room temperature. The reaction mixture was exposed to air and passed through celite to remove any precipitate and the toluene was removed. The products of the reaction mixture were purified by silica-gel column chromatography using a solvent ratio of 9 hexane : 1 toluene and recrystallized from a hexane solution.

\[ (\text{Z})-(\text{1-(2,3,4,5,6-pentafluorophenyl)ethene-1,2-diyl})\text{dibenzene} \ (7.2). \]  
\( ^{19}\text{F} \{ ^1\text{H} \} \) NMR (\( \text{CDCl}_3 \), 25 °C, 282.40 MHz): \( \delta \) –141.1 (AA'BB' second order multiplet, 2F, \( m-\text{C}_6\text{F}_5 \)) –155.8 (t, 1F, \( p-\text{C}_6\text{F}_5 \), \( \text{J}_{\text{FF}} = 21.0 \text{ Hz} \)); –162.3 (AA'BB' second order multiplet, 2F, \( o-\text{C}_6\text{F}_5 \)).
(1Z,3Z)-1-(2,3,4,5,6-tetrafluorophenyl)buta-1,3-diene-1,2,3,4-tetrayl)tetrabenzenes

(7.3). $^1$H NMR (CDCl$_3$, 27 °C, 300.13 MHz): $\delta$ 6.52 (s, 1H, ethylene–H); 6.89–7.32 (m, 20H, Ph–H). $^{19}$F($^1$H) NMR (CDCl$_3$, 25 °C, 282.40 MHz): $\delta$ −139.8 (AA'BB' second order multiplet, 2F, $m$–C$_6$F$_5$); −156.4 (t, 1F, $p$–C$_6$F$_5$, $^3$J$_{FF}$ = 20.9 Hz); −163.6 (AA'BB' second order multiplet, 2F, $o$–C$_6$F$_5$). $^{13}$C($^1$H) NMR (CDCl$_3$, 25 °C, 75.47 MHz): $\delta$ 117.9 (m, $p$–C$_6$F$_5$); 125.3, 126.2, 127.0, 127.1, 127.4, 127.9, 128.0, 128.2, 129.0, 129.2, 129.3, 129.7, 131.2, 134.7, 136.9, 138.8, 140.4, 141.2, 143.3, 150.7 (phenyl–C and ethylene–C); 137.4 (dm, $o$–C$_6$F$_4$H, $^1$J$_{CF}$ = 239.2 Hz); 137.9 (ips–C$_6$F$_5$); 143.9 (dm, $m$–C$_6$F$_4$H, $^1$J$_{CF}$ = 251.8 Hz).

(1E,3Z)-1-(2,3,4,5,6-pentafluorophenyl)buta-1,3-diene-1,2,3,4-tetrayl)tetrabenzenes

(7.4). $^1$H NMR (CDCl$_3$, 27 °C, 300.13 MHz): $\delta$ 6.81 (s, 1H, ethylene–H); 6.87–7.31 (m, 16H, Ar–H); 7.76 (dm, 2H, Ar–H, $^3$J$_{HH}$ = 7.7 Hz); 7.51 (dm, 2H, Ar–H, $^3$J$_{HH}$ = 7.7 Hz). $^{19}$F($^1$H) NMR (CDCl$_3$, 25 °C, 282.40 MHz): $\delta$ −139.1 (br d, 2F, $m$–C$_6$F$_5$, $^3$J$_{FF}$ = 21.1 Hz); −139.6 (br d, 2F, $m$–C$_6$F$_5$, $^3$J$_{FF}$ = 21.9 Hz); −155.3 (t, 1F, $p$–C$_6$F$_5$, $^3$J$_{FF}$ = 20.9 Hz); −163.4 (br second order multiplet, 2F, $o$–C$_6$F$_5$).

Reaction of 1,2,4,5-C$_6$F$_4$H$_2$, diphenylacetylene and catalytic amounts of Ni(COD)$_2$ and MeNC$_5$H$_4$N$i$Pr. To a solution of 1,2,4,5-C$_6$F$_4$H$_2$ (0.550 g, 2.80 mmol) and diphenylacetylene (1.0 g, 5.60 mmol) was added Ni(COD)$_2$ (0.154 g, 0.56 mmol) and MeNC$_5$H$_4$N$i$Pr (0.168 g, 1.12 mmol) in 30 mL of toluene. The reaction was stirred for 4 days at room temperature. The reaction mixture was exposed to air and passed through celite to remove any precipitate and the toluene was removed. The products of the reaction mixture were purified by silica-gel column chromatography starting with a solvent ratio of 4 hexane : 1 toluene to elute the first three fractions, 2.5 hexane : 1 toluene to elute the fourth fraction and 0.75 hexane : 1 toluene to elute the final two fractions, the products were all further purified by recrystallization from a hexane solution. Mass of isolated mixture was 0.908 g, which is approximately 60 % conversion, the remaining 40 % consists of left over diphenylacetylene and hexaphenylbenzene.

