Cooperative Bond Activation by an Electron-Deficient Pentanuclear Nickel Hydride Cluster

Manar Matti Shoshani
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Cooperative Bond Activation by an Electron-Deficient Pentanuclear Nickel Hydride Cluster

By
Manar Matti Shoshani

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

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Cooperative Bond Activation by an Electron-Deficient Pentanuclear Nickel Hydride Cluster

by

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Declaration of Co-Authorship/Previous Publication

I. Declaration of Co-Authorship

I hereby declare that this thesis incorporates material that is result of joint research, as follows: this thesis contains eight chapters, out of which four chapters have been previously published in peer-reviewed journals. Chapter two contains results published from the full paper “Facile Deep and Ultradeep Hydrodesulfurization by the [(tPr3P)Ni]3H6 Cluster Compared to Mononuclear Ni Sources.” Shoshani, M; Johnson; S. A. Inorganic Chemistry 2015, 54, 11977-11985. Chapter three contains results from the communication “Cooperative carbon-atom abstraction from alkenes in the core of a pentanuclear nickel cluster.” Shoshani, M. M.; Johnson, S. A.; Nature Chemistry 2017, 9 1282-1285. Chapter four contains results published from the full paper "Synthesis of Surface-Analogue Square-Planar Tetranuclear Nickel Hydride Clusters and Bonding to μ4-NR,-O and-BH Ligands."Shoshani, M. M.; Beck, R.; Wang, X.; McLaughlin, M. J.; Johnson, S. A. Inorganic Chemistry 2018, 57, 2438-2446 . Chapter five contains results published from the full paper “Mechanistic Insight into H/D Exchange by a Pentanuclear Ni–H Cluster and Synthesis and Characterization of Structural Analogue Structures of Potential Intermediates.” Shoshani, M. M.; Liu, J.; Johnson, S. A. Organometallics 2017, 37, 116-126. I acknowledge my supervisor as a co-author in this work as he made a significant contribution to the editing and preparation of these manuscripts. I acknowledge that other
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Abstract

This dissertation focuses on the activation and functionalization of inert-bonds by harnessing cooperativity between metals. Transition metal clusters can serve as molecular models for the poorly-understood solid-state catalysts used in most industrial scale processes. An understanding of how adjacent metals act together to coordinate substrates, cleave traditionally unreactive bonds and reform new skeletal bonds could inspire new classes of catalysts, both heterogeneous and molecular, that are able to utilize abundant and currently unusable species as chemical precursors.

The pentanuclear Ni hydride cluster \([\text{(iPr}_3\text{P})\text{Ni}]_5\text{H}_6\) is an electron-deficient nido cluster that facilitates ultra-deep hydrodesulfurization by cleaving both C−S bonds of 4,6 dimethyl dibenzothiophene and forming 3,3′-dimethylbiphenyl and the tetranuclear Ni sulfide cluster \([\text{(iPr}_3\text{P})\text{NiH}]_4(\mu_4\text{-S})\). The reaction of \([\text{(iPr}_3\text{P})_2\text{Ni}]_2(\mu_5\text{-N}_2)\) with 4,6-dimethyl dibenzothiophene gave no C−S activation product, which demonstrates the importance of intact cluster cooperativity in the activation this highly unreactive thiophene by \([\text{(iPr}_3\text{P})\text{Ni}]_5\text{H}_6\).

The pentanuclear Ni cluster \([\text{(iPr}_3\text{P})\text{Ni}]_5\text{H}_6\) undergoes CC and CH bond cleavage along with CH bond formation upon reaction with ethylene at −30 °C to make the pentanuclear Ni-carbide cluster \([\text{(iPr}_3\text{P})\text{Ni}]_5\text{H}_4(\mu_5\text{-C})\), along with ethane and methane. The process is highly selective as the reaction proceeds in high yields in the presence of various functional group containing molecules. Isolated intermediates obtained from reacting \([\text{(iPr}_3\text{P})\text{Ni}]_5\text{H}_6\) with styrene and isobutylene feature a triple CH bond activated organic substrate bound to all 5 Ni centers. These intermediates give direct insight into the cooperative involvement of all five Ni centres in the binding and activation of these
typically unreactive bonds. The reaction may give insight into the ability of Ni (1 1 1) surfaces to abstract C atoms from hydrocarbons selectivity at the step sites; this process is used to catalytically generate graphene on Ni metal surfaces.

Main group elements other than C can also serve as central bridging ligands supporting Ni clusters. Reactions of [(iPr3P)Ni]5H6 resulted in the formation of square plane or tetrahedral clusters Ni clusters that incorporate μ4−O, μ4−NCH2Ph, μ2−Cl, and μ4−BH. A study of H/D exchange with [(iPr3P)Ni]5H6 and unactivated arenes such as deuterated benzene revealed a first order dependence of rate on [(iPr3P)Ni]3H6 and arene, and first-order inhibition by P3Pr3. Structural analogues of likely intermediates were synthesized to give insight into this cooperative reactivity.

The potential for [(iPr3P)Ni]3H6 to facilitate C−O bond cleavage was studied using vinyl ethers. These reactions demonstrate the ability of these clusters to engage in cooperative CC, C(sp3)O, C(sp2)O, and CH bond cleavages with minimal energy barriers. The selectivity in C(sp3)O versus C(sp2)O C−O bond cleavage is dependent on the group attached to the oxygen, with tBu causing C(sp3)O bond activation and SiMe3 and 1-Ad causing C(sp2)O bond cleavage.

Functionalization of the carbide ligand in [(iPr3P)Ni]3H4(μ5−C) could allow for the use of ethylene as a catalytic C1 transfer reagent. However, reactivity studies with in [(iPr3P)Ni]3H4(μ5−C) demonstrate the utility of the carbide as an anchor-like ancillary ligand, which allows to access new cluster geometries and core oxidation states with the potential for improved stability under common catalytic conditions compared to [(iPr3P)Ni]3H6.
Dedicated to my father:

Matti Shaya Shoshani
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I wouldn’t be the man I am today if it was not for my father. He was my inspiration and in many ways, my idol. Dedicating this thesis to you was a no-brainer.
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# Glossary of Terms

The following abbreviations, most of which are commonly found in the literature, are used in this thesis.

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<td>BArF$_{26}$</td>
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<td>bond dissociation energy</td>
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<td>$\Delta S^\ddagger$</td>
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s  singlet

$sp^n$  n-hybridized $s$ and $p$ orbitals

syst  system

t  triplet or time

td  triplet of doublets

tm  triplet of multiplets

TMDSO  tetramethyldisiloxane

tq  triplet of quartets

T  temperature in Kelvin or °C

THF  tetrahydrofuran

$^{205}$Tl  thallium-205

$U(eq)$  equivalent isotropic displacement parameter (one third of the trace of the orthogonalized $U_{ij}$ tensor)

V  unit cell volume

vt  virtual triplets

$W_{1/2}$  width at half height

X  halide substituent

Z  asymmetric units per unit cell (X-ray crystallography) or $trans$ (opposite side)

$\alpha$  atom in the alpha position or angle label (X-ray crystallography)

$\beta$  atom in the beta position or angle label (X-ray crystallography)

$\gamma$  angle label (X-ray crystallography)

$\delta$  chemical shift in ppm
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Chapter 1 - Transition Metal Clusters Geared Towards Cooperative Inert-Bond Activation

1.1 General Introduction

The conversion of cheap and abundant hydrocarbons from crude oil distillates and potential biofuel sources to more commercially practical chemicals represents one of the greatest challenges facing chemists.\textsuperscript{1-13} The target products of these hydrocarbon-based
transformations have uses in natural product synthesis and liquid fuel formations.\textsuperscript{14-17} The starting materials bear unreactive CH, CC, and CO bonds, which make chemical transformation of these species difficult. Though organic transformations have been reported which can functionalize inert bonds, the requirement for large amounts of high energy reagents, and lack of selectivity renders many of these methods ineffective.\textsuperscript{5,10} Less energy intensive inert bond activation and functionalization has been realized through the design of transition metal catalysts.\textsuperscript{4,10} The use of soluble transition metal catalysts offers the benefit of milder conditions and higher selectivities in bond activation.\textsuperscript{18} In addition, soluble single-site transition metal-mediated transformations are amenable to mechanistic studies and can be tuned and improved via a rational approach.\textsuperscript{19-20}

A plethora of transition metals have been reported to facilitate various inert bond activations. The early transition metal centres, while capable of bond activations, tend to have a hard and oxophillic nature, which creates a thermodynamic sink when exposed to molecules containing N or O donors, and significantly hinders functional group tolerance.\textsuperscript{5} Complexes of the late 2\textsuperscript{nd} and 3\textsuperscript{rd} row transition metal centres, including Pd,\textsuperscript{6} Pt,\textsuperscript{21-22} Ir,\textsuperscript{23-24} and Rh,\textsuperscript{25-27} are generally less oxophillic and have a variety of accessible oxidation states which aid in facilitating a variety of transformation. Though a plethora of reports outlining complexes of the 2\textsuperscript{nd} and 3\textsuperscript{rd} row facilitating notoriously difficult bond transformations, these metals are considered precious, which hinders the efficiency of the processes.\textsuperscript{28} Complexes of the late 1\textsuperscript{st} row transition metal centres are significantly cheaper in comparison to their heavier congeners. Though there are several examples of Ni-mediated transformations,\textsuperscript{29-31} the scope of activation is relatively limited and generally requires
Transition Metal Clusters Geared Towards Cooperative Inert-Bond Activation

Chapter 1

Preactivation of substrates and high temperatures. A potential reason for this is the strength of the corresponding M−C bond formed, compared to the heavier congeners.9,32-33

Heterogeneous catalysts are widely utilized in industry to perform transformations on multi-ton scales daily.34 Heterogeneous catalysts such as metal surfaces have been postulated to be highly active due to having metal centres in close proximity which allows M-M cooperativity to facilitate difficult bond transformations.35 The main issue present in heterogeneous catalysis is a complete lack of selectivity in activation as well as difficulty in tuning and characterizing catalysts.36-37 Transition metal clusters can potentially serve as a hybrid to both avenues of catalysts, where M-M cooperative bond activations can still be achieved, yet the solubility of these complexes allow mechanistic studies to determine how bond transformations are facilitated.38-39 Transition metal clusters and polynuclear species in general have more recently been used to mimic cofactors in multimetallic enzymes such as the [MnO] cofactor in Photosystem II40-42 and the [FeMo] cofactor in Nitrogenase43-45 in attempts to harness nature’s ability to catalytically oxidize water and convert N₂ to ammonia under mild conditions.

This dissertation will focus on the ability of an electron-deficient pentanuclear Ni hydride cluster to both stoichiometrically and catalytically activate inert bonds at temperatures of 298 K or lower. Studies exploring cooperative CH, CS, CO, and CC bond activations are discussed and mechanistic studies were conducted to provide evidence that the transformations facilitated were a direct result of M-M cooperativity of the cluster. Additionally, reactivity studies of a pentanuclear Ni carbide cluster were explored and provided evidence of the interstitial carbide allowing the small clusters to accommodate
various oxidation states, electron counts, and cluster geometries. The ability for the interstitial carbon atom to allow the cluster to react with a variety of different substrates without decomposing draws comparison to the nitrogen functionalizing [FeMo] cofactor in \textit{Nitrogenase}, which exhibits a multi-coordinate carbide.

\section*{1.2 Overview of Ni Chemistry}

Ni is a late-first row transition metal centre with 10 $d$ electrons and significantly cheaper and more abundant than its heavier congeners. Due to Ni being considered a “soft” metal, it preferentially binds to soft ligands such as phosphines and carbon monoxide.\cite{46} Binding to ligands that can act as $\pi$-acceptors, such as CO, often stabilize Ni(0) complexes due to the excess $d$-electrons present, often rendering complexes of CO less reactive.

Soluble Ni complexes exist in a variety of oxidation states from Ni(0) – Ni(IV), with the most common being the Ni(II) and Ni(0) oxidation states. Ni(I) species are also quite common and take on a variety of geometries, including trigonal planar.\cite{47,48} Ni(III) and Ni(IV) are less common oxidation states for Ni complexes and many reported examples of the isolated species are cationic complexes.\cite{49,50,51,52} The most common geometry for organometallic Ni(II) complexes is square planar;\cite{53} however, several other geometries have been reported including trigonal planar, trigonal bipyramidal, octahedral and tetrahedral. Ni(0) complexes often take on a tetrahedral or trigonal planar geometry, especially in the presence of alkene ligands,\cite{48,54} some examples of the common geometries of the monometallic Ni species are shown in Figure 1.1.
Figure 1.1. Common geometries for monometallic complexes of Ni(0), Ni(I), and Ni(II) (L=neutral ligand)

Both Ni nanoparticles and Ni surfaces are used as heterogeneous catalysts in industrial processes such as the Fischer-Tropsch process,\textsuperscript{55} among others.\textsuperscript{56} However, their use in industrial homogenous catalysis is significantly more limited. Thermodynamic and kinetic challenges in a variety of bond activations exist, including the relatively weak Ni-C bond formed in comparison to Pd-C and Pt-C bonds.\textsuperscript{33} Though the ability for Ni centres to be stable in a variety of oxidation states makes Ni complexes ideal candidates for oxidative addition and reductive elimination mechanisms, the kinetic barrier in the activation steps for these transformations serve as a hindrance towards their use as catalysts for inert-bond functionalization. In addition, the propensity of stable Ni(I) species forming allows 1-electron transformations to proceed, which can form a variety of side products and in many cases, decomposes the catalyst.

1.3 Inert Bond Activation

1.3.1 General Overview

Numerous examples of inert-bond activations facilitated by 2\textsuperscript{nd} and 3\textsuperscript{rd} row late transition metal centres have been reported.\textsuperscript{10} Complexes of Pd are commonly used as
catalysts in a variety of cross coupling reactions, the discovery of which was awarded the Nobel prize in chemistry in 2005.\textsuperscript{57} Despite the discovery occurring nearly half-a-century ago, research in this area continues to flourish in order to expand the scope of species and optimize catalysis.\textsuperscript{58-59} Yet, the utility of the 2\textsuperscript{nd} and 3\textsuperscript{rd} row transition metals are not limited to cross coupling, which typically involved activated substrates such as aryl electrophiles, the role of the metals in functionalizing unactivated species is extensively reported.\textsuperscript{6, 60-61}

One of the reasons these complexes are used is due to the metals lacking oxophillic character, which greatly increases functional group tolerance and thus significantly increases scope of reactivity. In addition, the 2\textsuperscript{nd} and 3\textsuperscript{rd} row late transition metal complexes generally have a large variance of stable oxidation states reported, which is imperative for the common inert bond activation mechanism, oxidative addition.\textsuperscript{62-63} These conditions also apply for Ni complexes, as low-oxidation state Ni complexes are not very oxophillic, and Ni(0) – Ni(IV) oxidation states are known. However, the Ni-C bond formed through activation of C-R bonds is generally considered quite weak potentially due to poor orbital overlap between the 3\textit{d} orbital of Ni and the sp hybrid orbital of carbon. Despite this, a variety of Ni mediated inert-bond activations have been reported in the literature, among them CS,\textsuperscript{64} CH,\textsuperscript{7} CC\textsuperscript{65}, and CO\textsuperscript{66} bond activations.

\subsection*{1.3.2 C–S Bond Activations}

The presence of thiophene based compounds in petroleum feedstocks pose an environmental hazard as the combustion of these species convert them to harmful sulfur oxides. Though most C–S bonds are prone to classic oxidative addition, the thiophenes found in petroleum feedstocks are quite bulky, often containing dibenzo groups with bulky substituents present in the 4 and 6 sites, which render these bonds less reactive.\textsuperscript{67} The
presence of these bulky dibenzothiophenes has led researchers to focus efforts towards finding methods to extrude the sulfur and replace them with hydrogens in a process known as hydrodesulfurization. As a measure of transition metal’s capability to remove sulfur from these species three model compounds are commonly examined as a measure of degree of desulfurizing abilities. The three compounds are dibenzothiophene, 4-methyl dibenzothiophene, and 4,6 dimethyl dibenzothiophene; the processes of removing sulfur from these complexes are known as hydrodesulfurization, deep hydrodesulfurization, and ultra-deep hydrodesulfurization, respectively, as shown in Scheme 1.1.

**Scheme 1.1**: The three model compounds used to measure desulfurization ability, dibenzothiophene, 4-methyl dibenzothiophene, and 4,6 dimethyl dibenzothiophene, reacting with a metal and H₂ to produce the corresponding biphenyl product

### 1.3.3 CC Bond Activations

The activation of CC bonds represents one of the most difficult transformations in synthetic chemistry. One of the potential reasons is that breaking the CC bond in classic

*References begin on page 39*
oxidative addition mechanisms require the formation of two M-C bonds, which is likely a high-energy product of activation due to the directionality of the 2p orbitals of the carbon atom. Both cleavage of CC bonds and the microscope reverse, formation of CC bonds, are highly useful transformations, due to the abundance of alkanes, alkenes, and aromatics in crude oil distillates. Despite heavy emphasis on expanding the scope of CC bond activations and functionalizations, the area is still an emerging field. One of the first examples of soluble transition metal species cleaving CC bonds was reported nearly half a century ago by Eisch et al.\textsuperscript{68} and later work was further expanded by Jones,\textsuperscript{69-70} as shown in Scheme 1.2.

![Scheme 1.2](image-url)

**Scheme 1.2.** A) CC bond cleavage of biphenylene by Ni(PEt)\textsubscript{4} which oxidatively adds the CC bond to form a Ni(II) metallocycle. B) Ni mediated reversible CC bond cleavage of benzonitrile producing a Ni(II) square planar complex.

The example outlines the use of a Ni(0) source oxidatively adding the CC bond of the 4-membered ring in biphenylene to produce the Ni(II) metallocycle. Though this example

*References begin on page 39*
outlined an unprecedented transformation at the time, it is obvious that the thermodynamic driving force for this reaction lies in the relief of ring strain achieved by converting to a metallocycle. Jones followed up on the work of Eisch by expanding the biphenylene\textsuperscript{71} cleavages to a number of mid-late transition metals as well as outlining examples of cleaving CC bonds is alkyl\textsuperscript{70} and aryl\textsuperscript{3} nitriles, including reversible cleavage of benzonitrile using Ni(0) as shown in Scheme 1.2

One of the drawbacks of the listed examples is that they require preactivation of a substrate to be susceptible to activation. Milstein reported one of the first examples of a “unactivated” CC bond cleavage by a soluble transition metal complex. The reaction utilizes a specialized pincer ligand that forced a Rh centre in close proximity to an aromatic-\(sp^3\) CC bond and undergoes cleavage at 90 °C as shown in Scheme 1.3.\textsuperscript{72} The organic product made from CC bond cleavage of this substrate, is methane, producing methane as a result of CC bond cleavage offers mechanistic insight to the microscopic reverse, using methane as a C\(_1\) source for carbon-carbon bond.

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {\text{H}_3\text{C}};
\node (b) at (1,0) {\text{PPh}_2};
\node (c) at (2,0) {\text{CH}_3};
\node (d) at (3,0) {\text{PPh}_2};
\node (e) at (4,0) {\text{H}_3\text{C}};
\node (f) at (5,0) {\text{PPh}_2};
\node (g) at (0,-1) {\text{H}_3\text{C}};
\node (h) at (1,-1) {\text{PPh}_2};
\node (i) at (2,-1) {\text{PPh}_2};
\draw (a) -- (b);
\draw (b) -- (c);
\draw (c) -- (d);
\draw (d) -- (e);
\draw (e) -- (f);
\draw (g) -- (h);
\draw (h) -- (i);
\node (j) at (0,1) {\text{H}_3\text{C}};
\node (k) at (1,1) {\text{PPh}_2};
\node (l) at (2,1) {\text{Rh}};
\node (m) at (3,1) {\text{PPh}_3};
\node (n) at (4,1) {\text{H}_3\text{C}};
\node (o) at (5,1) {\text{PPh}_2};
\draw (j) -- (k);
\draw (k) -- (l);
\draw (l) -- (m);
\draw (m) -- (n);
\draw (n) -- (o);
\node (p) at (0,2) {\text{H}_3\text{C}};
\node (q) at (1,2) {\text{PPh}_2};
\node (r) at (2,2) {\text{Rh}};
\node (s) at (3,2) {\text{PPh}_3};
\node (t) at (4,2) {\text{H}_3\text{C}};
\node (u) at (5,2) {\text{PPh}_2};
\draw (p) -- (q);
\draw (q) -- (r);
\draw (r) -- (s);
\draw (s) -- (t);
\draw (t) -- (u);
\node (v) at (0.5,0.5) {\text{HRh(PPh}_3)_4};
\node (w) at (0.5,-0.5) {\text{-3 PPh}_3\text{-H}_2};
\node (x) at (3.5,0.5) {\text{H}_2\text{Rh(PPh}_3)_3};
\node (y) at (3.5,-0.5) {\text{90 °C -CH}_4};
\end{tikzpicture}
\end{center}

**Scheme 1.3.** Milstein’s initial report of Rh mediated unactivated CC bond cleavage of a chelating phosphine ligand. The Rh centre initially CH activated the methyl site upon binding to the phosphines. Upon heating, the CC bond is cleaved forming a Rh-C bond to the phenyl ring as well as an equivalent of methane.
The design of a pincer ligand to introduce strain and cleave the CC bond is an clever strategy to force an inert-bond activation, but also severely hinders the scope of substrates available for further functionalization. Cleaving or forming CC bonds of simple hydrocarbons is still a process that soluble transition metal complexes struggle reacting with, especially monometallic species.

1.3.4 H/D Isotope Exchange

There has been a rising need for selective isotope labelling at carbon centres to serve as radiotracers in drug development\(^7^3\) as well as internal standards for mass spectrometry\(^7^4\) and isotopic labelling experiments for mechanistic studies.\(^7^4\) High temperatures along with a D\(_2\)O source are known to incorporate deuterium into some activated and non-activated aromatic species, but very little regioselectivity is obtained, an example of which is shown in Scheme 1.4.\(^7^5\)

![Scheme 1.4](image)

**Scheme 1.4.** H/D exchange using D\(_2\)O without the presence of a catalyst and using high heat shows limited and non-selective deuterium incorporation into the substituted pyridine compound.

Acid catalyzed H/D exchange is a popular choice for incorporating deuterium into molecules as it can use D\(_2\)O, or C\(_6\)D\(_6\) as the source of deuterium and proceeds under more mild conditions; however, it generally relies of the site being activated towards exchange and can also lack selectivity, as can be seen in the example shown in Scheme 1.5a.\(^7^6\) Base-
catalyzed H/D exchange has also been explored extensively and shows high selectivity for sites with acidic C−H bonds, especially in carbonyl containing compounds, as shown in Scheme 1.5b. The high selectivity is sought after, but the lack of scope and requirement for acidic CH sites limits the utility of the base-catalyzed methods.

Heterogeneous catalysts have also been reported as catalysts for H/D exchange, especially late transition metals such as Ni, Co, Pd, and Rh. Heterogeneous catalysts have the benefit of not requiring significant efforts for purification as the catalysts are insoluble. An additional benefit is being able to use a variety of deuterium sources such as D₂O, D₂, and C₆D₆. However, the common issue of poor selectivity along with, dehalogenation, hydrogenation, and racemization become prevalent issues when dealing with heterogeneous catalysts. The activity of the catalysts, especially with aromatic systems is quite high, as shown in the examples listed in Scheme 1.5c. Scheme 1.5c also shows the ability of these catalysts to exchange effectively with the benzylic sp³ C−H sites. Early mechanistic studies outlined, that preactivating Pd catalysts with H₂ allowed for the increased activity of the catalysts, specifically towards the benzyl sites. Although, elucidating that preactivating the catalyst is crucial for activity, further mechanistic studies are severely limited due to insolvability of the catalysts, an area where homogenous catalysts thrive.
Scheme 1.5. A) Acid catalyzed H/D exchange showing the ability to incorporate deuterium into aromatic CH sites using D₂O with deuterated phosphoric acid serving as the catalyst. The transformation here is done at room temperature but does not exchange with the sp³ CH bonds. B) Base-catalyzed H/D exchange using NEt³ as the catalyst and D₂O as the source to exchange with the acidic CH bond site. C) H/D exchange catalyzed on heterogeneous bed of Pd/C. High heat is required and minimal selectivity is obtained, however non-activated sp³ CH bonds are activated. Also, the compound is slightly deoxygenated on the catalyst bed.
In addition to the ability to obtain detailed mechanistic insight from soluble transition metal mediated H/D exchange processes, the mild reaction conditions required, and the high functional group tolerance offer a very appealing alternative to the H/D exchange methods mentioned above. To add to this, good regioselectivity has been reported with a variety of compounds, both aromatic and aliphatic. The late 2nd and 3rd row transition metals are popular choice for H/D exchange catalyst, likely due to many of the mechanisms of H/D exchange relying on oxidative addition of CH bonds and requiring functional group tolerance. Fels and coworkers reported highly selective catalytic H/D exchange using Ir(I) for both aliphatic and aromatic carboxylic acids as shown in Scheme 1.6. 79

![Scheme 1.6](image)

**Scheme 1.6.** Fels reported examples of selective H/D exchange using an Ir(COD)acac catalyst that gives exchange with both aromatic and olefinic CH bonds under relatively mild conditions. The carboxylic acid group is necessary for coordination. (COD = 1,5 cyclooctadiene, acac = acetylacetonate)

Though these examples feature selectivity, the carboxylic acid group is necessary for the exchange to proceed, severely hindering the scope. Bergman also explored Ir catalyzed H/D exchange using Ir(III) metal complexes and tackled H/D exchange in significantly less
activated species, such as diethyl ether and toluene, as shown in Scheme 1.7.80-81 These transformations are very impressive, and the reaction conditions are quite mild; however, the minimal selectivity observed, and the requirement to use expensive Ir metal to catalyze this reaction leave room for improvement.

Scheme 1.7. Ir catalyzed H/D exchange of unactivated substrates such as toluene and diethyl ether. Relatively mild conditions and impressive bond activation in general; however, reaction is non-selective

Over the last decade Chirik and coworkers have developed powerful iron catalysts with redox active ligands that are capable of mild and regioselective isotope labelling.82 Using D₂ as the deuterium source they have reported deuteration as well as tritiation of a variety of pharmaceuticals. Their use of an iron catalyst with a redox-active ligand has proven very successful, the catalyst has also been subject to mechanistic studies to gain insight towards the transformation.

1.3.5 C–O Bond Activations

The potential to access the abundant and currently under-utilized lignocellulosic biomass towards biofuels has brought a lot of attention to C–O bond activation and
functionalization. Lignin is primarily composed of $sp^2$ and $sp^3$ hybridized carbon, along with oxygen, and hydrogen, with many of the bonds built by etheric linkages. The relative strength and stability of these linkages is what makes C–O bond activation a challenging transformation. The use of C–O functional group for cross-coupling also offers an appealing use in cross-coupling chemistry. Various transition metal complexes have been reported to facilitate $sp^2$ C–O bond cleavages, including catalytic examples by Ni(0) and Ni(II) sources in the presence of phosphine ligands. Wenkert outlined one of the first examples using $\text{Cl}_2\text{Ni}(\text{PPh}_3)_2$ as a catalyst in the presence of aryl ethers to cleave the $sp^2$ hybridized C–O bonds as shown in Scheme 1.8.

![Scheme 1.8](image)

**Scheme 1.8.** Ni catalyzed C–O bond cleavage of 2-methoxynapthalene. Reaction proceeds under relatively mild temperatures, but requires a Grignard reagent to proceed.

This initial result inspired several other reports using Ni catalysts in order to increase the scope and produce C–O bond activation products with substrates significantly milder than Grignard reagents. This has led to many breakthroughs in the field, among them was Hartwig’s recent report of nickel catalyzed hydrogenolysis of a series of substituted ethers using Ni(COD)$_2$ a carbene ligand and an atmosphere of H$_2$ in the presence of base, as shown in Scheme 1.9a. This report outlined how a change of ancillary ligand had a dramatic effect, as failed conversions of C–O bond cleavage were reported for similar conditions with the use of PCy$_3$ in lieu of a carbene ligand, shown in Scheme
1.9b. However, Ruben Martin and coworkers reported the use of Ni(COD)$_2$ and PCy$_3$ to cleave the C–O bond in a series of aromatic ethers, with the use of silanes as the source of hydrogen as shown in Scheme 1.9c.$^{87}$

![Scheme 1.9](image)

**Scheme 1.9.** A) Hartwig’s report of highly active *in situ* generated catalyst from Ni(0) and a carbene ligand that facilitates catalytic diphenyl ether hydrogenolysis with the addition of H$_2$ to produce benzene and phenol at 120 °C. B) The same Hartwig report shows that under identical conditions with the exception of using PCy$_3$ in lieu of the carbene ligand, only decomposition products of the phosphine are produced. C) Ruben Martin’s report of CO bond cleavage of 2-methoxynaphthalene using Ni(0) and PCy$_3$ with tetramethyldisiloxane as the source of hydrogen.
A common theme with the reported examples is the lack of well-defined complexes facilitating the bond activation of interest. Generally, an *in-situ* catalyst is produced, which hinders the mechanistic insight that can be obtained. For example, in the examples outlined in Scheme 1.9, two equivalents of ligand with respect to one equivalent of Ni are used, under the assumption mononuclear NiL₂ species facilitate the reactivity; however, recent work by Martin suggested that dinuclear Ni(I) species are formed under his C–O bond activation conditions. The presence of these dinuclear species suggests that, an alternate mechanism with di or perhaps polynuclear species may be present.

### 1.4 Transition Metal Clusters

#### 1.4.1 General Overview

Transition metal clusters have been reported in the literature for several decades and extensive research in the field has led to thousands of crystal structures of these clusters reported in the Cambridge structural database. The size of these reported clusters ranges from bearing three metal centres to hundreds, bridging the gap to solid state chemistry.

#### 1.4.2 Transition Metal Cluster Geometries and Electron Counting Rules

Transition metal clusters to come in a variety of geometries and incorporating a plethora of metal centres and ligands. The vast majority tend to fall under classifications outlined by the pioneers of cluster chemistry, Wade and Mingos. Though much of their work was with main group clusters, specifically boranes and carboranes, similarities between the main group and transition metal clusters allowed extension of the basic principles. They conducted extensive studies into the bonding patterns of various cluster geometries including closed polyhedrons, known as closo clusters, as well as stable clusters.
missing one or two vertices from being closed polyhedrons, knows as *nido* and *arachno* clusters.90-92

Lauher conducted extensive studies analyzing the stability of these clusters using a molecular orbital study.93 Assuming 9 MOs for each metal centre, the total number of metal based orbitals are taken into consideration, but the High Lying Antibonding Orbitals (HLAO) are subtracted from the total orbitals to obtain the number of cluster valence molecular orbitals (CVMO). Through these studies he determined for a range of cluster geometries the number of molecular orbitals that would need to be occupied in order for the species to be stable. The CVMO’s determined for a variety of geometries are shown in Table 1.1.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Vertices</th>
<th>Total Metal Orbitals (9 x Vertices)</th>
<th>High lying Anitbonding Orbitals</th>
<th>CVMO’s</th>
<th>CVE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer</td>
<td>1</td>
<td>9</td>
<td>0</td>
<td>9</td>
<td>18</td>
</tr>
<tr>
<td>Dimer</td>
<td>2</td>
<td>18</td>
<td>1</td>
<td>17</td>
<td>34</td>
</tr>
<tr>
<td>Trimer</td>
<td>3</td>
<td>27</td>
<td>3</td>
<td>24</td>
<td>48</td>
</tr>
<tr>
<td>Tetrahedron</td>
<td>4</td>
<td>36</td>
<td>6</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>Butterfly</td>
<td>4</td>
<td>36</td>
<td>5</td>
<td>31</td>
<td>62</td>
</tr>
<tr>
<td>Square Plane</td>
<td>4</td>
<td>36</td>
<td>4</td>
<td>32</td>
<td>64</td>
</tr>
<tr>
<td>Trigonal Bipyramid</td>
<td>5</td>
<td>45</td>
<td>9</td>
<td>36</td>
<td>72</td>
</tr>
</tbody>
</table>
Table 1.1. Lauher’s analysis on selected cluster geometries outlining how many orbitals, for each geometry, are considered too high energy for stable occupation, as well as the number of orbitals available for stable occupation (CVMO) and the number of cluster valence electrons expected for various geometries (CVE).

<table>
<thead>
<tr>
<th>Geometry</th>
<th>High Energy</th>
<th>Available</th>
<th>Stable</th>
<th>CVE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square Pyramid</td>
<td>5</td>
<td>45</td>
<td>8</td>
<td>37</td>
</tr>
<tr>
<td>Octahedron</td>
<td>6</td>
<td>54</td>
<td>12</td>
<td>43</td>
</tr>
</tbody>
</table>

Lauher conducted molecular orbital studies and compared clusters with the same nuclearity that took on different geometries. An example is shown in Figure 1.2. The comparison here outlines how the CVE changes for M₄ clusters with either tetrahedron, butterfly, or square plane geometries. The butterfly geometry lowers the energy of one of the previously HLAO, and it now becomes a CVMO giving a CVE of 62 electrons. Additionally, the square plane cluster geometry lowers the energy of the HLAO of the butterfly geometry to give a CVE of 64 electrons. A series of different clusters with similar nuclearity were compared and this pioneering study has proven correct for the vast majority of transition metal clusters reported in literature, examples of which are shown in Figure 1.3.⁹⁴
Figure 1.2: A molecular orbital figure adapted from Lauher’s seminal study showing how clusters of the same nuclearity (M₄) with different geometries can have different CVE counts, as a HLAO become a CVMO for both geometries, from left to right

A separate study by Lauher was dedicated to exploring reasoning for the lack of square plane transition metal clusters, as at the time the unstable, Os₄(CO)₁₆, was the only reported example. The study was of interest due to the several examples of square plane clusters existing for main group clusters. A molecular orbital study showed that, an essentially negligible steric influence was present, but an orbital symmetry problem is present, which allows no more than two in-plane metal-metal bonds.⁹⁵
Figure 1.3. Reported clusters of different geometries and nuclearities that follow the predicted CVE counts suggested by Lauher.

Lauher’s seminal computational study used bare clusters of Rh and were based on the assumption that stable monometallic transition metal species require 18 electrons to achieve stability. However, a variety of stable electron counts for mononuclear transition metals exist, among them 14 electron Au(I) species as well as group 10 M$^{2+}$ 16 electron species, which are known to form stable square-planar geometries. In Lauher’s seminal study, he outlines exceptions to the predicted CVE counts and specifically mentions that cluster of Pd and Pt metal centres may break the predicted counts and geometries often.

### 1.4.3 Mixed Transition Metal-Main Group Element Clusters

Clusters in no way are exclusive to transition metal species, their formation for main group elements are well-known, a few examples being the widely utilized tetrahedral $P_4$ cluster, as well as the polyhedral borane and carborane clusters. Naturally, the combination of the main group components and transition metals into clusters has been explored extensively. A plethora of examples of mixed transition metal-main group
element clusters exist, including many examples with boron and phosphorus incorporated into a transition metal cluster core. Fenske provided a family of examples which included several metal sulfide bearing clusters among many other main group elements from groups 5 and 6. The majority of the reported examples use late transition metals such as Ni, Cu, and Ag.

More recently, Kubiak has demonstrated a new class of mixed transition metal-main group element clusters composed of 3 Ni centres with a halide bridging all 3 Ni centres as well as an additional ligand which bridged the Ni centres, either an X ligand for neutral species, or an L ligand for a cationic cluster, a few of which are shown in Figure 1.4. Kubiak has demonstrated interesting properties of these clusters including their redox potential as well as their capabilities in electrochemical CO$_2$ reduction.

![Figure 1.4](image)

**Figure 1.4.** Ni clusters with triply bridged iodide ligands and various main group components bound on the top of the cluster. These class of Ni clusters are electron precise.
Though the CVE count of these trimers is 48 electrons, which is predicted based on Lauher’s work, alternative counting schemes have been described considering the main group elements as a vertex instead of a bridging ligand. This could potentially classify the cluster as a trigonal bipyramidal cluster instead of the described trimer. It should be noted that the classification of main group components as vertices can alter both the expected electron count as well as the observed CVE count. In many occasions these alternate classifications are used to justify electron counts that are not in agreement with expected electron counts.

1.5 Cooperative Inert Bond Activation

1.5.1 General Overview

The idea of using transition metal clusters for inert-bond activation was proposed several decades ago, when reports of isolated metal clusters started to crowd the literature. Seeing the success that monometallic species had in bond activation and catalysis led chemists to the notion that generating complexes which bear multiple metal centres proximal to one another could result in highly difficult bond activations. The idea that these metal clusters could serve as hybrids between soluble metal complexes amenable to mechanistic studies, and reactive metal surfaces that can activate and cleave known unreactive substrates, also appealed to multiple research groups.98

1.5.2 Study and Reactivity of Hydride-Bearing, Electron-Deficient Transition Metal Clusters

Despite the continued growth of transition metal clusters in the literature, most examples offered little more than structural intrigue. The continued trend seemed to be that transition metal clusters followed the guidelines set out by Lauher as well as Wade and
Mingos, and these clusters, which had the expected electron counts, had high thermal stability and modest reactivity. The majority of transition metal clusters fall under the classification of late metals with soft ligands such as CO or high oxidation state early metals with harder ligands such as halides. However, more recently transition metal clusters composed of early metals, hydrides and η⁵-substituted cyclopentadiene fragments as well as clusters composed of late metals, hydrides, and phosphines have shown some truly unprecedented cooperative reactivity, the common theme with these clusters is that the all seem to be electron deficient.

One of the first examples of the introduction of these class of clusters was the 44-electron ruthenium trimer with η⁵-pentamethylcyclopentadiene ligands and seven bridging hydride ligands, introduced by Suzuki and coworkers, as shown in Figure 1.5.

![Figure 1.5](image.png)

**Figure 1.5.** Ru cluster reported by Suzuki, electron deficient cluster composed of 3 Ru centres, 3 terminal pentamethylcyclopentadiene ligands and 5 hydride ligands.

The cluster has a triangular geometry and as mentioned in section 1.4, the expected CVE of trimers are 48 electrons, rendering Suzuki’s cluster electron deficient. This cluster was featured in multiple reports outlining multiple examples of dramatic cooperativity.
exhibited by this electron deficient Ru cluster. Examples of some reactivity include the reversible double NH bond activation of ammonia producing a bridging imido Ru cluster,\textsuperscript{100} as well as the facile hydrodesulfurization of dibenzothiophene producing the three-coordinate sulfide in the middle of the Ru cluster.\textsuperscript{101} The difficulty of hydrodesulfurization was outlined in section 1.3, the ability of the Ru trimer to cleave both CS bonds under relatively mild conditions also provides evidence of the cooperative nature of reactivity.\textsuperscript{101} Even more unprecedented reactivity was obtained when exposing the trimer to cyclopentadiene at room temperature, which instantly forced a CC-bond cleavage and skeletal rearrangement to form a methyl metallocycle.\textsuperscript{102} Until this example existed, CC bond cleavages by soluble transition metal species relied on preactivated substrates or ligands designed to force a metal centre proximal to a CC bond as shown in Section 1.3. Furthermore, exposing the trimer to \textit{n}-alkanes such as pentane, among others, led to the formation of a substituted metallocycle, as shown in the bottom right of Scheme 1.10.\textsuperscript{103} Alkanes are some of the most inert hydrocarbons known, so the ability for this soluble metal species to cooperatively enable this transformation, which involved six CH bond activations, was truly revolutionary.
Scheme 1.10. Cooperative reactivity exhibited by Suzuki’s Ru trimer including reversible ammonia activation, hydrodesulfurization as well as CC bond cleavage of cyclopentadiene at room temperature and CH bond activations of alkanes to form a Ru metallacycle.

More recently, a titanium trimer with η⁵-tetramethyltrimethylsilyl cyclopentadiene and seven hydride ligands was reported by the Hou and coworkers. This titanium cluster again is expected to have an electron count of 48 electrons, yet is incredibly deficient with a count of 34 electrons, as shown in Figure 1.6.¹⁰⁴

![Figure 1.6](image)

Figure 1.6. Highly electron deficient Ti trimer reported by Hou, composed of 3 Ti centres with 3 terminal tetramethyl trimethylsilyl cyclopentadiene ligands and 7 bridging hydride ligands.

The electron-deficient titanium trimer has exhibited dramatic cooperative reactivity. At room temperature the cluster cleaves the N≡N of atmospheric dinitrogen to make the triply bridged nitride titanium trimer shown on the left side of Scheme 1.11.¹⁰⁴ Tremendous focus in nitrogen fixation has catapulted many efforts towards cleaving the NN bond of nitrogen;¹⁰⁵ however, from a fundamental standpoint, the room temperature
cleavage of N$_2$ without the use of an additional substrate is very impressive. In addition, when the titanium trimer is exposed to benzene at 100 °C, it facilitates CC bond cleavage and skeletal rearrangement of benzene to produce the titanium metallocycle shown on the right of Scheme 1.11.\textsuperscript{106} The ability to cleave the CC bond of an aromatic species, under such mild conditions, is another dramatic example of cooperative bond activation. The only similar relativity reported was the CC bond cleavage of quinoxoline, which is somewhat activated due to the presence of two nitrogen containing groups. The naptha hydrocracking process forms similar ring-opening products, which further cements the comparisons made between these soluble transition metal clusters and solid-state catalysts used with high temperatures and high pressures of hydrogen.

**Scheme 1.11.** Impressive cooperative reactivity of Ti cluster including room temperature cleavage of dinitrogen as well as CC bond cleavage and skeletal rearrangement of benzene at surprisingly mild conditions.

These new class of clusters resurrected the notion of transition metal clusters acting as molecular models for solid-state catalysts. Activation of the most inert CC, CH, NN,
CS, NH, and many other bonds offered great promise towards passing the threshold of inert-bond activation and leading into avenues for impressive catalysis. However, one of the main issues when looking at these clusters for their use in catalysis is the functional group tolerance, these metal species severely lack tolerance to a variety of functional groups and therefore their uses as catalysts are significantly hindered. Late metal centres are employed in cross coupling, partly due to their extensive functional group tolerance. However, as mentioned earlier, late metal clusters are generally surrounded by ligands such as CO, which seem to render these clusters less reactive. Weller produced an octahedral Rh₆ octahedral cluster supported by purely electron rich ligands, including PPr₃ and 12 hydride ligands. This dicationic cluster has an overall electron count of 76 electrons, making it 10 electrons deficient of what is expected for octahedral species (86).¹⁰⁷ Weller’s cluster has the ability to add two equivalents of dihydrogen to achieve an 80 electron cluster with 16 hydride ligands, and the reaction is reversible through the use of vacuum or exposing the 80-electron cluster to 3,3-dimethyl-1-butene, as shown in Scheme 1.12.
**Scheme 1.12.** Weller’s electron-deficient octahedral Rh cluster reversibly adding two equivalents of hydrogen. Rare example of a cluster composed of solely late transition metal with electron-rich ligands and hydrides

An electron deficient cluster supported by purely electron rich metal species such as the rhodium cluster shown above was also reported for the group 10 metal Pt.\textsuperscript{108} This Pt\textsubscript{5} is also a closo cluster composed of 5 metal centres, 5 terminal phosphine ligands but has 8 hydride ligands giving a total electron count of 68, which is less than the expected count of 72 electrons. However, both Rh(I) and Pt(II) are known to form stable mononuclear 16 electron species, so it is possible that the expected electron count is not as relevant for these clusters as it may have been for the Ru and Ti clusters mentioned earlier in this section. The lack of reported reactivity studies of the Pt cluster may reflect the poor yield, or that the expected electron count actually reflects what the CVE of the Pt cluster bears.
Figure 1.7. Trigonal pyramidal platinum cluster, another rare example of a cluster composed solely of late metals and electron-rich ligands. The cluster has 5 terminal phosphine ligands and a total of 8 hydride ligands and is considered electron deficient with an electron-count of 68.

An area Lauher’s seminal study unfortunately does not clarify 93 is whether clusters of Ni complexes would follow the rules outlined by his study on bare Rh atoms, or whether they would be ruled as exceptions similar to Pd, and Pt complexes. The increase in reports of stable 16 electron Ni(II) species gives the notion that the expected electron counts may differ for these clusters, but reports of 15 electron Ni(I) species adds to the convolution of assigning how reactive a species, purely based off of the electron count. Analyzing oxidation states of species in attempts to determine the expected electron counts can help reason an electron count but using it in a predictive manner can be difficult.

Limberg and coworkers reported a polynuclear Ni complex in a linear shape with the terminal Ni centres bound to the diketiminato ligands reduced by K which are bound to the phenyl groups of the ligand, along with 4 bridged hydrides. 109 The metal centres here are assigned oxidation states of Ni(I)-Ni(II)-Ni(I). The complex, though not a traditional transition metal cluster still bears hydride ligands as facilitates cooperative reactivity. The trinuclear species was shown to facilitate CH bond activation at 60 °C, evidenced by exchanging its hydride ligands with deuterides from solvents such as deuterated benzene, as shown in Scheme 1.13. The complex is able to exchange its hydride ligands with
deuterides by exposing the Ni species to deuterium gas, suggesting the species is capable of achieving higher oxidation states.

Scheme 1.13. Cooperative reactivity of trinuclear Ni complex able to facilitate H/D exchange with unactivated substrates such as C₆D₆ under mild conditions. Deuterium becomes incorporated into the hydride ligands of the polynuclear Ni complex.

The ability to catalyze H/D exchange under mild conditions is not the only interesting property present with Limberg’s Ni complex. Through careful NMR studies, they showed that the Ni species has a low-lying triplet state accessible at room temperature that may be responsible for the observed reactivity. Though X-Ray crystallography is a powerhouse in determining solid-state structures of species, predicting geometries of these species in solution becomes increasingly difficult, however, it is imperative to consider the possibility that the solid-state structure is not the species responsible for the reactive nature observed, especially when low-lying triplet states are predicted.
A clever approach to the synthesis of transition metal clusters has been through a polynucleating ligand design. The last decade has seen the emergence of several reactive transition metal clusters which have strong M-M interactions through the forced proximal interaction between the metal centres. These clusters have shown significant potential in mediating multielectron redox processes, akin to cofactors in metalloenzymes.\textsuperscript{110-115}

1.5.3 Relation of Transition Metal Clusters to Reactive Metal Surfaces

This introduction chapter has mentioned the ultimate goal with transition metal clusters was to utilize them as hybrids to solid-state catalysts with the idea of gaining mechanistic insight, in mind. Limited reactivity even under harsh conditions, coupled with repeated confirmations of Lauher’s predictions, seemed to tarnish the idea of a molecular version of a reactive metal-surface. However, the influx of reactive clusters reported in the past few decades has resurrected hope in the area. Though gaining mechanistic data from solid-state catalysts is quite limited, any information gained can offer significant insight towards the requirements to mimic similar reactivity.

A study examining CC bond cleavages using Ni(111) surfaces with ethylene was reported a few decades ago. This study used scanning tunnel microscopy to analyze the surfaces prior to and after exposure to one atmosphere of ethylene gas. The study revealed the formation of carbidic surfaces, exclusively on the step sites of the Ni(111) surface after exposure at room temperature. The terraces of the Ni surface did not form carbidic surfaces until the temperature was increased to 500 °C. This dramatic change in reactivity demonstrates that reactivity, even in the solid state, requires more than proximal metal centres, a step site may offer the ideal geometry to facilitate a difficult bond cleavage such
as the CC bond of ethylene. However, gaining more information that this is difficult in the solid state.

1.6 Scope of Dissertation

Previous work done in our research group outlines the synthesis of an electron deficient pentanuclear Ni-H cluster with terminal PPr$_3$ ligands, [(P$_3$Pr)Ni]$_3$H$_6$ (1) in a square-pyramid nido geometry.$^{116}$ It is produced by exposing the dinuclear dinitrogen-bridging nickel bisphosphine complex to H$_2$ and is isolated in modest yield through recrystallization of n-pentane, as shown in Scheme 1.14. The Ni$_5^{6+}$ cluster has an electron count of 66 and is classified as electron deficient as the predicted electron count for this nido cluster is 74 electrons.