(E)-(1-(2,3,5,6-tetrafluorophenyl)ethene-1,2-diyl)dibenzene (7.5) A colourless solid. $^1$H NMR (CDCl$_3$, 27 °C, 300.13 MHz): $\delta$ 6.76 (s, 1H, ethylene–H); 6.99 (tt, 1H, $p$–C.
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((1Z,3Z)-1-(2,3,5,6-tetrafluorophenyl)buta-1,3-diene-1,2,3,4-tetrayl)tetrabenzene (7.6). A colourless solid. $^1$H NMR (hexane, 27 ºC, 300.13 MHz): $\delta$ 6.74 (tt, 1H, $p$-C$_6$F$_4$H, $^3$J$_{HF} = 9.6$ Hz, $^4$J$_{HF} = 7.2$ Hz); 6.76 (s, 1H, ethylene–H); 7.01–7.48 (m, 20H, Ar–H). $^{19}$F{$^1$H} NMR (hexane, 25 ºC, 282.40 MHz): $\delta$ –139.7 (dd, 2F, $m$–C$_6$F$_4$H, $^3$J$_{FF} = 23.0$ Hz, $^4$J$_{FF} = 12.6$ Hz); –140.6 (dd, 2F, $o$–C$_6$F$_4$H, $^3$J$_{FF} = 23.0$ Hz, $^4$J$_{FF} = 12.6$ Hz). $^{19}$F{$^1$H} NMR (CD$_2$Cl$_2$, 25 ºC, 75.47 MHz): $\delta$ 105.5 (t, $p$–C$_6$F$_4$H, $^2$J$_{CF} = 21.5$ Hz); 123.5 (t, ipso–C$_6$F$_4$H, $^3$J$_{HH} = 7.4$ Hz); 127.7, 127.9, 128.0, 128.1, 128.3, 128.6, 128.9, 129.4, 129.8, 132.5, 137.1, 140.2, 140.5, 141.1, 142.2, 144.3 (phenyl–C and ethylene–C); 144.6 (dm, C$_6$F$_4$H, $^1$J$_{CF} = 243.1$ Hz); 146.4 (dm, C$_6$F$_4$H, $^1$J$_{CF} = 245.0$ Hz). HMRS (EI) Calcd for C$_{34}$H$_22$F$_4$: M+, 506.1658. Found: m/z 506.1655.

((1E,3Z)-1-(2,3,5,6-tetrafluorophenyl)buta-1,3-diene-1,2,3,4-tetrayl)tetrabenzene (7.7). A colourless solid. $^1$H NMR (d$_8$-toluene, 27 ºC, 300.13 MHz): $\delta$ 6.11 (tt, 1H, $p$–C$_6$F$_4$H, $^3$J$_{HF} = 9.6$ Hz, $^4$J$_{HF} = 7.2$ Hz); 6.65–7.14 (m, 15H, Ar–H and ethylene–H); 7.32 (d, 2H, o–Ar–H, $^3$J$_{HH} = 7.4$ Hz); 7.47 (d, 2H, o–Ar–H, $^3$J$_{HH} = 7.4$ Hz); 7.58 (d, 2H, o–Ar–H, $^3$J$_{HH} = 7.4$ Hz). $^{19}$F{$^1$H} NMR (CD$_2$Cl$_2$, 25 ºC, 282.40 MHz): $\delta$ –140.4 (br m, 2F, $m$–C$_6$F$_4$H); –141.0 (br m, 1F, $o$–C$_6$F$_4$H); –141.3 (br m, 1F, $o$–C$_6$F$_4$H). $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$, 25 ºC, 75.47 MHz): $\delta$ 106.9 (t, $p$–C$_6$F$_4$H, $^2$J$_{CF} = 19.6$ Hz); 127.7, 127.9, 128.0, 128.1, 128.3, 128.6, 128.9, 129.4, 129.8, 132.5, 137.1, 140.2, 140.5, 141.1, 142.2, 144.3 (phenyl–C and ethylene–C); 144.6 (dm, C$_6$F$_4$H, $^1$J$_{CF} = 243.1$ Hz); 146.4 (dm, C$_6$F$_4$H, $^1$J$_{CF} = 245.0$ Hz). HMRS (EI) Calcd for C$_{34}$H$_22$F$_4$: M+, 506.1658. Found: m/z 506.1655.

((1Z)-1-(4-(((E)-1,2-diphenylvinyl)-2,3,5,6-tetrafluorophenyl)buta-1,3-diene-1,2,3,4-tetrayl)tetrabenzene (7.8). A colourless solid. $^{19}$F{$^1$H} NMR (CDCl$_3$, 25 ºC, 282.40 MHz): $\delta$ –139.4 (dd, 2F, $m$–C$_6$F$_4$H, $^3$J$_{FF} = 23.0$ Hz, $^4$J$_{FF} = 13.2$ Hz). $^{13}$C{$^1$H} NMR (CDCl$_3$, 25 ºC, 75.47 MHz): $\delta$ 104.9 (dd, 2F, $p$–C$_6$F$_4$H, $^3$J$_{FF} = 23.0$ Hz, $^4$J$_{FF} = 13.2$ Hz). $^{19}$F{$^1$H} NMR (CD$_2$Cl$_2$, 25 ºC, 75.47 MHz): $\delta$ 105.4 (t, $p$–C$_6$F$_4$H, $^2$J$_{CF} = 22.8$ Hz); 124.1 (t, ipso–C$_6$F$_4$H, $^2$J$_{CF} = 17.6$ Hz); 127.8 (s, Ar–C); 127.9 (s, Ar–C); 128.2 (s, Ar–C); 128.5 (s, ethylene–C); 128.6 (s, Ar–C); 129.1 (s, Ar–C); 129.5 (s, Ar–C); 135.1 (s, ipso–Ar–C); 135.6 (s, ipso–Ar–C); 138.3 (s, ethylene–C); 144.1 (dm, C$_6$F$_4$H, $^1$J$_{CF} = 246.0$ Hz); 146.0 (dm, C$_6$F$_4$H, $^1$J$_{CF} = 242.7$ Hz). HMRS (EI) Calcd for C$_{20}$H$_{12}$F$_4$: M+, 328.0875. Found: m/z 328.0860.
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((1E,3Z)-1-((E)-1,2-diphenylvinyl)-2,3,5,6-tetrafluorophenyl)buta-1,3-diene-
1,2,3,4-tetrayl)tetrabenzenes (7.9). A colourless solid. $^1$H NMR (CDCl$_3$, 27 ºC, 300.13 MHz): $\delta$ 6.73 (s, 1H, ethylene–H); 6.79–7.29 (m, 26H, Ar–H); 7.40 (d, 2H, o–Ar–H, $^3$J$_{HH}$ = 7.5 Hz); 7.53 (d, 2H, o–Ar–H, $^3$J$_{HH}$ = 7.5 Hz). $^{19}$F{1H} NMR (CDCl$_3$, 25 ºC, 282.40 MHz): $\delta$ –140.6 (br m, 1F, m–C$_6$F$_4$H); –141.0 (br m, 1F, m–C$_6$F$_4$H); –142.4 (dd, 2F, o–C$_6$F$_4$H, $^3$J$_{FF}$ = 23.6 Hz, $^4$J$_{FF}$ = 12.6 Hz).

Two symmetric double activation and insertion product, cannot distinguish which isomer has cis or trans disposed phenyl groups from the $^{19}$F NMR spectrum (7.10 and 7.11).

A colourless solid. $^{19}$F{1H} NMR (CDCl$_3$, 25 ºC, 282.40 MHz): $\delta$ –141.3 (s, 4F, C$_6$F$_4$H). A colourless solid. $^{19}$F{1H} NMR (CDCl$_3$, 25 ºC, 282.40 MHz): $\delta$ –141.9 (s, 4F, C$_6$F$_4$H).

Reaction of diphenylacetylene and trans-(MeNC$_5$H$_4$N$^i$Pr)NiF(C$_6$F$_5$). To a solution of diphenylacetylene (0.007 g, 0.037 mmol) was added trans-(MeNC$_5$H$_4$N$^i$Pr)NiF(C$_6$F$_5$) (0.020 g, 0.037 mmol) in 1 mL of CD$_2$Cl$_2$, C$_6$D$_5$Br or C$_6$D$_6$. The reaction mixtures were allowed to react at 60 ºC for 1 day. Analysis by $^{19}$F{1H} NMR was inconclusive, no reaction appears to have occurred, and the nickel complex appears to have decomposed in all three of the solvents.

Reaction of 1,2,4,5-C$_6$F$_4$HD, diphenylacetylene and catalytic amounts of Ni(COD)$_2$ and MeNC$_5$H$_4$N$^i$Pr. To a solution of 1,2,4,5-C$_6$F$_4$HD (0.424 g, 2.80 mmol) and diphenylacetylene (1.0 g, 5.61 mmol) was added Ni(COD)$_2$ (0.171 g, 0.62 mmol) and MeNC$_5$H$_4$N$^i$Pr (0.187 g, 1.24 mmol) in 30 mL of toluene. The reaction mixture was allowed to stir for three days at room temperature. The reaction mixture was then passed through a plug of celite and the products were separated by silica-gel column chromatography with a solvent ratio of 4 hexane : 1 toluene.