Scheme 1.14: Synthesis of square pyramid Ni-hydride cluster [(P$_3$Pr)Ni]$_3$H$_6$ (1), by exposing dinuclear nitrogen nickel complex to dihydrogen. The Ni$_5$ cluster is another rare example of a cluster composed of only later metals and electron rich ligands and is electron-deficient with 66 electrons, with an expected count of 74 electron for the nido cluster.
We reported the ability of cluster 1 to serve as a catalyst for H/D exchange of simple arenes such as deuterated benzene, deuterated toluene, as well as deuterium gas, at room temperature. This cooperative reactivity in CH bond activation was appealing to further explore. The deuterium incorporation into 1 occur at the hydride ligands similar to Limberg’s example, and creates a total of seven possible isotopologues 1-d\(^0\)-d\(^6\) as shown in Figure 1.8a. Evidence of deuterium incorporation when exposing 1 to C\(_6\)D\(_6\) into the cluster was found when looking at an increase of C\(_6\)D\(_5\)H signal through \(^1\)H and \(^{13}\)C\{\(^1\)H\} NMR studies, as well as analyzing the resonances of cluster 1 through \(^1\)H and \(^{31}\)P\{\(^1\)H\} NMR. Analyzing the hydride resonance of 1 in \(^1\)H NMR shows not only the diminished resonance of the hydride signal as the cluster exchages it’s hydrides with deuterides, but also the isotopologues of 1-d\(^0\)-d\(^5\) are observed. These isotopologues are observed in the \(^{31}\)P\{\(^1\)H\} NMR spectra of 1 after being exposed to C\(_6\)D\(_6\). The isotopologues have a separation ranging from 0.75-0.8 ppm, as shown in Figure 1.8b, which is quite drastic for a simple isotope effect. Additionally, \(^{31}\)P\{\(^1\)H\} NMR served as a helpful tool for determining the completion of the reaction, which took approximately 85 minutes to become mostly 1-d\(^6\).
Figure 1.8: A) Reaction of 1 with C$_6$D$_6$ at room temperature producing all permutations of isotopologues 1$d^0$-$d^6$. B) $^{31}$P{$^1$H} NMR of reaction of 1 with C$_6$D$_6$ over time showing the surprisingly large separations of chemical shift between the isotopologues.

The large chemical shift difference observed in $^{31}$P{$^1$H} NMR spectra of 1 was peculiar and warranted further investigation. Additional non-regularities were observed when looking at temperature effects on both the linewidth and chemical shift dependence of 1 with respect to temperature in $^{31}$P{$^1$H} NMR. This phenomena was attributed to a low-
lying triplet state and was later modelled, as shown in Figure 1.9, to provide evidence of a low-lying triplet state approximately 8.3 kcal/mol above the ground state.

**Figure 1.9:** Graphs showing temperature dependence of the linewidth of the resonance of 1 in $^{31}$P{$^1$H} NMR as well as temperature dependence on chemical shift of 1 in $^{31}$P{$^1$H} NMR. The latter was used to model the thermal Boltzmann population of a low-lying triplet state approximately 8.3 kcal·mol$^{-1}$ above the ground state.

There are seven additional chapters in this dissertation, that expand upon the cooperative reactivity of the Ni$_5$ cluster. Chapter 2 shows the ability of cluster 1 to facilitate hydrodesulfurization, deep hydrodesulfurization, and ultra-deep hydrodesulfurizations at room temperature. These transformations produced a tetrannuclear sulfide cluster as well as an unidentified paramagnetic species. These results were compared to that of mononuclear Ni phosphine complexes which facilitated hydro, and deep-hydrodesulfurization, but did not react with 4,6 dimethyldibenzothiophene, supporting the cooperative nature of 1.

Chapter 3 outlines the use of 1 to cleave CC bonds of unactivated alkenes such as ethylene at temperatures as low as –30 °C to produce a pentanuclear Ni carbide cluster along with
ethane and methane. Direct evidence that this unprecedented transformation proceeds through a cooperative nature was obtained when exposing 1 to isobutylene and styrene, which allowed the isolation of intermediates of carbon atom abstraction, which featured triple CH activation of the organic substrate bound to all 5 Ni centres. Chapter 4 describes a family of tetranuclear Ni square plane clusters with main group components bound to all 4 Ni centres, the main group atoms bound include O, NCH₂Ph, BH, and Cl to go along with the tetranuclear sulfide reported in Chapter 2. A neutron diffraction study of the Cl incorporated tetranuclear cluster is also included in Chapter 4 to confirm the position of the hydride ligands. Chapter 5 expands upon the work done in my undergraduate research, detailing a mechanistic study of the catalytic exchange reaction of 1 with simple deuterated aromatics. Kinetics studies were conducted showing rate dependences of 1, the arene, and PPr₃. Structural analogues of potential intermediates were also reported which features dissociation of the PPr₃ bound to the apical Ni centre, followed by η⁵ coordination of a cyclopentadiene or pentamethyl cyclopentadiene fragment. These analogues are also bound to either Tl, MgCp, or H. Chapter 6 focuses on expanding the carbon atom abstraction detailed in Chapter 3. This work looks at the reactivity of 1 with vinyl ethers and shows unexpected reactivity including both sp³ and sp² CO bond cleavages of vinyl ethers along with examples of CC and CH bond cleavages. Furthermore, these isolated clusters also provide evidence of cooperativity as they bind to multiple organic fragments upon cleavage. Despite an even electron count of two of the species, paramagnetism is observed with high magnetic anisotropy. Chapter 7 explores reactivity of the carbide cluster formed by reacting 1 with alkenes with various complexes, in part to find methods to extrude the carbide ligand. The carbide ligand however, served as a multinucleating
ligand in a variety of reactions, to stabilize new clusters of various oxidation states, electron counts, and geometry, offering a perspective in the carbide’s utility towards multielectron redox processes. The pentanuclear carbide cluster is also compared to the carbide-containing [FeMo] cofactor in Nitrogenase. Chapter 8 serves as a summary and looks into some future work with preliminary results focused on the observation of an even more electron-deficient cluster postulated to be composed of five Ni centres, 5 phosphine, and 4 hydride ligands, which is observed when exposing 1 to alkenes such as isobutylene. Evidence of this cluster, as well as attempts to isolate it are described. Preliminary carbide reactivity studies are also mentioned here. Lastly, a paramagnetic di nuclear Ni phosphine species with 3 bridging iodide ligands was synthesized and X-Ray and NMR details of this species are provided.
1.7 References


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Chapter 2- Facile Deep and Ultra Deep Hydrodesulfurization by the [(iPr_3P)Ni]_5H_6 Cluster Compared to Mononuclear Ni Sources

2.1 Introduction:

The chemistry of transition metal clusters has been of interest for several decades, but applications of clusters in inert-bond activation and catalysis are still an emerging field. Several examples of metal-hydride clusters activating traditionally inert bonds are known, including examples of clusters activating C=S bonds. Our group recently reported that the pentanuclear nickel cluster [(iPr_3P)Ni]_5H_6 undergoes H/D exchange with arenes such as benzene, as shown in Scheme 2.1. The mechanism of this reaction is of
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interest, because the functionalization of unactivated arenes such as benzene is typically difficult for Ni complexes;\(^{11-14}\) however, compared to mononuclear complexes, little is known about the reactivity pathways available to clusters supported solely by electronic rich phosphines and hydride ligands.\(^{15-20}\) In this work we show the propensity of \([\text{(iPr}_3\text{P})\text{Ni}]_5\text{H}_6\) (I) to react with even some of the least reactive C–S bonds under ambient conditions to give a tetranuclear \(\mu_4\)-sulfido complex.

![Scheme 2.1](image)

**Scheme 2.1** Room temperature catalytic H/D exchange of the C–H bonds in benzene by the pentanuclear Ni hydride cluster \([\text{(iPr}_3\text{P})\text{Ni}]_5\text{H}_6.\)

The last few decades have seen continued interest in C–S bond activation, due to the importance of removing sulfur from compounds in petroleum feedstocks.\(^{21-25}\) Transition metal complexes of expensive 2\(^{nd}\) and third row metals such as Pt, Pd, Ir, and Rh have proven effective for the hydrodesulfurization (HDS) of dibenzothiophenes,\(^{26-35}\) though cheaper first row metal complexes such as Ni are also capable.\(^{36-39}\) A challenge has been the “ultra-deep” desulfurization of C–S bonds in 4,6-dimethyldibenzothiophene (4,6-Me\(_2\)DBT). Few examples of ultra-deep desulfurization have been reported. For example, although the compounds Pt(PEt\(_3\))\(_3\) and (\(\eta^5\)-C\(_5\)Me\(_5\))RhPhH both react with 4-methyldibenzothiophene, both fail to activate the C–S bonds in 4,6-
dimethyldibenzothiophene, even at elevated temperatures.\textsuperscript{27, 29} Similarly, [(dippe)NiH]\textsubscript{2} (where dippe = 1,2-bis(diisopropylphosphino)ethane) reacts with 4-methyldibenzothiophene under mild conditions, but with 4,6-Me\textsubscript{2}DBT requires extended reactions times and high temperatures to give only poor conversions to an HDS product, as shown on the top of Scheme 2.2.\textsuperscript{39} A similar reaction of 4,6-Me\textsubscript{2}DBT with [(dippe)PtH]\textsubscript{2} requires heating to 120 °C for 6.5 h, whereas the already highly reactive mixture of Na and H\textsubscript{2} with Pt(PEt\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} required heating to 100 °C for 24 h to obtain a 30% yield of a C–S bond activation product.\textsuperscript{29} By using strongly basic nucleophiles such as MeMgBr it is possible to catalyse desulfurization using Ni(PEt\textsubscript{3})\textsubscript{4}, but even with the addition of these highly reactive stoichiometric reagents, temperatures of 111 °C and impractical reaction times of 5 days are required for complete conversion, as shown on the bottom of Scheme 2.2.\textsuperscript{40-43} Reactions of 4,6-Me\textsubscript{2}DBT that are suggested to involve heterogeneous components are known, such as the poorly understood reaction of a mixture of 90 equiv of NaBH\textsubscript{4} and 30 equiv Ni(II), which performs HDS under ambient conditions with a yield of 29% based on the 1 equiv of 4,6-Me\textsubscript{2}DBT used.\textsuperscript{44} Coordination of the electrophilic Mn(CO)\textsubscript{3}\textsuperscript{+} moiety to 4,6-Me\textsubscript{2}DBT to preactivate it towards nucleophilic attack by (Ph\textsubscript{3}P)\textsubscript{2}Pt(C\textsubscript{2}H\textsubscript{4}) provides one of the few examples of the C–S activation of 4,6-Me\textsubscript{2}DBT under ambient conditions by a well-defined molecular species.\textsuperscript{31} Well-defined complexes that react with 4,6-Me\textsubscript{2}DBT under ambient conditions without preactivation, to the best of our knowledge, have not been reported.
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Scheme 2.2. Previous stoichiometric and catalytic ultra-deep desulfurizations using the nickel complex \([(dippe)Ni]_2(\mu-H)_2\), where (dippe) = bis-1,2-(diisopropylphosphino)ethane and an example using Ni(PEt)_4.

Herein we report two nickel complexes, the cluster \([(Pr_3P)Ni]_5H_6\) and the dinuclear dinitrogen complex \([(Pr_3P)_2Ni]_2(\mu-N_2)\) (3), that are capable of stoichiometric hydrodesulfurization at room temperature. Although both these compounds are either composed of \(Pr_3P)Ni\) fragments, or in the case of the dinitrogen complex generates \(Pr_3P)Ni\) fragments in the presence of arenes, they exhibit different reactivities with bulky thiophene substrates, with the dinitrogen complex being able to perform deep desulfurization and the pentanuclear nickel hydride cluster being capable of both deep and ultra-deep hydrodesulfurization at room temperature.

2.2 Results and Discussions
2.2.1 HDS of Dibenzothiophenes with \([(Pr_3P)Ni]_5H_6\). The pentanuclear nickel hydride cluster, \([(Pr_3P)Ni]_5H_6\), reacts with dibenzothiophene (DBT) at room temperature over the course of a few hours in toluene. This hydrodesulfurization provides the tetranuclear nickel-hydride fragment, \([(Pr_3P)Ni]_4(\mu-H)_4(\mu-S)\) (2), the previously reported
mononuclear fragment, \((^3\text{Pr}_3\text{P})\text{Ni}(\eta^6\text{-toluene})\), and biphenyl, as shown in Scheme 2.3, where \(R^1 = R^2 = \text{H}\). The \(^{31}\text{P}\{^1\text{H}\}\) is indicative of a clean reaction; however, in addition to sharp resonances for 2, broad resonances were observed in the \(^1\text{H}\) NMR spectrum at \(\delta 2.6\) and \(25\) with a 6:1 ratio of integrals, which indicates a second product with a \(^3\text{Pr}_3\text{P}\) ligand bound to a paramagnetic Ni(I) centre. Kinetics studies were run with an excess of DBT and an internal integration standard. The ratio of integrals of 2 and the paramagnetic product were found to be constant over the course of the reaction, suggestive of two distinct reaction pathways. The \(^1\text{H}\) NMR spectrum showed 36% conversion to 2, but despite this modest conversion, 2.25 equivalents of biphenyl were produced for each equivalent of \([(^3\text{Pr}_3\text{P})\text{Ni}]_3\text{H}_6\) used. With both 4-Me-DBT and 4,6-Me_2-DBT, only 11% conversions to 2 were observed, but with significantly more of the unidentified paramagnetic product. The process forming the paramagnetic Ni product appears to be the source of the vast majority of the methylated biphenyls from the reactions of 4-Me-DBT and 4,6-Me_2-DBT, as shown in Scheme 2.3a, and support the hypothesis that the paramagnetic product observed in \(^1\text{H}\) NMR spectrum is the product of an alternate HDS pathway, and likely a \(^3\text{Pr}_3\text{P}\) supported Ni(I) sulfide. Kinetics studies of the HDS are shown in Scheme 2.3b. The HDS reaction takes about 2-3 hours, depending on the DBT used. Efforts to recrystallization the paramagnetic nickel by-product have proven unsuccessful, and all attempts to prepare this compound via alternative synthetic pathways failed to yield any amount of this product in the \(^1\text{H}\) NMR spectrum.

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Scheme 2.3. A) HDS of the model dibenzothiophenes with 1 B) Kinetics studies of ultra-deep HDS by 1
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Although all three DBTs tested undergo HDS with \((\text{iPr}_3\text{P})\text{Ni})_5\text{H}_6\) to provide 2, the yet unassigned paramagnetic byproduct made isolation of 2 extremely difficult, so alternate routes of synthesis were investigated via S-atom sources. The reaction of \((\text{iPr}_3\text{P})\text{Ni})_5\text{H}_6\) with \(\text{S}=\text{P}\text{Pr}_3\), as shown in Scheme 2.5, provides a higher yielding route to 1. This synthesis does not produce the unknown paramagnetic byproduct observed in reactions of the dibenzothiophenes with \((\text{iPr}_3\text{P})\text{Ni})_5\text{H}_6\).

Dark brown plates of 1 suitable for X-ray diffraction were grown by cooling a saturated hexamethyldisiloxane solution of the reaction mixture to –40 °C. The solid-state molecular structure of 1 is shown in Figure 2.1. Compound 1 features the sulfide lying above the approximate plane of the \([\text{Ni}_4]^{6+}\) core, with Ni-S-Ni bond angles of 112.10(6) and 120.00(6)°. The \(\mu_2\)-hydrides were located in an electron density difference map at each Ni-Ni edge. All hydride ligands are located just below the square-based nickel plane. The cluster has approximate \(C_{2v}\) rather than \(C_{4v}\) symmetry, due to P(1) and P(4) being approximately in the Ni(4) plane, whereas P(2) and P(3) bend away from the face bearing the sulfide. A solution based on a twinned monoclinic cell was determined for a partially twinned crystal. Some of the \(\text{iPr}_3\text{P}\) substituents have disorder associated with them, and this combined with twinning resulted structural data that is of modest quality.
There are two possible designations of cluster geometry and electron count with mixed transition-metal/main-group-element clusters. Complex 2 can be viewed as a *nido* cluster if the sulfur is considered as a vertex in a mixed transition metal-main group element.
cluster. For this assignment the electron count is 58, but the expected electron count is 64. Alternatively, the sulfide can be considered an X₂L ligand, which would render 2 an *arachno* cluster based on an octahedron with two vertices missing. This method gives an electron count of 56, counting only 6 of the 8 electrons in the valence shell of S²⁻ as involved in bonding; a pair of electrons residing on the sulfide in an orbital directed away from the centre of the cluster is presumably non-bonding. The expected electron count for a square-planar cluster is 64 electrons; however, these expected electron counts are based on is the 18-electron rule for transition metal complexes, whereas 16-electron mononuclear Ni complexes are common. Accounting for this, the predicted electron count for both designations is 56 electrons, which is in agreement with the assignment of 2 as an *arachno* cluster.

Unlike the electron-deficient precursor [(iPr₃P)Ni]₅H₆, sulfide 2 is thermally stable over a period of weeks at room temperature both in the solid state and in toluene and pentane solutions. The ³¹P{¹H} NMR spectrum of 2 is consistent with rapid fluxional exchange of the two phosphorus environments to give apparent C₄ᵥ symmetry in solution; a singlet at δ 54.9 was observed in the ³¹P{¹H} NMR spectrum in toluene as low as −95 °C. The methyne signal in the ¹³C{¹H} NMR spectrum could be modeled as a second order AXX'₂X'' spin system with a ¹J_PC of 15.5 Hz and a ³J_PP of 3.0 Hz. The ¹H NMR spectrum features a pair of resonances for the iPr substituents along with a second-order hydride multiplet at δ −22.55, which was modeled as an eight spin AA'A"A"XX"X" spin system using WINDNMR. The model was consistent with the 43.2 Hz span of the hydride multiplet equalling 2×(²J_PH + ³J_PH). The multiplet was best fit with a ²J_HH of 12.5 Hz and
an abnormally large \(^3J_{HH}\) value of 6.0 Hz, though these values could not be fitted with great accuracy.

There are many examples of multi-coordinate sulfide ligands bridging between 4 or more transition metals, including nickel\(^{50-55,56-60}\) However, the number of transition metal clusters with a tetranuclear square plane and a 4-coordinate sulfide ligand are more limited.\(^{61-66}\) A \(\mu_4\)-S bonding motif is found in nature at the active site for nitrous oxide reductase, where a sulfide anion is bridged by 4 Cu centres.\(^{67-68}\) Tetranuclear copper model complexes bearing a \(\mu_4\)-S ligand in a cluster have also been prepared due to their appeal in bioinorganic chemistry.\(^{61,69-70}\)

2.2.2 Reaction of Dibenzothiophenes with \([(iPr_3P)Ni]_2(\mu-N_2)\) (3). Many examples of the desulfurization of dibenzothiophenes using nickel complexes have involved a diphosphine nickel fragment.\(^{40-43}\) The reactivity of the cluster \([(iPr_3P)Ni]_5H_6\) in room-temperature deep and ultra-deep HDS could be due to the cluster acting as a source of a less sterically congested and more electron deficient monophosphine nickel fragment, \((iPr_3P)Ni\). The activation of C–S bonds in these systems is likely similar to C–F bond activation by Ni,\(^{11,71}\) in that the strengths of the bonds being broken and formed make the bond initial bond cleavage steps thermodynamically favourable, but a large activation barrier prevents facile activation. In dibenzothiophenes, steric congestion in the 4-methyl- and 4,6-dimethyl dibenzothiophenes appear to increase the barrier to activation. It is conceivable that monophosphine nickel complexes could perform more facile deep and ultra-deep HDS due to the smaller size of this fragment relative to the diphosphine nickel moiety. Monophosphine nickel moieties have also been implicated in C–O bond activation.\(^{72}\)
The dinitrogen complex \([(^{i}Pr_{3}P)_{2}Ni]_{2}(\mu-N_{2})\) (3) liberates \(N_{2}\) in aromatic solvents such as toluene to provide a monophosphine Ni source, \((^{i}Pr_{3}P)Ni(\eta^{6}-C_{7}H_{8})\) and free \(^{i}Pr_{3}P\). A mixture of 3 with dibenzothiophene in toluene over a period of 2 h provides \([(^{i}Pr_{3}P)Ni]_{3}(C_{12}H_{8})S\) (4), as shown in Scheme 2.4. Both \(^{1}H\) and \(^{31}P\{^{1}H\}\) NMR spectroscopy showed clean and complete conversion to 4. Due to the high solubility of 4, a modest 48% isolated yield was obtained after crystallization from pentane.

**Scheme 2.4.** Reactions of dibenzothiophenes with \([(^{i}Pr_{3}P)_{2}Ni]_{2}(\mu-N_{2})\).

Dark brown crystals of 4 suitable for X-ray diffraction were grown from a saturated hexamethyldisiloxane solution by cooling to −40 °C. The solid-state molecular structure is shown in Figure 2.2. The open-trinuclear structure features a metallacycle in which the central Ni(2) is in the plane of the biphenyldiyliyl and the two terminal nickel centres are \(\pi\)-bound to the biphenyldiyliyl, with the Ni(1)-C(2) and Ni(3)-C(8) distances significantly shorter than the Ni(1)-C(3) and Ni(3)-C(9) distances. The sulfide bridges all three of the Ni atoms in the formally \([Ni_{3}]^{4+}\) core. Other trinuclear nickel compound with three coordinate sulfide ligands have been reported, but most consist of 2 or more sulfides, with only one example having only one sulfide. Open trinuclear nickel monophosphine
compounds are not common, but related complexes have been reported before where a benzyne ligand is present in lieu the sulfide ligand seen in 4 and 5.\textsuperscript{77-78} It has been suggested that the mechanism of the desulfurization of dibenzothiophene by nickel phosphine complexes involves three nickel centres.\textsuperscript{79}

\begin{center}
\textbf{Figure 2.2} ORTEP diagram of X-ray crystal structure of 2 (carbons on phosphines omitted for clarity). Selected bond distances: Ni(1)-Ni(2) = 2.3983(6) Å; Ni(2)-Ni(3) = 2.4485(6) Å; Ni(1)-S(1) = 2.1866(10) Å, Ni(2)-S(1) = 2.1653(10) Å, Ni(3)-S(1) = 2.2149(10) Å; Ni(1)-C(2) = 1.980(3) Å; Ni(1)-C(3) = 2.206(4) Å; Ni(3)-C(8) = 1.960(3) Å; Ni(3)-C(9) = 2.281(3) Å; Ni(2)-C(2) = 1.973(3) Å; Ni(2)-C(8) = 1.965 Å. Selected bond angles: Ni(1)-S(1)-Ni(3) = 100.38(4)°
\end{center}

The \textsuperscript{31}P\textsuperscript{1}H NMR spectrum of 4 has a triplet central nickel phosphine resonance at $\delta$ 31.7 and a doublet from the phosphine ligands on the terminal nickels at $\delta$ 54.4, with a shared $J_{PP}$ of 32 Hz. Upon heating, exchange is observed between the two environments as both peaks broaden significantly; however, the compound begins to decompose at 353 K, prior to coalescence. The failure to observe exchange with free phosphine is consistent with an intramolecular exchange pathway. The Arrhenius activation energy for the

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fluctational process observed in 4 was calculated to be 20.2 kcal mol$^{-1}$. The $^1$H NMR spectrum has four resonances in the aromatic region along with four resonances for the two phosphines environments. All four $^1$H NMR resonances associated with the phosphines are broad at room temperature. Upon cooling to $-10 \, ^\circ\text{C}$, the resonances sharpen to observable multiplets.

The reaction of 4-methyldibenzothiophene with 3 occurred over 3 h to provide trinuclear $[(\text{iPr}_3\text{P})\text{Ni}]_3(\text{C}_{13}\text{H}_{10})\text{S}$ (5), as shown in Scheme 2.4, where $R^1 = \text{Me}$ and $R^2 = \text{H}$. Similar to the reaction with dibenzothiophene, $^1$H and $^{31}$P{$^1$H} NMR spectroscopy of the crude reaction mixture showed clean conversion, but an isolated yield of 49 % was obtained after crystallization due to the high solubility of 5. Dark brown crystals were grown from a hexamethyldisiloxane solution at $-40 \, ^\circ\text{C}$, and the solid-state molecular structure is shown in Figure 2.3. As expected, complex 5 is structurally similar to 4. The methyl group is proximal to the phosphine ligand associated with P(1), which causes some asymmetry. For example, the Ni(1)-C(3) distance of 2.388(4) Å is longer than that of the corresponding 2.247(4) Å distance between Ni(3)-C(9) on the terminal nickel not adjacent to the methyl group.
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Figure 2.3: ORTEP diagram of the X ray crystal structure of 3, with isopropyl substituents, P(3) disorder and hydrogens omitted for clarity. Selected bond distances: Ni(1)-Ni(2) = 2.4357(6) Å; Ni(2)-Ni(3) = 2.4533(7) Å; Ni(1)-S(1) = 2.1940(11) Å; Ni(2)-S(1) = 2.1593(10) Å Ni(3)-S(1) = 2.1994(11) Å; Ni(1)-C(2) = 1.963(3) Å; Ni(1)-C(3) = 2.388(4) Å; Ni(3)-C(8) = 1.951(3) Å; Ni(3)-C(9) = 2.247(4) Å. Selected bond angles: Ni(1)-S(1)-Ni(3) = 94.95(4)°; P(1)-Ni(1)-Ni(2) = 165.48(4)°; P(3A)-Ni(3)-Ni(2) = 167.61(19)°.

The 298 K ³¹P{¹H} NMR spectrum of 5 features a triplet with a broad central peak at δ 49.3 that overlaps with a broad resonance at approximately δ 49.0 with a peak width at half height of 280 Hz and a second similarly broad resonance at δ 28.0. By comparison to 4, this latter shift can be assigned to the phosphine bound to the central Ni. Upon cooling to −30 °C, the slow exchange spectrum is observed, and the central phosphine resonance sharpens to a doublet of doublets with coupling constants of 43 and 19 Hz from coupling to the terminal phosphines. The triplet transforms into a doublet at −30 °C with a coupling constant of 19 Hz and the overlapping broad resonance coalesces to a doublet with the corresponding coupling constant of 43 Hz. The variable-temperature ³¹P{¹H} NMR
spectrum linewidths were fit using WINDNMR,\textsuperscript{49} which provided an Arrhenius activation energy of 21.8 kcal-mol\textsuperscript{-1} for this process. The fluxional process involves the exchange of the central (\textit{i}Pr\textsubscript{3}P)Ni moiety with only one of the two possible terminal (\textit{i}Pr\textsubscript{3}P)Ni. The variable-temperature \textsuperscript{1}H NMR spectra of 3 was also consistent with this process. Although the similar activation energy observed for 2 would appear to imply that only the (\textit{i}Pr\textsubscript{3}P)Ni furthest from methyl substituent is in exchange with the central (\textit{i}Pr\textsubscript{3}P)Ni, a 1D gradient-enhanced nuclear Overhauser effect spectroscopy (GOESY) NMR experiment showed that the terminal (\textit{i}Pr\textsubscript{3}P)Ni moiety closest to the dibenzothiophene Me substituent was in exchange. The exact mechanism of the intramolecular exchange process is not known.

In contrast to the reaction that generated 4 and 5, [(\textit{i}Pr\textsubscript{3}P)\textsubscript{2}Ni\textsubscript{2}(\mu-N\textsubscript{2})] did not react with 4,6-dimethyldibenzothiophene. Even after heating a solution of 4,6-dimethyldibenzothiophene and 3 to 70 °C and monitoring the mixture by \textsuperscript{1}H and \textsuperscript{31}P{\textsuperscript{1}H} NMR spectra over a period of a week, no reaction was observed. This result suggests that the cluster 1 does not simply act as a source of the (\textit{i}Pr\textsubscript{3}P)Ni moiety in the initial C–S bond cleavage steps.

\textbf{2.2.3 Characterization of [(\textit{i}Pr\textsubscript{3}P)Ni\textsubscript{3}H\textsubscript{6}(S)] (6).} During the investigation for alternate routes for high yielding synthesis of 2, it was observed that the reaction with \textit{i}Pr\textsubscript{3}P=S proceeded by an observable intermediate, along with an equivalent of \textit{i}Pr\textsubscript{3}P derived from the sulfide source. A variety of characterization techniques support the assignment of this intermediate as [(\textit{i}Pr\textsubscript{3}P)Ni\textsubscript{3}H\textsubscript{6}(S)] (6).
Attempts to crystallize 6 under a variety of conditions proved unsuccessful and only provided crystals of 2; even at −40 °C slow conversion to 2 was observed. There is a slow equilibrium present between 6 and 2 which can be controlled by the addition or removal of dihydrogen, as shown in Scheme 2.5. Through the addition of hydrogen gas we were able to maintain 6 in solution and characterize it by multinuclear NMR spectroscopy. The room-temperature $^{31}$P{¹H} NMR spectrum of 6 features a singlet at δ 56.5. In the ¹H NMR spectrum, the hydride resonance at δ −18.00 is a 5.5 Hz sextet from coupling to five $^{31}$P nuclei. Relative to the signals for the $^{3}$PrP substituents, the hydride resonance integrates to six hydrogens. Furthermore, in the $^{31}$P NMR spectrum where the $^{3}$Pr ¹H resonances were selectively decoupled, a 5.5 Hz septet was observed, from to coupling to six hydrides. These observations support the proposed formulation [(¹Pr³P)Ni]₅H₆(S).
temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy provided further insight into the ground state structure. At $-90\,^\circ\text{C}$ the $^{31}\text{P}\{^1\text{H}\}$ displays two broad resonances in a ratio of $3:2$. An Arrhenius activation energy of 10.3 kcal/mol was estimated for the fluxional process that exchanges $^1\text{Pr}_3\text{P}$ environments in 6, though this determination was hampered by the lack of a slow exchange limit spectrum. The $^1\text{H}$ NMR spectrum did not show decoalescence of the single hydride resonance as low as $-100\,^\circ\text{C}$.

The 3 : 2 ratio of $^{31}\text{P}$ environments suggests that 6 takes on either a trigonal bipyramidal or an elongated square-based pyramid arrangement of Ni atoms. For the latter, either the fluxional exchange of two of the square-base Ni and the capping Ni occur by a facile Berry pseudorotation-like mechanism even at $-100\,^\circ\text{C}$, or two of the shifts are close enough that the true 2 : 2 : 1 ratio of peaks expected for the static structure are not resolved. Computational studies were performed to further investigate the nature of 6. The optimized geometry, $6^\text{DFT}$, features a sulfur atom bound $\mu_4$ to an elongated square base of four nickel centres, and opposite to a capping nickel, as shown in Figure 2.4. The framework of the structure is similar to $[(^1\text{Pr}_3\text{P})\text{Ni}]_5\text{H}_6$, however, the metal-metal distances of $6^\text{DFT}$ are elongated, and range from 2.576 Å-2.732 Å, with the shortest distances belonging to Ni(1)-Ni(5) and Ni(3)-Ni(5) and the longest distances between Ni(2)-Ni(5) and Ni(4)-Ni(5). The square base Ni-Ni distances are also long, and range from 2.666 to 2.679 Å. The optimized structure of $6^\text{DFT}$ has all of the hydrides lying on the edge of the two nickel centres they are bridging. In contrast, $[(^1\text{Pr}_3\text{P})\text{Ni}]_5\text{H}_6$ has four of its hydrides shared between the nickel centre edges of the square base, however, the two remaining hydrides are $\mu_3$ and are located in the plane of two adjacent nickel centres from the square base and the terminal nickel centre outside the square base. The differences in Ni-Ni distances can be
rationalized by the presence of hydrides H(16) and H(17), which shortens the Ni(1)-Ni(5) and Ni(3)-Ni(5) distances. The optimization also shows that the two diagonal nickel centres of the square base that have an additional hydride ligand shared with the terminal nickel centre, have a much lower P-Ni-S bond angle (134.4° and 137.3°) than the bond angle of the other two nickel centres (148.23° and 154.19°). The Ni-S bond lengths of \( \text{6}^{\text{DFT}} \) are also longer for the nickel centres that are bound to the additional hydride ligand (2.1852 Å) in comparison to the other nickel centres in the square base (2.143 Å). It also gives some insight as to why a 3:2 splitting is observed in the \( ^{31}\text{P}\{^1\text{H}\} \) NMR spectrum of \( \text{6} \) at low temperatures, as the Ni-S bond lengths and bond angles in the optimized structure suggests that the nickel centres bound to an additional hydride in the square base are chemically distinct. Geometry optimizations and frequency calculations were performed using B3LYP\(^{80}\) and the TZVP\(^{81}\) basis set in Gaussian 09.\(^82\)
Figure 2.4. GaussView depictions of the DFT optimized geometry of 6, with carbons and hydrogens associated with the 'Pr₃P moieties omitted for clarity. Selected bond distances: Ni(1)-Ni(2) = 2.665 Å; Ni(2)-Ni(3) = 2.672 Å; Ni(3)-Ni(4) = 2.679 Å; Ni(1)-Ni(4) = 2.678 Å; Ni(1)-Ni(5) = 2.576 Å; Ni(2)-Ni(5) = 2.732 Å; Ni(3)-Ni(5) = 2.606 Å; Ni(4)-Ni(5) = 2.736 Å; Ni(1)-S = 2.185 Å; Ni(2)-S = 2.143 Å; Ni(3)-S = 2.182 Å; Ni(4)-S = 2.143 Å; Ni(5)-S = 2.933 Å; Selected bond angles: Ni(1)-S-Ni(3) = 117.3°; Ni(2)-S-Ni(4) = 125.82°; P(11)-Ni(5)-S = 179.2°.
Complex 6 can be assigned as a nido cluster with a square-based pyramidal geometry, if the S is treated as an X₂L ligand. Complex 6 has an electron count of 70, and an expected electron count of 74 electrons based on the 18-electron rule. The 16-electron preference for Ni centres gives an expected electron count of 64 electrons. In relation to 2, complex 6 appears electron rich, which is in agreement with the propensity of complex 6 to convert to 2.

Complex 6 was also observed through NMR spectra from 2 and the addition of hydrogen and [(iPr₃P)₂Ni]₂(μ-N₂), with the latter acting as a source of an (iPr₃P)Ni moiety, as shown in Scheme 2.6. All attempts to utilize this equilibrium to crystallize 6 under H₂ failed, even at −80°C. This result is presumably due to the extreme solubility of 4.

![Scheme 2.6. Alternate route to 6 via equilibrium with 2.](image)

The presence of a slow equilibrium between 2 and 6 made the isolation of 2 in high yield problematic. To shorten the reaction time and isolate 2 in a convenient manner, Me₃SiCH=CH₂ was added to the mixture of 6 and 2 generated from the reaction of [(iPr₃P)Ni]₅H₆ and S=PPr₃. This cleanly and irreversibly converted the product mixture to 2 and (iPr₃P)Ni(η²-CH₂=CHSiMe₃)₂ (7). The trimethyl vinyl tin analogue of 7 has been
previously reported. Complex 2 is readily crystallized in the presence of 7 which renders this the most facile and high-yielding route to 2.

2.3 Conclusions

In summary, deep and ultra-deep HDS were achieved under ambient conditions using [(iPr₃P)Ni]₅H₆, providing a tetrannuclear nickel hydride sulfide complex 2, which features a μ₄-S moiety. In comparison, the species [(iPr₃P)₂Ni]₂(μ-N₂) only reacted with DBT and 4-methyl DBT, to give 4 and 5, respectively. Unidentified paramagnetic impurities hindered the isolation of 2, and an alternate route to 2 from the addition of S=PPr₃ to [(iPr₃P)Ni]₅H₆ was devised. This approach yielded [(iPr₃P)Ni]₅H₆(S) (6) as an intermediate, and the discovery of an equilibrium between 6 and 2 provided synthetic routes to both species. Other avenues of HDS were also explored as a means of comparison to the nickel hydride cluster’s capabilities. This was done using [(iPr₃P)₂Ni]₂(μ-N₂) to react with the various dibenzothiophenes. Upon reaction with the series of DBTs, it was shown that the dinitrogen bridging nickel complex was able to insert into the C−S bonds and facilitate the desulfurization of DBT and 4-methyl-DBT to synthesize the trinuclear metallacycles 4 and 5. A counterintuitive result is that [(iPr₃P)₂Ni]₂(μ-N₂), which serves as a source of (iPr₃P)Ni in aromatic solvents, is unreactive in ultradeep HDS, whereas the seemingly bulkier [(iPr₃P)Ni]₅H₆ cluster undergoes ultradeep HDS under ambient conditions.

Although catalytic HDS reactions were not possible, and the utility of highly reactive complexes such as [(iPr₃P)Ni]₅H₆ in HDS reactions is impractical, the Ni cluster reactivity provide insight into the ability of [(iPr₃P)Ni]₅H₆ to activate bonds, and generate
new unprecedented Ni clusters. The cluster [((Pr₃P)Ni)₅H₆ also undergoes H/D exchange with unactivated arenes, though little is known regarding what types of intermediates and mechanisms are viable for this cluster catalyzed reaction. This work broadens the scope of known reactivity for these electron-rich clusters featuring strongly electron-donating phosphines and hydride ligands.

2.4 Experimental:

2.4.1 General Procedures:

Unless otherwise stated, all manipulations were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or an MBraun glove-box. Dry, oxygen-free solvents were employed throughout. Anhydrous pentane, toluene, and THF were purchased from Alfa Aesar and were argon packed and dried with either activated sodium or molecular sieves. Benzene-\textit{d}₆ was dried by heating at reflux with Na/K alloy in a sealed vessel under partial pressure then trap-to-trap distilled and freeze–pump–thaw degassed three times. Toluene-\textit{d}₈ was purified in an analogous manner by heating at reflux over Na. THF-\textit{d}₈ was purified in an analogous manner by heating at reflux over K. Dibenzothiophene, 4-methyl dibenzothiophene and 4,6-dimethyl dibenzothiophene were purchased from Sigma-Aldrich and their purity was confirmed through NMR spectroscopy. \textsuperscript{1}H, \textsuperscript{31}P\{}\textsuperscript{1}H\}\ and \textsuperscript{13}C\{}\textsuperscript{1}H\}\ NMR spectra were recorded on a Bruker AMX Spectrometer operating at 300 MHz or 500 MHz with respect to proton nuclei. All chemical shifts are recorded in parts per million, and all coupling constants are reported in Hertz. \textsuperscript{1}H NMR spectra were referenced to residual protons (C₆D₅H, \(\delta\) 7.15; C₇D₇H, \(\delta\) 2.09; C₄D₇HO, \(\delta\) 1.73) with respect to tetramethysilane at \(\delta\) 0.00. \textsuperscript{31}P\{}\textsuperscript{1}H\}\ NMR spectra were referenced
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to external 85% H₃PO₄ at δ 0.00. \(^{13}\)C\(^{1}\)H NMR spectra were referenced relative to solvent resonances (C₆D₆, δ 128.0; C₇D₈, δ 20.4; C₄D₈O, δ 25.37) Elemental analyses were performed at the Center for Catalysis and Materials Research, Windsor, Ontario.

2.4.2 Synthesis, Characterization, and Reactivity of complexes

Synthesis and Characterization of [(iPr₃P)Ni]₄(µ-H)₄(µ-S) (2) using SP\(^{3}\)Pr\(_{3}\). To a stirring toluene solution of [(iPr₃P)Ni]₅H₆ (610 mg, 0.55 mmol) S=Pr\(^{3}\)P (105 mg, 0.55 mmol) was added. The solution was stirred for 2.5 hours, and a four-fold excess of vinyltrimethylsilane (200 mg, 1.99 mmol) was then added to the solution. The dark brown solution was then dried under vacuum, extracted with 10 mL of hexamethyldisiloxane and filtered through Celite. The solution was left at −40°C for 16 hours, which afforded dark brown plates suitable for X-ray diffraction. A second crop also afforded crystals and a combined yield of 235 mg (47.3 %) was obtained. \(^{1}\)H NMR (298 K, C₆D₆, 500 MHz). δ 1.35 (dd, \(^{3}\)J\(_{HH}\)= 7.1 Hz, \(^{3}\)J\(_{HP}\)= 12.9 Hz, 72 H, P(CH(CH\(_{3}\))₂)\(_{3}\) δ 2.20 (septet of d/apparent octet, \(^{3}\)J\(_{HH}\)=7.1 Hz, \(^{2}\)J\(_{HP}\)= 14.5 Hz 12 H, P(CH(CH\(_{3}\))₂)\(_{3}\) δ −22.55 (2\(^{nd}\) order multiplet, spin system AA'A''A'''XX''X''', full span = 2×(\(^{2}\)J\(_{PH}\) + \(^{3}\)J\(_{PH}\)) = 43.2 Hz, multiplet modeled with \(^{2}\)J\(_{HH}\)=12.5 Hz, \(^{3}\)J\(_{HH}\)=6.0 Hz, and \(^{3}\)J\(_{PP}\)=3.0 Hz, 4 H, Ni-H). \(^{31}\)P\(^{1}\)H NMR(298 K, C₆D₆, 202.5 MHz): δ 53.9 (s, 4P, P(CH(CH\(_{3}\))₂)\(_{3}\)) \(^{13}\)C\(^{1}\)H NMR (298 K, C₆D₆, 125.7 MHz) δ 20.7 (2\(^{nd}\) order multiplet, spin system AXX₂'X'', \(^{2}\)J\(_{CP}\)=4.0 Hz, \(^{3}\)J\(_{PP}\)=3.0 Hz, 24 C, P(CH(CH\(_{3}\))₂)) δ 26.2 (2\(^{nd}\) order multiplet, spin system AXX₂'X'', \(^{1}\)J\(_{CP}\)=15.5 Hz, \(^{3}\)J\(_{PP}\)=3.0 Hz, 12 C, P(CH(CH\(_{3}\))₂) Anal Calcd. for C\(_{36}\)H\(_{88}\)Ni\(_{4}\)P\(_{4}\)S: %C 47.56; %H 9.76. Found %C 47.07; %H 9.70.
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Reaction of [(Pr₃P)Ni]₅H₆ and Dibenzothiophene. Deuterated benzene was used to dissolve [(Pr₃P)Ni]₅H₆ (25 mg, 0.023 mmol) and three equivalents dibenzothiophene (13 mg, 0.070 mmol) which was then added to 1,4-dioxane (18 mg, 0.20 mmol), which was used as an internal ¹H integration standard. The solution was immediately transferred to an NMR tube and ³¹P{¹H} and ¹H NMR were used to monitor progression of the reaction. The immediate ¹H NMR and ³¹P{¹H} NMR spectra showed some conversion to 2 as well as (Pr₃P)Ni(η⁶-C₆D₆). Free biphenyl and broad peaks at δ 2.5 and 25 corresponding to an unknown paramagnetic complex were also seen in the ¹H NMR spectrum. After two hours an additional two equivalents of dibenzothiophene were added and NMR spectra were conducted again that showed almost full conversion of 2 to the HDS products.

Reaction of [(Pr₃P)Ni]₅H₆ and 4-Methyl dibenzothiophene. Deuterated benzene was used to dissolve [(Pr₃P)Ni]₅H₆ (26 mg, 0.023 mmol) and 1,4-dioxane (22 mg, 0.25 mmol) and was then used to dissolve three equivalents of 4-methyl dibenzothiophene (14 mg, 0.070 mmol). The solution was immediately transferred to an NMR tube and ³¹P{¹H} and ¹H NMR spectra were used to monitor progression of the reaction. The immediate ³¹P{¹H} NMR spectrum already showed conversion to 2 as well as (Pr₃P)Ni(η⁶-C₆D₆). ¹H NMR spectrum also showed resonances unique to 2 and (Pr₃P)Ni(η⁶-C₆D₆) as well as a new set of peaks in the aromatic region corresponding to free 3-methylbiphenyl. Broad peaks were observed in the ¹H NMR spectrum at δ 25 and 2.5 corresponding to the unidentified paramagnetic complex. After 3 h, NMR experiments were conducted again and showed almost full conversion to the HDS products.

Reaction of [(Pr₃P)Ni]₅H₆ and 4,6-Dimethyldibenzothiophene. Deuterated THF was used to dissolve [(Pr₃P)Ni]₅H₆ (25 mg, 0.023 mmol), 1,4-dioxane (18 mg, 0.20 mmol) and
was then used to dissolve 5 equivalents of 4,6-dimethyl dibenzothiophene (25 mg, 0.11 mmol). The solution was immediately transferred to an NMR tube and $^{31}$P{$^1$H} and $^1$H NMR spectroscopy were used to monitor progress of the reaction. The immediate $^{31}$P{$^1$H} NMR spectrum showed conversion to 2. The $^1$H NMR spectrum also showed resonances unique to 1 as well as a new set of peaks in the aromatic region corresponding to free 3,3'-dimethylbiphenyl. Broad peaks were observed in the $^1$H NMR spectrum at $\delta$ 25 and 2.5 corresponding to the unidentified paramagnetic complex. After approximately 3 hours, NMR spectra were collected again and showed almost full conversion to the HDS products.

**Attempted Isolation of Paramagnetic Nickel Complex.** To a stirred n-pentane solution of [($^{i}$Pr$_3$P)Ni]$_5$H$_6$ (217 mg, 0.20 mmol), one equivalent of 4,6-dimethyl dibenzothiophene (42 mg, 0.20 mmol) was added. The solution was stirred for 2 h, at which point $^1$H NMR spectrum showed that the paramagnetic nickel complex was formed and that no starting material was left. The solution was then filtered through a plug of Celite and kept at −40 °C for an extended period of time with no precipitate being produced. The n-pentane solution was then put under reduced pressure to remove all volatiles. The remaining material was dissolved in minimal hexamethyldisiloxane, filtered through a plug of Celite and cooled to −40 °C for an extended period of time, but again no solid was obtained.

**Synthesis and Characterization of [($^{i}$Pr$_3$P)Ni]$_3$C$_{12}$H$_8$(S) (4).** To a solution of [(Pr$_3$P)$_2$Ni]$_2$(µ-$N_2$) (725 mg, 0.92 mmol) in 10 mL of toluene and was added dibenzothiophene (113 mg, 0.61 mmol). The dark red solution was stirred for 2 h, at which point it turned dark brown. The toluene was removed under vacuum and the crude product was extracted with 15 mL of n-pentane and filtered through Celite. The solution was then stored at −40 °C for 16 hours, which afforded dark brown crystals suitable for X-ray
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diffraction. A yield of 236 mg was isolated (48 %).\(^1\)H NMR (298 K, C\(_6\)D\(_6\), 500 MHz): \(\delta\) 1.05 (broad s, \(W_{1/2}=30.3\) Hz 18 H, \(\text{P(\text{CH(\text{CH}_3)}_2)\text{]}_3\)) \(\delta\) 1.11 (broad s, \(W_{1/2}=31.6\) Hz, 18 H, \(\text{P(\text{CH(\text{CH}_3)}_2)\text{]}_3\)) \(\delta\) 1.21 (broad s, \(W_{1/2}=31.4\) Hz, 3 H, \(\text{P(\text{CH(\text{CH}_3)}_2)\text{]}_3\)) \(\delta\) 1.69 (broad m, \(W_{1/2}=29.6\) Hz, 6 H, \(\text{P(\text{CH(\text{CH}_3)}_2)\text{]}_3\)). \(\delta\) 6.75 (d, \(^3J_{HH}= 7.1\) Hz 2H, 1,8 or 4,5 site of metallacycle). \(\delta\) 7.01 (apparent t, \(^3J_{HH}= 7.1\) Hz, 2H, 2,7 or 3,6 site of metallacycle) \(\delta\) 7.12 (apparent t, \(^3J_{HH}= 7.1\) Hz, 2H, 2,7 or 3,6 site of metallacycle) \(\delta\) 7.72 (d, \(^3J_{HH}= 7.1\) Hz 2H, 1,8 or 4,5 site of metallacycle)

\(^31\)P\(\{}^1\)H\} NMR (298 K, C\(_6\)D\(_6\), 202.5 MHz): \(\delta\) 31.7 (t, 1P, \(^3J_{PP}= 32\) Hz) \(\delta\) 31.7 (d, 2P, \(^3J_{PP}= 32\) Hz)

\(^{13}\)C\{\(^1\)H\} NMR (298 K, C\(_6\)D\(_6\), 125.7 MHz) \(\delta\) 19.60 (s, 6C, \(\text{P(\text{CH(\text{CH}_3)}_2)\text{]}_3\)) \(\delta\) 20.0 (s, 6C, \(\text{P(\text{CH(\text{CH}_3)}_2)\text{]}_3\)) \(\delta\) 20.3 (s, 6C, \(\text{P(\text{CH(\text{CH}_3)}_2)\text{]}_3\)) \(\delta\) 22.10 (d, \(^1J_{CP}= 12.9\) Hz, 3C, \(\text{P(\text{CH(\text{CH}_3)}_2)\text{]}_3\)) \(\delta\) 24.15 (d, \(^1J_{CP}= 15.5\) Hz, 6C, \(\text{P(\text{CH(\text{CH}_3)}_2)\text{]}_3\)) \(\delta\) 109.5 (s, 2C, C-H) \(\delta\) 116.0 (s, 2C, C-H) \(\delta\) 121.8 (s, 2C, C-H) \(\delta\) 132.1 (s, 2C, C-H) \(\delta\) 151.2 (s, 2C, C-H) \(\delta\) 172.4 (2nd order multiplet, 2C, C-H) Anal Calcd. for C\(_{39}\)H\(_{71}\)Ni\(_3\)P\(_3\): %C 55.83; %H 8.54. Found %C 55.03; %H 8.51.

**Fluctual Exchange of 4.** Compound 4 (20 mg, 0.030 mmol) was dissolved in 0.6 mL of \(d_8\)-toluene and transferred to a J. Young NMR tube. \(^{31}\)P\{\(^1\)H\} NMR spectra were collected at 35 °C, 45 °C, 55 °C, 65 °C, and 75 °C to monitor exchange between the two environments. WINDNMR was used to model the spectra and corresponding rate constants of, 220 s\(^{-1}\), 620 s\(^{-1}\), 1400 s\(^{-1}\), 4000 s\(^{-1}\), and 10 000 s\(^{-1}\) were determined and using the Arrhenius equation, an \(E_a\) of 20.32 kcal·mol\(^{-1}\) was calculated.
Synthesis and Characterization of Ni₃(PᵢPr₃)₃C₁₃H₁₀S (5). To a stirring toluene solution of [(iPr₃P)₂Ni]₀(μ-N₂) (785 mg, 1.28 mmol) was added 4-methyldibenzothiophene (198 mg, 0.85 mmol). The dark red solution was stirred for 3 h at which point it turned to a dark brown. The toluene was then removed by vacuum and extracted with 15 mL of n-pentane and filtered through Celite. The solution was then stored at −40 °C for 16 hours and afforded dark brown crystals suitable for X-ray diffraction. A yield of 359 mg was obtained (49 %).