H/D-(E)-(1-(2,3,5,6-tetrafluorophenyl)ethene-1,2-diyl)dibenzene. $^{19}$F{1H} NMR (CDCl$_3$, 25 ºC, 282.40 MHz): $\delta$ –139.1 (dd, 2F, m–C$_6$F$_4$H, $^3$J$_{FF}$ = 22.7 Hz, $^4$J$_{FF}$ = 12.8 Hz).
19F NMR (CDCl3, 25 ºC, 282.40 MHz): \( \delta \) –139.1 (ddd, 2F, \( m \)-C6F4H, \( 3^J_{FH} = 9.6 \) Hz, \( 3^J_{FF} = 22.7 \) Hz, \( 4^J_{FF} = 12.8 \) Hz); –139.4 (dd, 2F, \( m \)-C6F4H, \( 3^J_{FF} = 22.7 \) Hz, \( 4^J_{FF} = 12.8 \) Hz); –141.5 (dd, 2F, \( o \)-C6F4H, \( 3^J_{FF} = 22.7 \) Hz, \( 4^J_{FF} = 12.8 \) Hz); –141.6 (dd, 2F, \( o \)-C6F4H, \( 3^J_{FF} = 22.7 \) Hz, \( 4^J_{FF} = 12.8 \) Hz).

**Reaction of (diphenylacetylene)bis(Ni(COD)2), MeNC5H4N’Pr and C6F5H.** To a solution of (diphenylacetylene)bis(Ni(COD)2) (0.030 g, 0.060 mmol) was added MeNC5H4N’Pr (0.018 g, 0.12 mmol) and C6F5H (0.010 g, 0.060 mmol) in 1 mL of C6D6. The reaction mixture was analyzed by 19F{1H} NMR spectroscopy, after 20 min a new complex is beginning to form with resonances at \( \delta \) –97.9, –154.5 and –166.3; however, after 2 days the reaction has formed a complex mixture of products.

**Reaction of (Cp2)Zr(Cl)(1-CH3-1-propenyl) and trans-(MeNC5H4N’Pr)NiF(C6F5).** To a solution of (Cp2)Zr(Cl)(1-CH3-1-propenyl) (0.010 g, 0.048 mmol) was added trans-(MeNC5H4N’Pr)NiF(C6F5) (0.017 g, 0.048 mmol) in 1 mL of C6D6. The reaction mixture was allowed to react at 70 ºC for 16 h. A large amount of precipitate formed and was filtered off, the 19F{1H} NMR spectrum of the filtrate indicated that there was a new organic product that had resonances at \( \delta \) –140.4 (dd, 2F, C6F4H2, \( 3^J_{FF} = 22.9 \) Hz, \( 3^J_{HF} = 13.0 \) Hz); –144.0 (dd, 2F, C6F4H2, \( 3^J_{FF} = 22.7 \) Hz, \( 3^J_{HF} = 13.0 \) Hz). There were also two minor unknown products with resonances at \( \delta \) –139.9 (s) and –144.6 (s).

**General Procedure for the reaction of a variety of alkynes with C6F5H and catalytic amounts of Ni(COD)2 and MeNC5H4N’Pr.** To a solution of C6F5H (0.014 g, 0.083 mmol) and 1,6-bis(perfluorophenyl)hexa-1,5-diyne, 1,2,3,4,5-pentafluoro-6-(phenylethynyl)benzene, 2-pentyne, 3-hexyne, 4-octyne, 1-phenyl-1-butyne, 1-hexyne, 2-butyne, ethynyltrimethylsilane, phenylethynyldimethylsilylene, 1-methyl-4-((4-trifluoromethyl)phenyl)ethynyl)benzene, or \( N,N \)-dimethyl-4-trifluoromethyl)phenyl)ethynyl)aniline (0.167 mmol) was added Ni(COD)2 (0.005 g, 0.0167 mmol) and MeNC5H4N’Pr (0.005 g, 0.033 mmol) in 1 mL of C6D6. The reaction
mixtures were allowed to react for three days at room temperature and were analyzed each day by $^{19}$F{1H} NMR spectroscopy.

The reaction with 3-hexyne produced two new nickel containing compounds with similar environments with resonances for one of the complexes at $\delta$ –108.6 (1F, $\alpha$–C$_6$F$_5$); –110.0 (1F, $\alpha$–C$_6$F$_5$); –158.4 (1F, $\rho$–C$_6$F$_5$); –164.1 (br m, 1F, $m$–C$_6$F$_5$); –164.7 (br m, 1F, $m$–C$_6$F$_5$). The second complex had resonances at $\delta$ 109.3 (1F, $\alpha$–C$_6$F$_5$); –110.5 (1F, $\alpha$–C$_6$F$_5$); –163.6 (1F, $p$–C$_6$F$_5$); –163.9 (m, 2F, $m$–C$_6$F$_5$).

The reaction with 2-butyne formed a new C–H bond alkenylation product with resonances at $\delta$ –142.2 (2F, $\alpha$–C$_6$F$_5$); –158.6 (1F, $p$–C$_6$F$_5$); –163.9 (2F, $m$–C$_6$F$_5$).

The reaction with phenylethynylmesitylene, formed approximately 60 % of a C–H alkenylation product with resonances at $\delta$ –141.9 (AA'BB' second order multiplet, 2F, $\alpha$–C$_6$F$_5$, $^3$$J_{FF} = 23.2$, $^4$$J_{FF} = 7.4$); –156.7 (t, 1F, $p$–C$_6$F$_5$, $^3$$J_{FF} = 21.5$); –163.2 (AA'BB' second order multiplet, 2F, $m$–C$_6$F$_5$, $^3$$J_{FF} = 22.4$, $^4$$J_{FF} = 7.6$). A nickel complex was also present in catalytic amounts with resonances at $\delta$ –117.4 (AA'BB' second order multiplet, 2F, $\alpha$–C$_6$F$_5$); –146.6 (AA'BB' second order multiplet, 2F, $m$–C$_6$F$_5$); –156.1 (t, 1F, $p$–C$_6$F$_5$, $^3$$J_{FF} = 21.7$).

The reactions with 1,6-bis(perfluorophenyl)hexa-1,5-diyne, 1,2,3,4,5-pentafluoro-6-(phenylethynyl)benzene, phenylacetylene, 1-phenyl-1-butyne, 2-pentyne, 4-octyne, 1-hexyne, ethynyltrimethylsilane, 1-methyl-4-((4-trifluoromethyl)phenyl)ethynyl)benzene, and N,N-dimethyl-4- trifluoromethyl)phenyl)ethynyl)aniline either did not react, decomposed or formed a complex mixture, which still needs to be analyzed further.

**Synthesis of (MeNC$_5$H$_4$N$^{i}$Pr)$_2$YI$_2$[N(TMS)$_2$], (7.12).**

To a stirred solution of MeNC$_5$H$_4$NH$i$PrI (2.1) (0.666 g, 2.40 mmol) in 25 mL of toluene, was added Y[N(TMS)$_2$]$_3$ (0.683 g, 1.20 mmol) at room temperature and the reaction mixture was allowed to stir for 72 h. The product precipitated out as a white solid and was recrystallized from cold THF to yield colourless crystals (0.837 g, 76 % yield). $^1$H NMR ($d_8$-THF, 27 ºC, 300.13 MHz): $\delta$ –0.01 (s, 9H, N(Si(CH$_3$)$_3$)$_2$); 0.22 (s,
Chapter 7 – Future Work and Conclusions

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9H, N(Si(CH₃)₃)₂; 0.93 (d, 12H, NCH(CH₃)₂, ³JHH = 5.9 Hz); 3.20 (s, 6H, NCH₃); 3.32 (septet, 2H, NCH, ³JHH = 5.9 Hz); 5.69 (d, 2H, C₆H₄N, ³JHH = 7.8 Hz); 5.81 (d, 2H, C₆H₄N, ³JHH = 7.5 Hz); 6.50 (d, 2H, C₆H₄N, ³JHH = 7.8 Hz); 6.67 (d, 2H, C₆H₄N, ³JHH = 7.5 Hz). ¹³C{¹H} NMR (d₈-THF, 27 °C, 75.47 MHz): δ 2.74 (s, N(Si(CH₃)₃)₂); 6.92 (s, NCH(CH₃)₂); 41.5 (s, NCH₃); 44.8 (s, N⁺CH₃); 104.7 (s, C₆H₄N); 117.5 (s, C₆H₄N); 135.2 (s, C₆H₄N); 138.3 (s, C₆H₄N); 153.8 (s, C₆H₄N).

**Reaction of 7.12 and LiAlH₄.**

To a stirred solution of **7.12** (0.500 g, 0.620 mmol) in 30 mL of THF, was added LiAlH₄ (0.050 g, 1.24 mmol) in 20 mL of THF drop wise at −40 °C. The solution turned orange after warming to room temperature and stirring for 24 h. The salt was removed by filtering through celite. The solvent was removed in vacuo and the product was recrystallized from a solution of THF at −40 °C. ¹H NMR (d₈-THF, 27 °C, 300.13 MHz): δ 0.05 (s, 36H, N(Si(CH₃)₃)₂); 1.36 (d, 6H, NCH(CH₃)₂, ³JHH = 5.7 Hz); 2.28 (s, 3H, N⁺CH₃); 3.08 (septet, 1H, NCH, ³JHH = 5.7 Hz ); 6.58 (d, 1H, C₆H₄N, ³JHH = 6.2 Hz); 7.18 (d, 1H, C₆H₄N, ³JHH = 6.7 Hz); 7.49 (s, 1H, C₆H₄N, ³JHH = 6.7 Hz); 7.83 (s, 1H, C₆H₄N, ³JHH = 6.2 Hz).