1H NMR (298 K, C₆D₆, 500 MHz): δ 1.11 (broad m, W½=39.6 Hz, 36 H, P(CH(CH₃)₂)₃) δ 1.25 (dd, JHH= 6.9 Hz, JHP= 9.9 Hz 18 H, P(CH(CH₃)₂)₃) δ 1.67 (broad m, W½=30.4 Hz 6 H, P(CH(CH₃)₂)₃) δ 1.78 (septet of virtual triplets, 3 H, P(CH(CH₃)₂)₃) δ 3.37 (s, 3 H, C-CH₃).

δ 6.05 (multiplet, 1 H, C-H) δ 6.92 (apparent t, JHH= 7.3 Hz, 1 H, C-H) δ 6.95 (apparent t, JHH= 6.9 Hz, H, C-H) δ 7.04 (overlapping multiplet, 2 H, C-H) δ 7.72 (overlapping doublet, JHH= 6.9 Hz, 2 H, C-H)

31P{¹H} NMR (298 K, C₆D₆, 202.5 MHz): δ 28.0 (broad s, 2P) δ 49.3(t, JPP= 8.4 Hz, 1P)

31P{¹H} NMR(233 K, C₇D₈, 121.2 MHz ): δ 31.9 (dd, JPP=19 Hz, 42 Hz, 1 P, central phosphine) δ 49.8(d, JPP= 42 Hz, 1P) δ 49.8(d, JPP= 19 Hz, 1P) ¹³C{¹H} NMR (298 K, C₆D₆, 125.7 MHz) δ 19.48 (d, JCP= 1.16 Hz, 3C, P(CH(CH₃)₂)₃) δ 19.90 (broad s, 12 C, P(CH(CH₃)₂)₃) δ 20.30 (d, JCP= 3.4 Hz, 3 C, P(CH(CH₃)₂)₃) δ 23.65 (broad d, JCP= 19.8 Hz, 6 C, P(CH(CH₃)₂)₃) δ 24.06 (d, JCP= 15.0 Hz, 3 C, P(CH(CH₃)₂)₃) δ 29.78 (s, 1C, C-CH₃) δ 104.91 (s, 1C, C-H) δ 116.30 (s, 1C, C-H) δ 116.49 (s, 1C, C-H) δ 121.73(s, 1C, C-H) δ 122.82 (s, 1C, C-H) δ 128.33 (s, 1C, C-H) δ 131.62 (d, JCP= 3.8 Hz, 1C, C-H) δ 132.16 (s, 1C, C-H) δ 147.65 (s, 1C, C-H) δ 152.54 (s, 1C, C-H) Anal Calcd. For C₄₀H₇₃Ni₃P₃S: %C 56.32; %H 8.63. Found %C 55.76; %H 8.69.
Fluctual Exchange of 5. Compound 5 (17 mg, 0.030 mmol) was dissolved in 0.6 mL of 
d$_8$-toluene and transferred to a J. Young NMR tube. $^{31}$P{$_1^1$H} NMR spectra were collected
at 0 °C, −5 °C, −10 °C, −15 °C, and −30 °C, to monitor exchange between the two
environments. WIN$^{31}$NMR was used to model the spectra and corresponding
rate constants of 120 s$^{-1}$, 85 s$^{-1}$, 40 s$^{-1}$, 15 s$^{-1}$, and 1 s$^{-1}$ were determined and using the Arrhenius equation,
an E$_a$ of 21.8 kcal·mol$^{-1}$ was calculated.

Attempted reaction of [(iPr$_3$P)$_2$Ni]$_2$(µ-N$_2$) and 4,6-Dimethyldibenethiophene. To a
solution of [(iPr$_3$P)$_2$Ni]$_2$(µ-N$_2$) (25 mg, 0.032 mmol) in 0.6 mL of $d_6$-benzene was added
one equivalent of 4,6 dimethyldibenzoethiophene (7 mg, 0.033 mmol). The solution was
then immediately transferred to an NMR tube. The solution was then heated to 70 °C for
an additional hour and $^{31}$P{$_1^1$H} and $^1$H NMR spectra showed no presence of any HDS
products.

Synthesis and Characterization of [(iPr$_3$P)Ni]$_5$H$_6$(S) (6). To a solution of [(iPr$_3$P)Ni]$_5$H$_6$
(27 mg, 0.025 mmol) in 0.8 mL of $n$-pentane was added 1.5 equivalent of SP$^3$Pr$_3$ (7 mg,
0.036 mmol) was then added to the solution which was then transferred to an NMR tube.
The solution was left at 0 °C for 16 h. $^{31}$P{$_1^1$H} and $^1$H NMR show near complete conversion
to 4. $^1$H NMR (298 K, C$_6$D$_6$, 500 MHz) δ 1.33 (dd, 90 H, $^3$J$_{HH}$=7.1 Hz, $^3$J$_{HP}$= 9.2 Hz
P(CH(CH$_3$)$_2$)$_3$) δ 2.12 (broad m, $^3$J$_{HH}$=7.1Hz, 15 H, P(CH(CH$_3$)$_2$)$_3$ δ −18.00 (sextet, 6 H,
$^3$J$_{HP}$= 5.5 Hz, Ni-H) $^{31}$P{$_1^1$H} NMR(298 K, C$_6$D$_6$, 202.5 MHz): δ 56.5 (s, 5P, P(CH(CH$_3$)$_2$)
$^{13}$C{$_1^1$H} NMR (298 K, C$_6$D$_6$, 125.7 MHz) δ 20.85 (s, 30C, P(CH(CH$_3$)$_2$) 26.61 (d, $^1$J$_{CP}$=
13.8 Hz, 15C, P(CH(CH$_3$)$_2$)).
Chapter 2 - Facile Deep and Ultra Deep Hydrodesulfurization by the [(iPr3P)Ni]5H6 Cluster Compared to Mononuclear Ni Sources

Variable-Temperature NMR Spectra of 6. A n-pentane solution of [(iPr3P)Ni]5H6 (90 mg, 0.082 mmol) was added to a two-fold excess of triisopropylphosphine sulfide (31 mg, 0.164 mmol) and quickly transferred to a J. Young NMR tube. The NMR tube is then put under vacuum and exposed to 1 atmosphere of dihydrogen. The solution is then left in an ice bath for 8 h. 31P{1H} NMR spectra were collected at −40 °C, −50 °C, −60 °C, −70 °C, −80 °C, and −90 °C in attempts to see decoalesence of the single resonance. WINDNMR was used to model the spectra and corresponding rate constants of 125 000 s⁻¹, 58 000 s⁻¹, 15 000 s⁻¹, 4000 s⁻¹, 720 s⁻¹, and 300s⁻¹ were determined and using the Arrhenius equation, an Ea of 10.8 kcal·mol⁻¹ was calculated.

Attempted Isolation of 6. To a stirred n-pentane solution of [(iPr3P)Ni]5H6 (220 mg, 0.20 mmol), two equivalents of triisopropylphosphine sulfide (80 mg, 0.41 mmol) were added at 0 °C. The solution was kept at 0 °C and stirred for 1 h, at which point an aliquot was taken for NMR and showed nearly clean conversion to 6. The solution was then concentrated and kept at −80 °C in a sealed flask for a week. Very minimal amorphous solid was formed and isolated, but NMR showed the precipitate to be 2.

Equilibrium between 2 and 6. A solution of [(iPr3P)Ni]5H6 (22 mg, 0.020 mmol) in 0.74 mL d8-toluene was added to a two-fold excess of S=PPr3 (8 mg, 0.041 mmol) and transferred to J. Young NMR tube. One atmosphere of dihydrogen was introduced to the NMR tube. After 1.5 h the 31P{1H} and 1H NMR spectra showed high conversion to product 6. The NMR spectra were collected again after 16 h and still showed mainly 6 with very minimal conversion to 2. Vacuum was then applied to the J. Young tube and NMR spectra were collected immediately and once again 0.5 h later that showed increased conversion to 1. A secondary peak was also observed in the 31P{1H} NMR spectrum, which

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Chapter 2 - Facile Deep and Ultra Deep Hydrodesulfurization by the [(iPr_3P)Ni]_5H_6 Cluster Compared to Mononuclear Ni Sources

is consistent with the iPr_3PNi(η^6-C_7D_8). One atmosphere of dihydrogen was then reintroduced to the J. Young tube and the 31P{^1H} and ^1H NMR spectra resonances associated with 6 grew in intensity, while the resonances associated with 1 and (iPr_3P)Ni(η^6-C_7D_8) adduct diminished in intensity.

Alternate Synthesis and Characterization of (iPr_3P)Ni(μ2-H_2C=CHSiMe_3) (7). To a solution of Ni(COD)_2 (2.0 g, 7.27 mmol) in 10 ml of toluene was added to 2 equivalents of trimethylvinylsilane (1.46 g, 14.5 mmol) and one equivalent of triisopropylphosphine (1.18 g, 7.27 mmol). The yellow solution immediately turned brown and an aliquot was then transferred to an NMR tube. ^1H NMR (298 K, C_6D_6, 500 MHz): δ 0.21 (s, 18H, Si(CH_3)_3) 0.97 and 0.99 (d, ^2J_HH= 7.4 Hz, 18H, P(CH(CH_3)_2)_3) 2.13 (m, 3H, P(CH(CH_3)_2)_3) 2.64 (dd, ^3J_HH=12.7 Hz, ^3J_HP=4.8 Hz, 2H, vinyl group) 2.71 (dd, ^3J_HH=15.9 Hz, ^2J_HP=9.4 Hz, 2H, vinyl group) 3.23 (ddd, ^3J_HH=12.7 Hz, ^3J_HP=15.9 Hz, ^2J_HP=3.8 Hz, 2H, vinyl group) 31P{^1H} NMR(298 K, C_6D_6, 202.5 MHz): δ 49.8 (s, 1P, P(CH(CH_3)_2)_3)

13C{^1H} NMR (298 K, C_6H_6, 125.7 MHz) δ 1.06 (s, 6C, Si(CH_3)_3) 19.40 (s, 3C, P(CH(CH_3)_2)_3) 19.59 (d, ^2J_CP= 3.3 Hz, 3C, P(CH(CH_3)_2)_3) 25.65 (d, ^1J_CP= 15.6 Hz, 3C, P(CH(CH_3)_2)_3) 54.65 (d, ^2J_CP=5.3 Hz, 2C, vinylic carbon) 54.96 (d, ^2J_CP=8.3 Hz, 2C, vinylic carbon)

Alternate route to 6 via reaction of [(iPr_3P)_2Ni]_2(μ-N_2) and 2 with H_2. Compound 2 (25 mg, 0.028 mmol) was dissolved in 0.6 mL of n-pentane and half an equivalent of [(iPr_3P)_2Ni]_2(μ-N_2) (11 mg, 0.014 mmol) was added. The solution was immediately transferred to a J. Young NMR tube and 31P{^1H} and ^1H NMR spectra were collected to see if any reaction would proceed; both showed that no reaction was occurring between the two species. The J. Young tube was then put under vacuum and exposed to an atmosphere
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of H_2. Both $^{31}$P[\text{H}] and $^1$H NMR spectra were collected immediately, and showed some conversion to compound 6.

2.5 X-Ray Crystallography

Table 2.1: Crystallographic Data for Compounds 2, 4, and 5

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2.6 Supporting Information

Full details of crystallographic information in CIF format for compounds 2, 4, and 5 along with experimental NMR spectra and optimized coordinates for 6^{DFT} can be found at: https://pubs.acs.org/doi/suppl/10.1021/acs.inorgchem.5b02383

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2.7 References

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Chapter 3- Cooperative Carbon-atom Abstraction from Alkenes in the Core of a Pentanuclear Nickel Cluster

Chapter 3 adapted from published work: DOI: 10.1038/nchem.2840

3.1 Introduction

Molecular clusters have the potential to react akin to metal surfaces in the catalysis of difficult bond transformations that feature multiple C–H bond activations and C–C bond skeletal rearrangements.1–6 The low activation barriers for these transformations on
surfaces can be ascribed to cooperative reactivity between metal centres; however, the presence of multiple adjacent metal sites is insufficient for cooperative catalysis, and the full potential of cooperative reactivity is rarely actualized. Even on heterogeneous surface catalysts, reaction sites are often structure sensitive.7-9 For example, catalysis on Ni (1 1 1) surfaces frequently occurs at steps rather than on terraces; these sites are so reactive that they facilitate the room temperature cleavage of ethylene to give nickel carbide, from multiple C−H and C=C bond cleavage.10 Model complexes for surface carbon-carbon bond cleavage and the more intriguing mechanistic microscopic reverse, carbon-carbon bond formation from C1 feedstocks, are entirely lacking.11 Although mononuclear complexes are known that cleave C−C bonds, many of these rely on activated substrates,12-15 or highly reduced metal centres incompatible with the majority of functional groups.1,3,6,16-17 Despite focused efforts to design reactive polynuclear complexes with both monodentate18-24 and polydentate ligands,25-32 few molecular clusters are known that selectivity react with hydrocarbons via multiple C−H and carbon-carbon bond activation2, and invariably the voracious reactivity and incompatibility of these complexes with functional groups limits their catalytic potential.

3.2 Results and Discussion

3.2.1 Reaction of 1 with Ethylene

The pentanuclear Ni-H cluster [(′Pr3P)Ni]3H6 (1) has been shown to perform catalytic H/D exchange with unactivated arenes,33 and ultra-deep hydrodesulfurization.34 Both reactions are slow at room temperature. The cleavage of strong unactivated C=C bonds in alkenes35 is a difficult transformation, typically accomplished via oxidative
processes. The addition of two equivalents of ethylene to a solution of the pentanuclear hydride 1 in n-pentane at room temperature gave immediate and clean conversion to [(tPr3P)Ni]5(μ-H)4(μ5-C) (8), as shown in reaction A in Figure 1. Cluster 8 has two fewer hydrides than 1, in agreement with the stoichiometric requirement of two equivalents of ethylene, one of which is hydrogenated to give ethane. The second equivalent of ethylene is converted to methane via the net loss of a carbon atom. The reaction of 1 with ethylene was conducted in an NMR probe cooled to −80 °C, and revealed that cluster 8, ethane and methane are produced upon warming above −30 °C.
Scheme 3.1. Cooperative carbon atom abstraction from alkenes by [( Pr₃P)Ni]₅H₆ (1). (A) Synthesis of 8 from reaction of ethylene with 1. (B) Synthesis of 9 from reaction of styrene with 1. (C) Conversion of 9 to 8 by reaction with H₂ and Pr₃P. (D) Synthesis of 10 from reaction of isobutene with 1. (E) Conversion of 10 to 8 by reaction with H₂.

An ORTEP depiction of the solid-state structure of 8, as determined by X-Ray crystallography, is shown on the bottom of Figure 2. The 68 electron [Ni₅]⁸⁺ carbide cluster
Chapter 3-Cooperative Carbon-atom Abstraction from Alkenes in the Core of a Pentanuclear Nickel Cluster

8, features a central carbide, C(1), which lies 0.372(2) Å above the approximate square base of Ni(2,3,4,5). The Ni(1) sits above this plane, bound only to C(1), P(1), Ni(1) and Ni(2). The Ni-C(1) distances to the Ni(2,3,4,5) square base vary from 1.818(2) to 1.854(2) Å. The Ni(1) site is disordered, and was modelled with this capping Ni(1A,1B,1C) bridging either Ni(2,3), Ni(2,4) or Ni(2,5), respectively.

Fig. 3.1. ORTEP depiction of the solid-state molecular structure of 8, with 50 % probability ellipsoids. Carbons and hydrogens associated with the phosphine ligands and disorder of Ni(1) omitted for clarity. Selected bond distances (Å): Ni(1)–Ni(2) 2.3763(7), Ni(1)–Ni(3) 2.520(8), Ni(2)–Ni(3) 2.5475(4), Ni(2)–Ni(5) 2.5282(5), Ni(3)–Ni(4) 2.5327(5), Ni(4)–Ni(5) 2.5210(5), Ni(1)–C(1) 1.872(2), Ni(2)–C(1) 1.854(2), Ni(3)–C(1) 1.818(2), Ni(4)–C(1) 1.820(2), Ni(5)–C(1) 1.823(2). Selected bond angles (°): Ni(2)–C(1)–Ni(4) 157.91(13), Ni(3)–C(1)–Ni(5) 155.11(13).
Solution nuclear magnetic resonance (NMR) spectroscopy of the crude reaction mixture demonstrates clean conversion to 8, which is fluxional. The $^{31}$P{$^1$H} NMR spectrum has a single resonance at $\delta$ 52.1. The $^1$H and $^{13}$C{$^1$H} NMR spectra confirm conversion to a single cluster, with a set of resonances corresponding to a five equivalent fluxional $^i$Pr$_3$P moieties and an upfield signal at $\delta$ −7.15 that integrates to four hydride ligands. The hydride signal is a sextet from coupling to five $^{31}$P nuclei with an average $J_{PH}$ of 2.5 Hz. The $^1$H NMR of the crude reaction mixture also has two singlets at $\delta$ 0.84 and $\delta$ 0.16, from ethane and methane. Similar to 1, cooling solutions of 8 as low as −90 °C did not slow the fluxional process enough to cause decoalescence of any of the $^1$H or $^{31}$P NMR resonances.

The reaction of 1 with $^{13}$C-labelled ethylene provided the $^{13}$C-labelled cluster (8-$^{13}$C). The $^{13}$C{$^1$H} NMR of 8-$^{13}$C has a sextet for the carbide from coupling to 5 phosphines, at a downfield shift of $\delta$ 446.4 with $^2J_{CP} = 20.5$ Hz. The $^{31}$P{$^1$H} NMR of 8-$^{13}$C features a doublet instead of a singlet, with $^2J_{CP}$=20.5 Hz. The $^{13}$C NMR of the crude reaction mixture allowed confirmation of the hydrocarbon products $^{13}$CH$_4$ and $^{13}$C$_2$H$_6$ as a pentet at $\delta$ −4.90 and second-order multiplet at $\delta$ 6.79 in deuterated tetrahydrofuran (d$_8$-THF), respectively.

3.2.2 Functional Group Tolerance and Carbon-13 Labelling Studies

To demonstrate the remarkable selectivity in the C=C bond activation, cluster 1 was mixed with a variety of functional group containing molecules, which included $n$-butanol, diisoprolyamine, 3-pentanone, isopropyl acetate, N-N dimethylformamide, 3-
hexyne, and neopentyl chloride. With two exceptions, the addition of ethylene to these mixtures at −40 °C produced an equivalent of ethane, methane, and carbide cluster 8, in greater than 70% NMR yield.

One exception was 3-hexyne, which also generated methane and 8, but an equivalent of 3-hexyne was hydrogenated to give 3-hexene in lieu of ethane. The second exception was the reaction in the presence of neopentyl chloride, which still provided ethane and methane from the selective activation of ethylene, but neopentyl chloride was observed to react with cluster 8; further work is underway to examine the reactivity of 8 and the nature of this product. Only a few functional groups were not tolerated. For example, both benzyl chloride and propionitrile were observed to rapidly react with 1 at −40 °C.

### 3.2.3 Identifying and Isolating Intermediates

The isolation of intermediates in reactions with alkenes other than ethylene gave insight into how the five Ni centres cooperatively abstract C from alkenes. When 1 was reacted with styrene, the immediate $^1$H and $^{31}$P{$^1$H} NMR spectra displayed an intermediate which converted to 8 over the course of 16 h. The addition of excess styrene to 1 in a solution of n-pentane at −40 °C followed by recrystallization, provided the intermediate to C=C bond cleavage $(\text{Pr}_3\text{P})_3\text{Ni}_5(\mu_2-\text{H})_3(\text{CCPh})(\text{H}_2\text{C}=\text{CPh})$ (9), as shown in reaction B in Figure 1. The stoichiometry of the reaction involves 5 equivalents of styrene. Two equivalents of styrene are incorporated in the product. One is triply C−H activated to give a bent PhCC fragment, and the second styrene acts as bridging ligand π-bound over 3 Ni centres. The complex has only three hydride ligands, and along with the three H lost from the activated styrene, the total of 6 hydrogens lost are all incorporated
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into ethyl benzene from the hydrogenation of three equivalents of styrene, as quantified by integration of the $^1$H NMR of the crude reaction mixture. The unactivated bridging styrene displaces two $^3$Pr$_3$P ligands from the cluster.

The solid-state structure of 9 was determined by X-Ray crystallography, and is displayed in Figure 3. The solid-state structure of cluster 9 features many similarities to that of cluster 8. The capping Ni(1) bonds to C(2) and retains short distances to only two of the Ni centres in the base, opening up the cluster to provide a binding pocket for the substrate. The Ni(2,3,4,5) centres distort away from square planar to a butterfly geometry, and all bind to the terminal C(1) of the PhCC fragment. Ni(5) features nearly equal bond lengths to both C(1) and C(2). The C(1)-C(2) bond length of 1.397(5) Å along with the bent C(1)-C(2)-C(3) bond angle are suggestive that the some double-bond character of styrene is maintained after the triple C–H bond activation. The π-bound styrene exhibits disorder where the two different faces of the vinyl group are bound. This disorder is maintained in solution, and results in a major and minor isomer being observed by $^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectroscopy. Unlike 1 and 8, the $C_1$ symmetric 72 electron [Nis]$^{6+}$ cluster 3 is not fluxional, and all anticipated resonances were accounted for and are in agreement with the presence of two isomers in the solid-state structure of 9. In an attached proton test (APT)-$^{13}$C{$^1$H} NMR spectrum the α and β carbons of the PhCC moiety, located at δ 150.4 (d) and δ 242.2 (dd) for the major isomer, were phased consistent with the absence of attached hydrogens. A $^1$H-$^{13}$C heteronuclear single quantum correlation (HSQC) NMR experiment also showed no proton correlation to the α and β carbons.
To confirm that cluster 9 is an intermediate of C–C bond cleavage rather than a result of a non-productive side reaction, an isolated sample of 9 in a solution of deuterated benzene (C₆D₆) was exposed to ᵃPr₃P and an atmosphere of dihydrogen as shown in Figure 3. After four hours, $^1$H and $^{31}$P{$^1$H} NMR spectra revealed the conversion of cluster 9 to cluster 8 along with ethyl benzene and toluene. The ethyl benzene is likely formed from hydrogenation of the $\pi$-bound styrene fragment, while the toluene is generated from carbon-carbon bond cleavage of the PhCC fragment and the incorporation of three hydrogen atoms.

**Fig. 3.2:** ORTEP depiction of the solid-state molecular structure of 9, with 50 % probability ellipsoids. Carbons and hydrogens associated with the phosphine ligands and disorder of C(9) and C(10) omitted for clarity. Selected bond distances (Å): Ni(1)–Ni(4)
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2.7279(7), Ni(1)–Ni(5) 2.3256(7), Ni(2)–Ni(3) 2.4913(7), Ni(2)–Ni(5) 2.5210(7), Ni(3)–Ni(4) 2.4189(7), Ni(4)–Ni(5) 2.6054(7), Ni(1)–C(2) 1.924(4), Ni(5)–C(2) 2.005(3), Ni(2)–C(1) 1.935(4), Ni(3)–C(1) 1.867(4), Ni(4)–C(1) 1.910(4), Ni(5)–C(1) 1.999(5), C(1)–C(2) 1.397(5), C(2)–C(3) 1.471(5). Selected bond angles (°): C(1)–C(2)–C(3) 125.8(3), Ni(2)–C(1)–Ni(4) 115.88(19), Ni(3)–C(1)–Ni(5) 146.4(2).

Cluster 9 demonstrates how the Ni$_5$ core of 1 can open to cooperatively triply C–H activate alkenes, and ultimately facilitate C–C bond cleavage to give 8 and the formation of three new C–H bonds to give toluene; however, the additional π-bound styrene is a factor in the isolation of 9 that may not be relevant to the activation of ethylene or other alkenes. To demonstrate the scope of substituted alkenes that can undergo carbon atom abstraction using 1, and reveal mechanistic similarities, the isolation of an intermediate using a different substrate was explored. The reaction of 1 with isobutylene yielded 8 along with an equivalent of both isobutane and propane, however, a short-lived intermediate (10) was also observed when the reaction was monitored by $^{31}$P${}^1$H and $^1$H NMR spectroscopy. Under typical reaction conditions, the isolation of 10 was impossible due to its rapid conversion to 8; however, the reaction of a large excess of isobutylene with 1 at 0 °C, followed by the application of vacuum allowed the characterization of [($^3$Pr$_3$P)Ni]$_5$(µ$_2$-H)$_5$(CC(Me)=CH$_2$) (10), as shown in reaction D in Figure 1. The removal of H$_2$ gas from the reaction using vacuum is necessary for the crystallization of 10, though the thermal instability of 10 prevented its isolation in the absence of 8. When hydrogen gas is added to a solution of 10, conversion to 8 along with propane occurs via carbon-carbon bond cleavage and the formation of three new C-H bonds, as shown in reaction E in Figure 1.
The solid-state structure of 10 is shown in Figure 4. The structure features multiple similarities to clusters 8 and 9, but with Ni(1) attached only to Ni(2). A hydride bridges this connection to the approximately square base of Ni(2,3,4,5). Similar to cluster 9, triple C-H bond activation of isobutylene is observed, which includes the vinylic C=CH$_2$ bonds and an $sp^3$ C–H bond of one of the Me groups. Two-site disorder was modelled for the bound isobutylene fragment. The C(2)-C(3) bond distance is 1.380(14) Å and the C(1)-C(2) bond distance is 1.475(9) Å. Short bonding contacts are observed between C(1) and all the Ni centres, with Ni(1) $\eta^3$-bound to the C(1)-C(2)-C(3) fragment.

The $^{31}$P{$_1^1$H} NMR spectrum of the 70 electron [Ni$_5$]$^{8+}$ intermediate 10, features a singlet at $\delta$ 47.3, and selective $^1$H decoupling of the isopropyl substituent hydrogens resulted in a sextet with a $J_{PH}$ of 6.5 Hz. The $^1$H NMR spectrum displays a similar 6.5 Hz sextet at $\delta$ –22.05 for the hydrides. This is consistent with the solid-state structure undergoing rapid fluxional exchange of the five hydride and phosphine environments. The $^1$H NMR spectrum of cluster 10 also reveals resonances for the triply C-H activated isobutylene, with the methyl group at $\delta$ 2.05, and a singlet at $\delta$ 2.90 for one of the inequivalent coordinated C=CH$_2$ hydrogens. The second C=CH$_2$ hydrogen features a temperature-dependent shift ranging from $\delta$ 1.62-1.78 between 283-288 K. Low-temperature $^{13}$C{$_1^1$H}-DEPT-Q (Distortionless Enhancement by Polarization Transfer) and $^{13}$C{$_1^1$H}-$^1$H-HSQC were collected to confirm these assignments.
Figure 3.3. ORTEP depiction of solid-state structure of cluster 10, with 50% probability ellipsoids. Carbons and hydrogens on phosphine ligands along with 2-site disorder on the top Ni centre and the bound isobutylene fragment omitted for clarity. Selected bond distances (Å): Ni(1A)–Ni(2) 2.437(2), Ni(2)–Ni(3) 2.4829(8), Ni(2)–Ni(5) 2.4762(8), Ni(3)–Ni(4) 2.4822(8), Ni(4)–Ni(5) 2.5157(8), Ni(1A)–C(1) 2.131(5), Ni(1A)–C(2A) 2.01(2), Ni(2)–C(1) 1.977(4), Ni(3)–C(1) 1.974(4), Ni(4)–C(1) 1.938(4), Ni(5)–C(1) 1.983(4), C(1)–C(2A) 1.475(9), C(2A)–C(3A) 1.380(14), C(2A)–C(4A) 1.523(18). Selected bond angles (°): Ni(2)–C(1)–Ni(4) 118.2(2), Ni(3)–C(1)–Ni(5) 134.1(2).

3.3 Conclusions

Although carbide formation is often viewed as a detrimental step for heterogeneous Ni catalysis, there has been modern interest in the use of surface nickel carbides in transformation that involve C-H and carbon-carbon bond transformations, with the
belief that reactivity occurs at four-coordinate square planar carbide sites. The facile transformations of C–H and carbon-carbon bond at [(Pr3P)Ni]5H6 demonstrate the dramatic effect of cooperativity by five metals, and offers possible insight into unforeseen mechanisms of CC bond making and breaking on metal surfaces at higher coordinate sites.

3.4 Experimental

3.4.1 General Procedures:

Unless otherwise stated, all manipulations were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or an MBraun glove-box. Dry, oxygen-free solvents were employed throughout. Anhydrous pentane, toluene, and THF were purchased from Alfa Aesar and were argon packed and dried with either activated sodium or molecular sieves. Benzene-$d_6$ and THF-$d_8$ was dried by filtering through a plug of activated alumina. Isobutylene was purchased from Sigma-Aldrich and dried with activated molecular sieves. Styrene and ethylene, and carbon-13-labelled ethylene were purchased from Sigma-Aldrich and their purity was confirmed through NMR spectroscopy. $^1$H, $^{31}$P{$^1$H} and $^{13}$C{$^1$H} NMR spectra were recorded on a Bruker AMX Spectrometer operating at 300 MHz or 500 MHz with respect to proton nuclei. All chemical shifts are recorded in parts per million, and all coupling constants are reported in Hertz. $^1$H NMR spectra were referenced to residual protons (C$_6$D$_5$H, $\delta$ 7.15; C$_7$D$_7$H, $\delta$ 2.09; C$_4$D$_7$HO, $\delta$ 1.73) with respect to tetramethylsilane at $\delta$ 0.00. $^{31}$P{$^1$H} NMR spectra were referenced to external 85% H$_3$PO$_4$ at $\delta$ 0.00. $^{13}$C{$^1$H} NMR spectra were referenced relative to solvent resonances (C$_6$D$_6$, $\delta$ 128.0; C$_7$D$_8$, $\delta$ 20.4; C$_4$D$_8$O, $\delta$ 25.37) Elemental analyses were performed at the Center for Catalysis and Materials Research, Windsor, Ontario.
3.4.2. Synthesis, Characterization and Reactivity of Complexes

Synthesis and Characterization of (8) [Ni(PiPr3)]5(µ-H)4(µ5-C)

A stirring solution of [(iPr3P)Ni]5H6 (550 mg, 0.50 mmol) in 100 mL of n-pentane, was exposed to 2 equivalents of ethylene (0.0246 L, 1 mmol) through a Schlenk line. The solution was stirred for 0.25 hours. The dark brown solution was then evacuated and filtered through a plug of Celite and was concentrated until the precipitation of product was observed. The solution was left at −40 °C for 40 hours, which afforded dark brown plates suitable for X-ray diffraction. A second crop also afforded crystals and a combined yield of 281 mg (46.5 %) was obtained. 1H NMR (298 K, C6D6, 500 MHz): δ −7.17 (sextet, 2JPH=2.45 Hz, 4 H, Ni-H), 1.40 (dd, 3JHH= 7.1 Hz, 3JPH= 12.4 Hz, 90 H, P(CH(CH3)2)3), 2.21 (septet of d/apparent octet, 3JHH=7.2 Hz, 2JPH= 7.6 Hz, 15 H, P(CH(CH3)2)3). 31P{1H} NMR (298 K, C6D6, 202.5 MHz): δ 52.4 (s, 5P, P(CH(CH3)2)3) 13C{1H} NMR (298 K, C6D6, 125.7 MHz): δ 20.7 (s, 30 C, P(CH(CH3)2)), 24.1 (d, 1JPC=12.1 Hz, 15 C, P(CH(CH3)2) Anal Calcd. for C46H109Ni5P5: %C 49.74; %H 9.89. Found %C 49.96; %H 10.21.

NMR Scale Synthesis of 8

A solution of 1 (27 mg, 0.025 mmol) in 0.5 mL of benzene was transferred to a J-Young tube. Ethylene was introduced to the room temperature solution, until the sample was saturated. The reaction was left to stir for 15 min. 1H NMR spectra was collected and showed the conversion of 1 to 8 as well as the growth of peaks corresponding to ethane and methane.
Synthesis and Characterization of (8*) [Ni(iPr3)5(µ-H)4(µ5-13C)]

A solution of [(iPr3P)Ni]5H6 (28mg, 0.025 mmol) in 0.5 mL of n-pentane was transferred to a J-Young tube. The pressure of the J-Young tube was then reduced using vacuum and 2 equivalents of carbon-13-labelled ethylene (1.22 mL, 0.050 mmol) were introduced to the J-Young tube and the reaction was left for 5 min. 1H and 31P{1H}, 13C{1H} NMR spectra were collected and show the conversion to 1* 31P{1H} NMR (298 K, C7D₈, 202.5 MHz): δ 50.5 (d, 2JPC=20.5 Hz, 5P, P(CH(CH3)2)13C{1H} NMR (298 K, C6D6, 125.7 MHz): δ 446.4 (sext, 2JPC=20.5 Hz, 1C, Ni-C);

Synthesis and Characterization of (9) Ni5(PiPr3)3(µ2-H)3(CCPh)(H2C=CHPh)

A solution of an excess of styrene [C8H8 (756 mg, 7.27 mmol) in 10 mL of n-pentane was cooled to −40 °C and added dropwise over the course of 0.25 h to a solution of [(iPr3P)Ni]5H6 (800 mg, 0.727 mmol) in 5mL of n-pentane. The dark brown solution was stirred at −40 °C for 0.5 h, then filtered through a plug of Celite and solvent was removed under vacuum until product precipitated. The solution was cooled to −40 °C and after 16 h dark brown blocks suitable for X-ray diffraction were isolated by filtration. A second crop also afforded crystals and a combined yield of 376 mg (52.7 %) was obtained. Isomer A 1H NMR (298 K, C6D6, 500 MHz): δ −21.12 (dd, 2JPH=30.2 Hz, 2JPH=10.3 Hz 1H, Ni-H), −15.77 (tm, 2JPH=15.4 Hz, 1H, Ni-H), −13.90 (d, 2JPH=22.4 Hz, 1H, Ni-H), 0.79-1.02 (4x dd, 3JHH= 7.2 Hz, 3JPH= 13.6 Hz, 36 H, P(CH(CH3)2)3), 1.42 (dd, 3JHH= 7.1 Hz, 3JPH= 12.7
Hz, 18 H, (CH(CH₃)₂)₃, 1.42 (septet of d/apparent octet, 3JHH=7.1 Hz, 2JPH= 14.5 Hz, 3H, P(CH(CH₃)₂), 1.78 (septet of d/apparent octet, 3JHH=7.1 Hz, 2JPH= 14.5 Hz, 3H, P(CH(CH₃)₂), 2.23(septet of d/apparent octet, 3JHH=7.3 Hz, 2JPH= 14.5 Hz, 15 H, P(CH(CH₃)₂)₃), 2.78(d, 3JHH=14.8 Hz, 1H, HC=CHH), 3.06(t, 3JHH=4.9Hz, 1H, Ar-H C₈H₈), 3.50(d, 3JHH=4.9 Hz, 1H, Ar-H C₈H₈), 3.88(dd, 3JHH=14.8 Hz, 3JHH=7.9 Hz, 1H, HC=CHH), 4.25(d, 3JHH=7.9 Hz, 1H, HC=CHH), 5.20 (overlapping m, 2H, Ar-H C₈H₈), 5.95(t, 3JHH=5.8 Hz, 1H, Ar-C C₈H₈), 7.00 (t, 1H, para-H C₈H₈), 7.11(m, 2H, meta-H C₈H₈), 7.69 (d, 3JHH=7.6 Hz, 2H, ortho-H C₈H₈). 3¹P{¹H} NMR (298 K, C₆D₆, 202.5 MHz): δ 30.3 (dd, 2JPP≈20.4, 3JPP=1.5 Hz 1P, P(CH(CH₃)₂), 57.58(dd, 2JPP=20.4, 3JPP=5.4 Hz 1P, P(CH(CH₃)₂), 57.77(d, 3JPP=1.5 Hz 1P, P(CH(CH₃)₂) 1³C{¹H} NMR (298 K, C₆D₆, 125.7 MHz): δ 19.9 (s, 3C, P(CH(CH₃)₂), 20.5(s, 3C, P(CH(CH₃)₂), 20.3-21.1 (4x d, 2JPC=4.6Hz, 12C, P(CH(CH₃)₂), 25.8 (d, 1JPC=14.4 Hz, 9 C, P(CH(CH₃)₂), 59.3(s, 1C, Ar-C C₈H₈), 59.6 (s, 1C, Ph-HC-CH₂), 61.6 (s, 1C, Ar-C C₈H₈), 69.8(s, 1C, Ar-C C₈H₈), 74.2 (s, 1C, Ar-C C₈H₈), 78.8 (s, 1C, Ar-C C₈H₈), 80.5(s, 1C, ipso-C C₈H₈), 89.1 (s, 1C, Ph-HC-CH₂), 124.6 (s, 1C, para-C), 127.1 (s, 2C, aromatic C), 130.5 (s, 2C, aromatic C), 150.4 (d, 2JPC= 4.0 Hz, 1C, Ni-C), 168.1(s, 1C, ipso-C C₈H₈), 242.4 (dd, 2JPC= 42.3 Hz, 2JPC= 24.7 Hz, 1C, Ni-C)  Isomer B ¹H NMR (298 K, C₆D₆, 500 MHz): δ −19.91 (dd, 2JPH=29.1 Hz, 2JPH=10.9 Hz 1H, Ni-H), −14.90 (dd, 2JPH=23.1 Hz, 3JPH=5.6 Hz, 1H, Ni-H), −14.80 (tm, 2JPH=16.1 Hz, 1H, Ni-H), δ 0.79-1.10 (4x dd, 3JHH= 7.2 Hz, 3JPH= 12.7 Hz, 36 H, P(CH(CH₃)₂)₃), 1.42 (dd, 3JHH=7.1 Hz, 3JPH= 11.8 Hz, 18 H, (CH(CH₃)₂)₃), 1.42 (septet of d/apparent octet, 3JHH=7.1 Hz, 2JPH= 14.5 Hz, 3H, P(CH(CH₃)₂), 1.83 (septet of d/apparent octet, 3JHH=7.3 Hz, 2JPH= 14.5 Hz, 3H, P(CH(CH₃)₂), 2.23(septet of d/apparent octet, 3JHH=7.3 Hz, 2JPH= 14.5 Hz, 15 H, P(CH(CH₃)₂)₃), 2.10 (d, 3JHH=14.9Hz, 1H, HC=CHH), 2.35(d, 3JHH=5.4
Chapter 3 - Cooperative Carbon-atom Abstraction from Alkenes in the Core of a Pentanuclear Nickel Cluster

Hz, 1H, Ar-H C₈H₈), 3.78(t, 3J_HH=5.4 Hz, 1H, Ar-H C₈H₈), 3.95(d, 3J_HH=8.2 Hz, 1H, Ar-H C₈H₈), 4.52(dd, 3J_HH=8.2 Hz, 3J_HHH=14.9Hz, 1H, HC=CHH), 5.41(t, 1H, 3J_HH=5.9Hz, Ar-H C₈H₈), 5.6(overlapping m, 2H, Ar-H C₈H₈), 7.00(t, 3J_HH=7.6 Hz, 1H, para-H), 7.11(m, 2H, meta-H), 7.61(d, 3J_HH=7.6 Hz, 2H, ortho-H). 31P{¹H} NMR(298 K, C₆D₆, 202.5 MHz): δ 29.4(dd, 2J_PP=17.6 Hz, 3J_PP=2.0 Hz, 1P, P(CH(CH₃)₂), 56.8(d, 3J_PP=2.0 Hz, 1P, P(CH(CH₃)₂), 58.2(d, 2J_PP=17.6 Hz, 1P, P(CH(CH₃)₂)) 13C{¹H} NMR (298 K, C₆D₆, 125.7 MHz): δ 19.5(s, 3C, P(CH(CH₃)₂), 20.4(s, 3C, P(CH(CH₃)₂), 20.3-20.9(4x d, 2J_PC=4.6 Hz, 12C, P(CH(CH₃)₂), 26.0(d, 1J_PC=14.4 Hz, 9 C, P(CH(CH₃)₂), 57.6(s, 1C, Ph-HC-CH₂), 61.1(s, 1C, Ar-C C₈H₈), 63.3(s, 1C, Ar-C C₈H₈), 67.3(s, 1C, Ar-C C₈H₈), 74.5(s, 1C, Ar-C C₈H₈), 80.1(s, 1C, ipso-C C₈H₈), 81.8(s, 1C Ar-C C₈H₈), 88.2(s, 1C, Ph-HC-CH₂), 124.6(s, 1C, para-C), 127.1(s, 2C, aromatic C), 130.5(s, 2C, aromatic C), 150.8(d, 3J_PC= 4.0 Hz, 1C, Ni-C), 170.0(s, 1C, ipso-C C₈H₅), 251.9(dd, 2J_PC= 41.9 Hz, 2J_PC= 25.0 Hz, 1C, Ni-C) Anal Calcd. for C₄₉H₇₉Ni₅P₃: %C 52.57; %H 8.10. Found %C 52.57; %H 8.24.

**Reaction of 9 with P₃Pr₃ + H₂**

A solution of 9 (10 mg, 0.010 mmol) in 0.5 mL of n-pentane was added to 2 equivalents of triisopropylphosphine (3 mg, 0.020 mmol) and transferred to a J-Young tube. 1 atmosphere of dihydrogen was introduced to the J-young tube until the solution was saturated, and the reaction was left to stir for 4 h. ¹H and 31P{¹H} NMR spectra were collected and showed the conversion of 9 to 8 and ¹H NMR showed the growth of peaks corresponding to toluene and ethylbenzene in a 1:1 ratio.
Synthesis and Characterization of (10) (Ni₅(PPr₃)₅(µ₂-H)₅(CC(Me)=CH₂)).

To a stirring solution of [(PPr₃)Ni]₅H₆ (600 mg, 0.55 mmol) in 100 ml of n-pentane at 273 K, isobutylene was introduced to the 500 mL Schlenk flask until the solution was saturated with isobutylene. The solution was stirred for 0.25 h. The head-space gas was then removed under vacuum, and the dark brown solution was filtered through a plug of Celite. The solution was concentrated by vacuum evaporation, and then cooled to −40 °C for 40 hours, which afforded dark brown plates of 1. A second crop also afforded crystals of a combination of 1 and 10 according to ¹H and ³¹P{¹H} NMR spectra. A third crop, which was also a mix of 1 and 10, was collected and dark brown plates of 10 were isolated which were suitable for X-Ray diffraction. ¹H NMR (298 K, C₆D₆, 500 MHz): δ ~22.05 (sextet, ²Jₜₜ=6.5 Hz, 5 H, Ni-H), δ 1.38 (dd, ³Jₜₜ= 7.3 Hz, ³Jₜₚ= 13.1 Hz, 90 H, P(CH(CH₃)₂)₃), δ 2.28 (septet of d/apparent octet, ³Jₜₜ=7.1 Hz, ²Jₜₚ= 7.5 Hz, 15 H, P(CH(CH₃)₂)₃), 1.62-1.78 (temperature-dependent s, 1H, isobutylene =CH₂), δ 2.09 (s, 3H, isobutylene CH₃), 2.91 (s, 1H, isobutylene =CH₂) ³¹P{¹H} NMR(298 K, C₆D₆, 202.5 MHz): δ 47.3 (s, 5P, P(CH(CH₃)₂)

Conversion of 10 to 8:

A solution of 10 contaminated with 8 in C₆D₆ was monitored over a period of 16 hours. ¹H and ³¹P{¹H} NMR spectra were collected throughout and revealed almost all of 10 had been converted to cluster 8 along with propane as an organic byproduct. The shifts
corresponding to the bound isobutylene fragment also disappeared, further supporting their assignment.

**Conversion of 1 to 8 in the Presence of added Functional Group Bearing Compounds:**

A solution of cluster 1 (22 mg, 0.02 mmol) in 0.6 mL of n-pentane was cooled to –40 °C along with a separate solution of approximately 1 equivalent of: a) n-butanol (2 mg, 0.027 mmol); b) diisopropyl amine (2 mg, 0.02 mmol); c) 3-pentanone (2 mg, 0.023 mmol); d) isopropyl acetate (2 mg, 0.02 mmol); e) N,N dimethyl formamide (2 mg, 0.024 mmol); f) 3-hexyne (2 mg, 0.023 mmol); g) neopentyl chloride (3 mg, 0.028 mmol); h) benzyl chloride (3 mg, 0.024 mmol); i) propionitrile (1 mg, 0.02 mmol) in 0.2 mL of n-pentane. The two solutions were added together at –40 °C, transferred to a J-Young tube and subsequently exposed to an excess of ethylene. Samples a-f showed conversion to cluster 8 in higher than 70 % NMR yield, as determined through integration of $^{31}$P{$^1$H} NMR spectra. Sample g formed a new cluster from the reaction of 1 with neopentyl chloride; the nature of this compound is under investigation, but the same species could be independently prepared from the reaction of 8 directly with neopentyl chloride. Methane was generated for samples a-g, and ethane was generated for samples a-e and g. In sample f, 3-hexyne was converted to 3-hexene in lieu of ethane formation. Reactivity that did not result in methane formation was observed when exposing additives h and i to cluster 1, where instantaneous reaction was observed before the addition of ethylene.

*Table 3.1: Reaction of Cluster 1 and Ethylene with Various Additives*
### Chapter 3 - Cooperative Carbon-atom Abstraction from Alkenes in the Core of a Pentanuclear Nickel Cluster

<table>
<thead>
<tr>
<th>Additive</th>
<th>Hydrogenation Product</th>
<th>Methane Generation</th>
<th>NMR Yield of 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) 1-Butanol</td>
<td>Ethane</td>
<td>Yes</td>
<td>80.2 %</td>
</tr>
<tr>
<td>b) Diisopropylamine</td>
<td>Ethane</td>
<td>Yes</td>
<td>82.6 %</td>
</tr>
<tr>
<td>c) 3-Pentanone</td>
<td>Ethane</td>
<td>Yes</td>
<td>77.1 %</td>
</tr>
<tr>
<td>d) Isopropyl Acetate</td>
<td>Ethane</td>
<td>Yes</td>
<td>82.3 %</td>
</tr>
<tr>
<td>e) N,N-Dimethyl formamide</td>
<td>Ethane</td>
<td>Yes</td>
<td>70.0 %</td>
</tr>
<tr>
<td>f) 3-hexyne</td>
<td>3-hexene</td>
<td>Yes</td>
<td>79.6 %</td>
</tr>
<tr>
<td>g) Neopentyl Chloride</td>
<td>Ethane</td>
<td>Yes</td>
<td>*</td>
</tr>
<tr>
<td>h) Benzyl Chloride</td>
<td>N/A</td>
<td>No</td>
<td>N/A</td>
</tr>
<tr>
<td>i) Propionitrile</td>
<td>N/A</td>
<td>No</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*8 reacts with neopentyl chloride after being formed.
Chapter 3-Cooperative Carbon-atom Abstraction from Alkenes in the Core of a Pentanuclear Nickel Cluster

3.5. X-Ray Crystallography

Table 3.2: Crystallographic data for 8-10

<table>
<thead>
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<th>Compound</th>
<th>8</th>
<th>9</th>
<th>10</th>
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<tr>
<td>Chemical Formula</td>
<td>C_{46}H_{109}Ni_{5}P_{5}</td>
<td>C_{43}H_{79}Ni_{5}P_{3}</td>
<td>C_{49}H_{115}Ni_{5}P_{5}</td>
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<td>Formula Weight</td>
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<td>140(2) K</td>
<td>143(2) K</td>
<td>143(2) K</td>
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<td>Monoclinic</td>
<td>Triclinic</td>
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<td>Space group</td>
<td>P-1</td>
<td>P21</td>
<td>P-1</td>
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<td>a/ Å</td>
<td>12.4070(14)</td>
<td>9.2461(7)</td>
<td>12.2549(6)</td>
</tr>
<tr>
<td>b/ Å</td>
<td>12.5366(13)</td>
<td>21.8005(19)</td>
<td>13.7326(7)</td>
</tr>
<tr>
<td>c/ Å</td>
<td>21.207(2)</td>
<td>11.6957(10)</td>
<td>19.9615(12)</td>
</tr>
<tr>
<td>α/ °</td>
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<td>90</td>
<td>85.283(2)</td>
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<tr>
<td>β/ °</td>
<td>89.969(3)</td>
<td>99.603(3)</td>
<td>80.495(3)</td>
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<tr>
<td>γ/ °</td>
<td>60.558(3)</td>
<td>90</td>
<td>64.795(2)</td>
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<td>V/ Å³</td>
<td>2868.1(5)</td>
<td>2324.5(3)</td>
<td>2997.5(3)</td>
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<td>F(000)</td>
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<td>R(int)</td>
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<td>8.78</td>
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<tr>
<td>R1 (I &gt; 2σ(I))(^{a})</td>
<td>3.70</td>
<td>2.88</td>
<td>4.51</td>
</tr>
<tr>
<td>R1(all)</td>
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<td>3.56</td>
<td>7.09</td>
</tr>
<tr>
<td>wR2(all)</td>
<td>7.55</td>
<td>4.88</td>
<td>10.70</td>
</tr>
<tr>
<td>GOF</td>
<td>1.014</td>
<td>1.131</td>
<td>1.170</td>
</tr>
</tbody>
</table>

3.6 Supporting Information
Chapter 3-Cooperative Carbon-atom Abstraction from Alkenes in the Core of a Pentanuclear Nickel Cluster

Full details of crystallographic information in CIF format for compounds 8, 9, and 10 along with experimental NMR spectra can be found at:

https://www.nature.com/articles/nchem.2840#supplementary-information
3.7. References

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Chapter 4- Synthesis of Surface-Analogue Square Planar Tetranuclear Nickel Hydride Clusters and Bonding to $\mu_4$- NR, O and BH Ligands.

4.1 Introduction:

There has been a surge of interest in the design$^{1-15}$ and study of reactive transition metal clusters for difficult bond transformations$^{16-24}$ and ultimately catalysis.$^{25-26}$ Cooperativity is often proposed as a means to render inert-bond activations facile,$^{27}$ though the full potential is rarely realized. Relative to monometallic and bimetallic complexes, little is known about how substrates bind and transform on clusters or similarly cooperative metal surfaces.
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The electron-deficient Ni-hydride cluster [(iPr$_3$P)Ni]$_5$H$_6$ (1) has been shown to perform catalytic H/D exchange with arenes,\textsuperscript{21} and ultra-deep hydrodesulfurization,\textsuperscript{22} as shown in Scheme 4.1. Recently, it was shown that 1 can abstract a carbon from alkenes by C–H activation and carbon-carbon bond cleavage.\textsuperscript{23} With ethylene this reaction occurs at temperatures as low as −30 °C, as shown on the right of Scheme 4.1. Reactions of 1 with styrene and isobutylene gave the same product, but via isolable intermediates. The intermediates revealed that the five Ni centres operate cooperatively in these remarkably facile hydrocarbon transformations to give a cluster containing a 5-coordinate carbide. Notably, step sites on Ni (1 1 1) surfaces are also capable of carbon atom abstraction from ethylene at room temperature to give carbides.\textsuperscript{28} The Ni (1 1 1) surfaces and step sites have been studied extensively for catalytic hydrocarbon conversions, and complex 1 provides an unusual analogue for these unique metal surface sites.

![Scheme 4.1](image-url)
Scheme 4.1. Reported cooperative bond activation reactivity of cluster 1 including aromatic H/D exchange, hydrodesulfurization, and carbene atom abstraction from alkenes.

Most clusters fall under the classifications of either multiple late-metal centers paired with \( \pi \)-acceptor ligands,\textsuperscript{29} or early transition metals with \( \pi \)-donor ligands.\textsuperscript{30} There are very few known clusters composed of late transition metals supported solely by electron-rich ligands, such as strong donor phosphines and hydrides.\textsuperscript{31-34} There are no closely related examples in the literature to help understand both the extreme selectivity and reactivity exhibited by cluster 1, which structurally resembles the chemistry of metal surfaces or sheets, though there has been computational and experimental interest in main-groups elements forced into unusual bonding environments coordinated to multiple transition metal centers.\textsuperscript{35-36} In this chapter, we report reactivity studies of \( [(\text{Pr}_3\text{P})\text{Ni}]_5\text{H}_6 \) (1) with main group element-containing precursors which produce novel tetranuclear mixed transition metal-main group clusters.

4.2. Results and Discussion:

4.2.1. Reactivity using \( [(\text{Ni}(\text{PPr}_3))_5\text{H}_6] \). We have previously reported several examples of unprecedented bond cleavage facilitated by the pentanuclear Ni-H cluster \( [(\text{Pr}_3\text{P})\text{Ni}]_5\text{H}_6 \) (1), in particular its ability to abstract a carbon atom to give a carbide complex.\textsuperscript{23} Nickel surfaces are known to catalyze several hydrocarbon transformations involving a source of oxygen, including steam reforming and the Sabatier reaction.\textsuperscript{37-38} The behaviour of cluster 1 in the presence of oxygen containing compounds was of interest.
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Initial studies found that trace oxygen impurities generated the compound $\left[(^3\text{Pr}_3\text{P})\text{Ni}\right]_4(\mu_2\text{-H})_4(\mu_4\text{-O})$ (11), a new tetranuclear Ni-H cluster bearing a central planar tetracoordinate oxide ligand. This species was also observed in trace amounts from the reduction of $(^3\text{Pr}_3\text{P})_2\text{NiCl}$ with Na/Hg, presumably due to trace oxide impurities. Attempts to generate 2 from reaction of 1 with stoichiometric oxygen or from reduction of $(^3\text{Pr}_3\text{P})_2\text{NiCl}$ with Na/Hg reacted with water, to provided increased oxide, provided only trace yields of 11. A synthetically useful synthesis was provided by the reaction of 1 with four equivalents of N-methylmorpholine oxide (NMO), as shown in Scheme 4.2. An immediate color change from dark brown to wine-red occurred and 11 was isolated in 58% yield after crystallization. The modest isolated yield can be attributed to high solubility of cluster 11. The $^{31}\text{P}\{}^{1}\text{H}\}$ and $^{1}\text{H}$ NMR spectra of the crude reaction mixture indicated conversion to a single soluble transition metal complex along with an equivalent of free $^3\text{Pr}_3\text{P}=\text{O}$, indicative of decomposition of the capping Ni in 1. The stoichiometry suggests the capping NiH$_2$ moiety is converted to NiO and water, though these were not identified. The addition of less than four equivalents of NMO gave incomplete conversion, whereas the use of an excess of NMO was not detrimental and underwent no further reaction.

Scheme 4.2. Formation of cluster 11

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The solid state molecular structure of 11 was obtained using X-Ray diffraction and shows four Ni centres in a square plane with bond distances ranging from 2.5451(3) – 2.5504(4) Å, and is featured in Figure 4.1. The oxo ligand sits in the centre of the square plane of nickels, trans to the four phosphine donors, which are also in the plane of the Ni centres, giving approximate $D_{4h}$ symmetry. The Ni–O bond distances range from 1.7987(3) – 1.8044(3) Å. The hydrides, located in the electron density difference map, bridge between each pair of adjacent Ni centres and also lie in the square Ni plane.

**Figure 4.1.** ORTEP Depictions of 11 with carbons and hydrogens on phosphines omitted for clarity. Selected bond lengths: Ni(1)–Ni(2) = 2.5451(3) Å; Ni(2)-Ni(1') = 2.5504(4) Å; Ni(1)-O(1) = 1.7987(3) Å; Ni(2)-O(1) = 1.8044(3) Å; Ni(1)-H(1) = 1.66(2) Å, Ni(2)-H(1)
Cluster 11 has a \([\text{Ni}_4]^{6+}\) core and is considered an *arachno* cluster as it is two vertexes deficient of being a closed polyhedron. The expected electron count for square plane clusters is 64 electrons.\(^{39}\) The electron count of cluster 11 is 58 electrons with the oxo ligand acting as an \(X_2L_2\) donor with both pairs of electrons in the oxygen valence shell contributing in bonding. Cluster 11 bears resemblance to previously reported sulfide cluster \([((i\text{Pr}_3P)\text{Ni})_4(\mu_2-\text{H})_4(\mu_4-S)]^{22}\); however, the sulfide ligand acts only as an \(X_2L\) ligand, because the sulfide ligand lies above the Ni plane. Reasoning for the supposed electron deficiency of cluster 11 can be attributed to the cluster counting rules being based on the 18 electron rule for transition metal centres,\(^{40}\) while 16 electron Ni compounds are very common.\(^{41}\) Accounting for the 2 electron difference for each Ni centre, the rule-based electron count of cluster 11 can alternatively be 56 electrons, which adds ambiguity as to whether 58-e cluster 11 is electron deficient, rich, or precise.

While the electron-deficient precursor \([((i\text{Pr}_3P)\text{Ni})_5\text{H}_6\) (1) decomposes slowly at room temperature, cluster 11 is thermally stable over a period of weeks at room temperature both in the solid state and in toluene and pentane solutions. The \(^{31}\text{P}\{^1\text{H}\}\) NMR of cluster 11 features a sharp singlet at \(\delta\ 71.8\) which is in agreement with the highly symmetric solid-state structure of 11. The \(^{13}\text{C}\{^1\text{H}\}\) NMR features a pair of resonances, with a singlet for the methyl and a doublet for the methine environments of the phosphine ligand. The \(^1\text{H}\) NMR features a pair of resonances for the phosphine ligands as well as a second-order multiplet at \(\delta\ −15.00\) from the AA’A”A”XX’X” spin system.
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Molecular transition metal complexes with square planar $\mu_{4}$-O ligands have been reported for a few 3d transition metals, which include Y, Ti, V, Mn, Co and Cu. However, no examples of square planar $\mu_{4}$-O coordinated to Ni are known; furthermore, in the known examples of square planar $\mu_{4}$-O, none of the species bear any resemblance to surface oxo-species, due to either the complete absence of direct metal-metal bonding interactions, or in case of many of the Cu species, long metal-metal separations above 2.7 Å consistent with weak interactions.

Despite the lack of Ni$_4$(µ$_4$-O) species comparable to 11, the closely related species Ni$_4$(µ$_2$-H)$_4$(µ$_4$-O) was postulated based on density functional theory (DFT) calculations as potentially stable enough to be observed using frozen matrix isolation techniques or as a transient species in the gas phase. The stability of square planar $\mu_{4}$-C and N species on surfaces and in 2-D structures has also been investigated by DFT. The latter structures have been posited as examples of triply aromatic species, though the use of the term aromatic is even more nebulous in this context than in hydrocarbon systems, and the use of word aromaticity in this sense and its measures have the subject of critical debate. The species M$_4$(µ$_2$-H)$_4$(µ$_4$-E) species (M=Cu, Ni and E=B, C, N, O) were assigned as nonaromatic due to their predicted negative $^1$H NMR chemical shifts, whereas the species Cu$_4$(µ$_2$-H)$_4$ was labelled aromatic; however, the ubiquitous positive shifts of d$^0$ and d$^{10}$ metal hydrides and negative shifts of d$^1$-d$^9$ metal hydrides are explained by more prosaic causes than aromaticity. Regardless, the $\mu_{4}$-O complex 11 shows good thermal stability, and is unreactive in refluxing toluene. The addition of iPr$_3$P gave no line-broadening in the $^{31}$P NMR at elevated temperature, which indicates that iPr$_3$P dissociation from 11 is not
facile. Similarly, the addition of alkenes such as cyclopentene under reflux in benzene gave no reaction.

Reaction with the nitrogen donor benzonitrile provides a related example of a (μ₄-NR) complex. Cluster 1 reacted with two equivalents of benzonitrile, and immediately changed from dark brown to the bright red complex [([Pr₃P]₄Ni₄)(μ₂-H)₄(μ₄-NCH₂Ph)] (12). This transformation occurs by transfer of two hydrogen atoms associated with 1 to the two-coordinate carbon atom of benzonitrile. Although the reaction provided no observable intermediates from which to ascertain the mechanism of the formation of 12, the microscopic reverse reaction of a μ₃-NCH₂Ph moiety to give benzonitrile on a Cu(1 1 1) surface has been proposed to occur by two subsequent β-elimination reactions at temperatures above 310 K.⁶³ The reaction of 1 with benzonitrile also produces a stoichiometric amount of a the trimeric Ni(0) species [(Pr₃P)Ni(N≡CPh)]₃ (13) as shown in Scheme 4.3. Both ³¹P{¹H} and ¹H NMR show quantitative conversion from cluster 1 to cluster 12 and trimer 13.

Cooling a solution of cluster 12 and trimer 13 in n-pentane at −40 °C over a period of 16 h led to the crystallization of bright red block crystals of the less soluble complex, cluster 12. The solid-state structure of 12 was determined by X-ray crystallography, and is featured in Figure 4.2, and showed many similarities of that of cluster 11. It features four Ni centers in a square plane with Ni-Ni bond lengths ranging from 2.484–2.507(6) Å. The four terminal phosphines, however, all lie slightly below the Ni square plane. The bridging hydrides were located on the electron difference map and were found to be in the Ni square plane bridging in between each adjacent Ni centre. The N-centre of the imido group was located approximately 0.660 Å above the square plane with opposing Ni–N–Ni bond.
angles of 137.2(6) ° and 140.7(6) ° and Ni–N bond distances ranging from 1.870(9) to 1.898(8) Å. The imido group in 12 lies above the Ni plane, unlike the oxide-ligand in 11, though similar to the sulfide in [(iPr3P)Ni]4(μ2-H)4(μ4-S). The C(1)–N(1) bond length of the imido group is 1.520(14) Å, consistent with single bond character. Although transition metal μ₄-NR species are not uncommon, the Cambridge Structural Database has no examples of Ni₄(μ₄-NR) species, and even molecular μ₃-NR imido complexes of Ni are rare.

Scheme 4.3. Formation of cluster 12 and trimer 13.
Similar to 11, the imido cluster 12 bears a [Ni$_4$]$^{6+}$ core, is stable at room temperature over a period of weeks in the solid state. Complex 12 is an arachno cluster with an expected electron count of 64 electrons, but unlike the oxo cluster 11, the imido donor is an XL$_2$ donor, similar to the sulfide ligand in [(tPr$_3$P)Ni$_4$(µ$_2$-H)$_4$(µ$_4$-S)]. This gives the cluster an overall electron count of 56 electrons. In this instance, accounting for the propensity of Ni to form stable 16 electron complexes, allows cluster 12 to be electron precise.

**Figure 4.2:** ORTEP Depiction of 12 (Carbons on phosphines and hydrogens on phosphines and imido ligand excluded for clarity) Ni(1)–Ni(2) = 2.507(2) Å; Ni(2)-Ni(3) = 2.500(2) Å; Ni(3)-Ni(4) = 2.484(2) Å; Ni(1)-Ni(4) = 2.491(2) Å; Ni(1)-N(1) = 1.898(8) Å; Ni(2)-N(1) = 1.891(9) Å; Ni(3)-N(1) = 1.874(9) Å; Ni(4)-N(1) = 1.870(9) Å; N(1)-C(1) = 1.520(14) Å; Ni(1)-H(1) = 1.71(12) Å, Ni(1)-H(4) = 1.56(13) Å; Ni(2)-H(1) = 1.60(12) Å; Ni(2)-H(2) = 1.55(12) Å; Ni(3)-H(2) = 1.74(12) Å; Ni(3)-H(3) = 1.64(12) Å; Ni(4)-
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H(4) = 1.56(13) Å; Ni(4)-H(4) = 1.48(13) Å; Selected Bond Angles: Ni(1)−Ni(2)−Ni(3) = 90.47(6) °; Ni(2)−Ni(3)−Ni(4) = 89.26(6) °; Ni(3)−Ni(4)−Ni(4) = 91.22(7); Ni(4)−Ni(1)−Ni(2) = 88.94(6) °; Ni(1)−N(1)−Ni(3) = 140.9(6 °); Ni(2)−N(1)−Ni(4) = 137.2(6) °; N(1)−C(1)−C(2) = 114.9(9) °

The $^{31}$P{$^1$H} NMR features a sharp singlet at approximately $\delta$ 63.2 which is consistent with apparent $C_{4v}$ symmetry. The $^{13}$C{$^1$H} NMR spectrum has a pair of doublet resonances for the phosphine ligand methyl and methine carbons with a $^2J_{PC}$ of 3.5 Hz and a $^1J_{PC}$ of 15.2 Hz. The benzyl carbon resonance appears as a pentet at $\delta$ 58.0 with a $^3J_{PC}$ of 1.8 Hz. Lastly, a set of 4 resonances are present in the aromatic region corresponding to the phenyl substituent of the imido ligand. The $^1$H NMR spectrum features a pentet at $\delta$ 3.11 for the benzyl protons, with a $^4J_{PC}$ of 2.6 Hz, along with resonances for the phosphine donors and the aromatic protons. The hydride resonance was observed as a second-order multiplet at $\delta$ −13.55 which integrates to 4 hydrogens. Similar to 1, the multiplet was modeled with an AA'A''A''''XX'X'X'' spin system.

The isolation of trimer 13 in the presence 12 proved difficult. An alternate synthesis from the reaction of Ni(COD)$_2$, PPr$_3$ and a slight excess of benzonitrile in toluene formed trimer 13 quantitatively, as shown in Scheme 4.4. The solid-state molecular structure of trimer 13 is shown in Figure 4.3. Each Ni center is bound to a terminal phosphine, one N-bound $\eta^1$-NCPh and one $\pi$-bound $\eta^2$-NCPh. The $\pi$-bound $\eta^2$-NCPh features Ni-C and Ni-N bond distances range from 1.839 – 1.855(3) Å and 1.918 – 1.935(2) Å, respectively. The C≡N bonds of the bound nitriles in 13 are elongated with bond distances of 1.230 – 1.238(4) Å, which is expected due to backbonding by the bound Ni centre. The Ni-N bond

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distances for the $\eta^1$-NCPh interaction range from 1.896(4) – 1.902(2) Å. These bond distances are consistent with reported Ni $\pi$-bound nitriles.$^{67-68}$

\[
3 \text{Ni(COD)}_2 + 3 \text{P}^3\text{Pr}_3 + 3 \text{Ph} = \equiv \equiv \text{N} \\
\text{toluene} \quad 298K \\
- 6(\text{COD}) \\
\frac{[\text{P}^3\text{Pr}_3\text{Ni(CNPh)}]}{3} \\
\text{13}
\]

**Scheme 4.4.** Alternate synthesis of trimer 13

**Figure 4.3.** ORTEP depiction of 13. Hydrogen atoms and iso-propyl carbon groups on phosphorus omitted for clarity. Selected bond lengths: Ni(1)-C(1) = 1.840(3) Å, Ni(1)-N(1) = 1.935(2) Å, C(1)-N(1) = 1.238(4) Å, Ni(2)-N(1) = 1.906(2) Å, Ni(2)-C(2) = 1.855(3) Å,
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Ni(2)-N(2) = 1.922(3) Å, C(2)-N(2) = 1.230(4) Å, Ni(3)-N(2) = 1.892(4) Å, Ni(3)-C(3) = 1.839(3) Å, Ni(3)-N(3) = 1.918(2), C(3)-N(3) = 1.227(4) Å, Ni(1)-N(3) = 1.900(2) Å.

The \( ^{31}\text{P}\{^1\text{H}\} \) NMR of trimer 13 features a sharp singlet at \( \delta 61.1 \), which is consistent with the apparent \( C_{3h} \) symmetry. The observation of second-order AXX'X" multiplets in the \( ^{13}\text{C}\{^1\text{H}\} \) NMR for both the ipso carbon at \( \delta 136.4 \) and the C≡N group at \( \delta 177.1 \) supports the trimeric nature of 13 in solution. In contrast the literature of nickel \( \pi \)-bound nitrile complexes\(^{69-74} \) features tetrameric structures,\(^{67} \) which includes examples with benzonitrile.\(^{68} \) A tetrameric structure may be less favourable in this scenario from a steric perspective, due to the large cone angle of \( \text{P}^3\text{Pr}_3 \). The remaining \(^1\text{H} \) and \( ^{13}\text{C}\{^1\text{H}\} \) NMR resonances are all consistent with the solid-state structure of 13.

4.2.2. Tetranuclear Nickel Chloride. The propensity of the \([\text{(Pr}_3\text{P)Ni}]_4\text{H}_4 \) fragment to adopt a square planar arrangement and bind in a \( \mu_4 \)-fashion to dianionic donors is well represented by complexes 11, 12 and \([\text{(Pr}_3\text{P)Ni}]_4(\text{µ}_2-\text{H})_4(\text{µ}_4-\text{S}) \). The stability of \( D_{4h} \) compounds bearing two monoanionic donors, like \([\text{(Pr}_3\text{P)Ni}]_4(\text{µ}_2-\text{H})_4(\text{µ}_4-\text{Cl})_2 \) seemed plausible, and its synthesis was explored. A successful synthesis of the complex \([\text{(Pr}_3\text{P)Ni}]_4\text{H}_4\text{Cl}_2 \) (14), with the desired molecular formula was obtained by the reaction of the dinitrogen complex \([\text{(Pr}_3\text{P)Ni}]_2\text{N}_2 \) with 2 equivalents of the Ni(I) chloride \((\text{Pr}_3\text{P})_2\text{NiCl} \)\(^{75} \) in \( n \)-pentane followed by exposure to 4 atm of dihydrogen for 1.5 h. Alternatively, the Ni(I) species \((\text{Pr}_3\text{P})_2\text{NiCl} \) can be made \textit{in situ} by reacting \((\text{Pr}_3\text{P})_2\text{NiCl}_2 \) with additional \([\text{(Pr}_3\text{P)Ni}]_2\text{N}_2 \), as shown in Scheme 4.5. Both the \(^1\text{H} \) and \( ^{31}\text{P}\{^1\text{H}\} \) NMR

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spectra are indicative of clean and complete conversion to cluster 14. Due to the high solubility of 14 a modest isolated yield of 49% was obtained.

Scheme 4.5: Synthesis of cluster 14

Dark brown crystals of cluster 14 suitable for X-Ray diffraction were obtained by cooling the reaction mixture to –40 °C. The solid-state molecular structure is shown in Figure 4.4. The four Ni centres adopt a tetrahedral arrangement. The chloride ligands bridge at two of the edges of the transition-metal core, with Cl(1) bridging between Ni(1) and Ni(3) and Cl(2) between Ni(2) and Ni(4). Each phosphine is directed trans to a Ni-Ni bond bridged by the chloride. The Ni–Ni bond distances have a large variance, and range from 2.3534(8) to 2.5907(8) Å, with the shorter distances for the Ni centres with the bridging chloride ligands. The chlorides bridge symmetrically, with Ni–Cl bond distances ranging from 2.2909(14) to 2.2939(13) Å. Although resonances corresponding to four equivalent hydride ligands were observed in the ¹H NMR, and four hydride ligands were located in the X-ray diffraction electron density difference map, there were discrepancies
in the Ni–H bond distances between the two Ni₄H₄ moieties in the unit cell. To further support both the presence and location of the hydride ligands in the solid-state structure, neutron diffraction studies were employed. The solid-state structure obtained from neutron diffraction revealed that 14 does in fact bear four hydride ligands and that each are bridged between three Ni centers with one short contact and two long contacts, as can be seen in Figure 4.4b. The hydride ligands trans-disposed to the chloride ligand have significantly shorter Ni–H bond distances, from 1.54(2) Å to 1.64(2) Å, in comparison to the two remaining Ni–H bond distances, which range from 1.86(2) Å to 2.095(19) Å. Additional details are provided in Table S2.

Cluster 14 features a [Ni₄]⁶⁺ core, but unlike 11, 12 and [(t²Pr₃P)Ni]₄(µ₂-H)₄(µ₄-S), it can be classified as a closo cluster. Cluster 14 has an electron count of 58 electrons with the chloride ligands treated as XL donors. The predicted electron count for tetrahedral clusters is 60 electrons,³⁹ which makes 14 electron deficient. Several tetrahedral nickel clusters have been reported that have the predicted electron count of 60,⁷⁶⁻⁷⁸ even in examples with the same core oxidation state as 14.⁷⁶
Figure 4.4: (a) ORTEP depiction of cluster 14 from X-ray diffraction data. Carbons and hydrogens on phosphine ligands omitted for clarity. Selected bond lengths: Ni(1)–Ni(2)= 2.3534(8) Å; Ni(1')-Ni(2) = 2.5907(8) Å; Ni(1)-Cl(1) = 2.2909(14) Å; Ni(2')-Cl(1)= 2.2939(13) Å; Ni(1)-Cl(1)-Ni(2')= 61.76(4)°. (b) Neutron diffraction structure. Atom thermal ellipsoids, including the hydrogen atoms (pink) were plotted at the 50% probability level. The observed negative nuclear scattering densities (cyan) are shown with an isosurface level of −1.0 fm·Å⁻³. Selected distances: H(1)—Ni(1) 1.60(2) Å, H1—Ni(1') 2.00(2) Å; H(1)—Ni(2) 2.078 (17) Å , H(2)—Ni(2) 1.642(2) Å; H(2)—Ni(2') 1.591(18) Å; H(2)—Ni(1) 1.874(16) Å.

The $^{31}\text{P}$($^1\text{H}$) NMR features a sharp singlet at δ 45.7, consistent with the apparent $D_{2d}$ symmetry of 14. The $^1\text{H}$ NMR features a pair of resonances corresponding to the phosphine ligands along with a singlet at δ −25.50 which integrates to four hydrides. The $^1\text{H}$ NMR spectrum was monitored upon cooling to 173 K and showed no effect on the hydride resonance. When deuterium gas was used in lieu of H₂ in the synthesis of 14, the deuterated analogue 14-d₄ was obtained, which displayed no hydride resonance observed in the $^1\text{H}$ NMR spectrum. The $^{13}\text{C}$$^1\text{H}$ NMR spectrum of 14 featured a pair of resonances.
corresponding to the phosphine ligands at δ 20.3 and 23.4. Both resonances are 2nd order multiplets, from a AXX'X''2 the spin system.

Complex 14 offers a route to other clusters by replacement of the chlorides via salt metathesis. With Ni clusters containing C, N, O, S and Cl as ligands now characterized, attempts were made to install a B containing group. The reaction of 14 with two equivalents of LiBH₄ in tetrahydrofuran for 20 minutes caused a color change from dark brown to dark purple, and the tetraneuclear Ni–H cluster [(iPr₃P)Ni₄(μ₂-H)₄(μ₄-BH)₂ (15)] was formed, with the liberation of two equivalents of LiCl and three equivalents of H₂, as can be seen in Scheme 4.6. While there is quantitative conversion from 14 to 15, a modest isolated yield of cluster 15 of 63% was obtained due to its high solubility in n-pentane.

Dark purple blocks of cluster 15 were isolated from recrystallization in n-pentane at −40 °C over a period of 16 h. The solid-state molecular structure of 15 was obtained using X-Ray diffraction, and is featured in Figure 4.5. The cluster features four Ni centres in a square plane in a similar fashion to clusters 11 and 12, and pseudo-D₄h symmetry, with the phosphine ligands lying in the Ni square plane. The four hydrides were located in an electron-density difference map and their positions and isotropic thermal parameters were refined. The BH ligands are located above and below the Ni plane with the opposing Ni-B-Ni bond angles ranging from 130.84(9) to 130.93(9) ° and Ni–B bond lengths ranging from 1.9995(14) to 2.0039(17) Å. The distance between the two boron centres is approximately 1.663(3) Å, which is in the range observed for B-B single bonds. By this measure 15 could be considered a metal stabilized complex of the B₂H₂ moiety, with the caveat that 15 undoubtedly features delocalized bonding between the Ni and BH vertices typical of clusters.
Scheme 4.6: Formation of cluster 15

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of cluster 15 features a sharp singlet at $\delta$ 41.2. The $^1\text{H}$ NMR spectrum features a pair of resonances for the phosphine ligands as well as a 2$\text{nd}$ order AA′A″XX′X″X‴ multiplet at $\delta$ −13.69, which integrates to four hydrides. The resonance associated with the two BH moieties was observed at $\delta$ 10.38 as an apparent broad doublet; the multiplet was successfully modeled as arising from coupling to quadrupolar $^{11}\text{B}$ with a $0.90 \text{ ms} \ T_1$ and a $^1J_{\text{BH}}$ of 158.3 Hz. Consistent with this interpretation, the $^{11}\text{B}$ NMR spectrum reveals a doublet $\delta$ 94.1 with the same $^1J_{\text{BH}}$. The $^{13}\text{C}\{^1\text{H}\}$ reveals a pair of 2$\text{nd}$ order resonances at $\delta$ 20.6 and 25.5 for the CH$_3$ resonances and CH of the phosphine moieties respectively. Both were successfully modelled using AXX′₂X‴ spin systems.
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Figure 4.5: ORTEP depiction of 15 with phosphine \(^3\)Pr substituents omitted for clarity.

Selected bond lengths: Ni(1)-Ni(2) = 2.5722(3) Å; Ni(1)-B(1) = 2.0008(17) Å; Ni(1)-B(1’)
= 2.0039(17) Å; Ni(2)-B(1) = 1.9989(17) Å; Ni(2)-B(1’) = 1.9995(17) Å; B(1)-B(1’) =
1.663(4) Å; Ni(1)-H(2) = 1.64(2) Å, Ni(2)-H(2) = 1.60(2) Å; Ni(2)-H(3) = 1.63(2) Å.
Selected bond Angles: Ni(1)–Ni(2)–Ni(1’) = 90.109(9) °; Ni(1)–B(1)–Ni(1’) = 130.93(9)
°; Ni(2)–B(1)–Ni(2’) = 130.84(9) °.

While the other clusters reported in this chapter have a core oxidation state that can be determined unambiguously, cluster 15 bears two borohydride ligands that has a B–B bond distance of 1.663(3) Å. As noted before, this distance is consistent with reports boron-boron single bond lengths. Thus, it becomes ambiguous whether cluster 15 bears two BH\(^2\)-ligands or one B\(_2\)H\(_2\)\(^2\)-ligand. This ligand designation would alter the core oxidation state from [Ni\(_4\)]\(^8+\) to [Ni\(_4\)]\(^6+\) respectively. In the former assignment, the Ni centres are all Ni\(^2+\),
and in support of this the Ni-Ni bond distances in 15 are longer than 11 and 12. In addition to the ambiguous assignment of oxidation state, the ligand designation also adds an obstacle in terms of cluster assignment. Considering the cluster as a mixed transition metal-main group cluster, it has the octahedral closo designation, with an expected electron count of 66 electrons, but has a count of 60 e\textsuperscript{-}. Alternatively, viewing the cluster as a square plane transition metal cluster with an arachno designation, the expected electron count is 64 e\textsuperscript{-}. Viewing the supporting ligand as BH gives the cluster an electron count of 56 e\textsuperscript{-}. Accounting for the previously discussed tendency for 16 electron Ni complexes, this would be electron precise. However, it is difficult to discount the potential closo designation of 15, as several clusters reported here do not agree with the predicted electron counts.

### 4.3. Conclusions

Tetranuclear square-planar clusters supported by hydrides and phosphines were synthesized that contained \( \mu_4\)-O, N and B atoms, in complexes 11, 12, and 15. These bonding modes are in contrast to the a \( \mu_5\)-C structure previously seen in \( [(\text{^3} \text{Pr}_3 \text{P})\text{Ni}]_5 \text{H}_4(C) \). Electron counts in these species are unexpectedly varied, and classic cluster counting rules are not always predictive of stability. Attempts to synthesize a similar square planar cluster with two bridging chlorides yielded the tetrahedral cluster 14. A summary of approximate bond lengths and formal oxidation states of clusters 1, 11, 12, 14, 15 and the related clusters \( [(\text{P}^\text{Pr}_3)\text{Ni}]_4 \text{H}_4\text{S} \) and \( [(\text{P}^\text{Pr}_3)\text{Ni}]_3 \text{H}_4\text{C} \) are shown in Figure 4.6. To date, little is known about the bonding modes and reactivity accessible to these small late-metal clusters. In some cases, the clusters appear to be models for surface bonding; however, with accessible alternate geometries, as observed in 14, a rich possibility for catalytic conversion reactions.
not possible on surfaces or bimetallic complexes can be envisioned. Further work in this direction is underway.

Figure 4.6. List of approximate bond lengths measured in Å and core oxidation states.
Chapter 4: Synthesis of Surface-Analogue Square Planar Tetranuclear Nickel Hydride Clusters and Bonding to $\mu_4$- NR, O and BH Ligands.

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 glove-box. Dry, oxygen-free solvents were employed throughout. Anhydrous pentane, toluene, and THF were purchased from Alfa Aesar and were argon packed and dried with either activated sodium or molecular sieves. Benzene-$d_6$ was dried by heating at reflux with Na/K alloy in a sealed vessel under partial pressure then trap-to-trap distilled and freeze–pump–thaw degassed three times. Cluster $1^{21}$ and [(Pr$_3$P)Ni]$_2$N$_2$$^{75}$ were synthesized as per literature procedures as N-methylmorpholine oxide, benzonitrile, and lithium borohydride were purchased from Sigma-Aldrich and their purity was confirmed through NMR spectroscopy. $^1$H, $^{31}$P{$^1$H} and $^{13}$C{$^1$H} NMR spectra were recorded on a Bruker AMX Spectrometer operating at 300 MHz or 500 MHz with respect to proton nuclei. All chemical shifts are recorded in parts per million, and all coupling constants are reported in Hertz. $^1$H NMR spectra were referenced to residual protons (C$_6$D$_5$H, $\delta$ 7.15) with respect to tetramethylsilane at $\delta$ 0.00. $^{31}$P{$^1$H} NMR spectra were referenced to external 85% H$_3$PO$_4$ at $\delta$ 0.00. $^{13}$C{$^1$H} NMR spectra were referenced relative to solvent resonances (C$_6$D$_6$, $\delta$ 128.0; C$_7$D$_8$, $\delta$ 20.4; C$_4$D$_8$O, $\delta$ 25.37). $^{11}$B{$^1$H} NMR spectra were referenced to external BF$_3$OEt$_2$ at $\delta$ 0.00. Elemental analyses were performed at the Center for Catalysis and Materials Research, Windsor, Ontario.

4.4.2: Synthesis and Characterization of Complexes

Synthesis and Characterization of [(Pr$_3$P)Ni]$_4$H$_4$(μ$_4$-O) (11). A solution of [(Pr$_3$P)Ni]$_3$H$_6$ (336 mg, 0.30 mmol) and four equivalents of N-methylmorpholine N-oxide
(143 mg, 1.22 mmol) in 20 mL toluene was stirred for 15 min to give a dark red solution. Volatiles were removed in vacuo and the residue was extracted with n-pentane (2 × 10 mL). The solution was cooled at −40 °C for 48 h, which provided bright red crystals suitable for X-ray diffraction. The mother liquor was then concentrated and multiple crops yielded a total of 159 mg of 12 (58.1%). Complex 11 is very stable in solid state and solutions of 11 remained unchanged for weeks at room temperature. Dark red blocks of 11 suitable for X-ray diffraction were isolated from cooling a saturated solution of 11 in n-pentane at −40 °C over a period of 16 hours.

1H NMR (298 K, C6D6, 500 MHz): δ −15.00 (AA’A”XX’X”X’” full span = 2×(2JPH + 3JPH) = 70.3 Hz, multiplet modeled with 2JHP=25.5 Hz, 3JHP=3.0 Hz, 2JHH=6.0 Hz, and 2JHH=10.2 Hz 4H, Ni-H), 1.37 (dd, 3JPH = 13.0 Hz, 3JHH = 7.1 Hz, 72H, P(CH(CH3)2)3), 2.31 (septet of d/apparent octet, 3JHH=7.5 Hz, 2JHP=7.9 Hz, 12H, P(CH(CH3)2)3). 31P{1H} NMR (298 K, C6D6, 121.5 MHz): δ 71.8 (s, 4P, NiP3). 13C{1H} NMR (298 K, C6H6, 75.5 MHz) δ 20.6 (d, 3JCH=1.8 Hz, 24C, P(CH(CH3)2)3), 26.7 (d, 3JCH=18.6 Hz, 12C, P(CH(CH3)2)3). Anal Calcd for C36H88Ni4OP4 (895.75): C, 48.41; H, 9.90; Found: C, 48.90; H, 9.98.

Synthesis and Characterization of [(iPr3P)Ni4(μ2-H)4(μ4-NCH2Ph)] (12). A solution of [(iPr3P)Ni]3H6 (200 mg, 0.18 mmol) and benzonitrile (47 mg, 0.45 mmol) in 15 mL toluene was stirred for 15 min, which gave a dark red solution. Volatiles were then removed in vacuo and the residue extracted with n-pentane (3 × 5 mL). The solution was cooled −40 °C for 16 h at which point dark red crystals suitable for X-ray diffraction were obtained. The mother liquor was concentrated and multiple crops yielded 115 mg of 12 (64.6%). 1H NMR (298 K, C6D6, 500 MHz): δ −13.55 (AA‘A”XX’X”X’” full span = 2×(2JPH + 3JPH)
Chapter 4: Synthesis of Surface-Analogue Square Planar Tetranuclear Nickel Hydride Clusters and Bonding to μ₄-NR, O and BH Ligands.

= 60.5 Hz, multiplet modeled with \(^2J_{HP}=22.4\) Hz, \(^3J_{HP}=2.2\) Hz, \(^2J_{HH}=7.2\) Hz, and \(^2J_{HH}=4.5\) Hz 4 H, Ni-H), 1.37 (dd, \(^3J_{PH}=12.5\) Hz, \(^3J_{HH}=7.1\) Hz, \(^2J_{HH}=72\) H, P(CH(CH₃)₂)₃), 2.24 (septet of d/apparent octet, \(^3J_{HH}=7.1\) Hz, \(^2J_{HP}=7.6\) Hz, 12 H, P(CH(CH₃)₂)₃), 3.11 (pentet, \(^4J_{PH}=2.6\) Hz, NCH₂). 6.91–7.35 (overlapping m, 5 H, aromatic C–H); \(^{31}P\{^1H\} NMR (298 K, C₆D₆, 121.5 MHz): \(\delta 63.20\) (s, 4 P, NiP₃iPr₃). \(^{13}C\{^1H\} NMR (298 K, C₆D₆, 125.7 MHz) \(\delta 21.04\) (d, \(^2J_{CP}=3.5\) Hz, 24 C, P(CH(CH₃)₂)₃), 26.97 (d, \(^1J_{CP}=15.2\) Hz, 12 C, P(CH(CH₃)₂)₃), 57.98 (p, \(^3J_{CP}=1.8\) Hz, 1 C, NCH₂), 125.40 (s, 1 C, ipso-C), 126.60 (s, 2 C, aromatic C), 128.25 (s, 2 C, aromatic C), 145.27 (s, 1 C, ipso-C)  Anal Calcd for C₄₃H₉₅Ni₄P₄ (981.71): C, 52.58; H, 9.76; N, 1.43; Found: C, 52.58; H, 9.14; N, 1.82.

Synthesis of 13. A solution of Ni(COD)₂ (500 mg, 1.82 mmol) in 15 mL of toluene was added to 1 equiv of iPr₃P (296 mg, 1.82 mmol) and a two-fold excess of benzonitrile (375 mg, 3.64 mmol) and dissolved in 10 mL of toluene. The solution was stirred for 15 min and the solution was dried under vacuum. The solid product was dissolved in 10 mL of n-pentane and filtered through Celite. The resulting solution was then cooled to −40 °C for 72 h, which provided bright orange crystals. The mother liquor was then concentrated and multiple crops yielded 450 mg of 13 (78.0%). \(^1H NMR (298 K, C₆D₆, 500 MHz) \(\delta 1.04\) (dd, \(^3J_{PH}=12.5\) Hz, \(^3J_{HH}=7.2\) Hz, 54 H, P(CH(CH₃)₂)₃), 1.66 (septet of d/apparent octet, \(^3J_{HH}=7.2\) Hz, \(^2J_{HP}=7.6\) Hz, 9 H, P(CH(CH₃)₂)₃), 6.96(t, \(^3J_{HH}=7.2\) Hz, 3 H, p-protons), 6.96(t, \(^3J_{HH}=7.2\) Hz, 3 H, p proton), 7.04 (apparent t/dd, \(^3J_{HH}=7.2\) Hz, \(^3J_{HH}=7.3\) Hz, 6 H, m-protons), 7.25(d, \(^3J_{HH}=7.3\) Hz, 6 H, o-protons). \(^{31}P\{^1H\} NMR (298 K, C₆D₆, 202.4 MHz): \(\delta 61.1\) (s, 4 P, PPr₃) \(^{13}C\{^1H\} NMR (298 K, C₆D₆, 125.7 MHz): \(\delta 20.30\) (s, 18 C, P(CH(CH₃)₂)₃), 24.61 (d, 9 C, \(^2J_{CP}=14.8\) Hz, P(CH(CH₃)₂)₃), 125.04 (s, 6 C, m/o–carbon

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N≡C–C₆H₅), 125.69 (s, 3C, $p$–carbon N≡C–C₆H₅), 127.47 (s, 6C, m/o–carbon, N≡C–C₆H₅), 136.36 (2$^\text{nd}$ order multiplet spin system AXX'Y, 3C, ipso–carbon N≡C–C₆H₅), 177.08 (2$^\text{nd}$ order multiplet spin system AXX'Y, 3C, N≡C–C₆H₅). Anal Calcd for Ni₃P₃C₄H₇₉N₃ (963.34): C, 59.79; H, 8.16; N, 4.36 Found: C, 60.20; H, 8.13; N, 4.54

Synthesis and Characterization of 14 [(Pr₃P)Ni]₄H₄Cl₂. The dinitrogen complex [(Pr₃P)₂Ni]₂(μ-N₂) (950 mg, 1.21 mmol) and 2 equivalents (Pr₃P)₂NiCl (1.00 g, 2.42 mmol) were dissolved in 150 mL of n-pentane. The solution was transferred to a 500 mL high pressure Schlenk flask, degassed under vacuum and subjected to 4 atm of dihydrogen with rapid stirring for 2.0 h, at which point the solution turned dark brown. After removal of excess dihydrogen, the solution was filtered through a plug of Celite, then concentrated and left at −40 °C for 16 h. Dark brown crystals suitable for X ray diffraction were obtained from the first crop giving a yield of 485 mg (49%). $^1$H NMR (298 K, C₆D₆, 500 MHz): δ −25.50 (s, 4H, Ni–H), 1.38 (d, $^3$J$_{HH}$ = 7.1 Hz $^3$J$_{HP}$ = 12.8 Hz, 36H, P(CH(CH₃)₂)₃), 2.09 (septet of d/apparent octet, $^3$J$_{HH}$ = 6.9 Hz, $^2$J$_{HP}$ = 7.1 Hz, 12H, P(CH(CH₃)₂)₃) $^{31}$P{$^1$H} NMR (298 K, C₆D₆, 202.5 MHz): δ 45.66 (s, 4P, P(CH(CH₃)₂)₃), 13C{$^1$H} NMR (298 K, C₆H₆, 75.5 MHz): δ 20.32 (2$^\text{nd}$ order multiplet, spin system AXX'2X''), $^3$J$_{CP}$ = 2.8 Hz, $^2$J$_{PP}$ = 17.6 Hz, 24C, P(CH(CH₃)₂)₃), 23.41 (2$^\text{nd}$ order multiplet, spin system AXX'2X''), $^2$J$_{CP}$ = 14.8 Hz, $^3$J$_{PP}$ = 17.6 Hz, 12C, P(CH(CH₃)₂)₃). Anal Calcd for C₃₆H₈₈Cl₂Ni₄P₄ (950.67) C, 45.65; H, 9.37, Found C, 45.73; H 9.27.

Synthesis of 14-d₄ [(Pr₃P)Ni]₄D₄Cl₂.

50 mL of n-pentane was used to dissolve the dinitrogen product [(Pr₃P)₂Ni]₂(μ-N₂) (2.7 g, 3.43 mmol) and 0.67 equivalents of (Pr₃P)₂NiCl₂ (1.03 g, 2.29 mmol) and was then
transferred to a 500 mL high pressure Schlenk flask. The solution was then evacuated and introduced to 4 atm. of deuterium gas and stirred for 2.0 h, at which point the solution became a dark brown colour. After removal of excess deuterium, the solution was filtered through a plug of Celite, concentrated and left at $-40 \, ^\circ\text{C}$ for 16 h. Dark brown crystals suitable for X-ray diffraction were obtained from the first crop giving a yield of 1.05 g (48.2%).

**Synthesis and Characterization of 15 [(^3\text{Pr}_3\text{P})\text{Ni}]_4\text{H}_4(\text{BH})_2.**

A solution of (Ni(P^3\text{Pr})_4\text{H})_4\text{Cl}_2 (471 mg, 0.50 mmol) in 20 mL of THF is added to 4 equivalents of LiBH$_4$ (44 mg, 2.0 mmol) at room temperature. The solution was stirred for 0.33 h at which point the solution changed to a dark violet color. The solution was then put under reduced pressure to remove all volatiles. The crude product was then extracted with 3 x 20 mL of $n$-pentane and filtered through a plug of Celite. The filtered solution was concentrated and left at $-40 \, ^\circ\text{C}$ for 16 h at which point bright red crystals suitable for X-ray diffraction were obtained. The mother liquor was then concentrated and additional crops were collected to give a combined yield of 285 mg (63%). $^1\text{H}$ NMR (298 K, C$_6$D$_6$, 500 MHz): $\delta$ −13.69 (apparent broad t, 2$^{\text{nd}}$ order multiplet AA’A”A’’XX’X’’”, 4H, $^2J_{\text{HF}}= 12.0 \, \text{Hz}$, $^3J_{\text{HF}}= 4.2 \, \text{Hz}$, Ni−H), 1.33(dd, $^2J_{\text{HF}}=7.0 \, \text{Hz}$ $^3J_{\text{HF}}=11.7 \, \text{Hz}$ 36H, P(CH(CH$_3$)$_2$)$_3$), 2.24 (septet of d/apparent octet, $^3J_{\text{HF}}=7.0 \, \text{Hz}$, $^2J_{\text{HF}}= 7.4 \, \text{Hz}$ 12H, P(CH(CH$_3$)$_2$)$_3$), 10.38 (apparent d, modeled T$_1 = 0.90 \, \text{ms}$, 2H, B−H). $^{31}\text{P}\{^1\text{H}\}$ NMR(298 K, C$_6$D$_6$, 202.5 MHz):$\delta$ 41.2 (s, 4P, P(CH(CH$_3$)$_2$)$_3$) $^{13}\text{C}\{^1\text{H}\}$ NMR (298 K, C$_6$H$_6$, 75.5 MHz): $\delta$ 20.58 (2$^{\text{nd}}$ order multiplet, spin system AXX’$^2$X”, $^2J_{\text{CP}} = 4.5 \, \text{Hz}$, $^3J_{\text{PP}} = 8.0 \, \text{Hz}$, 24C, P(CH(CH$_3$)$_2$)$_3$), 25.45 (2$^{\text{nd}}$ order multiplet, spin system AXX’$^2$X”, $^2J_{\text{CP}} = 11.2 \, \text{Hz}$, $^3J_{\text{PP}} = 8.0 \, \text{Hz}$, 12C,
Chapter 4: Synthesis of Surface-Analogue Square Planar Tetranuclear Nickel Hydride Clusters and Bonding to μ- NR, O and BH Ligands.

P(CH(CH$_3$)$_2$)$_3$ $^1$H NMR (298 K, C$_6$D$_6$, 160.5 MHz): δ 94.1 (broad d, $^1$J$_{BH}$=158.3 Hz, 2B, B$_2$H$_2$). Anal Calcd for C$_{36}$H$_{88}$B$_2$Ni$_4$P$_4$ (903.40): C, 47.98; H, 10.07. Found C, 47.75; H 10.26;

4.5 X-Ray Crystallography

Table 4.1: Crystallographic Information of Compounds 11-15

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References begin on page 139
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4.6 Supporting Information

Full details of crystallographic information in CIF format for compounds 11-15 along with experimental NMR spectra can be found at:

https://pubs.acs.org/doi/suppl/10.1021/acs.inorgchem.7b02546
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4.6: References

Chapter 4: Synthesis of Surface-Analogue Square Planar Tetranuclear Nickel Hydride Clusters and Bonding to $\mu^4$-NR, O and BH Ligands.