**Reaction of 7.12 and NaH.**

To a stirred solution of **7.12** (0.134 g, 0.166 mmol) in 20 mL of THF, was added NaH (0.008 g, 0.334 mmol) at room temperature and then allowed to stir for 72 hrs. The impurities were then filtered off through celite and the solvent was removed in vacuo. The product was recrystallized from cold toluene. ¹H NMR (d₈-THF, 27 °C, 300.13 MHz): δ 0.95 (d, 12H, N⁺CH(CH₃)₂, ³JHH = 7.5 Hz); 1.08 (s, 2H, Y–H); 2.21 (septet, 2H, NCH, ³JHH = 7.5 Hz); 3.22 (s, 6H, N⁺CH₃); 5.79 (d, 4H, C₆H₄N, ³JHH = 7.7 Hz); 6.53 (d, 2H, C₆H₄N, ³JHH = 7.7 Hz ); 6.68 (d, 2H, C₆H₄N, ³JHH = 7.7 Hz ).

**Synthesis of (MeNC₅H₄N⁺Pr)Y[N(TMS)₂]₂, (7.13).**

To a stirred solution of MeNC₅H₄NH⁺PrI (2.1) (0.500 g, 1.80 mmol) in 40 mL of pentane, was added Y[N(TMS)₂]₃ (2.4 g, 4.21 mmol) at room temperature and then
allowed to react for 72 h. The product precipitated out and was then filtered and washed with pentane to remove excess Y[N(TMS)₂]₃. The solid was recrystallized from cold THF to yield colourless crystals (0.516 g, 42 % yield). ¹H NMR (d₈-THF, 27 ºC, 300.13 MHz): δ 0.16 (s, 20H, N(Si(CH₃)₃)₂); 0.34 (s, 16H, N(Si(CH₃)₃)₂); 1.17 (d, 6H, NCH(CH₃)₂), ³J_HH = 9.0 Hz); 3.44 (s, 3H, +NC₃H₃); 3.57 (septet, 1H, NCH₃, ³J_HH = 9.0 Hz); 6.12 (t, 2H, C₆H₄N, ³J_HH = 6.0 Hz); 6.91 (d, 1H, C₆H₄N, ³J_HH = 6.0 Hz); 7.05 (d, 1H, C₆H₄N, ³J_HH = 6.0 Hz). ¹³C{¹H} NMR (d₈-THF, 27 ºC, 75.47 MHz): δ 2.7 (s, N(Si(CH₃)₃)₂); 7.8 (s, NCH(CH₃)₂); 23.9 (s, N⁺CH₃); 48.3 (s, NCH); 104.8 (s, C₆H₄N); 116.6 (s, C₆H₄N); 136.2 (s, C₆H₄N).

7.7 X-ray Crystallography

7.7.1 General Collection and Refinement Information

The X-ray structure of 7.3, 7.5, 7.7, 7.12, and 7.13 were obtained at −100 ºC, with the crystal covered in Paratone and placed rapidly into the cold N₂ stream of the Kryo-Flex low-temperature device. The data was collected using the SMART³⁸ software on a Bruker APEX CCD diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). A hemisphere of data was collected using a counting time of 10 s per frame. Data reductions were performed using the SAINT³⁹ software, and the data were corrected for absorption using SADABS.⁴⁰,⁴¹ The structures were solved by direct methods using SIR97⁴² and refined by full-matrix least-squares on F² with anisotropic displacement parameters for the non-H atoms using SHELX-97⁴³,⁴⁴ and the WinGX⁴⁵ software package, and thermal ellipsoid plots were produced using ORTEP32.⁴⁶ The hydrogen atoms were placed in idealized locations using the AFIX command in SHELX.

7.7.2 Crystallographic Data

Table 7.8. Crystallographic Data for (1Z,3Z)-1-(2,3,4,5,6-tetrafluorophenyl)buta-
1,3-diene-1,2,3,4-tetrayl)tetrabenzenne, 7.3.

Empirical formula  \( \text{C}_{34}\text{H}_{21}\text{F}_{5} \)

Formula weight  524.51

Temperature  173(2) K

Wavelength  0.71073 Å

Crystal system  Monoclinic

Space group  \( \text{P2(1)/c} \)

Unit cell dimensions  
\[
\begin{align*}
\text{a} &= 11.2260(13) \text{ Å} \\
\text{b} &= 8.5394(10) \text{ Å} \\
\text{c} &= 27.493(3) \text{ Å}
\end{align*}
\]

\[ \text{â}= 90^\circ. \]

\[ \beta= 100.9460(10)^\circ. \]

\[ \gamma= 90^\circ. \]

Volume  2587.6(5) Å
d

Density (calculated)  1.346 Mg/m
d

Absorption coefficient  0.102 mm
d

\( F(000) \)  1080

Crystal size  0.45 x 0.40 x 0.18 mm
d

Theta range for data collection  2.12 to 25.00°.

Index ranges  \(-13\leq h\leq 13, -10\leq k\leq 10, -32\leq l\leq 32\)

Reflections collected  23910

Independent reflections  4563 [R(int) = 0.0272]

Completeness to theta = 25.00°  100.0 %

Absorption correction  Semi-empirical from equivalents

Max. and min. transmission  0.9818 and 0.9554

Refinement method  Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters  4563 / 0 / 356

Goodness-of-fit on \( F^2 \)  1.026

Final R indices [I>2sigma(I)]  \( R_1 = 0.0365, wR_2 = 0.0905 \)

R indices (all data)  \( R_1 = 0.0455, wR_2 = 0.0989 \)

Largest diff. peak and hole  0.223 and –0.166 e.Å
d

References begin on page 262
Table 7.9. Crystallographic Data for (E)-(1-(2,3,5,6-tetrafluorophenyl)ethene-1,2-diyl)dibenzene, 7.5.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{20}H_{12}F_{4}, (C_{14}H_{12})</td>
</tr>
<tr>
<td>Formula weight</td>
<td>508.53</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(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></td>
</tr>
<tr>
<td>a</td>
<td>21.347(5) Å</td>
</tr>
<tr>
<td>b</td>
<td>5.6286(12) Å</td>
</tr>
<tr>
<td>c</td>
<td>21.574(5) Å</td>
</tr>
<tr>
<td>α</td>
<td>90°</td>
</tr>
<tr>
<td>β</td>
<td>103.933(2)°</td>
</tr>
<tr>
<td>γ</td>
<td>90°</td>
</tr>
<tr>
<td>Volume</td>
<td>2516.0(9) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.343 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.097 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1056</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.55 x 0.04 x 0.02 mm³</td>
</tr>
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<td>Theta range for data collection</td>
<td>2.41 to 27.50°</td>
</tr>
<tr>
<td>Index ranges</td>
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<td>Reflections collected</td>
<td>24739</td>
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<tr>
<td>Independent reflections</td>
<td>5601 [R(int) = 0.1361]</td>
</tr>
<tr>
<td>Completeness to theta = 27.50°</td>
<td>96.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.948 and 0.571</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>5601 / 0 / 347</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.257</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.1392, wR2 = 0.1644</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.2408, wR2 = 0.1848</td>
</tr>
</tbody>
</table>

References begin on page 262
Largest diff. peak and hole 0.423 and –0.374 e.Å⁻³

Table 7.10. Crystallographic Data for ((1E,3Z)-1-(2,3,5,6-tetrafluorophenyl)buta-1,3-diene-1,2,3,4-tetrayl)tetrabenzen, 7.7.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
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<td>Empirical formula</td>
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<tr>
<td>Formula weight</td>
<td>506.52</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>a</td>
<td>10.8708(13) Å</td>
</tr>
<tr>
<td>α= 90°</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>15.7197(19) Å</td>
</tr>
<tr>
<td>β= 98.0690(10)°</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>15.0315(19) Å</td>
</tr>
<tr>
<td>γ= 90°</td>
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</tr>
<tr>
<td>Unit cell dimensions</td>
<td>2543.2(5) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Volume</td>
<td></td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.323 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.096 mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>1048</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.38 × 0.33 × 0.21 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.59 to 27.50°</td>
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<tr>
<td>Index ranges</td>
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</tr>
<tr>
<td>Reflections collected</td>
<td>26957</td>
</tr>
<tr>
<td>Completeness to theta = 27.50°</td>
<td></td>
</tr>
<tr>
<td>98.2 %</td>
<td></td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<tr>
<td>Max. and min. transmission</td>
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<td>Goodness-of-fit on F²</td>
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<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0656, wR2 = 0.1412</td>
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</table>
R indices (all data)  
\[ R_1 = 0.0796, \ wR_2 = 0.1508 \]

Extinction coefficient  
\[ 0.0002(5) \]

Largest diff. peak and hole  
\[ 0.836 \text{ and } -0.254 \text{ e.Å}^{-3} \]