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Chapter 5 - Mechanistic Insight Into H/D Exchange by a Pentanuclear Ni–H Cluster and Synthesis and Characterization of Structural Analogues of Potential Intermediates

Chapter 5 adapted from published work: DOI: 10.1021/acs.organomet.7b00763

5.1 Introduction:

The last decade has seen several reports of transition metal clusters$^{1-2}$ undergoing unprecedented bond transformations with traditionally-inert bonds,$^{3-11}$ including the activation of C-C bonds in hydrocarbons such as benzene$^{4,9}$ and ethylene$^{11}$. This has spurred on increasing rational design of transition metal clusters and polynuclear
complexes, in an attempt to access similar cooperative reactivity. Interactions amongst proximal late-transition metal centres could be envisioned to facilitate metal surface-like transformations. Thousands of transition metal clusters have been reported in the Cambridge Structure Database with the vast majority of them comprised of either late-transition metals with π acceptor ligands like CO, or early transition metals with π donor ligands. Few examples of clusters are known that are composed of solely late transition metals and electron-rich phosphines and hydrides. Our group has reported examples of inert-bond activation by the electron-deficient pentanuclear Ni cluster, [(Pr₃P)Ni]₅H₆ (1), which includes ultra-deep hydrodesulfurization (HDS), CC bond cleavage of unactivated alkenes, and catalytic H/D exchange of unactivated aromatics such as benzene. Moreover, these transformations all proceed at room temperature. Cluster 1 is highly reactive in the presence of substrates such as unencumbered alkenes; however, 1 is surprisingly selective and functional group tolerant. Complex 1 does not react rapidly with amines, alcohols, or even water. Mechanistic studies of the CC bond cleavage reaction show that all five Ni centres in 1 aid in the binding of alkenes via initial triple C-H bond activation with minimal reaction barriers. Reactivity studies with 1 have shown the propensity of 1 to form stable tetranuclear clusters with bridging N, O, B, S, and Cl heteroatoms. Although these reactions give little direct insight into the mechanism of unactivated arene H/D exchange catalyzed by 1, the studies of CC bond cleavage suggest that it could occur with cooperativity from all five metal centres.
Chapter 5: Mechanistic Insight Into H/D Exchange by a Pentanuclear Ni–H Cluster and Synthesis and Characterization of Structural Analogues of Potential Intermediates

Scheme 5.1: Inert-bond activation facilitated by 1

Hydrogen-isotope-exchange (HIE) facilitated by transition metals is well-studied due to the application in selectively deuterating or tritiationg organic molecules that are used in pharmaceuticals.\textsuperscript{31-37} Though several techniques have been reported that are effective for HIE, in many cases the mechanisms are poorly understood and several require harsh conditions.\textsuperscript{38} The ability of 1 to catalyze H/D exchange of unactivated arenes such as benzene or toluene is of interest, particularly given that room-temperature activation of arene C-H bonds at Ni typically requires activating groups like ortho-F substituents.\textsuperscript{39-49} Herein we report mechanistic studies of the catalytic H/D exchange of 1. Although no intermediates could be observed or isolated in H/D exchange, reactivity studies are

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described that provide complexes that give insight into how these clusters could interact with arene $\pi$-ligands and facilitate H/D exchange.

5.2 Results and Discussion:

5.2.1 Stoichiometric H/D Exchange with 1. The stoichiometric reaction of 1 with an excess of deuterated arene provides a simple non-catalytic system to study H/D exchange. The room-temperature addition of 1 to deuterated arenes, such as C₆D₆ and C₇D₈, provides the isotopologues 1-$d_n$ (where $n = 1$-6), as shown in Scheme 5.2, along with isotopologues of the arene. These reactions proceed at room temperature, and the degree of H/D exchange into 1 is easily monitored by $^{31}$P{$^{1}$H} NMR, because the resonances for 1-$d_0$-$d_6$ have large temperature-dependent isotope shifts that arise due to a low-energy paramagnetic state. The extent of the isotope shift is dependent upon the degree of deuteration, with a separation between the 1-$d_0$ and 1-$d_1$ $^{31}$P{$^{1}$H} NMR shifts of 0.9 ppm, and a separation between the 1-$d_5$ and 1-$d_6$ shifts of 0.6 ppm, at 298 K. The incorporation of deuterium into 1 gives a statistical mixture of 1-$d_{0-6}$ that can be modelled to accurately determine the percent deuteration, and thus monitor the rate of H/D exchange.
Figure 5.1. a) H/D exchange of cluster 1 with arenes to form a series of isotopologues. b) $^{31}\text{P}\{^{1}\text{H}\}$ NMR of a statistical mixture of 1-d$_{0}$-6

H/D exchange reactions between 1 and C$_{6}$D$_{6}$ are first order with respect to overall Ni-H concentration in solution for several hours, but slowed as complex 1 gradually decomposed in solution at room temperature. The decrease in reaction rate suggested that $^{i}\text{Pr}_{3}\text{P}$ generated by decomposition of 1 was inhibiting the H/D exchange. By monitoring the kinetics of H/D exchange of 1 in the presence of different added concentrations of phosphine, it was found that the rate of reaction was inversely correlated to [$^{i}\text{Pr}_{3}\text{P}$], suggestive of an H/D exchange mechanism that involves phosphine dissociation at or
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before the rate-determining step. Similar experiments were conducted to determine the order of reaction of 1 and C₆D₆. These reactions were done with added iPr₃P to avoid errors associated with the thermal decomposition of 1 liberating iPr₃P. The rate of exchange was found to be 1ˢᵗ order with respect to both the concentration of Ni-H in 1-d₀₆ and in [C₆D₆]. The addition of partial pressures of H₂ as low as 1.3 × 10⁻⁶ atm caused a 10-fold decrease in rate, however, identical rates were observed at higher H₂ pressures of 1.3 × 10⁻⁵, and 6.6 × 10⁻⁵ atm. This observation can be rationalized by proposing two mechanisms of H/D exchange. One mechanism, which dominates in the absence of added H₂ is postulated to involve equilibrium loss of H₂ prior to a rate determining C–D bond activation. The second mechanism that dominates in the presence of even minimal added H₂ would have rate determining C–D bond activation occur without prior H₂ reductive elimination, either by an oxidative addition or σ-bond metathesis mechanism.

Both in arene solvents and pentane, the addition of higher pressures of dihydrogen to solutions of 1 gives an equilibrium amount of a new hydride containing species. Attempts to crystallize this equilibrium complex gave only low yields of its less soluble precursor 1, even under 4 atm H₂ and at −80 °C, so its characterization was limited to solution NMR. The complex features a broad hydride resonance at δ –19.0 and a broad resonance in the 3¹P{¹H} NMR spectrum that overlaps with 1. Increasing the pressure of dihydrogen gives an increase in the concentration of the unknown product. It is likely that this species is the 68 electron complex [(iPr₃P)Ni]₅H₈; the Pt analogue, [(tBu₂PhP)Pt]₅H₈, is known, though no reactivity studies have been reported.²⁶ Although the reaction of 1 with D₂ gives rapid incorporation of deuterium to give 1-d₁₋₆, catalytic incorporation of
deuterium into C₆H₆ was exceedingly slow using D₂ gas, due to the inhibition of the faster H/D exchange mechanism by added D₂.

To provide further mechanistic insight, the effects of temperature on the rate of H/D exchange were determined. A solution composed of 0.021 M of 1, 1.623 M of C₆D₆, and 0.095 M of iPr₃P in n-pentane was monitored at 15, 20, 25, and 30 °C by ³¹P{¹H} NMR to determine the rate of H/D exchange. The Eyring plot graphed showed a linear correlation and is provided in the supplementary information. The enthalpy and entropy of activation were 41.5 kcal·mol⁻¹ and 67.4 cal·K⁻¹·mol⁻¹. The large positive entropy of activation is typical of a dissociative mechanism. The influence of both iPr₃P dissociation and C₆H₆ association steps should give a net marginal entropy of activation. The large positive entropy of activation is consistent with the dominant mechanism involving further equilibrium loss of H₂ under these conditions, to give potentially the 68 electron species (C₆D₆)Ni[iPr₃P]₄(μ²-H)₄, which could then undergo rate-limiting C–D bond activation.

### 5.2.2 Catalytic H/D Exchange and Site Selectivity

Several mono-substituted arenes were exposed to a catalytic amount of 1 and C₆D₆ to monitor the regioselectivity of H/D exchange. Site-selectivity studies with cluster 1 and fluorobenzene revealed approximately equal meta and ortho H/D exchange with no observed para activation, as shown in Scheme 5.3a. The observed site selectivity is different from known mononuclear Ni C–H activation mechanisms which are generally ortho selective. The regioselectivity with fluorobenzene suggests that 1 does not dissociate into mononuclear fragments that then undergo reversible C-H bond oxidative addition. Cluster 1 and C₆D₆ were also exposed to 2-methoxynaphthalene, and ¹H and ¹³C{¹H} NMR spectra revealed deuterium incorporation in all aromatic C-H sites apart from the 1-site, which is electronically similar.
to the 3-site. The lack of reactivity at the 1-site is presumably due to the steric influence of the closest C-H bond on the adjacent ring. Peculiar regioselectivities were observed with a few of the analyzed substrates. For example, anisole showed a strong preference for meta H/D exchange, which was not observed for the electronically similar dimethylaniline. In addition, ortho H/D exchange was observed in anisole but not dimethylaniline. This latter fact may be rationalized by the larger steric influence of the NMe₂ group. A similar lack of regioselectivity was observed in α,α,α-trifluorotoluene, with no exchange at the sterically encumbered ortho positions, but near equal rates of exchange at the meta and para sites.

Competition reactions were conducted with a variety of mono-substituted arenes in the presence of catalytic amounts of 1 and C₆D₆, to monitor the effect of changing electronic parameters on the rate of H/D exchange, as shown in Scheme 5.3b. However, with the exception of α,α,α-trifluorotoluene and fluorobenzene, the change in substituents induced a minimal influence on the rate of H/D exchange. Although the most electrophilic arenes react fastest, the selectivities are not consistent with a nucleophilic attack at the arene. The electron-withdrawing nature of the CF₃ and F substituents may influence the arene-binding step of the mechanism, which would account for the increase in rate of exchange. The lack of typical selectivity in these reactions may indicate a transition state for C-H activation with little Ni-C bond formation.

When these competition reactions were run for extensive periods of time there was evidence of Ni metal particles formation that also facilitated H/D exchange, but with different selectivities. For example, when 1 was exposed to C₆D₆ and toluene, no initial H/D-exchange into the sp³ C-H bonds of toluene was observed, but after 16 h at room temperature, significant deuteration of the methyl sites was detected, consistent with H/D
exchange mediated by a Ni surface.\textsuperscript{52-53} The regioselectivities presented in Scheme 5.2c were determined from initial rates of exchange.

\textbf{Scheme 5.2.} a) The observed \textit{ortho} and \textit{meta} H/D-exchange between C$_6$D$_6$ and fluorobenzene with catalytic 1 b) Deuterium incorporation into all \textit{sp}² C-H sites of 2-methoxy naphthalene apart from the 1-site. c) General scheme for competition reactions conducted with various substituents. Relative rates between substrate C-H sites are shown beside their respective sites.

\textbf{5.2.3 H/D Exchange in the Presence of Hg.} The 1\textsuperscript{st} order kinetics observed in our kinetics studies are not consistent with Ni metal from the decomposition of 1 being the active species for H/D exchange; however, as noted in the absence of added \textit{iPr$_3$P} and over
extended reaction times a precipitate formed from solutions of \( \text{I} \), and H/D exchange reactions are observed that \( \text{I} \) is not capable of, such as the weaker \( \text{sp}^3 \) C–H bonds in the methyl group of toluene. In an attempt to amalgamate any Ni nanoparticles competing with cluster \( \text{I} \), mercury metal was added to solutions of \( \text{I} \) and \( \text{C}_6\text{D}_6 \). This reaction was monitored by \( ^1\text{H} \) and \( ^{31}\text{P}\{^1\text{H}\} \) NMR spectroscopy, and both showed the immediate disappearance of \( \text{I} \) and the formation of \([[(\text{Pr}_3\text{P})\text{Ni}](\text{H}_6)(\mu_4-\text{Hg})] \) (16) as shown in Scheme 5.3. This reaction proceeds rapidly at room temperature when a large excess of Hg metal is used. Despite the quantitative conversion observed by NMR spectroscopy, an isolated yield of approximately 58% was obtained after recrystallization from \( n \)-pentane.

![Scheme 5.3: Reaction of cluster 1 with Hg to give the heterometallic cluster 16](image)

The \(^{31}\text{P}\{^1\text{H}\} \) NMR spectrum of 16 features a broad peak centred at approximately \( \delta \) 37.5 with a \( W_{1/2} \) of 1250 Hz (\( W_{1/2} \) = peak width at half height). At \(-40 \, ^\circ\text{C}\) the slow exchange limit \(^{31}\text{P}\{^1\text{H}\} \) NMR spectrum was observed, which features a doublet at \( \delta \) 37.2 with a \( J_{PP} = 12.9 \, \text{Hz} \) that corresponds to the 4 phosphines in the basal plane, and a pentet at \( \delta \) 94.5 for the capping Ni with the same \( J_{PP} = 12.9 \, \text{Hz} \) but also \(^{199}\text{Hg} \) satellites \((I = 1/2, 3/2)\).
16.8 %) with a $J_{\text{PHg}}$ of 1208 Hz. The observation of coupling to the Hg centre for the phosphine on the capping Ni but not for the phosphines on the Ni centres in the square base is unique to 16, and not observed in structurally related $\mu_4$-Hg Au clusters, where the $^2J_{\text{HgP}}$ coupling to the phosphines in the basal plane is large. Antipodal ligands in carborane, and metallocarborane clusters have been reported to influence chemical shifts, but not coupling constants. The $^1$H NMR spectrum has the expected PCH and Me resonances for the five $\text{^iPr}_3\text{P}$ in rapid exchange, along with a resonance for the six hydrides at $\delta$ $-28.62$. The hydride resonance is exchange broadened, with a $W_{1/2}$ of 450 Hz. Cooling the solution of cluster 16 to $-60$ °C gave the slow exchange limit for the hydride region of the $^1$H NMR spectrum, which has two singlets at $\delta$ $-34.75$ and $\delta$ $-16.30$ in a 4 : 2 ratio. An Arrhenius activation energy of 8.1 kcal·mol$^{-1}$ was calculated for the exchange process. The $^{13}$C{$^1$H} NMR of 16 displays a pair of resonances for the methyl and methine environments of the phosphine ligand, with the latter coupling to the phosphine to give a doublet. Despite our best efforts, $^{199}$Hg{$^1$H} NMR spectra yielded no resolvable signal from a chemical shift range of $\delta$ $-5000$ to 5000, even at $-60$ °C.

The crystallization of 16 is facile, and yields seemingly perfect cubic crystals that diffract well; however, the solid-state structure from single-crystal X-ray diffraction could not be determined accurately, likely due to twinning, and only connectivity could be confirmed. Around 82 % of the diffraction data indexed to a tetragonal P unit cell with a volume of approximately 5800 Å$^3$, but weaker diffraction fit to an apparent tetragonal cell with four times the volume. In multiple different data sets it proved difficult to assign both the unit cell and space group, though in many attempted space groups the Ni$_5$Hg core could be observed, but with complete disorder of the supporting ligands. Further details
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are provided in the Supporting Information. Cluster 16 features a \([\text{Ni}_5\text{Hg}]^{6+}\) core in an octahedral geometry and could be considered an octahedral closo cluster. It bears an electron count of 76 electrons which is considered electron deficient compared to the anticipated 86 electrons. The Wade-Mingos electron counting rules are based on the 18-electron rule for transition metal complexes,\(^{58}\) while many 16 electron complexes are known for Ni centres.\(^{59}\) Accounting for the 2-electron difference per Ni centre, cluster 16 is electron precise. Only a few Ni-Hg complexes have been reported in the Cambridge Structural Database;\(^{60-67}\) Kubiak has reported a Hg centre bound to four Ni centres, albeit in a distorted planar-Hg geometry.\(^{67}\) The closest structural analogues with respect to the capping \(\mu_4\)-Hg environment in 16 have been reported in Au, Au/Pd, and Au/Pt clusters.\(^{68-69}\) Similarly to 1, samples of 16 in \(\text{C}_6\text{D}_6\) were found to undergo H/D-exchange with the solvent, which could be monitored by a decrease of the hydride resonance intensity in the \(^1\text{H}\) NMR and an increase in the intensity of the \(\text{C}_6\text{D}_5\text{H}\) resonance. The exchange with 16 in neat \(\text{C}_6\text{D}_6\) is significantly slower than with 1, with a \(t_{1/2}\) of \(4.76 \times 10^4\) s versus the \(t_{1/2}\) of \(1.8 \times 10^3\) s for 1.

5.2.4 Reactions of 1 with Cyclopentadienide Moieties and Cyclopentadiene

Cyclopentadienylthallium was reacted with cluster 1 at room temperature, with the intention that the CpTl fragment would bind in a similar manner to Hg in complex 16. The \(^{31}\text{P}\{^1\text{H}\}\) and \(^1\text{H}\) NMR showed immediate conversion to a new hydride bearing complex along with the loss of an equivalent of \(^3\text{Pr}_3\text{P}\). Rather than having a TlCp fragment bound to the square plane of the cluster, \((\eta^5\text{-Cp})\text{Ni}[(^3\text{Pr}_3\text{P})\text{Ni}]_4(\mu_2\text{-H})_4(\mu_4\text{-Tl})\) (17) was formed, which features Tl bound to the 4 Ni of the basal square plane, with the Cp ligand replacing the phosphine on the capping Ni along with the loss of one equivalent of dihydrogen, as

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Cluster 17 was isolated through recrystallization from n-pentane at $-40 \, ^\circ C$ in a yield of 66%.

Scheme 5.4. Reaction of cluster 1 with TlCp to synthesize the Cp bearing cluster 17

The solid-state structure of 17 is shown in Figure 5.2. The molecule has four Ni centres in a square plane with Ni–Ni bond distances ranging from 2.5107(4) to 2.5228(4) Å and a capping Ni bound to all four Ni centres with Ni–Ni bond lengths ranging from 2.3696(4) to 2.3730(4) Å. The four phosphine centres all lie in the plane of the Ni square base. The four bridging hydride ligands were located in an electron density difference map and are also in the square plane. The $\eta^5$-Cp ligand is bound to the capping Ni with a Ni(1)-Cp centroid distance of 1.788 Å. The Tl centre is located opposite of the capping Ni of the cluster and is bound to the four Ni centres in the square plane with Ni–Tl bond distances ranging from 2.6798(3) to 2.7334(3) Å. The $\text{C}_\text{p}_{\text{centroid}}$–Ni(1)–Tl(1) bond angle is 178.15°.
Figure 5.2. ORTEP depiction of cluster 17. Phosphine isopropyl groups and hydrogens on the Cp ligand are omitted for clarity. Selected bond distances (Å): Ni(1)–Ni(2) 2.3697(4), Ni(1)–Ni(3) 2.3696(4), Ni(1)–Ni(4) 2.3718(4), Ni(1)–Ni(5) 2.3730(4), Ni(1)–C_{centroid} 1.788, Ni(2)–Ni(3) 2.5228(4), Ni(3)–Ni(4) 2.5124(4), Ni(2)–Ni(5) 2.5107(4), Ni(4)–Ni(5) 2.5132(4), Ni(2)–Tl(1) 2.7334(3), Ni(3)–Tl(1) 2.6798(3), Ni(4)–Tl(1) 2.7302(3), Ni(5)–Tl(1) 2.7158(3). Selected bond angles (°): Tl(1)–Ni(1)–C_{centroid} 178.15, Ni(3)–Tl(1)–Ni(5) 81.838(9), Ni(2)–Tl(1)–Ni(4) 81.825(9).

The $^{31}$P{$^1$H} NMR spectrum of 17 features a singlet at $\delta$ 31.4. The $^{13}$C{$^1$H} NMR spectrum displays a singlet for the $^{1}$Pr methyl groups, whereas a second-order AXX'2X'' multiplet with $^2J_{PC}=10.9$ Hz is observed for the methine environment. A singlet at $\delta$ 85.2 is observed from the Cp carbons. The $^1$H NMR spectrum displays a pair of resonances corresponding to the $^1$Pr substituents and a singlet at $\delta$ 5.20 for the Cp ligand. The hydride resonance $\delta$ –24.20 is a pentet with $J_{PH} = 2.8$ Hz that integrates to 4 hydrides relative to the four phosphine ligands. The observation of a binomial pentet suggests that this is an...
average coupling to all four phosphines, and a fluxional process exchanges hydride environments; the same is not true in related complexes with a square planar Ni₄H₄ core.¹⁰ The $^{205}\text{Tl}\{^1\text{H}\}$ NMR spectrum features a broad singlet at $\delta$ 821.1.

Similar to 16, cluster 17 is a closo cluster with an octahedral core geometry. Overall, the four hydride ligands and the Cp ligand give cluster 17 five anionic X ligands. The thallium centre is best considered as formally cationic, consistent with thallium’s most common oxidation state, Tl(I). The electron count of cluster 17 of 68 electrons, and once again the apparent deficiency could be explained by the propensity of Ni complexes to form stable 16 electron compounds. Transition metal thallium complexes are reported in literature; however, examples of Ni–Tl complexes are quite rare,⁷⁰-⁷² though an example of a trinuclear Ni cluster with a Tl–I fragment was reported by Kubiak.⁷² The capping $\mu_4$-Tl binding mode of Tl in 17 is unprecedented in any Tl containing transition metal cluster.

Cyclopentadienyl complexes are well documented in the organometallic chemistry of Ni,⁷³ and have also found use as a supporting ligand in Ni clusters.²⁹ Of interest in H/D exchange with 1 is that the formally anionic $(\eta^5$-Cp)$(i\text{Pr}_3\text{P})_4\text{Ni}_5$($\mu_2$-H)$_4^-$ fragment in 17 is isoelectronic to the proposed intermediate for H/D exchange via the H₂ dissociation mechanism, $(\eta^6$-C₅D₅)Ni[(i\text{Pr}_3\text{P})\text{Ni}]$_4$($\mu_2$-H)$_4$. The formal anionic fragment in 17 is stabilized by strong covalent interactions afforded by the soft cation Tl, so attempts were made to synthesize an analogous cluster with a harder cation that would afford only ionic interactions. The reaction of [(i\text{Pr}_3\text{P})\text{Ni}]$_5$H$_6$ with one equivalent of Cp₂Mg at room temperature gave dark brown $(\eta^5$-Cp)$(i\text{Pr}_3\text{P})_4\text{Ni}_5$($\mu_2$-H$_6$)($\mu_4$-MgCp) (18) and an equivalent of $i$Pr₃P, as shown in Scheme 5.4. Contrary to the reaction forming 17, no loss of dihydrogen is observed, and 18 retains six hydride ligands. Although the $^{31}\text{P}\{^1\text{H}\}$ and $^1\text{H}$

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NMR spectra showed near quantitative conversion to 18, an isolated yield of 68% was obtained after recrystallization from n-pentane at −40 °C.

Scheme 5.5. Reaction of cluster 1 with Cp₂Mg to give 18.

The solid-state structure of 18 was obtained by X-Ray crystallography and is shown in Figure 5.3. The structure features two-fold disorder of the CpNi₅MgCp core. The proximal carbon atoms of the C(1)–C(5) and C(6)–C(10) cyclopentadienyl rings were constrained to have identical thermal parameters. The nickel hydrides, which should also be two-fold disordered could not be accurately located in the electron density difference map, and thus were not included in the model. Cluster 18 features a distorted square pyramid geometry composed of 5 Ni centres, with the square base Ni–Ni bond distances ranging from 2.417(10) to 2.502(10) Å and the Ni–Ni bond distances from the capping Ni to the square base Ni centres ranging from 2.485(10) – 2.650(10) Å. Four terminal phosphine ligands are bound to each of the Ni centres in the square base, while the capping Ni(1) has an η⁵-Cp. The bond distance from the capping Ni(1) to the Cp centroid is 1.794 which is similar to the Ni–Cpk centroid distance featured in 17. The bottom face of the cluster...
features a MgCp fragment that is bound to the 4 Ni centres in the square base with Ni–Mg distances ranging from 2.562(10) to 2.947(13) Å. The Cp ligand bound to the Ni centre lies almost directly above the Ni centre along with the MgCp fragment below with a \( \text{Cp}_{\text{centroid}}-\text{Ni}(1)-\text{Mg}(1) \) bond angle of 170.1°.

**Figure 5.3.** ORTEP depiction of cluster 18, with disorder not shown. Carbons and hydrogens on phosphine ligands excluded for clarity. Hydride ligands were not located. Selected bond distances (Å): Ni(1)–Ni(2A) 2.616(9), Ni(1)–Ni(3A) 2.497(4), Ni(1)–Ni(2B) 2.651(10), Ni(1)–Ni(3B) 2.485(10), Ni(1)–C(1–5)$_{\text{centroid}}$ 1.763, Ni(2A)–Ni(3A) 2.417(10), Ni(3A)–Ni(2B) 2.435(10), Ni(2B)–Ni(3B) 2.502(10), Ni(3B)–Ni(2A) 2.485(10), Ni(2A)–Mg(1) 2.682(16), Ni(3A)–Mg(1) 2.562(10), Ni(2B)–Mg(1) 2.713(16), Ni(3B)–Mg(1) 2.947(13). Selected bond angles (°): Mg(1)–Ni(1)–C(1–5)$_{\text{avg}}$ 176.24, Ni(2A)–Mg(1)–Ni(2B) 81.5(4), Ni(3A)–Mg(1)–Ni(3B) 76.5(3).
Although the solid-state structure of 18 did not reveal the hydride locations, the room temperature $^1$H NMR had a sharp singlet hydride resonance at $\delta$ –22.23 that integrates to six. The CpNi and CpMg resonances were observed at $\delta$ 5.91 and $\delta$ 6.78. Cooling a sample of 18 in n-pentane as low as –90 °C did not cause decoalescence of the hydride resonance. The $^{31}$P{${^1}$H} NMR spectrum had a singlet at $\delta$ 51.5, consistent with the $C_{4v}$ symmetry of cluster 18. Selective decoupling of the non-hydride resonances was attempted to further confirm the assignment of 6 hydride ligands; however, coupling to the hydride ligands only caused broadening of the $^{31}$P NMR resonance. The $^{13}$C{${^1}$H} NMR spectrum features a pair of resonances corresponding to the methyl and methine environments on the phosphine ligands, at $\delta$ 20.6 and $\delta$ 24.8, respectively. The methyl peak is a singlet, but the methine resonance is a 2nd order multiplet consistent with the spin system $AXX'X''$ and a $^2J_{PC} = 11.1$ Hz. Two additional singlets are observed at approximately $\delta$ 85.8 and $\delta$ 97.3, for the CpNi and CpMg fragments.

Cluster 18 has six hydride ligands in comparison to cluster 17 which only has four. The difference corresponds to a change in core oxidation state with 18 bearing a formally [Ni$_5$]$^{8+}$ core in comparison to 17 which bears a [Ni$_5$]$^{6+}$ core. This result has implication on the potential mechanism for H/D exchange, with the Ni$_5$ core being able to support a capping $\pi$-ligand with both six and four hydride ligands.

The pentanuclear Ni cluster [($^{i}$Pr$_3$P)Ni]$_5$H$_6$ also reacts immediately with one equivalent of freshly distilled cyclopentadiene at room temperature to give dark brown ($\eta^5$-Cp)Ni[($^{i}$Pr$_3$P)Ni]$_4$(μ$_2$-H)$_4$(μ$_5$-H) (19), as shown in Scheme 5.6. The reaction produces one equivalent of dihydrogen and releases an equivalent of $^{i}$Pr$_3$P. The $^1$H and $^{31}$P{${^1}$H} NMR
spectra shows quantitative conversion to 19, and an isolated yield of 56% was obtained after crystallization from $n$-pentane at $-40^\circ$C.

$$\text{Scheme 5.6. Reaction of cluster 1 with cyclopentadiene to form the 5-coordinate hydride bearing cluster 19}$$

The solid-state structure of 19 was determined by X-ray crystallography, and is shown in Figure 5.4. Complex 19 has Ni centres in a distorted square pyramidal geometry. The bond distances between the square-base Ni centres range from 2.5273(5) to 2.5531(5) Å. The Ni–Ni bond distances are considerably shorter to the capping Ni centre, and range from 2.3643(5)-2.3752(5) Å. A phosphine donor is bound to each Ni centre in the square base, and the capping Ni(1)-Cp$_{\text{centroid}}$ distance is 1.7381 Å. The five hydride ligands were located in the electron density difference map. Four are $\mu_2$-bound between the basal Ni centres, in the Ni$_4$ square plane. The distinct hydride ligand is located in the Ni square plane, below the capping Ni(1) with a short Ni(1)-H(5) distance of 1.54(5) Å. The Ni–H(5) distances for the Ni centres in the square plane are longer, and range from 1.77(5)-1.82(5) Å. Only one other example of a 5-coordinate hydride complex has been reported.$^{74}$
Figure 5.4. ORTEP depiction of Cluster 19. Carbons and hydrogens on and hydrogens on Cp ligand excluded for clarity. Selected bond distances (Å): Ni(1)–Ni(2) 2.3649(5), Ni(1)–Ni(3) 2.3752 (5), Ni(1)–Ni(4) 2.3643(5), Ni(1)–Ni(5) 2.3719(5), Ni(1)–Cp centroid 1.738, Ni(1)–H(5) 1.54(5), Ni(2)–Ni(3) 2.5273(5), Ni(3)–Ni(4) 2.5487(5), Ni(2)–Ni(5) 2.5414(5), Ni(4)–Ni(5) 2.5531(5), Ni(2)–H(5) 1.77(5), Ni(3)–H(5) 1.82(5), Ni(4)–H(5) 1.81(5), Ni(5)–H(5) 1.80(5). Selected bond angles (°): Cp centroid–Ni(1)–H(5) 174.76, N(3)–H(5)–Ni(5) 179.39(19), Ni(2)–H(5)–Ni(4) 178.46(15).

The $^{31}$P{${}^1$H} NMR of 19 has a sharp singlet at about $\delta$ 48.5, consistent with apparent $C_{4v}$ symmetry. The $^1$H NMR features a pair of resonances corresponding to the phosphine ligands along with a singlet at $\delta$ 5.56 for the protons on the Cp ligand. The hydride region has a single broad resonance at $\delta$ –29.66 for all five hydride ligands. This is consistent with a fluctional process that exchanges the $\mu_5$-H hydride ligand and the four $\mu_2$-H. When 19 in $n$-pentane is cooled to –60 °C, the hydride resonance decoalesces to give two peaks in a
4:1 ratio at δ –30.52 and δ –22.28, respectively. The variable-temperature $^1$H NMR spectra linewidths were used to determine an Arrhenius activation energy of 21.1 kcal·mol$^{-1}$ for exchange. The $^{13}$C{$^1$H} NMR features singlets for the methyl group and and a broad resonance with a $W_{1/2} = 25.3$ Hz for the methine environments, which is presumably due to an unresolved 2$^{nd}$ order-multiplet. A resonance is also observed at δ 85.4 for the Cp ligand.

Cluster 19 bears a [Ni$_3$]$^{6+}$ core in a square pyramidal geometry and can be considered a nido cluster that is one vertex deficient of being a closed polyhedron. The suggested stable electron count for these clusters is 74 electrons, however 1 bears 68 electrons; once again the deficiency may arise from the propensity of Ni centres to disobey the 18-electron rule. Cluster 1 is stable at room temperature in the solid-state and in solution over a period of days.

The pentamethyl cyclopentadienide (Cp*) analogue ($\eta^5$-$\text{Cp*}$)Ni[($i$Pr$_3$P)Ni]$_4$(μ$_2$-H)$_4$(μ$_5$-H) (20) was synthesized from either the reaction of [($i$Pr$_3$P)Ni]$_3$H$_6$ with pentamethylcyclopentadiene, or by reaction with an excess of Cp*Li in THF over a period of 2 days. It is believed that the latter reaction occurs because Cp*Li slowly deprotonates THF to generate pentamethylcyclopentadiene, and no initial direct reaction of Cp*Li with 1 to generate an analogue of 18 was observed. Both routes to 20 proceed quantitatively as observed by $^{31}$P{$^1$H} and $^1$H NMR, and 20 was isolated with a yield of 55 % after crystallization at –40 °C from n-pentane.
Scheme 5.7. Reaction of cluster 1 with lithium pentamethylcyclopentadienide to form the 5-coordinate hydride bearing cluster 20

The solid-state structure of 20 was determined by X-Ray crystallography and is shown in Figure 5.5. All five hydride ligands in 20 were found in the electron density map and lie approximately in the Ni(2) to Ni(5) square plane, with the shortest Ni–H distance of 1.50(7) Å belonging to the capping Ni(1) and the 5-coordinate H(5).
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Figure 5.5. ORTEP depiction of Cluster 20. Carbons and hydrogens on phosphine ligands and hydrogens on methyl groups of Cp* excluded for clarity. Selected bond distances (Å): Ni(1)–Ni(2) 2.3991(6), Ni(1)–Ni(3) 2.3852 (7), Ni(1)–Ni(4) 2.4063(7), Ni(1)–Ni(5) 2.3977(6), Ni(1)–C_centroid 1.748, Ni(1)–H(5) 1.50(7), Ni(2)–Ni(3) 2.5659(6), Ni(3)–Ni(4) 2.5528(6), Ni(2)–Ni(5) 2.5510(7), Ni(4)–Ni(5) 2.5570(5), Ni(2)–H(5) 1.77(5), Ni(3)–H(5) 1.82(5), Ni(4)–H(5) 1.81(5), Ni(5)–H(5) 1.80(5). Selected bond angles (°): Ni(1)–C_avg–H(5) 177.29, N(3)–H(5)–Ni(5) 176(5), Ni(2)–H(5)–Ni(4) 174(5).

The $^{31}$P$\{^1$H$\}$ NMR of 20 has a singlet at $\delta$ 46.4, which is consistent with apparent $C_{4v}$ symmetry. The $^1$H NMR is similar to 19, with a pair of resonances is observed for the methyl and methine signal of the phosphine ligands along with a sharp singlet at $\delta$ 2.18 for the methyl peak of the Cp* ligand. A broad hydride resonance, which integrates to five hydrides with respect to the phosphine environments, is observed at $\delta$ –29.02. Cooling an isolated sample of 20 to –65 °C gave the slow-exchange spectrum, where the hydride resonance split into two peaks in a 4:1 ratio at $\delta$ –31.1, and $\delta$ –21.1 respectively. The variable-temperature $^1$H NMR linewidths were modelled to give an Arrhenius activation energy of 15.9 kcal·mol$^{-1}$, which is 5.2 kcal·mol$^{-1}$ lower than in 19. The $^{13}$C$\{^1$H$\}$ NMR of 2 features a pair of singlets, for the methyl and methine carbons of the phosphine ligands, at $\delta$ 20.9 and $\delta$ 25.3. Two singlets are also observed at $\delta$ 13.0 and $\delta$ 92.2 for the methyl and pentadienyl carbons on the Cp* ligand, respectively.

Cluster 20 shares many electronic similarities to 19; the core oxidation state of [Ni$_3$]$^{6+}$ and electron count of 68 electrons are identical. The bond distances and bond angles are also very similar. One important conclusion from the structure of 20 is that these

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clusters can bind even sterically encumbered π-ligands to the capping Ni centre without much of an effect on the neighbouring metal centres or supporting ligands. In fact, the Ni(1)-Cp\textsuperscript{centroid} bond distance in 20 is practically identical to Ni(1)-Cp\textsuperscript{centroid} distance in 19. This has the implication that in the H/D exchange mechanism of 1, the arene-binding step may not be greatly influenced by arene size, consistent with the observed reactivity of larger substituted naphthalenes. Clusters 17-20 serve as structural analogues of potential intermediates for H/D exchange by 1. Cluster 20 also facilitated H/D exchange in neat C\textsubscript{6}D\textsubscript{6}, observed by the pseudo-first order decrease of the \textsuperscript{1}H NMR hydride integral, with a half-life of 5.62 \times 10\textsuperscript{4} s. Incorporation of deuterium into the methyl sites of the Cp\textsuperscript{*} ligand was also observed, but at a slower rate and not with first-order kinetics. A likely mechanism for H/D exchange into the Cp\textsuperscript{*} ligand is via a tuck-in complex, though the slow decomposition of 20 under these conditions prevented a complete analysis.

The observed regioselectivity of 1 in H/D exchange noted in Scheme 5.2 is not fully consistent with a nucleophilic mechanism for H/D exchange, but the failure of fluorobenzene to perform exchange at the para-site could be explained by such a mechanism.\textsuperscript{50} A species isoelectronic to 19 and 20, (η\textsuperscript{5}-C\textsubscript{6}D\textsubscript{6}H)Ni[(\textsuperscript{1}Pr\textsubscript{3}P)Ni\textsubscript{4}(\textmu\textsubscript{2}-H)\textsubscript{4}(\textmu\textsubscript{5}-H)], is a potential intermediate for H/D exchange by a mechanism that does not include H\textsubscript{2} dissociation. This intermediate could be formed from 1 by \textsuperscript{1}Pr\textsubscript{3}P dissociation and by hydride transfer to benzene-\textsubscript{d6} to give the C\textsubscript{6}D\textsubscript{6}H anion. In an attempt to make the protio species (η\textsuperscript{5}-C\textsubscript{6}H\textsubscript{7})Ni[(\textsuperscript{1}Pr\textsubscript{3}P)Ni\textsubscript{4}(\textmu\textsubscript{2}-H)\textsubscript{4}(\textmu\textsubscript{5}-H)] directly, 1 was reacted with both 1,4- and 1,3-cyclohexadiene as shown in Scheme 5.8a. In both cases, 1 was not immediately consumed, but acted as a hydrogen-transfer catalyst, forming equivalent amounts of benzene and cyclohexene immediately at room temperature. Similar reactivity with nickel
complexes has been reported. Over the course of an hour, the cyclohexene produced reacted with 1, forming multiple products that included the known carbide cluster, \([\text{Pr}_3\text{P}]\text{Ni}\cdots\text{H}_4(\mu_5\cdots\text{C})\), from CC bond cleavage. In an attempt to avoid the thermodynamic driving force provided by aromatization in these reactions, 1,4-pentadiene was reacted with 1 in an attempt to make the acyclic analogue \((\eta^5\cdot\text{C}_5\text{H}_7)\text{Ni}[\text{Pr}_3\text{P}]\text{Ni}_4(\mu_2\cdots\text{H})_4(\mu_5\cdots\text{H})\). Instead the previously reported cluster \([\text{Pr}_3\text{P}]\text{Ni}\cdots\text{H}_4(\mu_5\cdots\text{C})\) (8) was formed rapidly a room temperature, along with a series of organic products from isomerization, hydrogenation and carbon atom abstraction, including, pentane, 1-pentene, 2-pentene, butane, 1-butene, 2-butene, and propane, as shown in Scheme 8b.

![Scheme 5.8.](image)

**Scheme 5.8.a** Reaction of 1 with 1,4 pentadiene forming the known carbide cluster \([\text{Pr}_3\text{P}]\text{Ni}\cdots\text{H}_4(\mu_5\cdots\text{C})\) (8) **b** Catalytic conversion of 1,3 and 1,4 cyclohexadiene to cyclohexene and benzene by 1
5.3. Conclusions:

In summary, mechanistic insight was obtained from kinetics experiments conducted with 1. It was shown that the rate of H/D exchange was first order with respect to the concentration of 1 and arene, whereas iPr₃P showed first-order inhibition. Temperature effects on the rate of exchange determined a large positive value for the entropy of activation, indicative of a dissociative mechanism, which is in support of the dominant mechanism in the absence of added H₂ involving H₂ reductive elimination prior to the rate determining step. Similar rates of catalytic ortho and meta-H/D exchange in fluorobenzene suggests a very different mechanism of H/D exchange than the C–H bond oxidative addition or H-atom transfer known for mononuclear Ni(0)-phosphine complexes.

The competition of mono-substituted arenes with a wide array of electronic parameters, demonstrated an unusual lack of selectivity in H/D exchange for Ni complexes. Exposing 1 to arenes in the presence of Hg led to the coordination of Hg to the Ni square plane forming the heterometallic cluster 16. Exposing 1 to the isolobal TlCp yielded cluster 17 which featured a cationic Tl centre bound to the 4 Ni centres of the square base and the Cp ligand dissociating the phosphine of the capping Ni. Three additional Cp bearing clusters (18-20) were synthesised by exposing 1 to MgCp₂, cyclopentadiene, and LiCp* respectively; with 19 and 20 featuring a 5-coordinate hydride ligand. The dissociation of the phosphine ligand to bind an arene supports the kinetics data provided indicating phosphine inhibition and a dissociative type of mechanism. Moreover, clusters 17-20 range in the amount of hydride ligands they bear with four hydrides on 17, six hydrides on 18 and five hydrides in 19 and 20. The isolation of analogues of potential intermediates of H/D exchange with a range of hydride ligands has major mechanistic implications by
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showing that 1 can potentially bind an arene and maintain structural integrity upon loss of H₂ or transfer of a hydride ligand. Cluster 1 has shown remarkable reactivity at room temperature with unactivated substrates including unactivated hydrocarbons such as benzene and ethylene. To date, little remains known regarding the chemistry of small clusters supported solely by electron-rich donor ligands. The electron counts and accessible core oxidation states and ligand bonding modes seen here all provide some insight into the possible transformations accessible via these unique species.

5.4. Experimental:

5.4.1 General Procedures:

Unless otherwise stated, all manipulations were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or an MBraun glove-box. Dry, oxygen-free solvents were employed throughout. Anhydrous pentane, toluene, and THF were purchased from Alfa Aesar and were argon packed and dried with either activated sodium or molecular sieves. Benzene-d₆ was dried by heating at reflux with Na/K alloy in a sealed vessel under partial pressure then trap-to-trap distilled and freeze–pump–thaw degassed three times. 2-methoxynaphthalene, fluorobenzene, mercury, thallium cyclopentadieneide, magnesium cyclopentadieneide, pentamethyl cyclopentadiene, lithium cyclopentadieneide, 1,3 cyclohexadiene, 1,4 cyclohexadiene, and 1,3 pentadiene were purchased from Sigma-Aldrich and their purity was confirmed through NMR spectroscopy. Cyclopentadiene was purchased from Sigma Aldrich and was distilled prior to use. ¹H, ³¹P{¹H} and ¹³C{¹H}NMR spectra were recorded on a Bruker AMX Spectrometer operating at 300 MHz or 500 MHz with respect to proton nuclei. All chemical
shifts are recorded in parts per million, and all coupling constants are reported in Hertz. $^1$H NMR spectra were referenced to residual protons ($C_6D_6H$, $\delta$ 7.15) with respect to tetramethylsilane at $\delta$ 0.00. $^{31}$P{$^1$H} NMR spectra were referenced to external 85% $H_3PO_4$ at $\delta$ 0.00. $^{13}$C{$^1$H} NMR spectra were referenced relative to solvent resonances ($C_6D_6$, $\delta$ 128.0; $C_7D_8$, $\delta$ 20.4; $C_4D_8O$, $\delta$ 25.37). $^{205}$Tl{$^1$H} NMR spectra were referenced to external 85% $Tl_2SO_4$ at $\delta$ 0.00. Elemental analyses were performed at the Center for Catalysis and Materials Research, Windsor, Ontario.

5.4.2 Isotope Exchange Studies

Reaction of 1 with $C_6D_6$ and Characterization of 1-d$_n$ (n = 1-6).

Complex 1 (20 mg, 0.018 mmol) was dissolved in $C_6D_6$ (600 mg, 7.68 mmol). At 5 minutes, the $^{31}$P{$^1$H} NMR spectrum featured resolved peaks for the isotopologues 1-d$_1$, 1-d$_2$, and 1-d$_3$. After 25 minutes, the $^{31}$P{$^1$H} NMR spectrum had resolved peaks for all isotopologues (1-d$_0$ to 1-d$_6$). Through modeled spectra, it was determined at this point the mixture was a 1:6:15:20:15:6:1 statistical mixture of 1-d$_0$ : 1-d$_1$ : 1-d$_2$ : 1-d$_3$ : 1-d$_4$ : 1-d$_5$ : 1-d$_6$ arising from a 50 % deuterium incorporation into the hydride sites of 1. At 85 min, the solution of 1 was found to have only 13 % Ni–H remaining, with 87 % deuteration.

$^1$H NMR (298 K, $C_6D_6$, 500 MHz): $\delta$ –26.57 (1-d$_1$), –26.55 (1-d$_2$), –26.54 (1-d$_3$), –26.53 (1-d$_4$), –26.51(1-d$_5$) (s, 6H, Ni–H). $^{31}$P{$^1$H} NMR (298 K, $C_6D_6$, 121.5 MHz): $\delta$ 59.8 (1-d$_1$), 59.1 (1-d$_2$), 58.3 (1-d$_3$), 57.6 (1-d$_4$), 56.9 (1-d$_5$), 56.1 (1-d$_6$) (s, 5P, NiPPr$_3$).

H/D Exchange Rate vs [1]. A stock solution of $^3$Pr$_3$P (63 mg, 0.38 mmol) was dissolved in 5 mL of $C_6D_6$. 1.575 g of the solution was used to dissolve 101 mg of complex 1 to make...
solution B. Approximate masses of 74 mg, 123 mg, 202 mg, 450 mg and 800 mg of solution B were weighed directly into 5 NMR tubes and diluted to 0.800 mL by stock solution A. The NMR tubes were kept in liquid nitrogen to avoid H/D exchange until the reaction could be monitored to obtain initial rates. The probe was preset to 298 K to avoid changes in chemical shift and the ratio of the metal hydride complex to the initial ratio was recorded versus time by the use of $^{31}$P{^1}H NMR spectroscopy and modelled using the stochastic kinetics simulation program Tenua. Using the determined rate law, initial rates were calculated to be: $4.30 \times 10^{-5}$, $9.18 \times 10^{-5}$, $1.18 \times 10^{-4}$, $2.68 \times 10^{-4}$, and $5.64 \times 10^{-4}$ mol·L$^{-1}$·s$^{-1}$. The plot of concentration of complex 1 vs rate was linear, consistent with a 1$^{st}$ order dependence of [1] on rate of H/D exchange.

**H/D Exchange Rate vs [C$_6$D$_6$].** A stock solution was made by dissolving 1 (95 mg, 0.086 mmol) and iPr$_3$P (60 mg, 0.38 mmol) in 5 mL of pentane. Approximately 400 mg of stock solution was weighed directly into 5 different NMR tubes, followed the addition of 75, 40, 28, 10, and 7 mg of C$_6$D$_6$ into each NMR tube. The NMR tubes were then diluted with n-pentane to a total volume of 0.900 mL. The NMR tubes were kept in liquid nitrogen to avoid unmonitored H/D exchange. The NMR probe was preset to 298 K to avoid changes in chemical shift and the ratio of the metal hydride complex to the initial ratio was recorded versus time by the use of $^{31}$P{^1}H NMR spectroscopy modelled using Tenua. Using the rate-law, $k_{obs}$ values were determined to be: $4.32 \times 10^{-4}$, $2.68 \times 10^{-4}$, $1.95 \times 10^{-4}$, $6.17 \times 10^{-5}$, and $4.55 \times 10^{-5}$ s$^{-1}$. The plot of concentration of C$_6$D$_6$ vs $k_{obs}$ was linear, consistent with a 1$^{st}$ order dependence of [C$_6$D$_6$] on rate of H/D exchange.

**H/D Exchange Rate vs [P$i$Pr$_3$].** A solution of 1 (100 mg, 0.082 mmol) in 2.1 mL of n-pentane was made. 215 mg of stock solution was weighed directly into four different NMR
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tubes. Varying amounts of PPr₃ were added amounting to 16 mg, 8 mg, 4 g, and 2 mg, each in 0.5 ml of n-pentane. Finally, 100 mg of C₆D₆ was added to each NMR tube. The NMR tubes are kept in liquid nitrogen to avoid unmonitored H/D exchange. The probe was preset to 298 K to avoid changes in chemical shift and the ratio of the metal hydride complex to the initial ratio was recorded versus time by the use of ³¹P{¹H} NMR spectroscopy and modelled with Tenua. Using the rate-law, kₐₒₛ values were determined to be: 5.83 x 10⁻⁵, 9.33 x 10⁻⁵, 1.12 x 10⁻⁴, 1.43 x 10⁻⁴, and 4.57 x 10⁻⁴ s⁻¹. A plot of 1/[PPr₃P] vs kₐₒₛ is near linear.

**H/D Exchange of 1 and C₆D₆ in the presence of H₂.** A stock solution of 1 (100 mg, 0.088 mmol), triisopropylphosphine (25 mg, 0.16 mmol), and C₆D₆ (720 mg, 8.57 mmol) was diluted with 3 mL of n-pentane. The solution was quickly transferred to 4 J-Young NMR tubes and frozen in liquid nitrogen. Three of the samples were placed under vacuum to remove the headspace and subsequently exposed to 1.3 × 10⁻⁵, 6.6 × 10⁻⁵, and 1.3 × 10⁻⁶ atm of H₂. The samples were warmed up in the NMR probe which was preset to 298 K to avoid changes in chemical shift. The overall % deuteration of 1 was recorded versus time using ³¹P{¹H} NMR spectroscopy and revealed kₐₒₛ values of 1.2 × 10⁻⁵, 1.3 × 10⁻⁵, and 1.6 ×10⁻⁵ s⁻¹, respectively. The kₐₒₛ value of the control sample was 1.35 × 10⁻⁴ s⁻¹.

**Catalytic site-selectivity studies with fluorobenzene.** A solution of 1 (52 mg, 0.047 mmol), triisopropylphosphine (15 mg 0.093 mmol), C₆D₆ (450 mg, 4.69 mmol), and fluorobenzene (60 mg, 0.63 mmol) was diluted with 1.3 mL of n-pentane. Deuterium exchange into fluorobenzene was monitored by ¹H, ¹⁹F{¹H}, and ¹³C{¹H} NMR early in the reaction. The relative rates of incorporation into the ortho, meta and para sites were obtained by modelling peak intensities by line-fitting using TOPSPIN.
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Catalytic site-selectivity studies with 2-methoxynaphthalene. A C₆D₆ solution of 1 (25mg, 0.023 mmol) and 2-methoxynapthalene (100 mg, 0.63 mmol) was left at room temperature for 16 h and then filtered through a plug of Celite. The selectivity of D incorporation was determined by ¹H, and ¹³C{¹H} NMR.

Mono-substituted arene competition reactions Solutions of 1 (5-25 mg, 0.0045-0.023 mmol) in C₆D₆ were made and designated amounts of monosubstituted arenes were added. The following proportions were used with each competition: (a) C₆H₅F (118 mg, 1.23 mmol) vs. C₆H₅N(Me)₂ (150 mg, 1.23 mmol); (b) C₆H₅F (164 mg, 1.71 mmol) vs. C₆H₅CH₃ (161 mg, 1.71 mmol); (c) C₆H₅F (150 mg, 1.56 mmol) vs. C₆H₅CF₃ (228 mg, 1.56 mmol); (d) C₆H₅CF₃ (225 mg, 2.08 mmol) vs. C₆H₅OCH₃ (60 mg, 0.41 mmol). The solutions were left to react at room temperature for 16 hours and then were filtered through a plug of Celite. Degree of deuteration was determined through the use of ¹³C{¹H} NMR, either by modeling the relative intensity of the resulting C-D coupling multiplet, or by the isotope shift caused by adjacent deuterium incorporation. The NMR spectra were modeled through TOPSPIN and used to determine the relative rate of each site.

H/D Exchange of 1 and C₆D₆ at variable temperatures. A stock solution of Ni₅L₅H₆ (100 mg, 0.088 mmol), triisopropylphosphine (60 mg, 0.37 mmol), and C₆D₆ (600 mg, 7.14 mmol) was dissolved in 4.4 mL of pentane. The stock solution was transferred evenly into 4 different NMR tubes. The NMR tubes are kept in liquid nitrogen to avoid unmonitored H/D exchange. 4 different temperatures were preset in the NMR probe, 20º C, 25º C, 30º C, and 35º C and the rate constants for each temperature was recorded by the use of ³¹P{¹H} NMR spectroscopy and modelled with Tenua. Using the determined rate constants, an
Eyring plot was produced and an enthalpy of activation of 41.5 kcal mol$^{-1}$ and an entropy of activation of 67.4 cal K$^{-1}$ mol$^{-1}$.

5.4.3 Synthesis, Characterization, and Reactivity of Complexes

Synthesis and characterization of [(iPr$_3$P)Ni]$_5$H$_6$(µ$_4$-Hg) (16). A solution of [(iPr$_3$P)Ni]$_5$H$_6$ (550 mg, 0.50 mmol) in 15 mL $n$-pentane was stirred in the presence of an excess of elemental Hg (9.4 g, 47.1 mmol) for 2.5 h. All volatiles were then removed in vacuo and the residue extracted with $n$-pentane (2 x 10 mL). The solution was then left at $-40 \, ^\circ$C for 48 h at which point dark brown block crystals suitable for X-ray diffraction were obtained. The mother liquor was then concentrated and multiple crops yielded 373 mg of 1 (57.4%). $^1$H NMR (298 K, C$_6$D$_6$, 500 MHz): $\delta$ –28.62 (broad s, $W_{1/2}$=453.4 Hz, 6H, Ni–H), 1.40 (dd, $^3J_{PH}$ = 11.8 Hz, $^3J_{HH}$ = 7.0 Hz, 90H, PCHMe$_2$), 1.96 (apparent octet, $^3J_{HH}$ = 7.0 Hz, $^2J_{HP}$ = 6.7 Hz, 15H, PCH). $^{31}$P{$^1$H} NMR (298 K, C$_6$D$_6$, 121.5 MHz): $\delta$ 37.51 (broad s, $W_{1/2}$=1235.4 Hz, 5P, NiP$_{i}$Pr$_3$). $^{13}$C{$^1$H} NMR (298 K, C$_6$D$_6$, 75.5 MHz) $\delta$ 20.21 (s, 30 C, PCHMe$_2$) 24.80 (d, $^2J_{PC}$=11.9 Hz, 15C, PCH). $^1$H NMR (233 K, $n$-pentane, 500 MHz) $\delta$ –34.75 (s, 4H, Ni–H) –16.30 (s, 2H, Ni–H) $^{31}$P{$^1$H} NMR (233K, $n$-pentane, 121.5 MHz) 37.16 (d, $^3J_{PP}$=12.9 Hz, 4P, square base NiP$_{i}$Pr$_3$) 94.20 (p with Hg satellites, $^3J_{PP}$=12.9 Hz, $^3J_{Hgg}$=1208 Hz, 1P, cap NiP$_{i}$Pr$_3$). Anal Calcd for C$_{45}$H$_{111}$HgNi$_5$P$_5$ (1298.38): C, 41.53; H, 8.60; Found: C, 41.23; H, 8.74.

Synthesis and characterization of (η$^5$-C$_5$)Ni[(iPr$_3$P)Ni]$_4$(µ$_2$-H)$_4$(µ$_4$-Tl) (17) A solution of [(iPr$_3$P)Ni]$_5$H$_6$ (600 mg, 0.55 mmol) in 15 mL toluene was stirred in the presence of an excess of thallium(I) cyclopentadiene (2.4 g, 8.9 mmol) for 0.25 h. All volatiles were then removed in vacuo and the residue extracted with $n$-pentane (2 x 10 mL). The solution was
cooled to −40 °C for 16 h at which point dark brown block crystals suitable for X-ray diffraction were obtained. The mother liquor was then concentrated and multiple crops yielded 432 mg of 1 (66.1%). $^1$H NMR (298 K, C$_6$D$_6$, 500 MHz): δ −24.20 (p, $^2$J$_{PH}$ = 2.8 Hz, 4H, Ni–H), 1.39 (dd, $^3$J$_{PH}$ = 12.2 Hz, $^3$J$_{HH}$ = 7.1 Hz, 72H, PCHMe$_2$), 2.01 (apparent octet, $^3$J$_{HH}$ = 7.2 Hz, $^2$J$_{PH}$=7.4 Hz, 12H, PCH), 5.25 (s, 5H, Cp).

$^{31}$P{$^1$H} NMR (298 K, C$_6$D$_6$, 121.5 MHz): δ 31.39 (s, 4P, NiP$i$Pr$_3$).

$^{13}$C{$^1$H} NMR (298 K, C$_6$D$_6$, 75.5 MHz) δ 20.41 (s, 24 C, PCHMe$_2$) 25.28 (dd, $^2$J$_{CP}$=6.6 Hz, $^3$J$_{CP}$=4.6 Hz, 12C, PCH), 85.31 (s, 5C, NiCp) $^{207}$Tl{$^1$H} NMR (298 K, C$_6$D$_6$, 288.73 MHz). δ 821.1 (broad s, W$_{1/2}$ = 796.2 Hz, 1 Tl, Ni$_4$Tl).  

Anal Calcd for C$_{41}$H$_{93}$Ni$_5$P$_4$Tl (1204.27): C, 40.77; H, 7.78. Found: C, 40.40; H, 7.87.

**Synthesis and characterization of (η$^5$-Cp)Ni[(iPr$_3$P)Ni]$_4$H$_6$(μ$_4$-MgCp) (18).** A solution of [($^3$Pr$_3$P)Ni]$_4$H$_6$ (550 mg, 0.50 mmol) in 10 mL toluene was stirred with one equivalent of Cp$_2$Mg (77 mg, 0.50 mmol) for 0.25 h. All volatiles were then removed *in vacuo* and the residue extracted with *n*-pentane (2 × 10 mL). The solution was then left at − 40 °C for 16 h at which point dark brown block crystals suitable for X-ray diffraction were obtained. The mother liquor was then concentrated and multiple crops yielded 396 mg of 1 (68.2%).

$^1$H NMR (298 K, C$_6$D$_6$, 500 MHz): δ −22.23 (s, 6H, Ni–H), 1.38 (dd, $^3$J$_{PH}$ = 11.1 Hz, $^3$J$_{HH}$ = 7.4 Hz, 72H, PCHMe$_2$), 1.78 (apparent octet, $^3$J$_{HH}$ = 7.4 Hz, $^2$J$_{HP}$ = 6.9 Hz 12H, PCH), 5.91 (s, 5H, CpNi) 6.78 (s, 5H, CpMg). $^{31}$P{$^1$H} NMR (298 K, C$_6$D$_6$, 121.5 MHz): δ 51.5 (s, 4P, NiP$i$Pr$_3$). $^{13}$C{$^1$H} NMR (298 K, C$_6$H$_6$, 75.5 MHz) δ 20.60 (s, 24 C, PCHMe$_2$) 24.82 (2$^{nd}$ order multiplet, spin system AX’2XX”, $^2$J$_{PC}$ = 11.1 Hz, $^3$J$_{PP}$=14.2 Hz, 12C, PCH) 85.81 (s, 5C, NiCp) 107.33 (s, 5C, MgCp) Anal Calcd for C$_{46}$H$_{106}$MgNi$_5$P$_4$ (1090.34): C, 50.46; H, 9.24; Found: C, 50.70; H, 9.23.
Synthesis and characterization of (η5-Cp)Ni[(η3Pr3P)Ni]4(μ-2-H)4(μ-5-H) (19). A solution of [(η3Pr3P)Ni]3H6 (550 mg, 0.50 mmol) in 5 mL of n-pentane was stirred at room temperature in the presence of one equivalent of freshly distilled cyclopentadiene (33 mg, 0.50 mmol) for a total of 0.1 hours. The dark brown solution was filtered through a plug of Celite and concentrated by removing volatiles until precipitate was formed. The solution was then left at −40 °C for 16 h. Dark brown block-crystals suitable for X-Ray diffraction were collected. Solid collected from the first crop and an additional crop from the mother liquor yielded a total of 281 mg of product (56% yield). 1H NMR (298 K, C6D6, 500 MHz): δ –29.49 (s, 5H, Ni–H), 1.35 (dd, 3JPH = 10.1 Hz, 3JHH = 7.5 Hz, 72H, PCHMe2), 2.04 (broad m, W1/2=29.6 Hz, 12H, PCH), 5.56 (s, 5H, CpNi). 31P{1H} NMR (298 K, C6D6, 121.5 MHz): δ 48.55 (s, 4P, NiPPr3). 13C{1H} NMR (298 K, C6H6, 75.5 MHz) δ 20.96 (s, 24 C, PCHMe2) 26.45 (s, 12C, PCH) 84.80(s, 5C, NiCp) Anal Calcd for C41H94Ni5P4 (1004.54): C, 49.02; H, 9.47; Found: C, 49.05; H, 9.09.

Synthesis and characterization of (η5-Cp*)Ni[(η3Pr3P)Ni]4(μ-2-H)4(μ-5-H) (20). A solution of [(η3Pr3P)Ni]3H6 (600 mg, 0.545 mmol) in 5 mL of tetrahydrofuran was stirred at room temperature with 5.2 equivalents of lithium pentamethylcyclopentadienide (420 mg, 3.0 mmol) for a total of 4 hours. All volatiles were removed from the dark brown solution and the precipitate was extracted with 4 × 10 mL of n-pentane and filtered through a plug of Celite. The solution was then left at −40 °C for 16 hours. Dark brown block-crystals suitable for X-ray diffraction were formed and collected. Precipitate collected from the first crop along with precipitate from the mother liquor yielded a total of 322 mg of product (55% yield). 1H NMR (298 K, C6D6, 500 MHz): δ –29.02 (s, 5H, Ni–H), 1.37 (dd, 3JPH = 12.2 Hz, 3JHH = 7.4 Hz, 72H, PCHMe2), 2.06 (apparent octet, 3JHH = 7.4 Hz, 2JHP = 7.1 Hz,
Chapter 5: Mechanistic Insight Into H/D Exchange by a Pentanuclear Ni−H Cluster and Synthesis and Characterization of Structural Analogues of Potential Intermediates

12H, PCH), 2.18 (s, 15H, C5Me5); 31P{1H} NMR (298 K, C6D6, 121.5 MHz): δ 46.36 (s, 4P, NiP3Pr3). 13C{1H} NMR (298 K, C6H6, 75.5 MHz) 13.02 (s, 5C, C5Me5) δ 20.91 (s, 24 C, PCHMe2) 25.31 (m, 12C, PCH) 92.19(s, 5C, C5Me5) Anal Calc’d for C46H104Ni5P4 (1074.68): C, 51.41; H, 9.75; Found: C, 51.58; H, 10.09.

Reaction of 20 with C6D6. Cluster 20 (5 mg, 0.00466 mmol) was dissolved in 0.525 mL of C6D6 and transferred to an NMR tube. The NMR tubes are kept in liquid nitrogen to avoid unmonitored H/D exchange. The solution was monitored by 31P{1H} and 1H NMR to model the hydride resonance intensity over the course of the reaction. A half-life of 5.62 × 104 s was determined.

Transfer hydrogenation with 1 and cyclohexadienes. Cluster 1 (55 mg, 0.05 mmol) was dissolved in 0.6 mL of n-pentane followed by either 1,3-cyclohexadiene, or 1,4-cyclohexadiene (4 mg, 0.057 mmol). The solution was monitored by 31P{1H} and 1H NMR and resonances consistent with the formation of C6H6 and cyclohexene were observed immediately, along with the disappearance of resonances of the corresponding diene.

Reaction of 1 with 1,4 pentadiene. Cluster 1 (55 mg, 0.05 mmol) was dissolved in 0.6 mL of C6D6 followed by 1,4-pentadiene (4 mg, 0.059 mmol). The solution was then transferred to an NMR tube and was studied by 31P{1H}, 13C{1H} and 1H NMR, which showed resonances consistent with several alkanes and alkenes including n-pentane, 1-pentene, 1-butene, n-butane, and propane. Both NMR spectra also revealed quantitative conversion to the known carbide cluster, [(iPr3P)Ni]5H4(μ5-C).

Variable-temperature NMR spectra of 16. A n-pentane solution of 16 (20 mg, 0.018 mmol) was transferred to a J. Young NMR tube. 31P{1H} and 1H NMR spectra were
collected at 0 °C, −30 °C, −40 °C, −50 °C, −60 °C, and −70 °C in attempts to track decoalescence of the single hydride resonance. WINDNMR was used to model the spectra, and corresponding rate constants of 2500 s\(^{-1}\), 400 s\(^{-1}\), 145 s\(^{-1}\), 58 s\(^{-1}\), 33 s\(^{-1}\), and 15 s\(^{-1}\) were determined. Using the Arrhenius equation, an \(E_a\) of 8.13 ± 0.70 kcal·mol\(^{-1}\) was calculated.

**Variable-temperature NMR spectra of 19:** A \(n\)-pentane solution of 19 (50 mg, 0.050 mmol) was transferred to a J. Young NMR tube. \(^{31}\)P\{\(^1\)H\} and \(^1\)H NMR spectra were collected at −10 °C, −20 °C, −30 °C, −40 °C, and −60 °C in attempts to see decoalescence of the single resonance. WINDNMR was used to model the spectra and corresponding rate constants of 10 000 s\(^{-1}\), 3800 s\(^{-1}\), 1200 s\(^{-1}\), 98 s\(^{-1}\), and 1 s\(^{-1}\) were determined. Using the Arrhenius equation, an \(E_a\) of 21.1 ± 0.48 kcal·mol\(^{-1}\) was calculated.

**Variable-temperature NMR spectra of 20.** A \(n\)-pentane solution of 20 (50 mg, 0.051 mmol) was transferred to a J. Young NMR tube. \(^{31}\)P\{\(^1\)H\} and \(^1\)H NMR spectra were collected at 0 °C, −25 °C, −40 °C, −55 °C, and −70 °C in attempts to see decoalescence of the single resonance. WINDNMR was used to model the spectra and corresponding rate constants of 30 000 s\(^{-1}\), 2600 s\(^{-1}\), 280 s\(^{-1}\), 45 s\(^{-1}\), and 1 s\(^{-1}\) were determined. Using the Arrhenius equation, an \(E_a\) of 15.9 ± 0.49 kcal·mol\(^{-1}\) was calculated.

5.5. X-Ray Crystallography

**Table 5.1.** Crystallographic information of 17-20

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References begin on page 183
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Chapter 5: Mechanistic Insight Into H/D Exchange by a Pentanuclear Ni−H Cluster and Synthesis and Characterization of Structural Analogues of Potential Intermediates

5.6. Supporting Information

Full details of crystallographic information in CIF format for compounds 17-20, as well as crystallographic information of 16, along with experimental NMR spectra and kinetics studies can be found at:

https://pubs.acs.org/doi/suppl/10.1021/acs.organomet.7b00763

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5.7. References.


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Chapter 6 - Dismantling of Vinyl Ethers by Pentanuclear [(iPr₂P)Ni]₅H₆: Facile Cooperative C–O, C–C and C–H Activation Pathways

6.1. Introduction

Despite recent progress in the activation of both CC₁ and CO₂⁻³ bonds, large thermodynamic barriers in transition metal-mediated functionalization hinder further advancement. These bonds have garnered interest due to their presence in crude oil distillates and potential biofuels such as lignin.⁴⁻⁵ The opportunity to use these abundant materials as low-cost chemical feedstocks has led to significant progress in transition metal-mediated CO bond activation,²⁻⁶⁻²³ as well as the microscopic reverse, CO bond formation.²⁴⁻²⁹ Cooperative reactivity between multiple proximal transition metal centres
Chapter 6: Dismantling of Vinyl Ethers by Pentanuclear \[\{\text{Pr}_3\text{P}\}\text{Ni}_3\text{H}_6\]: Facile Cooperative C–O, C–C and C–H Activation Pathways

in clusters provides a strategy towards bond activation and functionalization,\(^{30}\) reminiscent of surface chemistry or polynuclear enzymes. Although transition metal clusters are plentiful, highly reactive clusters capable of difficult bond transformations remain an emerging field.\(^{31-39}\) Late transition metal clusters are generally supported by \(\pi\)-acceptor ligands,\(^{40}\) or multi-electron bridging donor ligands such as sulfides.\(^{41}\) The combination of only late transition metal centres and electron-rich ligands such as alkylphosphines and hydrides is a rare combination for polynuclear species.\(^{42-46}\)

We have recently demonstrated the ability of the electron-deficient cluster \[\{\text{Pr}_3\text{P}\}\text{Ni}_3\text{H}_6\ (1)\] to selectively abstract a carbon atom from unactivated alkenes and rearrange C-H bonds to give the carbide cluster \[\{\text{Pr}_3\text{P}\}\text{Ni}_5(\mu_5-\text{C})(\mu_5-\text{C})\] under very mild conditions, as shown in Scheme 6.1a.\(^{39}\) This reaction proceeds selectively at \(-30\) °C, even in the presence of added ketones, alcohols, amines, esters, amides alkynes and alkyl halides. Isolated intermediates from the reaction of 1 with isobutylene and styrene, shown in Scheme 6.1b, reveal a triple CH bond activation mechanism that utilizes cooperative substrate binding to the Ni\(_5\) centres prior to CC bond cleavage. In this chapter, we describe reactions of 1 with alkoxy substituted alkenes via a surprising variety in mechanistic manifolds that all involve facile inert-bond activations, with rearrangement of C-H bonds and C-O bond activation.

6.2. Results and Discussions
Scheme 6.1: a) Previously reported cooperative carbon atom abstraction from ethylene by 1 at temperatures as low as −30 °C. b) isolated intermediates of carbon atom abstraction using isobutylene and styrene, which reveal cooperative activation by a robust Ni$_5$ core.$^{39}$

6.2.1 C(sp$^3$)O bond cleavage

The reaction of 1 with tert-butyl vinyl ether is complete within 10 minutes at room-temperature. The new 70 e$^−$ pentanuclear Ni-H cluster [(iPr$_3$P)Ni)$_5$H$_4$(C)(CO) (21) was observed in the $^{31}$P{$_1$H} and $^1$H NMR, along with an equivalent of isobutylene, as shown in Scheme 6.2a. Although a balanced reaction would generate a combined three equivalents tert-butyl ethyl ether and/or H$_2$, the exact stoichiometry proved difficult to verify due to alternate reaction pathways. Complex 21 arises from the cleavage of CC, C(sp$^3$)O and CH

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bonds in \(H_2C=CHO')Bu\), as shown in Scheme 6.2b. Activation of C(sp\(^3\))O and C(sp\(^3\))O bonds are both of interest; however, C(sp\(^3\))O bond activation is a more challenging transformation.\(^{47}\)

**Scheme 6.2.** a) Reaction of 1 with \(t\)-butyl vinyl ether to form cluster \(21\) and an equivalent of isobutylene, from tandem CC and C(sp\(^3\))O bond cleavage b) Depiction of the \(t\)-butyl vinyl ether CC and C(sp\(^3\))O bonds undergoing cleavage to give \(21\). c) Paramagnetic products \(22a\) and \(23a\) from an alternate C(sp\(^3\))O cleavage pathway, identified by \(^1\)H NMR and the synthesis of analogues.

The solid-state structure of \(21\) determined by X-Ray crystallography is shown in Figure 6.1. Cluster \(21\) features a highly distorted pyramid of 5 Ni centres, where the capping Ni(1) and the basal Ni(2) are bridged by a carbonyl ligand. There is a butterfly distortion of the
Chapter 6: Dismantling of Vinyl Ethers by Pentanuclear \([(iPr_3P)Ni]_5H_6\): Facile Cooperative C–O, C–C and C–H Activation Pathways

square base that is evident from the near linear bond angle of 176.0(2)° for Ni(2)-C(1)-Ni(4) compared to 157.2(2)° for Ni(3)-C(1)-Ni(5). The Ni(1)-Ni(3) and Ni(1)-Ni(5) distances of 2.7908(6) Å and 2.8876(6) are long. The Ni(1)–Ni(4) distance of 2.6757(6) Å is modestly shorter, whereas the Ni(1)-Ni(2) bond bridged by the CO ligand is the shortest at 2.4457(6) Å. The five-coordinate carbide ligand has Ni–C bond distances ranging from 1.802-1.865(3) Å, with the longest bond to Ni(1). The four hydride ligands were located and their positions in the in the Ni(2)-Ni(5) base were refined. The room-temperature NMR spectra reveals this structure to be fluxional, with a single broad $^{31}$P environment at $\delta$ 47.6 and $^1$H hydride at environment at $\delta$–9.28. At 203 K a slow exchange spectrum consistent with the approximately $C_s$ symmetric solid-state structure of 21 was observed, with two $^1$H NMR hydride environments and four $^{31}$P NMR environments, in a 2:1:1:1 ratio. The IR spectrum of 21 has a bridging CO stretch at 1761 cm$^{-1}$. Samples of 21 were invariably contaminated with 8 and paramagnetic impurities 22a and 23a (vide infra). Alternate routes to pure 21 were explored, including the addition of stoichiometric quantities of CO or Cr(CO)$_6$ to carbide 8. Although the resonances corresponding to 21 were observed in both these reactions, neither provided high-yielding routes to 21, due to the facile reactivity of 21 with additional equivalents of CO at a similar rate to 8, and subsequent decomposition

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Figure 6.1. ORTEP depiction of 21 Carbons and hydrogens on phosphine ligands excluded for clarity. Selected bond distances (Å): Ni(1)–Ni(2) 2.4457(6), Ni(1)–Ni(3) 2.7908(6), Ni(1)–Ni(4) 2.6757(6), Ni(1)–Ni(5) 2.8876(6), Ni(2)–Ni(3) 2.6016(5), Ni(2)–Ni(5) 2.5758(6), Ni(3)–Ni(4) 2.5682(6), Ni(4)–Ni(5) 2.5461(5), Ni(1)–C(1) 1.865(3), Ni(2)–C(1) 1.822(3), Ni(3)–C(1) 1.807(3), Ni(4)–C(1) 1.822(3), Ni(5)–C(1) 1.802(3), Ni(1)–C(2) 1.872(3), Ni(2)–C(2) 1.901(4), C(2)–O(1) 1.189(4). Selected bond angles (°): Ni(1)–C(2)–Ni(2) 80.81 (13); N(2)–C(1)–Ni(4) 176.01(19), Ni(3)–C(1)–Ni(5) 157.20(18).

Integration of the $^1$H NMR of the reaction of 1 with tert-butyl vinyl ether using an internal standard revealed that despite 21 being the major product in the $^{31}$P{$^1$H} NMR, the conversion to 21 was only 25 %. Carbide 8 was observed as a minor diamagnetic impurity, in a 7 % yield. Furthermore, resonances for both methane and ethane were also observed,
inconsistent with the stoichiometry required for the formation of 21. The additional paramagnetically shifted $^1$H NMR resonances were assigned after the synthesis of analogues (vide infra) as [(iPr$_3$P)Ni$_4$H$_4$(C-CH$_3$)]NiO'Bu (22a) and [(iPr$_3$P)Ni$_4$H$_4$(C-CH$_2$O'Bu)]NiO'Bu (23a), shown in Scheme 6.2c, where R= 'Bu. Complex 22a is a 66 e$^-$ cluster, not including $\pi$-donation from the O'Bu ligand. Complex 22a likely arises from 1 by either loss of H$_2$ or hydrogenation of an equivalent of t-butyl vinyl ether, followed by cleavage of the C(sp$^3$)-O bond in H$_2$C=CHO'Bu, and rearrangement of the CH=CH$_2$ group to C-CH$_3$. Complex 22a has a $^1$H NMR dominated by dipolar shifted resonances, with the phosphine resonances at $\delta$ 7.3 (72 H) and 12.9 (12 H), O'Bu group at $\delta$ –17.9 (9 H). The CCH$_3$ and hydride resonances were not observed, likely due to Fermi contact broadening.

Complex 23a is assigned as analogous to 22a, with the C-CH$_3$ group replaced by CCH$_2$O'Bu. The $^1$H NMR of 23a features resonances at $\delta$ 7.4 (72 H) and 13.3 (12 H) for the P$i$Pr$_3$ groups, and two sharp resonances integrating $\delta$ –4.9 (9 H) and $\delta$ –19.9 (9 H) for $^1$Bu environments in the CCH$_2$O'Bu and O'Bu groups, respectively. Additionally, a Fermi contact broadened resonance at $\delta$ –4.2 (2H) is observed for the CCH$_2$O environment. The conversions to 22a and 23a were determined to be 9 and 22 %, respectively; combined with 21 and 8 this accounts for 63 % of the cluster 1 used in the reaction. Complex 22a is not thermally stable, and converts to 8 along with the production of methane. Although the loss of $^1$BuOH is implied in this conversion to 8, it was not observed, possibly due reaction with the other products. The initial ratio of products 21, 22a and 23a formed from 1 was not influenced by H$_2$C=CHO'Bu concentration.

6.2.2 C(sp$^3$)O bond cleavage
Chapter 6: Dismantling of Vinyl Ethers by Pentanuclear [(t\(^3\)Pr\(_3\)P)Ni\(_3\)]\(_3\)H\(_6\): Facile Cooperative C–O, C–C and C–H Activation Pathways

In attempts to isolate analogues of the paramagnetic species 22a or 23a, cluster 1 was reacted with trimethylsilyl vinyl ether. It was anticipated that both the strong Si-O bond and weak Si=C bond could prevent the bond cleavage events that lead to 21. Reaction of 1 with H\(_2\)C=CHO\(_2\)SiMe\(_3\) gave the paramagnetic 22a analogue [(t\(^3\)Pr\(_3\)P)Ni\(_4\)]H\(_4\)(C\(_2\)CH\(_3\))NiOSiMe\(_3\) (22b) after 0.5 h, which featured a similarly paramagnetically shifted NMR to 22a. The high solubility of 22a in n-pentane hampered attempts to obtain a crystalline solid. This was addressed by using a substrate with the less solubilizing SiMe\(_2\)Bn functional group (Bn = benzyl). The reaction of 1 with H\(_2\)C=CHO\(_2\)SiMe\(_2\)Bn gave the additional analogue [(t\(^3\)Pr\(_3\)P)\(_4\)Ni\(_5\)]H\(_4\)(C\(_2\)CH\(_3\))(O-SiMe\(_2\)Bn) (22c) after 0.5 h. Complex 22c crystallized as dark brown crystals from pentane. The net reaction involves the dissociation of a phosphine ligand, loss of an equivalent of dihydrogen, and the cleavage of the C(sp\(^2\))O bond, followed by the CH bond rearrangement of the CH=CH\(_2\) moiety to a \(\mu_4\)-CCH\(_3\) moiety that binds below the square-base, as shown on the left side of Scheme 6.3. Although \(^1\)H NMR spectroscopy indicated that 22b and 22c were the only transition metal species formed through reaction of 1 with SiMe\(_3\) and SiMe\(_2\)CH\(_2\)Ph, an NMR yields of 27 and 25 % were determined. This suggested an alternate pathway of reactivity which leads to an NMR silent product, or a highly thermally unstable complex. Indeed, by tracking the reaction by \(^1\)H NMR resonances corresponding to the R = SiMe\(_3\) and SiMe\(_2\)Bz analogue of 23a were observed early in the reaction, but decomposed at a rate similar to their rate of formation. Despite the propensity of the \(^t\)Bu cluster 22a to form methane and 8 through decomposition, cluster 22c is much more thermally robust, and even when exposed to phosphine and dihydrogen, cluster 8 and methane are not formed.
Scheme 6.3. a) Reaction of 1 with vinyl ethers H₂C=CHOR to give crystalline analogues of 22a and 23a via C(sp²)-O cleavage, where R= b) SiMe₃; c) SiMe₂CH₂Ph; d) 1-Ad.

The solid-state structure of 22c was determined by X-Ray crystallography, and is shown in Figure 6.2. The structure features a square-planar Ni₄ base with relatively equal Ni-Ni bond lengths ranging from 2.5201-2.5549(5) Å. The hydride ligands were located, and bridge the basal Ni in the approximate square-plane. Phosphine donors are coordinated to each of these basal Ni. The capping Ni(1) features shorter bonds to the four basal Ni that range from 2.4100(5)-2.4588(5) Å. Other than the four Ni-Ni bonds, the capping Ni(1) is bound only to the siloxide ligand, with a Ni–O distance of 1.780(2) Å and a near linear
Ni–O–Si bond angle of 173.48(17)°. The C–CH\(_3\) fragment is located below the square Ni-plane with diagonal Ni–C–Ni bond angles of 143.16(5)° and 144.05(15)° and Ni–C bond distances ranging from 1.884-1.893(2) Å. The C–C bond length of 1.544 (4) Å is consistent with single-bond character. The three hydrogens bound to the CCH\(_3\) fragment were also observed in an electron-density difference map.

The paramagnetic cluster 22c is formally a [Ni\(_3\)]\(^{8+}\) cluster, akin to the diamagnetic [Ni\(_3\)]\(^{8+}\) clusters 8 and 21. The Evans’ method \(\mu_{\text{eff}}\) of 3.46 \(\mu_B\) in C\(_6\)D\(_6\) at 298 K can be accounted for by a species with two unpaired electrons (S=1, spin only \(\mu_{\text{eff}} = 2.83 \mu_B\)) with very significant spin-orbit coupling. This is consistent with the \(^1\)H NMR spectra, where the spin-orbit coupling and resultant magnetic anisotropy manifest as large dipolar shifts. Analysis of variable-temperature \(^1\)H NMR spectra demonstrates that the majority of paramagnetic shifts observed are almost exclusively from pseudo-contact dipolar effects. All the resonances associated with the siloxide ligand are reasonably sharp, and the multiplicity resolved, with resonances ranging from 4.4 to –22.2 ppm. The resonances associated with the phosphine ligands however, are broader and are positively shifted, resonating at \(\delta\) 7.7 and \(\delta\) 16.4. The hydride ligands are not observed by \(^1\)H NMR likely due to a large Fermi contact contribution. The CCH\(_3\) resonance is observed at \(\delta\) –15.7 and likely has a large contact contribution, with a \(W_{1/2}\) of 109 Hz, potentially due to the proximity to the Ni\(_5\) core. The change in sign of the shifts from the anticipated diamagnetic complex values for the phosphine ligands in comparison to the siloxide and carbyne ligand can be rationalized by the \(3\cos^2\theta–1\) geometry parameter\(^{48}\) associated will dipolar shifts in pseudoadxial symmetric cluster 22c, as depicted in Figure 6.3a. Variable-temperature \(^1\)H NMR studies demonstrate that the chemical shift of the resonances on the siloxide ligand have
the anticipated approximate $1/T^2$ temperature dependence at the high temperature limit, with changes in shifts ranging from 4-15 ppm over an 80° range as shown in Figure 6.3b. The NMR data allows for the determination of the magnetic anisotropy, $\chi_{||} - \chi_{\perp}$, which when combined with the Evans method measurement of the average $\chi$ allows an estimation of $\chi_{\perp} = 0.0059$ and $\chi_{||} = 0.0032$ emu·mol$^{-1}$ at 298 K. The latter is consistent with the anticipated spin only value for an $S=1$ system of 0.00336 emu·mol$^{-1}$, which suggests that the magnetic anisotropy increases $\chi_{\perp}$ from spin orbit coupling around the approximate molecular $\perp$ axes. The magnitude of the magnetic anisotropy in the paramagnetic complexes 22 and 23 appear similar to complexes of the heavy lanthanides.\textsuperscript{50-51}

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{image.png}
\caption{ORTEP depiction of cluster 22c. Carbons and hydrogens on phosphine ligands excluded for clarity and only the ipso-carbon C(6) of the phenyl group is shown. Selected bond distances (Å): Ni(1)–Ni(2) 2.4100(5), Ni(1)–Ni(3) 2.4215(5), Ni(1)–Ni(4) 2.4588(5), Ni(1)–Ni(5) 2.4643(5).}
\end{figure}

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Ni(1)–Ni(5) 2.4373(5), Ni(2)–Ni(3) 2.5488(5), Ni(2)–Ni(5) 2.5549(5), Ni(3)–Ni(4) 2.5201(5), Ni(4)–Ni(5) 2.5256(5), Ni(1)–O(1) 1.780 (2), Ni(2)–C(1) 1.886(2), Ni(3)–C(1) 1.884(2), Ni(4)–C(1) 1.886(2), Ni(5)–C(1) 1.893(2), C(1)–C(2) 1.544(4). Selected bond angles (°): Ni(1)–O(1)–S(1) 173.48 (); N(1)–C(1)–C(2) 174.79 (19), (); Ni(2)–C(1)–Ni(4) 144.05(15), Ni(3)–C(1)–Ni(5) 143.16(5).

Figure 6.3. a) solid state structure with selected groups in the approximately axially symmetric 22c overlayed with the +ve and –ve region of the dipolar shifts predicted from the 3cos^2θ-1/r^3 geometric dependence of dipolar shifts on axially symmetric species. b) The negatively shifted portion of the VT \(^1\)H NMR of 22c showing shifted yet sharp resonances of bound siloxide. The broadened CCH\(_3\) group shows the competing influence of dipolar and Fermi-contact effects.

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A stable analogue to 23a was prepared by exposing 1 to H₂C=CHOAd (Ad =1-adamantyl). The adamantyl group features a similar electronic influence to tert-butyl, but ring strain prevents elimination to give an alkene in the manner that isobutylene is generated in the production of 21, as was previously shown in Scheme 6.2a. The reaction of 1 with three equivalents of H₂C=CHOAd gave the paramagnetic species [(iPr₃P)₄Ni₅]H₄(C-CH₂OAd)(O-Ad) (23d) after 0.75 h. The net reaction involves production of one equivalent of 1-adamantyl ethyl ether along with the dissociation of one equivalent of phosphine, and the production of ethane, as shown in the right side of Scheme 6.3. Although the NMR yield of 23d is similar to that of 23a (29.2%), the absence of a β-H on the adamantyl group halts the formation of 21. By monitoring the reaction by ¹H NMR, resonances corresponding to a 1-adamatyl analogue of 22a-c, [(iPr₃P)₄Ni₅]H₄(C-CH₃)(O-Ad) (22d), were observed immediately, but similar to 22a it proved thermally unstable. The previously reported tetranuclear cluster [(iPr₃P)Ni]₄O₅² featuring square-planar oxygen, was also observed in the ¹H NMR after extended periods at room temperature. It is plausible that [(iPr₃P)Ni]₄O is formed through cleavage of both CO bonds. Cooling a n-pentane solution of the reaction mixture allowed for the separation of the organic 1-adamantyl ethyl ether, and further concentration and cooling gave a mix of crystals of 23d and 8.

The solid-state structure of 23d was determined by X-ray crystallography. The larger crystals of this complex were plagued by non-merohedral twinning, which presented as a two-fold disorder which rotated the cluster so that the chemically different adamantyl
groups were nearly overlapped. A structure obtained on a weakly diffracting needle with negligible twinning issues provided unambiguous characterization, as shown in Figure 6.4. The structure features multiple similarities to 22c, with the basal square-plane Ni bearing terminal phosphines and the capping Ni bound to an alkoxide ligand with Ni(1)–O(1) 1.762 (5) Å. The Ni(1)–O(1)–C(13) of 143.3(5)° is significantly more bent than the corresponding bond angle in 22c. The bond distances of the Ni centres in the square plane to the µ4-carbyne ligand are also similar to the corresponding distances of 22c. The key difference in the solid-state structures of 23d and 22c is in the presence of the second oxy adamantyl group bound to C(2).
Figure 6.4: ORTEP depiction of cluster 23d. Carbons and hydrogens on phosphine ligands excluded for clarity. Selected bond distances (Å): Ni(1)–Ni(2) 2.4247(12), Ni(1)–Ni(3) 2.3981(12), Ni(1)–Ni(4) 2.4409(12), Ni(1)–Ni(5) 2.4259(12), Ni(2)–Ni(3) 2.5222(12), Ni(2)–Ni(5) 2.5245(12), Ni(3)–Ni(4) 2.5249(12), Ni(4)–Ni(5) 2.5372(12), Ni(1)–O(1) 1.762(5), Ni(2)–C(1) 1.948(6), Ni(3)–C(1) 1.904(12), Ni(4)–C(1) 1.938(6), Ni(5)–C(1) 1.978(6), C(1)–C(2) 1.391(9). Selected bond angles (°): N(1)–C(1)–C(2) 175.3(5), Ni(2)–C(1)–Ni(4) 134.6(3), Ni(3)–C(1)–Ni(5) 133.3(3).

Cluster 23c bears a [Ni₅]⁸⁺ core, identical to 8, 21, and 22c with an electron count of 66 plus 4π electrons from the alkoxide ligand on the capping Ni centre. The ¹H NMR of 23d has positively shifted resonances for the phosphine ligands at δ 7.68 and 13.58 with half-height linewidths (W₁/₂) of 20.4 and 31.1 Hz, respectively. The resonances corresponding to the adamantyl sites were all located but had a wide range of chemical shifts from δ –36.84 to 14.08; Variable temperature NMR confirms that dipolar coupling is the dominant cause of these shifts, but complex 23d can no longer be approximated as axially symmetric to give predictive shifts for the nuclei; it is not clear if this is due to the bent alkoxide moiety, the bending of P(3) away from the adamantyl group associated with O(2), or rotation around the C(2)-O(2) bond giving significant distortion in solution. Similar to 22b, the hydride ligands are not observed due Fermi contact. The resonances of the protons on the adamantyl groups are all relatively sharp with W₁/₂ < 20 Hz. Comparatively, the resonance for the C-CH₂ fragment, at δ – 9.88, is significantly broader with a W₁/₂ of approximately 70.2 Hz, again due a more significant Fermi-contact contribution. The additional contact contribution can be rationalized due to proximity of
the protons of the C-CH\(_2\) fragment with respect to the molecular orbitals bearing the unpaired electrons. Variable-temperature \(^1\)H NMR studies reveal a temperature dependence on chemical shift and linewidth of the resonances of 23d similar to that shown for 22c.

### 6.3. Conclusions

Previous studies of nickel C-O activation\(^{21-22}\) have suggested that in lieu of the more classic Ni(0)-Ni(II) oxidative addition mechanism, Ni(I) species, including dinuclear complexes, are viable intermediates for C-O bond activation.\(^{23}\) This work demonstrates the viability of larger Ni clusters in C-O bond cleavage reactions. The cooperative nature of the reactivity allows for the rapid cleavage and rearrangement of multiple inert bonds under ambient conditions, which is atypical for nickel C-O transformations.\(^{21-22}\) At this point little is known about the fundamental bonding of these Ni\(_5\) late metal clusters.\(^{53}\) The paramagnetism and large magnetic anisotropy of complexes 22 and 23 is entirely unexpected given their even electron counts and strong field ligands; this data may aid in the identification of related clusters that could be unexpected intermediates in previously reported catalytic transformations that utilize Ni and similarly sized phosphines, such as PCy\(_3\). The Ni\(_5\) core demonstrates a remarkable propensity to remain intact, despite the multitude of inert bond activation steps and variety in substrates and products. The search for mechanistic insight into these facile cooperative bond cleavages continues, with the additional goal of catalytic applications.

### 6.4. Experimental

#### 6.4.1 General Procedures
Unless otherwise stated, all manipulations were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or an MBraun glove-box. Dry, oxygen-free solvents were employed throughout. Anhydrous pentane, toluene, and THF were purchased from Alfa Aesar and were argon packed and dried with either activated sodium or molecular sieves. Benzene-$d_6$ was dried by filtering through a plug of activated alumina. Tert-butyl vinyl ether, vinyl trimethylsilane, acetaldehyde, dimethylbenzylsilyl chloride, triethylamine, 1-Bromo adamantane, ethylene glycol, carbon tetrabromide, and triphenylphosphine were purchased from Sigma-Aldrich or Alfa Aesar and their purity was confirmed through NMR spectroscopy. 1-adamantyl vinyl ether was synthesized via reported preparation.$^1$ $^1$H, $^{31}$P{$^1$H} and $^{13}$C{$^1$H} NMR spectra were recorded on a Bruker AMX Spectrometer operating at 300 MHz or 500 MHz with respect to proton nuclei. All chemical shifts are recorded in parts per million, and all coupling constants are reported in Hertz. $^1$H NMR spectra were referenced to residual protons ($\text{C}_6\text{D}_5\text{H}$, $\delta$ 7.15; $\text{C}_7\text{D}_7\text{H}$, $\delta$ 2.09; $\text{C}_4\text{D}_7\text{HO}$, $\delta$ 1.73) with respect to tetramethylsilane at $\delta$ 0.00. $^{31}$P{$^1$H} NMR spectra were referenced to external 85% $\text{H}_3\text{PO}_4$ at $\delta$ 0.00. $^{13}$C{$^1$H} NMR spectra were referenced relative to solvent resonances ($\text{C}_6\text{D}_6$, $\delta$ 128.0; $\text{C}_7\text{D}_8$, $\delta$ 20.4; $\text{C}_4\text{D}_8\text{O}$, $\delta$ 25.37)

6.4.2 Synthesis, Characterization, and Reactivity of Complexes

Synthesis and Characterization of 21 [(Pr$_3$P)Ni]$_5$(µ-H)$_4$(µ$_5$-C)(µ$_2$-CO)

A solution of [(Pr$_3$P)Ni]$_5$H$_6$ (920 mg, 0.84 mmol) in 15 mL of $n$-pentane was stirred at room temperature and then charged with a solution with 15 equiv of tert-butyl vinyl ether (1.25 g, 11.25 mmol) in 3 mL of $n$-pentane. The dark brown solution was stirred for approximately 2 h at 298 K, at which point the reaction was put under vacuum to remove
all volatiles, which included excess vinyl ether. The resulting residue was extracted with 3 × 5 mL of n-pentane and filtered through a plug of Celite. The resulting solution was left at −40 °C for 40 hours and dark brown crystals suitable for X-Ray diffraction were obtained. The mother liquor was concentrated and afforded a 2nd crop contaminated with 8 [(tPr3)Ni]5H4(µ-C) along with 23a with a combined yield of the mixture of 375 mg.

1H NMR (298 K, C6D6, 500 MHz): δ −9.28(s, 4H, Ni−H), 1.36 (dd, 2J_HH = 6.9 Hz, 3J_HP = 12.2 Hz, 90H, PCH(CH3)2), 2.29 (apparent octet, 2J_HH = 6.9 Hz, 2J_HP = 7.2 Hz, 15H, PCH(CH3)2). 31P{1H} NMR (298 K, C6D6, 202.5 MHz) δ 47.6 (broad s, W1/2 = 168.2 Hz, 5P, Ni–P) 13C{1H} NMR (298 K, C6D6, 75.5 MHz) δ 21.0 (s, 30 C, PCH(CH3)2) 24.8 (d, 1J_CP=13.9 Hz, 15 C, PCH(CH3)2). 1H NMR (203 K, n-pentane, 500 MHz): δ −11.15 (s, 2H, Ni−H) −7.96 (s, 2H, Ni−H) 31P{1H} NMR (203 K, n-pentane, 202.5 MHz): δ 56.7 (s, 1P, Ni−P(tBu) 49.7 (s, 2P, Ni−P(tBu) 44.9 (s, 1P, Ni−P(tBu) 34.6 (s, 1P, Ni−P(tBu). IR (solid) 1761 cm−1

NMR Scale Characterization of 22a [(tPr3)Ni]4H4(C-CH3)NiO\textbf{tBu} and 23a [(tPr3)Ni]4H4(C-CH2O\textbf{tBu})NiO\textbf{tBu}

A solution of 1 (27 mg, 0.025 mmol) in 0.6 mL of C6D6 is frozen and thawed in the presence of 10 equiv of tert-butyl vinyl ether (25 mg, 0.25 mmol) in 0.2 mL of C6D6 and quickly transferred to a pre-cooled NMR tube and subsequently frozen with liquid nitrogen. The frozen sample was then warmed to 298 K in the NMR probe and the reaction was monitored over time until all of 1 was consumed. Resonances for 22a 1H NMR (298 K, C6D6, 500 MHz): −17.00 (s, W1/2 = 11.6 Hz, 9H, \textbf{tBu}), 6.95 (broad s, W1/2 = 15.1 Hz, 72 H, PCHCH3), 13.4 (broad s, W1/2= 28.3 Hz, 12 H, PCHCH3).Resonances for 23a 1H NMR (298 K, C6D6,
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500 MHz): $-19.05$ (s, $W_{1/2} = 13.2$ Hz, 9H, O'Bu), $-4.95$ (s, $W_{1/2} = 6.1$ Hz, 9H, CCH$_2$O'Bu), $-3.82$ (s, $W_{1/2} = 99.5$ Hz, 2H, CCH$_2$) 7.49 (broad s, $W_{1/2} = 16.1$ Hz, 72 H, PCHCH$_3$), 13.31 (broad s, $W_{1/2} = 26.2$ Hz, 12 H, PCHCH$_3$).

**Attempted Alternate Syntheses of 21**

a) A solution of 8 (27 mg, 0.025 mmol) in C$_6$D$_6$ (0.6mL) was transferred to a 2.3 mL J-Young NMR tube. The J-Young tube was equipped with a gas adapter and attached to a Schlenk line. The J-young tube was frozen with liquid nitrogen and the nitrogen in the headspace was removed through vacuum, the solution was then warmed to room temperature. A gas cylinder of CO was attached to the Schlenk line and one equivalent of CO (202 torr, 0.025 mmol) was exposed to the J-young tube. $^1$H and $^{31}$P{$^1$H} revealed the formation of cluster 21, however the presence multiple other resonances in the hydride region in $^1$H NMR along with multiple resonances in $^{31}$P{$^1$H} NMR proved this synthesis of 21 to be low-yielding. b) A solution of 8 (56 mg, 0.050 mmol) in C$_6$D$_6$ (0.6mL) was used to dissolve 1/3 equivalents of Cr(CO)$_6$ (4 mg, 0.017 mmol) and transferred to an NMR tube. The reaction was monitored over time and $^1$H and $^{31}$P{$^1$H} revealed the formation of cluster 21, however the formation of an additional majority project proved this synthesis of 21 to be low yielding.

**Synthesis and Characterization of 22b \([\text{Pr}_3\text{P})\text{Ni}]_4\text{H}_4(\text{C-CH}_3)\text{NiO}\text{SiMe}_3\)**

A solution of vinyl trimethylsilyl oxide (116 mg, 1.0 mmol) in 10 mL of n-pentane was added in a dropwise manner over the course of 0.25 h to a stirred solution of 1 (550 mg, 0.5 mmol) in 10 mL of n-pentane. After 0.25 h of stirring at room temperature, an aliquot of the solution was used to confirm that all of 1 had been consumed, shifts associated to

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22b were present, however, the reaction conditions did not allow for the observation of the thermally unstable 23b. The solution was then concentrated and filtered through a plug of Celite and left at −40 °C over the course of a week, however, the high solubility of complex 22b in n-pentane and P₃iPr rendered the isolation of 22b impossible. ¹H NMR (298 K, C₆D₆, 500 MHz): −15.24 (s, W₁/₂ = 10.3 Hz, 9H, SiMe₃), −12.31 (broad s, W₁/₂ = 111.9 Hz, 3H, Ni-CCCH₃), 7.69 (broad s, W₁/₂ = 16.2 Hz, 72 H, PCHCH₃), 16.36 (broad s, W₁/₂ = 26.2 Hz, 12 H, PCHCH₃).

NMR Scale Synthesis and Characterization of 23b [(iPr₃P)Ni]₄H₄(C-CH₂OSiMe₃)NiOSiMe₃

A solution of 1 (27 mg, 0.025 mmol) in 0.6 mL of C₆D₆ is frozen and thawed in the presence of 3 equiv of trimethyl silyl vinyl ether (9 mg, 0.075 mmol) in 0.2 mL of C₆D₆ and quickly transferred to a pre-cooled NMR tube and subsequently frozen with liquid nitrogen. The frozen sample was then warmed to 298 K in the NMR probe and the reaction was monitored over time until all of 1 was consumed. Resonances associated with 22b are reported above, resonances assigned to thermally sensitive 23b are given. ¹H NMR (298 K, C₆D₆, 500 MHz): −17.28 (s, W₁/₂ = 8.5 Hz, 9H, OSiMe₃), −6.19 (s, W₁/₂ = 6.8 Hz, 9H, CCH₂OSiMe₃), 8.32 (broad s, W₁/₂ = 15.6 Hz, 72 H, PCHCH₃), 16.20 (broad s, W₁/₂ = 25.7 Hz, 12 H, PCHCH₃).