**Table 7.11. Crystallographic Data for (MeNC₅H₄NⁱPr)₂Y₂N(TMS)₂, 7.12.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>( \text{C}<em>{36}\text{H}</em>{60}\text{I}_2\text{N}_5\text{O}_3\text{Si}_2\text{Y} )</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1009.78</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>( \text{C}_2/\text{c} )</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>( a = 18.913(2) \text{ Å } \quad \alpha = 90°. )</td>
</tr>
<tr>
<td></td>
<td>( b = 14.2300(18) \text{ Å } \quad \beta = 98.4010(10)°. )</td>
</tr>
<tr>
<td></td>
<td>( c = 17.231(2) \text{ Å } \quad \gamma = 90°. )</td>
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<tr>
<td>Volume</td>
<td>4587.7(10) \text{ Å}^3</td>
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<tr>
<td>( Z )</td>
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<tr>
<td>Density (calculated)</td>
<td>1.462 Mg/m³</td>
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<tr>
<td>Absorption coefficient</td>
<td>2.705 mm(^{-1})</td>
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<tr>
<td>( F(000) )</td>
<td>2032</td>
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<tr>
<td>Crystal size</td>
<td>0.34 x 0.29 x 0.25 mm(^3)</td>
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<tr>
<td>Theta range for data collection</td>
<td>2.07 to 27.49°</td>
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<tr>
<td>Index ranges</td>
<td>(-24 \leq h \leq 24, -18 \leq k \leq 17, -21 \leq l \leq 21)</td>
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<tr>
<td>Reflections collected</td>
<td>25183</td>
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<tr>
<td>Completeness to theta = 27.49°</td>
<td>97.3 %</td>
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<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<tr>
<td>Max. and min. transmission</td>
<td>0.5512 and 0.4598</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on ( F^2 )</td>
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<tr>
<td>Data / restraints / parameters</td>
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<tr>
<td>Goodness-of-fit on ( F^2 )</td>
<td>1.055</td>
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Final R indices [I>2sigma(I)] \[ R_1 = 0.0437, \text{wR}_2 = 0.0997 \]
R indices (all data) \[ R_1 = 0.0612, \text{wR}_2 = 0.1091 \]
Largest diff. peak and hole \[ 0.957 \text{ and } -0.491 \text{ e.Å}^{-3} \]

Table 7.12. Crystallographic Data for (MeNC₅H₄NⁱPr)Y[I[N(TMS)₂]₂, 7.9.

<table>
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<th>Property</th>
<th>Value</th>
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<tbody>
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<td>Empirical formula</td>
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<tr>
<td>Formula weight</td>
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<td>Temperature</td>
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<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
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<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
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<td>Space group</td>
<td>P2(1)2(1)2(1)</td>
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<td>Unit cell dimensions</td>
<td>a = 12.4064(17) Å, [\alpha=90^\circ]</td>
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<tr>
<td></td>
<td>b = 16.307(2) Å, [\beta=90^\circ]</td>
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<tr>
<td></td>
<td>c = 16.623(2) Å, [\gamma=90^\circ]</td>
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<tr>
<td>Volume</td>
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<td>Z</td>
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<td>Density (calculated)</td>
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<td>F(000)</td>
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<td>Crystal size</td>
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<td>37642</td>
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<td>Completeness to theta = 27.50°</td>
<td>99.2 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.6034 and 0.5402</td>
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<td>Refinement method</td>
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<td>Goodness-of-fit on F²</td>
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Chapter 7 – Future Work and Conclusions

Final R indices [I>2sigma(I)]  \[ R_1 = 0.0355, \text{ wR}^2 = 0.0794 \]
R indices (all data) \[ R_1 = 0.0487, \text{ wR}^2 = 0.0843 \]
Absolute structure parameter \[ -0.027(5) \]
Largest diff. peak and hole \[ 1.139 \text{ and } -0.440 \text{ e.Å}^{-3} \]
Chapter 7 – Future Work and Conclusions

7.8 References


References begin on page 262


(38) SMART, Molecular analysis research tool; Bruker AXS Inc. Madison, WI, 2001.
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(39) SAINTPlus, Data reduction and correction program; Bruker AXS Inc.: Madison, WI, 2001.


Appendix
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Jillian Hatnean

July 8, 2011
Appendix


I, Jacob Matthews, give Meghan Doster permission to use the results and ideas published in the paper entitled “A mechanistic investigation of carbon-hydrogen bond stannylation: synthesis and characterization of nickel catalysts” in her doctoral dissertation. I synthesized and characterized the active catalyst complex and conducted other mechanistic investigation under the supervision of Dr. Samuel A. Johnson.

Jacob Matthews

October 31, 2012

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Manar Shoshani
Oct 31, 2012
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