Synthesis and Characterization of H₂C=CHOSiMe₂(CH₂Ph)

A solution of dimethylbenzylsilyl chloride (3.2g, 0.0173 mol) and freshly distilled triethylamine (4.86 mL, 0.0346 mol) in 40 mL of anhydrous acetonitrile was cooled to 0 °C in a two-neck Schlenk flask. 1 equivalent of acetaldehyde (0.97 mL, 0.0173 mol) was
added to the Schlenk flask dropwise over the course of 10 min. The reaction was stirred at room temperature for 16 hours at which point the solvent was carefully evaporated on a rotovap under 300 torr vacuum (dimethylbenzyl silyl vinyl ether is volatile). The residue was extracted with 3 × 25 mL of n-pentane and filtered through a plug of Celite. The solvent was once again carefully removed using a rotovap. The remaining residue was fractionally distilled (bp 32 °C at 40 mTorr) to yield 1.62 g of compound 1 (58%).

\[ \text{Synthesis and Characterization of 22c } [(\text{iPr}_3\text{P})\text{Ni}]_4\text{H}_4(\text{C-CH}_3)\text{NiOSiMe}_2\text{CH}_2\text{Ph} ]
\]

A solution of dimethylbenzyl silyl vinyl ether (316 mg, 1.636 mmol) was diluted with 5 mL n-pentane and cooled to −40 °C. It was then added dropwise over the course of 5 minutes to a −40 °C solution of [(\text{iPr}_3\text{P})\text{Ni}]_3\text{H}_6 (900 mg, 0.82 mmol) in 15 mL of n-pentane. The dark brown solution stirred at room temperature for 30 minutes, at which point the solution turned olive coloured. An aliquot of the solution reveals that 23c is also formed, yet thermally unstable and decomposes at a similar rate to its formation. The solution was concentrated and filtered through a plug of Celite and then cooled to −40 °C. After 16 hours, dark green crystals suitable for X-Ray diffraction were isolated by filtration. The mother liquor was concentrated and afforded a 2nd crop giving a combined yield of 330 mg.

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(35.7%) contaminated with the hydrogenated vinyl ether. The solid was dissolved in 2 mL of n-pentane and cooled to −40 °C for 72 h, dark green crystals were then isolated giving an isolated yield of 146 mg (15.8 %) with significantly less organic siloxanes.

$^1$H NMR (298 K, C6D6, 500 MHz): −19.96 (s, 2H, SiCH2Ph), −15.71 (broad s, $W_{1/2} = 108.6$ Hz, 3H, Ni-CCH3), −27.18 (s, $W_{1/2} = 126.6$ Hz, 6H, SiMe2), −1.07 (d, $^3J_{HH} = 8.3$ Hz, 2H, o) 3.77 (t, $^3J_{HH} = 7.3$ Hz, 1H, m) 7.66 (broad s, $W_{1/2} = 16.2$ Hz, 72 H, PCHC3), 16.42 (broad s, $W_{1/2}= 28.4$ Hz, 12 H, PCHCH3).

$^1$H NMR (193 K, C4D8O, 500 MHz): −39.29 (s, $W_{1/2} = 196.3$ Hz, 2H, SiCH2Ph), −27.13 (s, $W_{1/2} = 160.6$ Hz, 6H, SiMe2), −16.60 (broad s, $W_{1/2} = 1260.6$ Hz, 3H, Ni-CCH3), −7.87 (s, $W_{1/2} = 60.1$ Hz, 2H, o) 12.55 (broad s, $W_{1/2}= 281$ Hz, 72 H, PCHCH3), 28.74 (broad s, $W_{1/2}= 1276.6$ Hz, 12 H, PCHCH3).

NMR Scale Synthesis and Characterization of 23c [(Pr3P)Ni]4H4(C-CH2OSiMe2CH2Ph)NiOSiMe2CH2Ph

A solution of 1 (27 mg, 0.025 mmol) in 0.6 mL of C6D6 was frozen and thawed in the presence of 3 equiv of dimethylbenzyl silyl vinyl ether (11 mg, 0.075 mmol) in 0.2 mL of C6D6 and quickly transferred to a pre-cooled NMR tube and subsequently frozen with liquid nitrogen. The frozen sample was then warmed to 298 K in the NMR probe and the reaction was monitored over time until all of 1 was consumed. Resonances associated with 22c are reported above, resonances assigned to thermally sensitive 23c are given. $^1$H NMR (298 K, C6D6, 500 MHz): −22.85 (s, $W_{1/2} = 14.6$ Hz, 2H, SiCH2Ph), −17.02 (s, $W_{1/2}=11.5$ Hz, 6H, SiMe2), −6.16 (s, $W_{1/2}=5.1$ Hz, 6H, H2CCOSiMe2), −5.58 (s, $W_{1/2} = 4.4$ Hz, 2H, CCH2OSiCH2Ph), 8.37 (broad s, $W_{1/2} = 14.9$ Hz, 72 H, PCHCH3), 16.44 (broad s, $W_{1/2}= 25.4$ Hz, 12 H, PCHCH3).

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Synthesis and Characterization of 23d Ni₅(Pr₃)₄(OAd)(µ-H)₄(µ-CCH₂OAd)

A solution of 1-adamantyl vinyl ether (534 mg, 3.0 mmol) was dissolved in 10 mL of n-pentane and added in a drop-wise manner to a stirring solution of a third of an equivalent of 1 (1.100 g, 1.0 mmol) over the course of 0.25 h. The solution was stirred at room temperature for an additional 0.5 h, at which point an aliquot of the reaction solution was taken to confirm that all of 1 had been consumed, and shifts associated to 23d were present, however, the reaction conditions did not allow for the observation of the thermally unstable 22d. The solution was then concentrated, filtered through a plug of Celite and cooled to –40 °C. After 8 h a gray solid precipitated from solution corresponding to a mixture of 23d, 8, and primarily 1-adamantyl ethyl ether. After concentration of the filtrate, the solution was cooled to –40 °C for an additional 48 h which produced dark brown X-ray quality crystals of both 23d and 8. The solid was dissolved in 5 mL of n-pentane and cooled once again to –40 °C for 16 h, at which point the precipitate was collected giving an overall yield of 155 mg (12.2 %). ¹H NMR (298 K, C₇D₈, 500 MHz): –36.56 (s, W₁/₂ = 15.5 Hz, 6H, OAd), –9.87 (broad s, W₁/₂ = 76.6 Hz, 2H, Ni-CCH₂), –8.47 (d, ²JHH= 10.3 Hz, 3H, OAd), –7.68 (d, ²JHH= 10.3 Hz, 3H, OAd) –6.47 (s, W₁/₂ = 9.0 Hz, 6H, OAd), –2.71 (d, ²JHH= 9.8 Hz, 3H, OAd) –1.73 (s, W₁/₂ = 11.2 Hz, 3H, OAd) –0.93 (d, ²JHH= 9.8 Hz, 3H, OAd) 7.55 Hz, 3H, OAd) –1.93 (d, W₁/₂ = 13.9 Hz, 72 H, PCHCH₃), 13.37 (broad s, W₁/₂= 24.7 Hz, 12 H, PCHCH₃) 13.87 (s, W₁/₂ = 9.7 Hz, 3H, OAd). ¹H NMR (208 K, C₇D₈, 500 MHz): –58.14 (s, W₁/₂ = 144 Hz, 6H, OAd), –14.66(s, W₁/₂ = 30.7 Hz, 3H, OAd), –13.40 (s, W₁/₂ = 20.7 Hz, 3H, OAd) –12.37 (s, W₁/₂ = 22.5 Hz, 6H, OAd), –9.00 (broad s, W₁/₂ = 1016 Hz, 2H, Ni-CCH₂), –5.67 (s, W₁/₂= 18.9 Hz, 3H, OAd) –4.16 (s, W₁/₂ = 18.6 Hz, 3H, OAd) –2.74 (s, W₁/₂=...
20.2 Hz, 3H, OAd) 11.62 (broad s, $W_{1/2} = 180.1$ Hz, 72 H, PCHCH$_3$), 18.39 (s, $W_{1/2} = 32.1$ Hz, 3H, OAd) 20.22 (broad s, $W_{1/2}= 302.2$ Hz, 12 H, PCHCH$_3$).

**NMR Scale Synthesis and Characterization of 22d [(Pr$_3$P)Ni]$H_4$(C-CH$_3$)NiOAd**

A solution of 1 (27 mg, 0.025 mmol) in 0.6 mL of C$_6$D$_6$ is frozen and thawed in the presence of 3 equiv of 1-adamantyl vinyl ether (10 mg, 0.075 mmol) in 0.2 mL of C$_6$D$_6$ and quickly transferred to a pre-cooled NMR tube and subsequently frozen with liquid nitrogen. The frozen sample was then warmed to 298 K in the NMR probe and the reaction was monitored over time until all of 1 was consumed. Resonances associated with 23d are reported above, resonances assigned to thermally sensitive 22d are given. $^1$H NMR (298 K, C$_6$D$_6$, 500 MHz): −35.25 (s, $W_{1/2} = 14.7$ Hz, 6H, OAd), −9.87 (broad s, $W_{1/2} = 76.6$ Hz, 2H, Ni-CCH$_2$), −7.66 (d, $^2J_{HH}= 10.1$ Hz, 3H, OAd), −7.10 (d, $^2J_{HH}= 10.1$ Hz, 3H, OAd), 7.01 (broad s, $W_{1/2} = 14.6$ Hz, 72 H, PCHCH$_3$), 13.36 (broad s, $W_{1/2}= 31.5$ Hz, 12 H, PCHCH$_3$) 16.65 (s, $W_{1/2} = 12.5$ Hz, 3H, OAd)

**Reaction of 1 with vinyl ethers in the presence of an internal standard**

A solution composed of C$_6$D$_6$ (600 mg), THF as an internal standard (10-13 mg), and 5 equivalents of vinyl ether (0.05 mmol) was used to dissolve 1 equivalent of 1 (0.01 mmol). The solutions were quickly transferred to an NMR tube and frozen with liquid N$_2$. The solutions were then warmed in the NMR probe pre-set to 298 K and $^1$H NMR spectra were collected to determine NMR yield of CC and CO bond cleavage products as can be seen in Table 6.1.
Chapter 6: Dismantling of Vinyl Ethers by Pentanuclear \((\text{tPr}_3\text{P})\text{Ni}_5\)\(_6\): Facile Cooperative C–O, C–C and C–H Activation Pathways

Table 6.1: NMR yields of cluster 8 and 21-23 with different vinyl ethers

<table>
<thead>
<tr>
<th>Vinyl Ether</th>
<th>time (min)</th>
<th>NMR Yield of 8 (%)</th>
<th>NMR Yield of 21 (%)</th>
<th>NMR Yield of analogue of 22 (%)</th>
<th>NMR Yield of analogue of 23 (%)</th>
<th>Equivalents of hydrogenated ether produced</th>
<th>Equivalents of C(_2)H(_6) produced</th>
<th>Equivalents of CH(_4) produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>tBu</td>
<td>10</td>
<td>7.3</td>
<td>25.5</td>
<td>8.7</td>
<td>22.4</td>
<td>1.2</td>
<td>0.14</td>
<td>0.03</td>
</tr>
<tr>
<td>SiMe(_3)</td>
<td>30</td>
<td>0</td>
<td>0</td>
<td>27.4</td>
<td>4.1</td>
<td>0.16</td>
<td>0.38</td>
<td>0.14</td>
</tr>
<tr>
<td>SiMe(_2)CH(_2)P(h)</td>
<td>30</td>
<td>0</td>
<td>0</td>
<td>25.9</td>
<td>3.8</td>
<td>0.10</td>
<td>0.37</td>
<td>0.05</td>
</tr>
<tr>
<td>1-Ad</td>
<td>45</td>
<td>11.7</td>
<td>0</td>
<td>11.2</td>
<td>25.7</td>
<td>1.15</td>
<td>0.20</td>
<td>0.08</td>
</tr>
</tbody>
</table>

S5: Magnetic Measurements of 22c

Table 6.2: Solid-State Parameters of 22c used in estimates of anisotropy. (Bond distances with respect to top Ni centre (assuming location of unpaired electron lied in top Ni centre although this may not be true; calculations using the centre of the cluster or the centre of the basal plane had a modest impact on the calculated values))
<table>
<thead>
<tr>
<th></th>
<th>Ni-CH₃</th>
<th>Ni-SiCH₂</th>
<th>para C-H</th>
<th>meta C-H</th>
<th>ortho C-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.444E-08</td>
<td>4.466E-08</td>
<td>4.412E-08</td>
<td>4.332E-08</td>
<td>4.092E-08</td>
<td>9.395E-08</td>
</tr>
<tr>
<td>147.72</td>
<td>163.02</td>
<td>149.92</td>
<td>148.85</td>
<td>146.08</td>
<td>143.32</td>
</tr>
<tr>
<td>1.144348E-514</td>
<td>1.744141E-641</td>
<td>1.246369E-482</td>
<td>1.197263E-069</td>
<td>1.065791E-473</td>
<td>0.929536E-3</td>
</tr>
<tr>
<td></td>
<td>6.39647E+21</td>
<td>6.66909E+21</td>
<td>1.01163E+21</td>
<td>1.23368E+21</td>
<td>2.59498E+21</td>
</tr>
</tbody>
</table>
Chapter 6: Dismantling of Vinyl Ethers by Pentanuclear \([(^3\text{Pr}_3\text{P})\text{Ni}]_5\text{H}_6\): Facile Cooperative C–O, C–C and C–H Activation Pathways

Table 6.3: Temperature Dependence on Chemical Shift of 22c

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>ortho</th>
<th>meta</th>
<th>para</th>
<th>CH$_2$-Ph</th>
<th>CH$_3$</th>
<th>CCH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paramagnetic shifts (ppm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>-1.31</td>
<td>4.401</td>
<td>-20.03</td>
<td>-15.11</td>
<td>-16.87</td>
<td></td>
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<tr>
<td>273</td>
<td>-2.232</td>
<td>4.053</td>
<td>-22.75</td>
<td>-16.76</td>
<td>-17.46</td>
<td></td>
</tr>
<tr>
<td>258</td>
<td>-3.028</td>
<td>3.737</td>
<td>-25.1</td>
<td>-18.28</td>
<td>-17.84</td>
<td></td>
</tr>
<tr>
<td>243</td>
<td>-3.804</td>
<td>3.444</td>
<td>-27.4</td>
<td>-19.62</td>
<td>-18.02</td>
<td></td>
</tr>
<tr>
<td>Diamagnetic shifts (ppm)</td>
<td>6.6</td>
<td>7.3</td>
<td>6.6</td>
<td>2.06</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Difference in shifts</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>-7.91</td>
<td>2.899</td>
<td>-22.09</td>
<td>-15.11</td>
<td>-16.87</td>
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<tr>
<td>273</td>
<td>-8.832</td>
<td>3.247</td>
<td>-24.81</td>
<td>-16.76</td>
<td>-17.46</td>
<td></td>
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<tr>
<td>258</td>
<td>-9.628</td>
<td>3.563</td>
<td>-27.16</td>
<td>-18.28</td>
<td>-17.84</td>
<td></td>
</tr>
<tr>
<td>243</td>
<td>10.404</td>
<td>3.856</td>
<td>-29.46</td>
<td>-19.62</td>
<td>-18.02</td>
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</table>

Table 6.4: Estimate of Magnetic Anisotropies (in emu·mol$^{-1}$) of 22c at Different Temperatures

<table>
<thead>
<tr>
<th>Temp</th>
<th>ortho</th>
<th>meta</th>
<th>SiCH$_2$</th>
<th>CH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298 K</td>
<td>-0.00183593</td>
<td>-0.00142</td>
<td>-0.00199</td>
<td>-0.00142</td>
</tr>
<tr>
<td>278 K</td>
<td>-0.002049929</td>
<td>-0.00159</td>
<td>-0.00224</td>
<td>-0.00158</td>
</tr>
<tr>
<td>253 K</td>
<td>-0.002234682</td>
<td>-0.00174</td>
<td>-0.00245</td>
<td>-0.00172</td>
</tr>
<tr>
<td>233 K</td>
<td>-0.002414794</td>
<td>-0.00188</td>
<td>-0.00266</td>
<td>-0.00185</td>
</tr>
</tbody>
</table>

References begin on page 219
Table 6.5: Ratios of the change in shifts at different temperatures between different environments in 22c showing consistency in ratio of changes in shift, providing evidence that shifts are primarily dipolar

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>ratio of change in shift</th>
<th>ortho and meta</th>
<th>ortho and SiCH2Ph</th>
<th>ortho and Si(CH3)2</th>
<th>meta and SiCH2Ph</th>
<th>meta and Si(CH3)2</th>
<th>SiCH2Ph and Si(CH3)2</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td></td>
<td>2.728527</td>
<td>0.358080</td>
<td>0.523494</td>
<td>0.131235</td>
<td>0.191859</td>
<td>1.461945</td>
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<tr>
<td>273</td>
<td></td>
<td>2.720049</td>
<td>0.355985</td>
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<td>1.480310</td>
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<tr>
<td>258</td>
<td></td>
<td>2.70221</td>
<td>0.354491</td>
<td>0.526695</td>
<td>0.131185</td>
<td>0.194912</td>
<td>1.485776</td>
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<td>243</td>
<td></td>
<td>2.698132</td>
<td>0.353156</td>
<td>0.530275</td>
<td>0.130889</td>
<td>0.196534</td>
<td>1.501529</td>
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</table>

Evans Method on 23d

A solution of 23d with a concentration of 8.22 mmol/L (accounting for the presence of the known [(IPr3P)Ni]4H4(µ4−O) impurity) in C6D6 was prepared and transferred to a capillary tube. An NMR tube was filled with 0.4 mL of C6D6 and the capillary tube was then carefully inserted into the NMR tube. The tubes were then taken to the 500 MHz NMR spectrometer where a 1H NMR experiment was conducted and a separation of 80.0 Hz was measured between the C6D5H signal in the capillary tube and the C6D5H signal outside the capillary tube. Using the measured values an effective magnetic moment of approximately 3.46 Bohr magnetons is calculated. This value lies between the expected effective magnetic moment value of 2 unpaired electrons (2.83) and 3 unpaired electrons (3.88). The high
effective magnetic moment of 23d, assuming 2 unpaired electrons, can be rationalized by the high degree of spin-orbit coupling present in cluster 23d.

**Estimate of $\chi_\perp$**

Using the calculated $\mu_{\text{eff}}$ of 3.45 we can determine the $\chi_mT$ through the approximation of $\mu_{\text{eff}} = 2.83(\chi_mT)^{0.5}$ which gives us a $\chi_m(\chi_{\text{ave}})$ value of 0.00502. Using the calculated magnetic anisotropy values $(\chi_{zz} - \chi_{\text{ave}})$ of $-0.0018$ in 22c from the ortho environment, we can then calculate the $\chi_{zz}$ from the equation $\chi_{zz} = (\chi_{zz} - \chi_{\text{ave}}) + \chi_m$, giving a value of $\chi_{zz}(\chi_\parallel)$ of 0.00322.

Then we can use the equation: $\chi_\parallel - \chi_\perp = 3/2(\chi_{zz} - \chi_{\text{ave}})$ to give us a value of $-0.0027$. Lastly, we can use this value to determine $\chi_\perp$, as $\chi_\perp = \chi_\parallel (-0.0027) = 0.00592$.

**6.5. X-Ray Crystallography**

Table 6.6. Crystallographic Information of Compounds 21, 22c, and 23d

<table>
<thead>
<tr>
<th>Compound</th>
<th>21</th>
<th>22c</th>
<th>23d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>C$<em>4$H$</em>{109}$ONi$_5$P$_4$</td>
<td>2(C$<em>{47}$H$</em>{104}$ONi$_5$P$_4$Si)C$<em>5$H$</em>{12}$</td>
<td>C$<em>{58}$H$</em>{120}$O$_2$Ni$_5$P$_4$</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>1138.74</td>
<td>2333.78</td>
<td>1266.96</td>
</tr>
<tr>
<td>Temp</td>
<td>173(2) K</td>
<td>173(2) K</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>P2(1)/n</td>
<td>P2(1)/c</td>
</tr>
<tr>
<td>a/ Å</td>
<td>11.8384(11)</td>
<td>14.4352(10)</td>
<td>12.9129(16)</td>
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<tr>
<td>b/ Å</td>
<td>12.8461(12)</td>
<td>29.027(10)</td>
<td>21.088(3)</td>
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<tr>
<td>c/ Å</td>
<td>21.625(2)</td>
<td>14.5531(10)</td>
<td>23.407(3)</td>
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<tr>
<td>$\alpha$/ °</td>
<td>86.932(2)</td>
<td>90</td>
<td>90</td>
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<td>$\beta$/ °</td>
<td>86.330(3)</td>
<td>90.693(2)</td>
<td>91.273(5)</td>
</tr>
<tr>
<td>$\gamma$/ °</td>
<td>63.466(2)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V/ Å$^3$</td>
<td>2935.2(5)</td>
<td>6097.5(8)</td>
<td>6372.3(14)</td>
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</table>
Chapter 6: Dismantling of Vinyl Ethers by Pentanuclear \([iPr_3P]Ni)_3H_6\): Facile Cooperative C–O, C–C and C–H Activation Pathways

<table>
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<td>Z</td>
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<td>D_{calc}/g cm^{-3}</td>
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<td>\mu(Mo-K\alpha)/mm^{-1}</td>
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<td>1.671</td>
<td>1.588</td>
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<td>F(000)</td>
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<td>2736</td>
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<tr>
<td>Independent reflections</td>
<td>13461</td>
<td>13983</td>
<td>11214</td>
</tr>
<tr>
<td>No. of Parameters</td>
<td>578</td>
<td>634</td>
<td>752</td>
</tr>
<tr>
<td>R(int)</td>
<td>5.96</td>
<td>6.69</td>
<td>19.15</td>
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<td>R1 (I &gt; 2\sigma(I))^a</td>
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<td>3.93</td>
<td>7.36</td>
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<tr>
<td>R1(all)</td>
<td>6.63</td>
<td>7.07</td>
<td>15.01</td>
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<td>wR2(all)</td>
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<td>8.26</td>
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<td>GOF</td>
<td>1.0440</td>
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6.6. Supporting Information

Full details of crystallographic information in CIF format for compounds 21, 22c, and 23d along with experimental NMR spectra can be found on supplementary USB provided.
Chapter 6: Dismantling of Vinyl Ethers by Pentanuclear \(\{(\text{Pr}_3\text{P})\text{Ni}\}_3\text{H}_6\): Facile Cooperative C–O, C–C and C–H Activation Pathways

6.7. References


Chapter 6: Dismantling of Vinyl Ethers by Pentanuclear \((\text{i-Pr}_3\text{P})\text{Ni})_5\text{H}_6\): Facile Cooperative C–O, C–C and C–H Activation Pathways


References begin on page 219
Chapter 6: Dismantling of Vinyl Ethers by Pentanuclear \{({}^{1}Pr_{3}P)Ni\}_{5}H_{6}: Facile Cooperative C–O, C–C and C–H Activation Pathways


7.1. Introduction

Focused efforts towards the design and synthesis of polynuclear transition metal species has gained popularity over the last decade. In part, these efforts stem from attempts to mimic the transformations facilitated by polynuclear metalloenzymes which enable redox processes, that allows the enzyme to facilitate difficult transformations.\textsuperscript{1-8} Examples include the Mn-O cofactor in \textit{Photosystem II},\textsuperscript{3,5,9} as well as the carbide bearing\textsuperscript{10-13} [FeMo] cofactor in \textit{Nitrogenase}.\textsuperscript{14-15} Although a plethora of transition metal clusters have been reported,\textsuperscript{16} most are highly stable species, likely due to the extensive use of \textit{\pi}-acceptor
ligands such as CO, and molecular orbital configurations that feature large HOMO/LUMO gaps. Towards the goal of designing transition metal clusters that have a more reactive nature and can potentially facilitate reactivity akin to cofactors in metalloenzymes, several research groups have produced specialized ligands intended to facilitate M-M interactions, some examples are shown in Figure 7.1.

Figure 7.1 Previously reported transition metal clusters which use a specialized ligand to coordinate several transition metal centres to form a cluster (ligand in b: hexapyridyl 1,3,5 triarylbenzene)
Chapter 7: A Multi-Coordinate Carbide Ligand as an Anchor for Stabilizing Small Transition Metal Clusters

Though the multielectron redox abilities of these clusters have been explored, the species ability towards cooperative bond activation is also an area of interest due to the comparisons made to reactive metal surfaces.\textsuperscript{35} As mentioned earlier, transition metal clusters are ubiquitous in literature but most species are unreactive. The past few decades however, has provided several examples of highly reactive transition metal clusters with mononucleating ligands.\textsuperscript{36-46} The cooperative reactivity exhibited by these species further strengthens the comparisons made to metal-surface chemistry, but the lack of a polynucleating ligand anchoring the transition metal species together often leads to decomposition.

Our group previously reported the facile CC bond cleavage\textsuperscript{47} of unactivated alkenes by the [(iPr\textsubscript{3}P)Ni\textsubscript{5}]H\textsubscript{6} cluster leading to the formation of the pentanuclear carbide cluster [(iPr\textsubscript{3}P)Ni]\textsubscript{5}H\textsubscript{4}(\mu_{5}-\text{C}) (8), shown in Figure 7.1d. The Peters’ group recently reported the use of a specialized ligand featuring a carbide bound to multiple phosphine centres bridging a single Fe centre, which led to catalytic N\textsubscript{2} functionalization.\textsuperscript{48-49} In this chapter, we investigate potential methods to form bonds with the carbide ligand, but also explore the utility of the carbide ligand as an anchor for accessing strained geometries leading to bond activations, as well as experimental evidence for multielectron redox processes.

7.2. Results and Discussion

7.2.1 Deciphering Nucleophilic Character of Carbide

In previous chapters we have demonstrated the ability for the electron-deficient [(iPr\textsubscript{3}P)Ni\textsubscript{5}]H\textsubscript{6} cluster to facilitate unprecedented bond cleavages including C–S, C–H, C=O, and C=C, under mild conditions. The CC bond cleavages have been theorized to
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proceed due to the thermodynamic driving force from the formation of carbide 8. Although a major interest is exploring methods to form bonds with the functionalized carbon atom, in search of catalytic pathways, exploring the ability of the carbide to serve as a bridging ligand offers a rare example of an atom serving as an anchor to hold polynuclear complexes together.\textsuperscript{50-51} Understanding whether bridging five Ni centres results in nucleophilic or electrophilic character of the carbide in 8 can offer insight to selecting reagents that are more likely to form bonds with the carbide ligand. To help determine this we exposed 8 to ammonia-borane and observed the immediate formation of [(Pr\textsubscript{3}P)Ni\textsubscript{5}H\textsubscript{4}(μ\textsubscript{5}−CBH\textsubscript{3})] (24) along with the release of ammonia, as shown in Scheme 7.1. An immediate colour change from dark red to purple occurred and 24 was isolated by recrystallization from n-pentane in 55.9 % yield. The modest yield of 24 can be attributed to the high solubility of cluster 24 in n-pentane, as NMR spectra indicate quantitative conversion. The selective formation of 24 indicates that the carbide ligand in 8 bears nucleophilic character.

\[ \text{Ni}_5^{8+} \quad \text{B-C length } \sim 1.58 \, \text{Å} \]

\[ \text{Ni}_5^{8+} \]

\textbf{Scheme 7.1:} Reaction of 8 with ammonia-borane to form cluster 24 and release NH\textsubscript{3}. 

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The solid-state molecular structure was obtained through X-Ray diffraction, as shown in Figure 7.2, and features an unusual geometry with the Ni₅ systems. The Ni centres are no longer in the familiar capped-square plane motif; however, three of the Ni centres, Ni(1), Ni(2), and Ni(3), lie above the 5-coordinate carbide ligand with non-bonding Ni–Ni distances, while two of the Ni centres, Ni(4), and Ni(5) lie below the carbide ligand with a Ni(4)-Ni(5) of 2.5009(10) Å. A very interesting aspect of this cluster is the B–C bond that is formed with a bond distance of approximately 1.583(9) Å. Cluster 24 bears seven bridging hydride ligands with 3 of the hydride ligands bridged between the boron centre and Ni(1-3).

**Figure 7.2:** ORTEP depiction of 24. Carbons and hydrogens on phosphine ligands excluded for clarity. Selected bond distances (Å): Ni(1)–Ni(5) 2.4700(11), Ni(2)–Ni(4) 2.5247(11), Ni(3)–Ni(4) 2.5303(11), Ni(4)–Ni(5) 2.5009(10), Ni(1)–C(1) 1.960(6), Ni(2)–C(1) 1.951(6), Ni(3)–C(1) 1.948(6), Ni(4)–C(1) 1.904(6), Ni(5)–C(1) 1.890(6), Ni(1)–B(1) 2.097(7), Ni(2)–B(1) 2.127(7), Ni(3)–B(1) 2.127(7), C(1)–B(1) 1.583(9).
Cluster 24 has approximate $C_{2v}$ symmetry and is thermally stable at room temperature as a solid over the course of a few days but slowly decomposes in solution. The $^{31}P\{^1H\}$ NMR spectrum of 24 features a singlet at $\delta$ 47.1, presumably due to a process of fluxional exchange. Upon cooling to $-95$ °C, decoalescence is observed to three resonances at $\delta$ 41.9, 50.7, and 53.9, in a 2:2:1 ratio, respectively. However, significant broadening of the resonance at $\delta$ 41.9 at $-95$ °C, indicates that at the low-temperature limit, there is still an exchange process occurring. The $^1H$ NMR spectrum features a pair of resonances corresponding to the methyl and the methine environment of the triisopropylphosphine ligand. In the hydride region, a broad resonance is present at approximately $\delta$ $-15.00$ with a $W_{1/2}$ of 105.2 Hz that integrates to seven, with respect to the 5 phosphine ligands. The one resonance for both the BH bonds bridged between the Ni centres, and the hydrides which are purely bridged by Ni, are in exchange. Cooling a solution of 24 to $-95$ °C caused decoalescence of the hydride ligands to five resonances is observed at $\delta$ $-24.07$, $-22.37$, $-16.59$, $-10.13$, and $-1.77$ in a 2:1:1:1:2 ratio, respectively. An Arrhenius activation energy of 9.0 kcal/mol was calculated. A $^{11}B\{^1H\}$ NMR spectrum further supported the presence of boron in 24 with a resonance appearing at $\delta$ $-3.9$. Lastly, the $^{13}C\{^1H\}$ NMR spectrum of 24 featured a pair of resonances corresponding to the methyl and the methine carbons, at $\delta$ 20.9 and 25.1, respectively.

The geometry of cluster 24, not only strays from the similar Nis systems shown in this dissertation, but also deviates from classical cluster geometries, which renders assigning a predicted electron count for the cluster, difficult. The main ambiguity is present when considering the potential for boron centres to serve as vertices in mixed transition
metal-main group element clusters, rather than ligands in clusters. However, the bond length of 1.583(9) Å suggests a σ-bond is present between the boron centre and the carbide ligand. The fluctional hydride resonance observed in $^1$H NMR along with lack of an IR stretch in a solid sample of 24 from the range of 1600-2900 cm$^{-1}$, suggests that the borane fragment has metal hydride character. The borane fragment overall can be considered to contribute four electrons to the cluster, with each BH bond contributing two electrons to the bound Ni centre and the C–B bond forming, involving two electrons. This cluster assignment gives 24 a [Nis]$^{8+}$ core with an overall electron count of 72.

The formation of cluster 24 is interesting from a variety of perspectives; first, the observation of a bonding interaction between the boron centre of borane and the carbide provides evidence that the carbide ligand is nucleophilic in character, which offers insight to the bonding interactions between the Ni centres and the carbide ligand. Another interesting outlook is that cluster 24 assembles into a new, unprecedented geometry to accommodate the borane ligand binding to the carbide centre. In similar Nis systems without a carbide ligand, we reported decomposition of a Ni centre to form tetranuclear clusters that can stabilize main group containing elements.$^{52}$ The ability to alter geometry to accommodate the inclusion of small molecules bears resemblance to the [FeMo] cofactor in Nitrogenase, because an interstitial carbide ligand bridging the metal centres is a factor that allows the active site to alter geometry.$^{53}$

### 7.2.2 Cluster 8 Facilitating A 1-Electron Oxidation, Accessing [Nis]$^{9+}$

To further explore the abilities of the carbide ligand in 8 to form new bonds via nucleophilic reactivity, mild carbon-based electrophiles were sought to react with 8.
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However, when 8 was reacted with an equivalent of neopentyl chloride, instead of a bonding interaction at the carbon atom, a one-electron oxidation occurred to form the new paramagnetic cluster \([({\text{iPr}}_3\text{P})\text{Ni}]_5(\mu_5-\text{C})(\mu_2-\text{Cl})\) (25), as shown in Scheme 7.2. The dark red solution turns into a dark green upon addition of neopentyl chloride, and the neopentyl group homodimerizes to form half an equivalent of 2,2,5,5 tetramethylhexane. Reacting 8 with neopentyl chloride in toluene results in the formation of neopentane and biphenyl, suggesting that the reaction proceeds through a single electron transfer mechanism. A combined yield of 66.5 % is obtained from recrystallization of 25 from n-pentane.

![Scheme 7.2: Reaction of 8 with neopentyl chloride to form paramagnetic cluster 25 and facilitate homodimerization of the neopentyl fragment to form 2,2,5,5 tetramethylhexane.](image)

The solid-state molecular structure of 25 was determined using X-Ray diffraction and is shown in Figure 7.3. Cluster 25 features approximate \(C_{2v}\) symmetry, with a chloride bridged between Ni(1) and Ni(3) with Ni(1)-Cl(1) of 2.2833(12) Å and Ni(3)-Cl(1) 2.4081(12) Å. The carbide ligand is pushed further into the Ni square plane, in comparison
to 8, with Ni(2)-C(1)-Ni(4) bond angle of 169.7(3) ° and a Ni(3)-C(1)-Ni(5) bond angle of 166.0(3) °. The Ni-Ni distances in the square plane are relatively consistent ranging from 2.5728(8)- 2.5753(7) Å. The Ni(1) centre bears the longest Ni-C bond at 1.976(4) Å and has a Ni(1)-Ni(3) bond distance of approximately 2.4525(8) Å, the remaining Ni-Ni bonds from Ni(1) are substantially longer, including a Ni(1)-Ni(2) bond distance of 2.7369(8) Å and a Ni(1)-Ni(4) bond distance of 2.8484(8) Å. The four hydride ligands are all bridged between adjacent Ni centres in the square plane and are located in the square plane as well. Although P(2) and P(4) lie in the Ni square plane, P(3) and P(5) lie well below the Ni square plane. The torsion angle of P(1)-Ni(1)-Ni(3)-P(3) is approximately 5.4 °, which resembles known dinuclear Ni monophosphine complexes with bridging chloride and hydride ligands.
Figure 7.3: ORTEP depiction of 25 with carbons and hydrogens on phosphines omitted for clarity. Selected bond lengths: Ni(1)−Ni(2) = 2.7369(8) Å; Ni(1)-Ni(3) = 2.4525(8) Å; Ni(1)-Ni(4) = 2.8484(8) Å; Ni(2)-Ni(3) = 2.5753(7) Å; Ni(3)-Ni(4) = 2.5728(8) Å; Ni(4)-Ni(5) = 2.5272(8) Å; Ni(2)-Ni(5) = 2.5313(8) Å; Ni(1)-Cl(1) = 2.2833(12) Å; Ni(3)-Cl(1) = 2.4081(12) Å; Ni(1)-C(1) = 1.976(4) Å; Ni(2)-C(1) = 1.813(5) Å; Ni(3)-C(1) = 1.836(4) Å; Ni(4)-C(1) = 1.804(5) Å; Ni(5)-C(1) = 1.804(4) Å; Ni(2)-H(1) = 1.69(5) Å; Ni(3)-H(2) = 1.57(5) Å; Ni(4)-H(2) = 1.56(4) Å; Ni(4)-H(3) = 1.57(5) Å; Ni(5)-H(3) = 1.47(5) Å; Ni(5)-H(4) = 1.74(4) Å; Ni(2)-H(4) = 1.56(4) Å. Selected Bond Angles: Ni(1)−Cl(1)−Ni(3) = 79.99(16) °; Ni(2)−C(1)−Ni(4) = 169.7(3) °; Ni(3)-C(1)-Ni(5) = 166.0(3) °.

Cluster 25 is paramagnetic with a [Ni5]9+ core. Evan’s method57 was used to determine an effective magnetic moment of 1.68 Bohr magnetons, which corresponds to one unpaired electron.58 Cluster 25 is 31P{1H} silent, but two broad resonances are observed in the 1H NMR spectrum, at δ 1.74 with a W1/2 of 140 Hz and δ 8.86 with a W1/2 of 520 Hz. The two resonances integrate to a 6:1 ratio, indicating that they correspond to the methyl and methine environments and that 25 is fluxional. The EPR spectrum of a solution cooled with liquid nitrogen revealed a signal with a gz value of 2.05 and nearly coincident gx and gy values of 2.22 and 2.24. The EPR linewidths of 50 Hz were broad enough to hinder the observation of potential hyperfine coupling to the phosphine or hydride ligands.

Cluster 25 is considered a distorted-nido cluster with one vertex deficient of an octahedron, akin to 8 and similar systems reported by our group.45-46 The cluster bears an
electron count of 71 electrons with the Cl ligand having the geometry to be an XL donor. Although the electron count for 25 is considered deficient for a nido cluster with 5 vertices (74 electrons),\textsuperscript{59} the electron counting rules for clusters is based on the premise that monometallic species require 18 electrons to form stable adducts.\textsuperscript{60} However, a variety of stable electron counts have been reported in literature for Ni species including 16 electron Ni\textsuperscript{II} square planar complexes,\textsuperscript{61} and potentially more applicable for 25, 15 electron Ni\textsuperscript{I} trigonal planar complexes are also well-known.\textsuperscript{62} The potential two- or three-electron differences per Ni centre in the anticipated count gives a wide variance of potential stable electron counts and renders and rationalization of the structure of 25 using Wade’s rules, weak. Discrepancies between the predicted electron count and the observed electron count could also be present due to the elongated distances between Ni(1) and Ni(2), Ni(4), and Ni(5), which cause the geometry to stray from the square-pyramid assignment.

As mentioned earlier, redox transformations are particularly important in multimetallic systems due to the attempts to mimic multielectron redox processes that occur in metalloenzymes such as the cofactors of Nitrogenase.\textsuperscript{15} Recent reports by the Betley group, have outlined the ability of polynuclear species to access multiple oxidation states through cyclic voltammetry and synthetic studies.\textsuperscript{21, 23, 63} While the transformation of cluster 8 to 25 only shows an overall increase from a [Ni\textsubscript{5}]\textsuperscript{8+} to [Ni\textsubscript{5}]\textsuperscript{9+}, 8 is formed when the known cluster, [(\textit{i}Pr\textsubscript{3}P)Ni]\textsubscript{3}H\textsubscript{6} (1), with a [Ni\textsubscript{5}]\textsuperscript{6+} core is exposed to various alkenes.\textsuperscript{43} The ability for the Ni\textsubscript{5} systems to access a variety of oxidation states further strengthens the comparisons to the carbide-bearing cofactor of [FeMo] Nitrogenase.

7.2.3 Oxidative addition by 8
In attempts to expand the scope of reactivity of 8 with potential XL ligands, oxidative addition with NH bonds was explored, with the anticipation that 1-electron processes would not be accessible. The reaction of 8 with 2,6-bis(trifluoromethyl)aniline gave the new pentanuclear carbide cluster \([\text{([iPr}_3\text{P})\text{Ni–H}]_5(\mu_4–\text{C})(\text{HN-C}_6\text{H}_3(\text{CF}_3)_2)}} \) (26), as shown in Scheme 7.3. Carbide cluster 26 is formed by reversible oxidative addition of one of the NH bonds of the aniline moiety. Due to the equilibrium present, an excess of aniline is required to achieve a near complete conversion of 26.

**Scheme 7.3.** Reaction of 8 with 2,6 bis(trifluoromethyl)aniline reversibly producing cluster 26 from oxidative addition of the NH bond.

The solid-state molecular structure of 26 was obtained by X-Ray diffraction and is featured in Figure 7.4, and shows \(C_1\) symmetry. The structure shows four Ni centres in a square plane with bond distances ranging from 2.5272 – 2.6297(4) Å, with the Ni(2)-Ni(3) distance substantially longer than the rest. The Ni(1) centre lies above the Ni(2)-Ni(3) bond and Ni(1)-Ni(2) distance of 2.3847(4) Å is significantly shorter than the rest of the Ni-Ni bonds. The Ni(1)-Ni(3) bond distance is approximately 2.5035(4) Å, which is similar to
the Ni-Ni bond distances in the square plane. The short Ni-Ni bond distance of Ni(1)-Ni(3) is associated with the bridging amido ligand with Ni(1)-N(1) distance of 1.9534(18) Å and Ni(2)-N(1) distance of 2.1044(17) Å. Unlike clusters 8, 24, and 25, the carbide ligand is bridged between only 4 of the Ni centres, with the Ni(1) centre not bonding to C(1). The carbide ligand lies in the approximate Ni(2)-Ni(5) square plane with diagonal bond angles Ni(2)-C(1)-Ni(4) of 168.49(12) ° and Ni(3)-C(1)-Ni(5) of 178.13(12) °. Similar to 25, the phosphine ligands on the Ni centres bridging the XL amido ligand are bent, which causes the phosphine on Ni(2) to lie below the Ni(2)-Ni(5) square plane, while the phosphines on Ni(3)-Ni(5) lie approximately in the square plane.

Figure 7.4. ORTEP Depictions of 26 with carbons and hydrogens on phosphines, and aromatic hydrogens on aniline omitted for clarity. Selected bond lengths: Ni(1)-Ni(2) = 2.3847(4) Å; Ni(1)-Ni(3) = 2.5035(4) Å; Ni(2)-Ni(3) = 2.6297(4) Å; Ni(3)-Ni(4) =
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2.5354(4) Å; Ni(4)-Ni(5) = 2.5272(4) Å, Ni(2)-Ni(5) = 2.5493(4) Å; Ni(1)-N(1) = 1.9534(18) Å; Ni(2)-N(1) = 2.1044(17) Å; Ni(2)-C(1) = 1.8258(19) Å; Ni(3)-C(1) = 1.8212(19) Å; Ni(4)-C(1) = 1.7965(19) Å; Ni(5)-C(1) = 1.7959(19) Å; Ni(1)-H(2) = 1.47(3) Å; Ni(3)-H(2) = 1.73(3) Å; Ni(2)-H(3) = 1.69(3) Å; Ni(2)-H(4) = 1.71(3) Å; Ni(3)-H(5) = 1.67(3) Å; Ni(4)-H(5) = 1.58(3) Å; Ni(4)-H(6) = 1.57(3) Å; Ni(5)-H(6) = 1.62(3) Å; Ni(5)-H(3) = 1.51(3) Å. Selected Bond Angles: Ni(2)-Ni(1)-Ni(3) = 65.037(12) °; Ni(1)-N(1)-Ni(2) = 71.88(6) °; Ni(2)-C(1)-Ni(4) = 168.49(12) °; Ni(3)-C(1)-Ni(5) = 178.13(12) °.

Attempts to purify 26 by recrystallization gave a mixture, that both $^{31}\text{P}^{1}\text{H}$ and $^{1}\text{H}$ NMR, identified as 26, carbide 8, and 2,6-bis(trifluoromethyl)aniline, presumably, due to the equilibria between these species. The $^{31}\text{P}^{1}\text{H}$ NMR spectrum of the mixture revealed three singlets associated with 26 appearing at δ 45.2, 47.7, and 52.3 in a 2:2:1 ratio, supporting a mechanism of fluxional exchange for the $C_1$ symmetric 26. Upon cooling to −55 °C, decoalescence of the resonance at δ 47.7 into a singlet at δ 47.2 and a doublet at δ 47.3 occurred, and the resonance at δ 52.3 was also a doublet with corresponding coupling constant of 17.8 Hz. The resonance at 45.2 broadens, but does not decoalesce, which suggests that there are two separate mechanisms of fluxional exchange. The $^{1}\text{H}$ NMR spectrum at 25 °C of 26 reveals several broad resonances in the phosphine region, corresponding to the methyl and methine environments of the phosphine ligands. A sharp singlet at δ 3.18 integrating to 1 H corresponds to the NH environment. In the aromatic region a sharp singlet is present at δ 6.79 corresponds to the para environment on the bound
aniline and two broad singlets, with $W_{1/2}$ of 20.6 Hz, at $\delta$ 6.75 and 8.78 correspond to the ortho environments of the aniline fragment. The broadness of the resonances are associated with exchange from rotation of the aniline ring and this is supported by the sharpening of the resonances upon cooling. The sizeable chemical shift difference between the two ortho environments is likely due to a significant paramagnetic contribution to the NMR shielding constant, $\sigma_p$, from the proximity of one of the ortho environments to Ni(1). The hydride region of the $^1$H NMR has three broad resonances in a 1:1:3 ratio at $\delta$ −14.48, −6.96 and −5.74, indicative of a fluxional process of exchange. Cooling down a solution of 26 to −95 °C gave decoalescence of the peak integrating to 3 H into unique environments at $\delta$ −27.96, −8.37 and −6.29. The fluxional exchange in the hydride region was modeled and an Arrhenius activation energy of 8.6 kcal/mol was calculated. The two remaining hydride resonances sharpened to reveal apparent triplet multiplicities with $^2J_{HP} = 17.5$ Hz and $^2J_{HP} = 16.5$ Hz.

The reversible process of oxidative addition was confirmed when monitoring the production of 26 versus 8 and 2,6-bis(trifluoromethyl)aniline. Due to the entropic favourability of the right side of the reaction in Scheme 7.3, higher temperatures should produce more of cluster 8 and free aniline, As can be seen in Figure 7.5, the resonance corresponding to the aniline increases upon heating to 55 °C and the resonance corresponding to an aromatic proton of 26 decreases, immediately after heating, the sample was cooled to room temperature and $^1$H NMR revealed the immediate increase in 26 and decrease in 8 and 2,6- bis(trifluoromethyl)aniline, thus confirming the oxidative addition process is reversible. The lack of broadening in both $^1$H and $^{19}$F{$^1$H} NMR of the free aniline upon heating suggests that the exchange process is slow on the NMR timescale.
Initial attempts reacting 2,6-bis(trifluoromethyl)aniline with ethylene, styrene, and 3-hexyne in the presence of 8 gave no evidence of hydroamination; further substrates and conditions are currently being tested.

![Chemical structure](image)

**Figure 7.5.** Variable temperature $^1$H NMR studies of reaction of 8 with 2,6-bis(trifluoromethyl)aniline showing the reversible oxidative NH bond addition.

Cluster 26 has a $[\text{Ni}_5]^{10+}$ core and the overall electron count is 72 electrons with the amido group serving as an XL donor. The observation of the increased oxidation state to
the [Ni₅]¹⁰⁺ provides further experimental evidence of the redox potential of the Ni₅ systems. Granted that square-planar Ni₅ complexes are ubiquitous in literature,⁶⁰ pentanuclear clusters with a bridging carbide ligand composed of entirely Ni₅ species are unprecedented. Attaining a [Ni₅]¹⁰⁺ core oxidation state is an interesting result considering the reaction of 8 with neopentyl chloride only facilitates a one-electron oxidation opposed to the oxidative addition of an NH bond. Oxidative addition of NH bonds have been reported in literature, including examples of ammonia oxidative addition.⁶⁴-⁶⁵ Additionally, Brookhart reported aniline NH bond activation by Ir⁶⁶ and Ozerov reported the NH oxidative addition of an aryl-NH bond incorporated into ligand design, by Ni(0).⁶⁷ The observation of reversible oxidative addition of the NH bond suggests a low barrier to activation which bodes well for potential catalysis towards hydroamination. Though reports of early transition metals facilitating hydroaminations are well known,⁶⁸,⁶⁹ as well as examples of mononuclear and dinuclear Ni species,⁷⁰-⁷² examples of polynuclear Ni complexes are not currently known. In addition, the oxidative addition of the NH bond causes the top Ni to lie directly above one of the Ni-Ni edges which causes the top Ni to lose bonding interaction with the carbide ligand. Once again, the carbide ligand displays versatility to account for bonding preferences in the other components of the cluster, here bridging four Ni centres.

The addition of Cl and NH bonds to 8 causing different core oxidation states and overall electron counts suggests that the cluster can accommodate various donors and various amounts of electrons. Our group has previously demonstrated the incorporation of sulfur into our Ni₅ systems through the use of S=PPr₃ with [(PPr₃)Ni]₃H₆, which proceeded through an observable Ni₅ intermediate, but leads to the decomposition to a mononuclear
and tetranuclear species. To provide further evidence that the carbide ligand provides stabilization to the Ni\textsubscript{5} system, 8 was reacted with one equivalent of S=PPr\textsubscript{3} to form the new pentanuclear Ni carbide cluster \([([\text{Pr}_3\text{P}]\text{Ni})_3\text{H}_4\text{C}(\text{S}) (27)]\), as shown in Scheme 7.4. The dark red solution turns dark brown after 0.25 h of stirring in toluene and one equivalent of PPr\textsubscript{3} is formed, recrystallization of 27 from \textit{n}-pentane affords a combined yield of 55.5%.

\begin{equation}
\text{Ni}_5^{8+} + \text{S} + \text{PPr}_3 \rightarrow \text{[Ni}_5^{10+}]_4\text{H}_4(\mu_7\text{-C})(\mu_7\text{-S})
\end{equation}

\textbf{Scheme 7.4:} Reaction of 8 with triisopropyl phosphine sulfide yielding cluster 27 along with the loss of one equivalent of phosphine

Though crystalline samples of 27 were obtained, X-Ray diffraction proved troublesome, as issues stemming from twinning are present which hampered attempts to identify the correct space group. However, all solutions lead to a similar core structure which feature five Ni centres with terminal phosphines along with an interstitial carbide ligand and a bridged sulfide ligand
The $^{31}$P{$^{1}$H} NMR spectrum of 27 features two resonances at $\delta$ 53.6 and 48.2 in a 2:3 ratio. Cooling down a solution of 27 revealed that phosphines were fluxional as the $^{31}$P{$^{1}$H} NMR spectrum at $-40 \, ^{\circ}C$ revealed decoalescence into a 1:2:1:1 ratio, the two equivalent phosphine ligands potentially corresponding to two of the phosphine centres bridging the sulfide ligand. The room-temperature $^{1}$H NMR spectrum of 27 reveals four resonances corresponding to the phosphine ligands, two methyl resonances and two methine resonances in a 3:2 ratio, in agreement with the room-temperature $^{31}$P{$^{1}$H} NMR spectrum. The hydride region features two resonances, a triplet of quartets at $-4.82$ with $^{3}J_{HP} = 5.6 \, Hz$ and $^{2}J_{HP} = 18.1 \, Hz$ and a broad resonance is at $\delta -11.42$, in a 1:3 ratio, respectively. Upon cooling to $-40 \, ^{\circ}C$, decoalescence of the broad resonance into a 1:2 ratio is then observed. An Arrhenius activation energy of 9.9 kcal·mol$^{-1}$ was calculated for this process. The $^{13}$C{$^{1}$H} NMR also shows two separate phosphine environments with four total resonances, two for the methyl environments, nearly coincident at $\delta 21.0$, and two doublets for the methine environments at $\delta 24.8$ and 25.6 with $^{1}J_{CP}$ of 13 and 12 Hz, respectively. The low-temperature NMR data suggests that 27 may take a trigonal bipyramid cluster geometry with hydrides potentially lying on the four Ni–Ni edges between the axial and equatorial Ni centres, apart from two Ni–Ni edges which are likely bridging the sulfide ligand. However, a distorted square pyramid cluster geometry is also a plausible assignment for 27. The use of electron counts to support a cluster geometry is widely used in cluster chemistry; however, the majority of the clusters in this dissertation do not agree with the expected electron count.

Once again, cluster 27 bears a [Ni$_5$]$^{10+}$ core through the addition of the X$_2$L$_n$ sulfur ligand, which gives an overall electron count of at least 72 electrons, similar to 26. As
mentioned above, the electron counting rules do not necessarily apply for these Ni\textsubscript{5} systems due to the variance in electron counts for stable mononuclear Ni moieties. Further support that the carbide ligand acting as a stabilizing agent is provided by the fact that a similar system lacking a carbide ligand, (1), decomposes the Ni\textsubscript{5} core while the carbide ligand allows the formation for a thermally stable Ni\textsubscript{5} adduct.

7.3. Conclusions:

In summary, the use of 8 to synthesize clusters 24-27 which bear varying core oxidation states, electron counts, and overall geometries outlines the versatility that the carbide ligand offers in cluster formation. This displays the ability of the carbide ligand to accommodate various electronic and steric influences the cluster imposes. Additionally, the ability for 8 to facilitate reversible NH bond oxidative addition expands on more cooperative reactivity previously reported on the Ni\textsubscript{5} systems. Our previous work coupled with these new results shows a net increase from [Ni\textsubscript{5}]^{6+} to [Ni\textsubscript{5}]^{10+}, which provides experimental evidence for capabilities in multielectron redox processes. The evidence for the cofactor in [FeMo] Nitrogenase revealing a carbide ligand bound to multiple transition metal centres further cements the comparisons of 8, and 24-27 to metalloenzymes. Further work in cooperative bond activation, and investigations into core oxidation state changes, with the Ni\textsubscript{5} systems is underway.

7.4. Experimental

7.4.1 General Procedures:

Unless otherwise stated, all manipulations were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or an MBraun glove-box. Dry, oxygen-
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free solvents were employed throughout. Anhydrous pentane, toluene, and THF were purchased from Alfa Aesar and were argon packed and dried with either activated sodium or molecular sieves. Benzene-\textit{d}6 was dried by heating at reflux with Na/K alloy in a sealed vessel under partial pressure then trap-to-trap distilled and freeze–pump–thaw degassed three times. Cluster 8 was synthesized as per literature procedures. as neopentyl chloride, ammonia-borane complex, 2,6-bis(trifluoromethyl)aniline and sulfur were purchased from Sigma-Aldrich and their purity was confirmed through NMR spectroscopy. $^1$H, $^{31}$P{$^1$H} and $^{13}$C{$^1$H}NMR spectra were recorded on a Bruker AMX Spectrometer operating at 300 MHz or 500 MHz with respect to proton nuclei. All chemical shifts are recorded in parts per million, and all coupling constants are reported in Hertz. $^1$H NMR spectra were referenced to residual protons (C$_6$D$_5$H, $\delta$ 7.15) with respect to tetramethylsilane at $\delta$ 0.00. $^{31}$P{$^1$H} NMR spectra were referenced to external 85\% H$_3$PO$_4$ at $\delta$ 0.00. $^{13}$C{$^1$H} NMR spectra were referenced relative to solvent resonances (C$_6$D$_6$, $\delta$ 128.0; C$_7$D$_8$, $\delta$ 20.4; C$_4$D$_8$O, $\delta$ 25.37). $^{11}$B{$^1$H} NMR spectra were referenced to external BF$_3$OEt$_2$ at $\delta$ 0.00. Elemental analyses were performed at the Center for Catalysis and Materials Research, Windsor, Ontario.

7.4.2 Synthesis, Characterization, and Reactivity of Complexes

Synthesis and Characterization of [($^\text{i}$Pr$_3$P)Ni]$_3$H$_4$($\mu_5$-C)($\mu_3$-BH$_3$) (24)

A solution of 8 (900 mg, 0.81 mmol) in 25 mL of \textit{n}-pentane was reacted with an equivalent of ammonia-borane complex (25 mg, 0.81 mmol) with vigorous stirring. After 0.25 h, all volatiles were removed from the purple solution and the residue was extracted with $3 \times 15$ mL of \textit{n}-pentane and filtered through a plug of Celite. The solution was then concentrated and cooled at $-40$ °C for 8 h, which gave purple crystals suitable for X ray diffraction.
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second crop was also collected to give a combined yield of 628 mg (55.9%). $^1$H NMR (298 K, C$_6$D$_6$, 500 MHz): $\delta$ −14.99 (broad s, $W_{1/2}$ = 105.2 Hz, 7H, Ni−H), 1.34 (dd, $^3$J$_{HH}$ = 7.0 Hz $^3$J$_{HP}$ = 12.6 Hz, 54H, P(CH(CH$_3$)$_2$)$_3$), 2.04 (septet of d/apparent octet, $^3$J$_{HH}$ = 6.5 Hz, $^2$J$_{HP}$ = 6.9 Hz, 15H, P(CH(CH$_3$)$_3$)$_3$), $^3$P{$^1$H} NMR (298 K, C$_6$D$_6$, 202.5 MHz): $\delta$ 48.3 (s, 5P, P(CH(CH$_3$)$_2$)$_3$), $^{11}$B{$^1$H} (298 K, C$_6$D$_6$, 160.5 MHz): $\delta$ −3.9 (s, 1B, C−BH$_3$), $^{13}$C{$^1$H} NMR (298 K, C$_6$D$_6$, 75.5 MHz): $\delta$ 20.9 (s, 30C, P(CH(CH$_3$)$_2$)$_3$), 25.4 (d, $^1$J$_{CP}$ = 12.8 Hz, 15C, P(CH(CH$_3$)$_2$)$_3$).

$^1$H NMR (178 K, n-pentane, 500 MHz): $\delta$ −24.07 (s, 3H, Ni−H) −22.37 (s, 1H, Ni−H) −16.59 (s, 1H, Ni−H) −10.13 (s, 1H, Ni−H), −1.77 (s, 1H, Ni−H). $^3$P{$^1$H} NMR (178 K, n-pentane, 202.5 MHz): $\delta$ 53.9 (broad s, $W_{1/2}$ = 405.8 Hz 1P, P(CH(CH$_3$)$_3$)$_3$) 50.7 (broad s, $W_{1/2}$ = 209.7 Hz 2P, P(CH(CH$_3$)$_3$)$_3$) 41.9 (broad s, $W_{1/2}$ = 220.5 Hz 2P, P(CH(CH$_3$)$_3$)$_3$)

**Synthesis and Characterization of [({iPr$_3$P)Ni$_5$H$_4$}(µ$_4$-C)(µ$_2$-Cl) (25).** A solution of [{iPr$_3$P)Ni$_5$H$_4$} (600 mg, 0.54 mmol) and 1 equivalent of neopentyl chloride (58 mg, 0.54 mmol) in 15 mL of n-pentane was stirred for 15 min, which gave a dark green solution. Volatiles were removed in vacuo and the residue extracted with n-pentane (3 × 5 mL). The solution was concentrated and cooled −40 °C for 16 h at which point dark green crystals suitable for X-ray diffraction were obtained. The mother liquor was concentrated and multiple crops yielded 416 mg of 25 (66.5%). $^1$H NMR (298 K, C$_6$D$_6$, 500 MHz): $\delta$ 1.74 (broad s, $W_{1/2}$=141 Hz, 90 H, P(CH(CH$_3$)$_2$)$_3$), 8.86 (broad s, $W_{1/2}$=519 Hz, 15H, P(CH(CH$_3$)$_3$)$_3$), Anal Calcd for C$_{46}$H$_{109}$ClNi$_5$P$_5$: C, 48.20; H, 9.59; Found: C, 48.07; H, 9.59.

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Synthesis and Characterization of [(i\(\text{Pr}_3\)P)Ni]_3H_5(\(\mu_4\)-C)(HN-C_6H_3(\(m\)-CF_3))_2 (26). A solution of 8 (550 mg, 0.49 mmol) in 10 mL of toluene was exposed to four equivalents of 2,6–bis(trifluoro)methyl aniline (451 mg, 1.96 mmol) while stirring vigorously. After 2 h of stirring, all volatiles were removed and the residue was extracted with 3 \times 15 mL of \(n\)-pentane and filtered through a plug of Celite. The solution was then concentrated and cooled to \(-40\) °C for 16 h, at which point dark brown crystals suitable for X-ray diffraction were obtained. A second crop was also collected giving a combined yield of 342 mg (52.1%).

\(^1\)H NMR (298 K, C_4D_8O, 500 MHz): \(\delta -14.48\) (broad s, \(W_{1/2} = 430\) Hz, 3 H, Ni-H), : \(-6.96\) (broad s, \(W_{1/2} = 117\) Hz, 1 H, Ni-H), 0.98 (broad s, \(W_{1/2} = 103.8\) Hz, 36 H, P(CH(CH_3)_2)_3), 1.74 (broad s, \(W_{1/2} = 81.1\) Hz, 6 H, P(CH(CH_3)_2)_3) 2.32 (broad s, \(W_{1/2} = 68.2\) Hz, 9 H, P(CH(CH_3)_2)_3) 3.18 (s, 1 H, HN-aryl) 6.75 (broad s, \(W_{1/2} = 20.6\) Hz, 1 H, o-H) 6.79 (s, 1 H, p-H) 8.78 (broad s, \(W_{1/2} = 20.6\) Hz, 1 H, o-H) \(^{31}\)P{\(^1\)H} NMR (298 K, C_6D_6, 121.5 MHz): \(\delta 45.2\) (s, 2 P, NiP\(i\)Pr_3) 47.7 (s, 2 P, NiP\(i\)Pr_3) 52.3 (s, 1 P, NiP\(i\)Pr_3). \(^{19}\)F{\(^1\)H} NMR (298 K, C_6H_6, 470.5 MHz) \(\delta -62.9\) (s, 3 F, C-CF_3) -62.2 (s, 3 F, CF_3). \(^1\)H NMR (193 K, C_4D_8O, 500 MHz): \(\delta -27.96\) (s, 1 H, Ni-H) \(-8.37\) (s, 1 H, Ni-H) \(-6.79\) (apparent t, \(^2\)J_{HF} = 17.5 Hz, 1 H, Ni-H) \(-6.29\) (s, 1 H, Ni-H) \(-5.58\) (apparent t, \(^2\)J_{HF} = 16.5 Hz, 1 H, Ni-H). \(^1\)H NMR (253 K, C_4D_8O, 500 MHz): \(\delta 0.88\) (broad m, 18 H, P(CH(CH_3)_2)_3) 0.97 (broad m, 18 H, P(CH(CH_3)_2)_3) 1.29 (overlapping m, 18 H, P(CH(CH_3)_2)_3) 1.36 (dd, \(^{31}\)P{\(^1\)H} NMR (253 K, C_4D_8O, 121.5 MHz): \(\delta 45.0\) (s, 2 P, NiP\(i\)Pr_3) 47.2 (s, 1 P, NiP\(i\)Pr_3) 47.3 (d, \(^3\)J_{PP} = 17.8 Hz, 1 P, NiP\(i\)Pr_3).
Synthesis and Characterization of \([([\Pr_3P]Ni)_3H_4(C)S)\) (27). A solution of 8 (555 mg, 0.5 mmol) in 10 mL of toluene was reacted with an equivalent of triisopropylphosphinesulfide (96 mg, 0.5 mmol) while stirring vigorously. After 0.25 h of stirring, all volatiles were removed and the residue was extracted with 3 × 10 mL of n-pentane and filtered through a plug of Celite. The solution was then concentrated and cooled to −40 °C for 16 hours at which point, dark brown crystals suitable for X-ray diffraction were obtained from the first crop. A second crop was also collected giving a combined yield of 317 mg (55.5%). \(^1\)H NMR (298 K, C\(_6\)D\(_6\), 500 MHz): \(\delta -11.47\) (broad m, 3H, Ni–H), −4.82 (tq, \(^3J\_\text{HP} = 5.6\) Hz, \(^2J\_\text{HP} = 18.1\) Hz, 1H, Ni–H) 1.34 (dd, \(^3J\_\text{HH} = 7.0\) Hz, 3J\(_{\text{HP}} = 12.6\) Hz, 54H, P(CH(C\(_3\))\(_2\))\(_3\)), 1.35 (dd, \(^3J\_\text{HH} = 7.1\) Hz, \(^3J\_\text{HP} = 12.4\) Hz, 36H, P(CH(C\(_3\))\(_2\))\(_3\)), 2.04 (septet of d/apparent octet, \(^3J\_\text{HH} = 6.8\) Hz, \(^2J\_\text{HP} = 7.2\) Hz, 9H, P(CH(CH\(_3\))\(_2\))\(_3\)), 2.34 (septet of d/apparent octet, \(^3J\_\text{HH} = 7.0\) Hz, \(^2J\_\text{HP} = 7.3\) Hz, 6H, P(CH(CH\(_3\))\(_2\))\(_3\)), \(^{31}\)P\({}^1\)H NMR (298 K, C\(_6\)D\(_6\), 202.5 MHz): \(\delta 48.2\) (broad s, \(W_{1/2} = 1272\) Hz, 3P, P(CH(CH\(_3\))\(_2\))\(_3\)), 53.6 (broad s, \(W_{1/2} = 235\) Hz, 2P, P(CH(CH\(_3\))\(_2\))\(_3\)), \(^{13}\)C\({}^1\)H NMR (298 K, C\(_6\)D\(_6\), 75.5 MHz): \(\delta 21.0\) (s, 18C, P(CH(CH\(_3\))\(_2\))\(_3\)), 21.0 (s, 12C, P(CH(CH\(_3\))\(_2\))\(_3\)), 24.8 (d, \(1^J\_\text{CP} = 13\) Hz, 9C, P(CH(CH\(_3\))\(_2\))\(_3\)), 25.6 (d, \(1^J\_\text{CP} = 12\) Hz, 6C, P(CH(CH\(_3\))\(_2\))\(_3\)). \(^1\)H NMR (233 K, n-pentane, 500 MHz): \(\delta -11.91\) (s, 2H, Ni–H) −10.81 (s, 1H, Ni–H) −5.02 (t, \(^2J\_\text{HP} = 21.9\) Hz, 1H, Ni–H). \(^{31}\)P\({}^1\)H NMR (233 K, n-pentane, 202.5 MHz): \(\delta 58.4\) (s, 1P, P(CH(CH\(_3\))\(_2\))\(_3\)), 56.1 (s, 2P, P(CH(CH\(_3\))\(_2\))\(_3\)), 47.9 (s, 1P, P(CH(CH\(_3\))\(_2\))\(_3\)), 32.2 (s, 1P, P(CH(CH\(_3\))\(_2\))\(_3\)). Anal Calcd for C\(_{46}\)H\(_{109}\)Sn\(_3\)P\(_5\)_4 (1142.754) C, 48.35; H, 9.61, Found C, 48.78; H 9.65.

Variable-temperature NMR spectra of 24. A n-pentane solution of 24 (20 mg, 0.018 mmol) was transferred to a J. Young NMR tube. \(^{31}\)P\({}^1\)H and \(^1\)H NMR spectra were
collected at −10 °C, −25 °C, −40 °C, −55 °C, and −75 °C in attempts to track decoalescence of the single hydride resonance. WINDNMR was used to model the spectra, and corresponding rate constants of 60000 s$^{-1}$, 17000 s$^{-1}$, 5200 s$^{-1}$, 1100 s$^{-1}$, and 220 s$^{-1}$ were determined. Using the Arrhenius equation, an $E_a$ of 8.98 kcal·mol$^{-1}$ was calculated.

Variable-temperature NMR spectra of 26. A $d_8$-THF solution of 26 (20 mg, 0.018 mmol) was transferred to a J. Young NMR tube. $^{31}$P{$^1$H} and $^1$H NMR spectra were collected at 25 °C, 0 °C, −20 °C, −45 °C, and −80 °C in attempts to track decoalescence of the single hydride resonance. WINDNMR was used to model the spectra, and corresponding rate constants of 250000 s$^{-1}$, 75000 s$^{-1}$, 22000 s$^{-1}$, 3000 s$^{-1}$, and 150 s$^{-1}$ were determined. Using the Arrhenius equation, an $E_a$ of 8.57 kcal·mol$^{-1}$ was calculated.

Variable-temperature NMR spectra of 27. A n-pentane solution of 27 (20 mg, 0.018 mmol) was transferred to a J. Young NMR tube. $^{31}$P{$^1$H} and $^1$H NMR spectra were collected at 25 °C, 10 °C, −10 °C, −20 °C, and −40 °C in attempts to track decoalescence of the single hydride resonance. WINDNMR was used to model the spectra, and corresponding rate constants of 3000 s$^{-1}$, 800 s$^{-1}$, 270 s$^{-1}$, 120 s$^{-1}$, and 25 s$^{-1}$ were determined. Using the Arrhenius equation, an $E_a$ of 9.88 kcal·mol$^{-1}$ was calculated.

NMR scale reaction of 8 with neopentylchloride in toluene

A solution of 8 (20 mg, 0.018 mmol) in $d_8$-toluene was exposed to two equivalents of neopentylchloride (4 mg, 0.036 mmol) and transferred to an NMR tube. A $^1$H NMR of the sample was obtained and showed the formation of cluster 25 as well as a singlet corresponding to neopentane, but no resonances for the homodimerized compound 2,2,5,5 tetramethylhexane.
Evans Method on 25

A solution of 25 with a concentration of 0.057 mol/L in C₆D₆ was prepared and transferred to a capillary tube. An NMR tube was filled with 0.4 mL of C₆D₆ and the capillary tube was then carefully inserted into the NMR tube. The tubes were then taken to the 500 MHz NMR spectrometer where a ¹H NMR experiment was conducted and a separation of 101.6 Hz was measured between the C₆D₅H signal in the capillary tube and the C₆D₃H signal outside the capillary tube. Using the measured values an effective magnetic moment of approximately 1.67 Bohr magnetons is calculated. This value corresponds to the expected effective magnetic moment expected for 1 unpaired electron.

Catalytic hydroamination attempts of 2,6-bis(trifluoromethyl)aniline with substrates using 8

A solution of 8 (11 mg, 0.01 mmol) was dissolved in 0.6 mL of C₆D₆ and the solution was used to transfer 20 equivalents of 2,6 bis(trifluoromethyl)aniline (46 mg, 0.2 mmol) and is exposed to an excess of alkene or alkyne a. (styrene: 21 mg, 0.2 mmol) b. (ethylene: 2.4 mL, 3.3 mmol) c. (3-hexyne: 16 mg, 0.2 mmol). The resulting solution is monitored using ¹H and ³¹P{¹H} NMR spectroscopy immediately, after 1 h, after 4 hours, and after 16 hours. No immediate reaction is observed with the exception of the formation of 26, over time decomposition of 8 leads to hydrogenation of the different substrates.

7.5. X-Ray Crystallography

Table 7.1. Crystallographic data for 24-26

<table>
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<th>Compound</th>
<th>24</th>
<th>25</th>
<th>26</th>
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</thead>
</table>

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<table>
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<th>Chemical Formula</th>
<th>$2(C_{46}H_{112}Ni_5P_5B)$</th>
<th>$C_{46}H_{106}Ni_5P_5Cl$</th>
<th>$(C_{54}H_{114}FeNNi_5P_5)<em>2C_3H</em>{12}$</th>
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<td>2751.86</td>
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<td>170(2) K</td>
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<td><strong>Space group</strong></td>
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<td>Pbca</td>
<td>P2(1)/n</td>
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<td>13.1179(12)</td>
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<td><strong>γ/ °</strong></td>
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<td>8.10</td>
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7.6. Supporting Information

Full details of crystallographic information in CIF format for compounds 24-26 along with selected experimental NMR spectra can be found on supplementary USB provided.
Chapter 7: A Multi-Coordinate Carbide Ligand as an Anchor for Stabilizing Small Transition Metal Clusters

7.7. References


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8.1. Future Work and Preliminary Results

8.1.1 Attempted Isolation and Characterization of [(iPr,P)Ni]3H4

Obtaining a better understanding of the carbon atom abstraction facilitated by 1 is a goal of our research group. Intermediates of CC bond cleavage were isolated and showed triple CH bond activation products indeed; however, low temperature studies of 1 with alkenes revealed an additional intermediate was observed by NMR. In particular, when 1 was reacted with isobutylene at 10 °C in d8-THF the observable intermediate 28 was
formed, as evidenced by a septet at approximately δ 4.3. Generally, a shift at this resonance would be attributed to an alkene, either bound to a metal centre or unbound; however, when the same reaction was conducted in C₆D₆, H/D scrambling into the compound allowed the confirmation of the assignment of this shift as the PCH resonance. The deuterium scrambling offers a significant amount of information. As seen in Figure 8.1, there is a large separation of approximately 0.1 ppm between the 5 isotopologues chemical shifts. Additionally, we observe a septet multiplicity for all isotopologues. This data is consistent with the resonance at δ 4.3 corresponding to a PPr₃ methine environments of a cluster, and the five isotopologues correlate to permutations present for a cluster bearing four hydride ligands.

Figure 8.1: ¹H NMR showing resonances corresponding to methine environment of all 5 isotopologues of cluster 28 from the reaction of 1 with isobutylene in C₆D₆. Top spectrum obtained after 10 minutes. Lower spectra show changes over time from increased deuterium incorporation into this tetrahydride complex over 30 minutes.
Despite conducting the reaction of 1 and isobutylene in various solvents, no other resonances could be found that correspond to the proposed intermediate. The downfield shift could be reasoned by the cluster having a low-lying paramagnetic state, which would also explain the lack of a $^{31}\text{P}\{^1\text{H}\}$ NMR resonance. The lack of an observable methyl resonance could be reasoned by the multiple resonances located in the alkyl region such as isobutylene, isobutane, propane, 1, carbide cluster 8, and isobutylene intermediate 10. Correlation spectroscopy could offer insight, though the short-lived nature of cluster 28, makes the experiment more difficult. The formation of an identical product from the reaction of 1 with other alkenes, such as di-tert-butylethylene, and diphenylacetylene, suggest that the alkene group is not bound to intermediate 28, which is likely composed of 5 Ni centres, with 5 terminal phosphines, and 4 hydride ligands, $[(\text{Pr}_3\text{P})\text{Ni}]_3\text{H}_4$, as shown in Scheme 8.1.
Scheme 8.1: Proposed reaction of cluster 1 isobutylene to form short-lived intermediate cluster 28 which subsequently reacts with isobutylene to form 10.

Cluster 28 may offer insight for variety of reasons. The consistent observation of hydrogenation of an equivalent of alkene when a variety of alkenes are exposed to 1 suggest that cluster 1 is not the active species, but generates 28 in the presence of alkenes, which facilitates the CC bond cleavage outlined in Scheme 8.1. Isolating the potential active species that facilitates the cooperative carbon-atom abstraction could lead to much more interesting reactivity, especially considering 28 is even more electron deficient. The reactivity of 28 towards simple alkanes could also be explored; however, the current synthesis of 28 through hydrogenation of alkenes by 1 invariably generates carbide 8 as an impurity from subsequent reactivity with alkenes. Additionally, in Chapter 5, we discussed the role of 1 as a catalyst for H/D exchange in simple arenes, and reported that the addition of dihydrogen inhibits catalysis despite slow scrambling into the cluster. In a similar scenario, if cluster 28 is the actual active catalyst, inhibition by dihydrogen is plausible, as the formation of cluster 28 under an atmosphere of dihydrogen is likely hindered.

The potential to use cluster 28 and study its reactivity with hydrocarbons such as alkanes, alkenes, and aromatics led us to explore different methods of synthesizing the cluster. One potential route is reacting 1 with a hydride abstracting agent that would likely generate dihydrogen, by removing one of the hydride ligands, and form a cationic cluster, subsequent addition of a base could then potentially remove the HX salt to generate cluster 28, as shown in Scheme 8.2.
As outlined in this dissertation, 1 is a highly reactive species, and tends to dissociate into a tetranuclear square plane fragment in the presence of a variety of X type ligands, shown in chapter 4. To mediate this issue, yet still generate a cationic cluster, a non-coordinating anion was sought after. Tetrakis [3,5-bis(trifluoromethyl)phenyl] borate (BArF\(^{26}\)) is a known non-coordinating and relatively inert species,\(^1\) additionally, Ph\(_3\)C\(^+\) BArF\(^{26}\) is extensively documented in literature for its use as a hydride abstractor, a role that is ideal for reactivity with 1. When 1 is reacted with to Ph\(_3\)C\(^+\) BArF\(^{26}\), both the \(^{31}\)P{\(^1\)H} and \(^1\)H NMR spectra indicate that 1 is consumed immediately and resonances corresponding to the intended [(\(^i\)Pr\(_3\)P)Ni\(_5\)]\(_6\)H\(_5\)X\(^+\) [BArF\(^{26}\)]\(^-\) (29) are observed; yet, several broad resonances in the \(^1\)H NMR spectrum at chemical shifts ranging from 4 to 15ppm appear. These broad resonances likely correspond to the radical cationic cluster [(\(^i\)Pr\(_3\)P)Ni\(_5\)]H\(_6\)X\(^+\) [BArF\(^{26}\)]\(^-\). Even under different temperature and concentration conditions, both clusters are formed in similar amounts, as shown in Scheme 8.3.

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Scheme 8.3: Reaction of cluster 1 with a triphenyl methyl BArF\textsuperscript{26} forming a mixture of cluster 29 and proposed radical cationic cluster \(((iPr_3P)Ni)_5H_6^+[BArF^{26}]^-.\)

Cluster 29 was isolated through recrystallization; however, the crystals were not suitable for structure elucidation purposes for X-Ray crystallography purposes. Poor resolution data was obtained that showed the presence of five Ni centres along with five phosphine ligands and the BArF\textsuperscript{26} counterion, but not much more data could be obtained from the data.

\(^{31}\text{P}\{^1\text{H}\}\) NMR studies of cluster 29 revealed a single resonance at \(\delta 67.8\) which indicates that 29 is fluctional. Variable-temperature \(^{31}\text{P}\{^1\text{H}\}\) NMR also reveal a large temperature dependence on chemical shift, similar to that of cluster 1, with cooling to \(-60^\circ\text{C}\) causing a 16.2 ppm shift. Further cooling of the solution of 29 to \(-95^\circ\text{C}\) caused decoalescence to two broad singlets in a 4:1 ratio at \(\delta 47.6\) and 58.0, respectively, suggesting a square pyramidal cluster geometry. Cluster 29 may bear a low-lying triplet state, similar to that of 1, which causes the dramatic temperature dependence. \(^1\text{H}\) NMR reveals a pair of resonances corresponding to the methyl and methine resonances of the phosphine ligands.
and a broad resonance at $\delta$ −27.65 corresponding to the hydride ligands which integrates to five with respect to the five phosphine ligands. Resonances corresponding to the BArF$^-\text{counterion}$ are also present in both $^1\text{H}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra. Low temperature $^1\text{H}$ NMR studies caused decoalescence of the hydride resonance at $-95 \degree\text{C}$, into a 4:1 ratio at $\delta$ −26.45 and −37.61, which supports the assignment of 5 hydride ligands, and suggest that the reaction of 1 with the triphenyl methyl BArF$^{26}$ removes one of the triply bridged hydride ligands as shown in Scheme 8.3.

Testing the reactivity of cluster 29 with various bases and deprotonating agents such as methyl lithium or benzyl potassium, under mild conditions should be undertaken, as it can potentially serve as an alternate method of producing 29, without having an alkene in the vicinity resulting in further reactivity. In addition, exploring different non-coordinating anions such as the known carboranes$^2$ may be beneficial, as they may generate analogues of 29 and avoid the formation of the analogue of the radical cationic cluster. Additionally, isolating the proposed radical cationic cluster, [(/Pr$_3$P)Ni)$_5$H$_6^+$[BArF$^{26}$]$^-$, should be investigated, gaining more information about effects of core oxidation state on reactivity is an area that was explored in Chapter 7, but with carbide cluster 8, the opportunity to explore potential change in reactivity by changing the core oxidation state through the use of 1 should be taken advantage of.

8.1.2 Building Towards Catalysis, Functionalizing the Carbide Ligand

Though the CC bond cleavage on unactivated alkenes is an incredible transformation, the reactivity observed is purely stoichiometric, and can be vastly improved by finding methods to make the carbon-atom abstraction catalytic. Chapter 7 demonstrated that carbide cluster 8 is reactive in nature with the ability to directly bond heteroatoms to
the carbide ligand as well as access multiple core oxidation states by undergoing 1 and 2 electron additions. Two potential directions to focus on with cluster 8 is to expand on the bond activations facilitated by cluster 8 towards catalysis, as well as finding methods to extrude the carbide ligand in the presence of hydrogen to generate 1, with the similar goal of catalysis. Both these directions can greatly benefit from an increase in thermal stability and a change in electronic process, both of which can be achieved through the use of NHC-carbenes.

Carbene ligands have been popularized over the past few decades due to serving as strong donors (in comparison to phosphines) and have been widely using in catalysis,\textsuperscript{3-5} and in many cases have been optimized by replacing the previously used phosphine ligands as the complexes seem to be more thermally robust.\textsuperscript{6} Substituting phosphine ligands with N-heterocyclic carbene ligands should be explored, as shown in Scheme 8.4, and reactivity studies of these new set of carbene ligated Ni\textsubscript{5}C clusters should be conducted in order to find ways of extruding the carbide ligand to lead to catalysis, as well as further establishing the role of the carbide ligand as an anchor in accessing novel cluster geometries.

Preliminary studies show the facile displacement of phosphine ligands in 8 when exposed to NHC carbenes. In particular, reaction of 8 with $^R\text{NHC}^\text{Me}$, where $R=$ isopropyl as shown in Scheme 8.4, has resulted in the formation of a new transition metal cluster presumably with 3 phosphine ligands and two carbene ligands. Further characterization of this species as well as early reactivity studies should be conducted to explore the effects that addition of different ligands have on the reactivity of the cluster.
Scheme 8.4: Proposed reaction of carbide cluster 8 with NHC-carbenes to displace phosphine ligands and form new carbide clusters.

8.1.3 Exploring Alternate Routes to Polynuclear Complexes

Cluster 1 is formed in modest yield from the dinuclear dinitrogen bridging complex as shown in Chapter 1; however, the use of two equivalents of PPr₃ per Ni centre is wasteful as cluster 1 is composed of 5 Ni monophosphine fragments. In addition to the waste of phosphine generated, the residual phosphine dramatically increases the solubility of 1 from the reaction mixture which decreases yield of 1 from recrystallization. This led to the exploration of different methods to synthesize 1 as well as related clusters that may exhibit similar cooperative reactivity. The dinuclear dinitrogen bridging compound also limits the phosphine ligands that can be explored, as only the complex with PCy₃ and PPr₃ are known. The known 16 electron (Pr₃P)Ni(η²-H₂CCHSiMe₃) (7) is easily synthesized from the convenient Ni(0) source, Ni(COD)₂ and when is exposed to ¾ equivalents of 1,2 dioiodethane, the novel Ni dimer with three bridging iodide ligands [(Pr₃P)Ni]₂(µ₂-I₃) (30) was formed, as shown in Scheme 8.5. The dimer is highly insoluble in n-pentane and allows for relatively easy recovery of dissociated ligand. Dimer 30 is
paramagnetic and Evan’s method\textsuperscript{10} yielded a magnetic moment of 3.45 Bohr magnetons which suggests that the dimer has 3 unpaired electrons.

Scheme 8.5: Reaction of (\textit{iPr}_3\textit{P})_2\textit{Ni}(\textit{η}^2\textit{H}_2\textit{CCHSiMe}_3) with 1,2-diiodoethane which forms the paramagnetic dinuclear Ni complex 30

X-ray quality crystals of 30 were grown and were used to determine the solid-state structure of 30, which is shown in Figure 8.2. The dinuclear structure has a Ni-Ni bond of 2.4649(4) Å and has Ni-I bonds ranging from 2.6000 – 2.6278 (3) Å. The Ni(2)-Ni(1)-P(1) of 176.261(19) ° and Ni(1)-Ni(2)-P(2) bond angle of 176.59(2) ° show a nearly linear Ni-phosphine dimer, similar to dinuclear LNi(I)-Ni(I)L dimers with bridging chloride ligands, for both carbenes\textsuperscript{11-12} and phosphines.\textsuperscript{13-14} The dinuclear compound bearing 3 unpaired electrons and likely has significant spin orbit coupling contributions. The \textsuperscript{1}H NMR features a pair of broad resonances at δ 15.5 and δ 122.2 corresponding to the methyl and methine resonances respectively.
Figure 8.2: ORTEP depiction of 30. Hydrogens on phosphine ligands omitted for clarity

Selected bond lengths: Ni(1)-Ni(2) = 2.4649(4) Å, Ni(1)-I(1) = 2.6278(3) Å, Ni(1)-I(2) = 2.6054(3) Å, Ni(1)-I(3) = 2.6091(3) Å, Ni(2)-I(1) = 2.6000(3) Å, Ni(2)-I(2) = 2.6161(3) Å, Ni(2)-I(2) = 2.6134(3) Å. Selected bond angles: Ni(1)-Ni(2)-P(2) = 176.59(2) °, Ni(2)-Ni(1)-P(1) = 176.261(19) °.

The use of dinuclear complex 30 as a precursor to transition metal clusters should be explored, particularly through the use of a reducing agent and hydride bearing reagents such as LiBEt$_3$H or LiAlH$_4$. EPR studies of 30 should be conducted as should SQUID measurements to explore the potential of 30 as a single molecule magnet (SMM). The precursor to 30 can likely be made with a variety of similarly sized phosphine ligands, analogues with carbene ligands are also known. Exploring studies of analogues of dinuclear complex 30 with different ancillary ligands should also be explored to offer an extensive study of the rare dinuclear complexes with 3 unpaired electrons, and their potential in uses as SMMs.

8.2. Summary.
Chapter 8: Summary, Future Work, and Preliminary Results

This dissertation outlines a body of work demonstrating the cooperative nature of the reactivity exhibited by [(Pr₃P)Ni]₅H₆ (1). The potential use of transition metal clusters as hybrids of homogeneous and heterogeneous species was postulated many decades ago; however, only the past few decades have shown promise in this regard. Recently clusters composed of early and mid transition metals in high oxidation states with hydride ligands have shown dramatic examples of cooperativity, which include CC bond cleavage of dienes and benzene. Prior to our findings, the literature lacked examples of functional-group tolerant transition metal clusters that undergo similar unreactive bond transformations. Four of the chapters in this dissertation outline different cooperative reactivity facilitated by 1. The most impressive of these transformations was described in Chapter 3, which described the ability of 1 to cleave the CC bonds of simple alkenes, to generate the novel Ni-carbide cluster (8). Other chapters expand on the cooperative reactivity and describe the ability of 1 to activate inert CS, CH, and CO bonds. The incorporation of main group elements into these Ni₅ clusters were undertaken in attempts to expand on the carbide cluster obtained from carbon atom-abstraction, yet instead, produced a series of tetranuclear clusters that feature square-planes of Ni centres. Lastly, the potential for the carbide atom as an interstitial ligand to generate unfavourable cluster geometries and various core oxidation states in the Ni₅ unit was explored, with the carbide-bearing [FeMo] cofactor of Nitrogenase serving as inspiration. Inert-bond activation using the thermally stable carbide was also examined. This body of work vastly increased the knowledge of cooperative bond activations facilitated by transition metal clusters and brings us closer to the long-theorized proposal of using soluble transition metal clusters for the next
generation of catalysts that can access the voracious reactivity of heterogenous surface sites and the selective nature of homogenous species.

8.3. Glossary of Complexes

The transition metal clusters reported in this dissertation are vastly different than the plethora of known metal clusters in literature, most of which are based on ML₃ fragments. Their unique nature is confirmed by the poor correlation of cluster stability with Lauher’s electron counting principles, as well as the increased reactivity and range of accessible geometries and oxidation state in comparison to classic transition metal cluster chemistry. It is hoped that the relation between the reactive nature of these clusters and the cluster geometry and electron count can be better understood in the future. A better theoretical understanding could help target potential polynuclear clusters for the next generation of catalysts. A summary of the clusters prepared in this thesis are given below, which shows the diversity of electron counts and core oxidation states accessible.
8.4 Experimental

8.4.1. General Procedures:

Unless otherwise stated, all manipulations were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or an MBraun glove-box. Dry, oxygen-free solvents were employed throughout. Anhydrous pentane, toluene, and THF were purchased from Alfa Aesar and were argon packed and dried with either activated sodium or molecular sieves. Benzene-$d^6$ was dried by heating at reflux with Na/K alloy in a sealed vessel under partial pressure then trap-to-trap distilled and freeze–pump–thaw degassed three times. ($^{i}$Pr$_3$P)$_2$Ni(η$^2$-H$_2$CCHSiMe$_3$), [Ph$_3$C]+[BArF$_{26}$]$^-$, $^{i}$PrNHCMe were synthesized as per literature procedures.$^1, 15, 17$ 1,2 diiodoethane was purchased from Sigma-Aldrich and its purity was confirmed through NMR spectroscopy. $^1$H, $^{31}$P{$^1$H} and $^{13}$C{$^1$H}NMR spectra were recorded on a Bruker AMX Spectrometer operating at 300 MHz.
MHz or 500 MHz with respect to proton nuclei. All chemical shifts are recorded in parts per million, and all coupling constants are reported in Hertz. $^1$H NMR spectra were referenced to residual protons ($C_6D_5H$, δ 7.15) with respect to tetramethylsilane at δ 0.00. $^{31}$P{$^1$H} NMR spectra were referenced to external 85% H$_3$PO$_4$ at δ 0.00. $^{13}$C{$^1$H} NMR spectra were referenced relative to solvent resonances ($C_6D_6$, δ 128.0; $C_7D_8$, δ 20.4; $C_4D_8O$, δ 25.37). $^{11}$B{$^1$H} NMR spectra were referenced to external BF$_3$OEt$_2$ at δ 0.00. Elemental analyses were performed at the Center for Catalysis and Materials Research, Windsor, Ontario.

8.4.2. Synthesis and Characterization of Complexes

NMR Scale Synthesis and Characterization of [(i$^2$Pr$_3$P)Ni]$^5$H$_4$ (28-d$_0$-d$_4$)

A solution of 1 (27 mg, 0.025 mmol) in 0.6 mL of $C_6D_6$ was transferred to a J-Young NMR tube which was subsequently connected to a Schlenk line. The solution is then put under three of freeze-pump-thaw cycles and was exposed to 1 atmosphere of isobutylene which was added through the Schlenk line. The J-young tube is then frozen with liquid nitrogen and allowed to warm to room temperature in the NMR probe. The reaction is monitored through $^1$H and $^{31}$P{$^1$H} NMR and resonances for isotopologues of [(i$^2$Pr$_3$P)Ni]$^5$H$_4$ appear and disappear as the reaction proceeds. $^1$H NMR (298 K, $C_6D_6$, 500 MHz): (28-d$_0$) δ 4.25 (septet, $^3$J$_{HH}$=6.8 Hz, 15 H, P(CH(CH$_3$)$_2$)$_3$) (28-d$_1$) δ 4.03 (sep, $^3$J$_{HH}$=6.8 Hz, 15 H, P(CH(CH$_3$)$_2$)$_3$) (28-d$_2$) δ 3.85 (sep, $^3$J$_{HH}$=6.8 Hz, 15 H, P(CH(CH$_3$)$_2$)$_3$) (28-d$_3$) δ 3.66 (sep, $^3$J$_{HH}$=6.8 Hz, 15 H, P(CH(CH$_3$)$_2$)$_3$) (28-d$_4$) δ 3.45 (sep, $^3$J$_{HH}$=6.8 Hz, 15 H, P(CH(CH$_3$)$_2$)$_3$).

Synthesis and Characterization of [(i$^2$Pr$_3$P)Ni]$^5$H$_5$+[BArF$_{26}$]$^-$ (29)
Equimolar amounts of 1 (650 mg, 0.59 mmol) and triphenyl methyl BArF$_2$ were added to an Erlenmeyer flask and cooled to −40 °C, at which point 15 mL of THF was transferred and the reaction was stirred vigorously for 20 min while warming to room temperature. Volatiles were then removed in vacuo and the residue is washed with n-pentane (3 × 25 mL). The remaining residue is extracted with 10 of THF and 10 mL of hexamethyldisiloxane and filtered through a plug of Celite. The solution was cooled −40 °C for 72 h at which point dark brown crystals suitable for X-ray diffraction were obtained. The mother liquor was concentrated and multiple crops yielded 220 mg of __ (18.9%). $^1$H NMR (298 K, C$_4$D$_8$O, 500 MHz): δ −27.65 (broad s, 5 H, Ni-H), 1.41 (broad s, 90H, P(CH(CH$_3$)$_2$)$_3$), 2.12 (broad m, 15H, P(CH(CH$_3$)$_2$)$_3$), 7.57(s, 4H, p-B(C$_6$H$_3$(CF$_3$)$_2$)$_4$), 7.79(s, 8H, o-B(C$_6$H$_3$(CF$_3$)$_2$)$_4$); $^{31}$P{${^1}$H} NMR (298 K, C$_4$D$_8$O, 121.5 MHz): δ 67.8 (s, 5P, NiP$_3$Pr$_3$).; $^{19}$F{${^1}$H} NMR (298 K, C$_4$D$_8$, 470.5 MHz): δ −63.4 (s, 24 F, B(C$_6$H$_3$(CF$_3$)$_2$)$_4$).

$^1$H NMR (178 K, C$_4$D$_8$O, 500 MHz): δ −26.45(s, 4H, µ$_2$-H), −37.61(s, 1H, µ$_3$-H) $^{31}$P{${^1}$H} NMR (178 K, C$_4$D$_8$O, 121.5 MHz): δ 47.6(s, 4P, basal Ni-P) 58.0(s, 1P, apical Ni-P)

**Synthesis and Characterization of [(iPr$_3$P)Ni]$_2$(µ$_2$-I)$_3$ (30)**

A solution of (iPr$_3$P)$_2$Ni(η$_2$-H$_2$CCHSiMe$_3$) (3.05 g, 7.27 mmol) in 25 mL of n-pentane and a separate solution of 1,2 diiodoethane (1.54 g, 5.45 mmol) in 5 mL n-pentane were pre-cooled to was cooled to −40 °C. With vigorous stirring, the solution of 1,2 diiodoethane was added dropwise to the solution of (iPr$_3$P)$_2$Ni(η$_2$-H$_2$CCHSiMe$_3$), over the course of 10 minutes, at which point the solution changed colour from light brown to a dark green colour, and gas was evolved from the solution. Volatiles were then removed in vacuo and the residue extracted with n-pentane (4 × 15 mL). The solution was cooled −40 °C for 16
h at which point dark green crystals suitable for X-ray diffraction were obtained. The
mother liquor was concentrated and multiple crops yielded 2.47 g of \( \_ \) (83.2%). \(^1\)H NMR
(298 K, C\(_6\)D\(_6\), 500 MHz): \( \delta \) 15.57 (broad s, \( \text{W}_{1/2}=68.5 \text{ Hz} \), 36H, P(CH(CH\(_3\))\(_2\))\(_3\)), 122.14
(broad s, \( \text{W}_{1/2}=133.8 \text{ Hz} \), 6H, P(CH(CH\(_3\))\(_2\))\(_3\)), Anal Calcd for C\(_{18}\)H\(_{52}\)Ni\(_2\)I\(_3\) (766.71): C,
26.41; H, 5.17; Found: C, 25.86; H, 5.15;

**Evans Method on \([\text{Pr}_3\text{P}]\text{Ni}_2(\mu_2-\text{I}_3)\)**

A solution of \( \text{30} \) with a concentration of 0.073 mol/L in C\(_6\)D\(_6\) was prepared and transferred
to a capillary tube. An NMR tube was filled with 0.4 mL of C\(_6\)D\(_6\) and the capillary tube
was then carefully inserted into the NMR tube. The tubes were then taken to the 500 MHz
NMR spectrometer where a \(^1\)H NMR experiment was conducted and a separation of 695.8
Hz was measured between the C\(_6\)D\(_5\)H signal in the capillary tube and the C\(_6\)D\(_5\)H signal
outside the capillary tube. Using the measured values an effective magnetic moment of
approximately 3.45 Bohr magnetons is calculated. This value corresponds to the expected
effective magnetic moment expected for 3 unpaired electrons.

**8.5: Crystallographic Information**

**Table 8.1. Crystallographic Information of Compound 30**

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8.6 Supporting Information

Full details of crystallographic information in CIF format for compound 30 along with selected experimental NMR spectra can be found on supplementary USB provided.

8.7 References
Chapter 8: Summary, Future Work, and Preliminary Results

Appendix
Appendix

Title: Mechanistic Insight into H/D Exchange by a Pentanuclear Ni-H Cluster and Synthesis and Characterization of Structural Analogues of Potential Intermediates

Author: Manar M. Shoshani, Junyang Liu, Samuel A. Johnson

Publication: Organometallics
Publisher: American Chemical Society
Date: Jan 1, 2018
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Copyright permission for the joint publication entitled Synthesis of Surface-Analogue Square-Planar Tetranuclear Nickel Hydride Clusters and Bonding $\mu_4$-Nr, -O and –BH Ligands” (Shoshani, M. M., Liu, J., & Johnson, S. A. (2018). *Inorganic Chemistry*

I, Matthew McLaughlin, give Manar Shoshani permission to use the results and ideas published in the paper entitled “Synthesis of Surface-Analogue Square-Planar Tetranuclear Nickel Hydride Clusters and Bonding $\mu_4$-Nr, -O and –BH Ligands” in his doctoral dissertation. I completed the reactivity studies with respect to the nickel-nitrogen trimer, under the supervision of Dr. Samuel. A. Johnson.

Matthew McLaughlin

April 11th, 2018

I, Junyang Liu, give Manar Shoshani permission to use the results and ideas published in the paper entitled "Mechanistic Insight into H/D Exchange by a Pentanuclear Ni–H Cluster and Synthesis and Characterization of Structural Analogues of Potential Intermediates" in his doctoral dissertation. We were the principle investigators on this joint paper, under the supervision of Dr. Samuel A. Johnson.

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April, 11, 2018
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