INVESTIGATING NEW REACTIONS FOR COORDINATED DINITROGEN

by

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Abstract

The chemistry of the tantalum dinitrogen complex ([NPN]Ta(μ-H)2(μ-η^1:η^2-N2)Ta-[NPN], 1, where [NPN] represents the acyclic tridentate ligand [(PhNSiMe2CH2)2-PPh]2), with primary alkenes, group IV and V metallocene complexes, and GaCp* is explored.

The reaction of 1 with 1-pentene and 1-hexene occurs via olefin-insertion into the metal-hydride bond to give two new complexes, ([NPN]Ta(CH2)4CH3)2(μ-η^1:η^1-N2), 10, and ([NPN]Ta(CH2)5CH3)2(μ-η^1:η^1-N2), 11, which were characterized using NMR spectroscopy. The solid-state structure of 11 was established and revealed that N2 has been transformed into a bridging end-on mode. In contrast to its C₃ symmetry in solution, the solid-state structure of 11 is C₂ symmetric; a VT-NMR study was performed and showed that 11 exists as an equilibrium between two isomers in solution: a C₂ symmetric isomer 11A, which is the predominant isomer at room temperature, and a C₂ symmetric isomer 11B, which is the minor isomer.

The reactivity of 1 with group IV and V metallocenes was investigated. The reaction of 1 with Cp₂Hf(PMe₃)₃(Me₃SiCCSiMe₃) produces [N(IA-P=N)N]Ta(μ-H)₂(μ-N(Hf-Cp₂))Ta[NPN], 14, in which N₂ is cleaved and new Hf-N and P=N bonds have formed. The reaction of 1 with group V metallocene hydrides Cp₂MH₃ (M = Nb, Ta) was also attempted however these complexes do not react with 1.

The reaction of 1 with GaCp* produces a new complex, [NPN]Ta(μ-N(GaCp*))Ta(=NPh)[NPh], 18, which was characterized using NMR spectroscopy. Complex 18 decomposes over several days in solution, and one product of decomposition
that was isolated was [(PhNH)(N\(\mu\)-N)Ta]_2, 19. The solid-state structure of 19 showed that the [NPN] ligand was cleaved at the N-Si bond, similar to that observed for the reaction of 1 with 9-BBN and HB(C_6H_5)_2. A mechanism for the formation of complexes 18 and 19 is proposed.
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Glossary of Terms

Å
Angström (10⁻¹⁰ m)

Anal.
analysis

atm
atmosphere

9-BBN
9-borabicyclonane (HB(C₈H₁₄))₂

°Bu
isobutyl group (-CH₂CH(CH₃)₂)

n°Bu
normal butyl group (-CH₂CH₂CH₂CH₃)

°Bu
tertiary butyl group (-C(CH₃)₃)

°C
degrees Celsius

¹³C
carbon -13

Calcd.
calculated

cm⁻¹
reciprocal centimeters (wavenumbers)

COSY
correlated spectroscopy

C₅

cyclopentadienyl group ([C₅H₅]⁻)

C₅*
pentamethylcyclopentadienyl group ([C₅Me₅]⁻)

DIBAL
diisobutylaluminium hydride (HA1(CH₂CH(CH₃)₂)₂

d
doublet

D
deuterium

2D	two-dimensional

δ
delta

Δ
heat

dd
doublet of doublets

deg (°)
degrees

DFT
density functional theory

dppe
bis(diphenylphosphino)ethane

Eₐ
Activation Energy

equiv
equivalent

g
grams

HIPT
hexa-isopropylterphenyl substituent
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>HSQC</td>
<td>Heteronuclear Single Quantum Coherence</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>$^{1}J_{AB}$</td>
<td>coupling constant between nuclei A and B over n bonds</td>
</tr>
<tr>
<td>K</td>
<td>degrees Kelvin</td>
</tr>
<tr>
<td>kcal</td>
<td>kilocalories</td>
</tr>
<tr>
<td>kJ</td>
<td>kilojoules</td>
</tr>
<tr>
<td>L</td>
<td>ligand group</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>M</td>
<td>metal</td>
</tr>
<tr>
<td>M-H</td>
<td>metal hydride</td>
</tr>
<tr>
<td>Me</td>
<td>methyl substituent</td>
</tr>
<tr>
<td>m</td>
<td>multiplet</td>
</tr>
<tr>
<td>m</td>
<td>meta-position of aryl ring</td>
</tr>
<tr>
<td>mg</td>
<td>milligrams</td>
</tr>
<tr>
<td>MgADP</td>
<td>adenosine diphosphate, magnesium salt</td>
</tr>
<tr>
<td>MgATP</td>
<td>adenosine triphosphate, magnesium salt</td>
</tr>
<tr>
<td>mol</td>
<td>mole</td>
</tr>
<tr>
<td>mmol</td>
<td>millimoles</td>
</tr>
<tr>
<td>MOs</td>
<td>molecular orbitals</td>
</tr>
<tr>
<td>$^{15}$N</td>
<td>nitrogen-15</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>[NPN]</td>
<td>[PhP(CH$_2$SiMe$_2$NPPh)$_2$]$^2^-$</td>
</tr>
<tr>
<td>$\eta^n$</td>
<td>hapticity of order n</td>
</tr>
<tr>
<td>o</td>
<td>ortho-position of aryl ring</td>
</tr>
<tr>
<td>ORTEP</td>
<td>Oakridge Thermal Ellipsoid Plotting Program</td>
</tr>
<tr>
<td>$\rho$</td>
<td>para-position of aryl ring</td>
</tr>
<tr>
<td>$^{31}$P</td>
<td>phosphorous-31</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl group (-C$_6$H$_5$)</td>
</tr>
<tr>
<td>$\pi$</td>
<td>pi</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>py</td>
<td>pyridine group</td>
</tr>
<tr>
<td>'Pr</td>
<td>isopropyl group (-CH(CH₃)₂)</td>
</tr>
<tr>
<td>R</td>
<td>alkyl or aryl group</td>
</tr>
<tr>
<td>rt</td>
<td>room temperature</td>
</tr>
<tr>
<td>s</td>
<td>singlet</td>
</tr>
<tr>
<td>σ</td>
<td>sigma</td>
</tr>
<tr>
<td>r</td>
<td>triplet</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMS</td>
<td>tetramethylsilane ((CH₃)₄Si)</td>
</tr>
<tr>
<td>VₙNN</td>
<td>stretching frequency of N-N bond</td>
</tr>
<tr>
<td>X</td>
<td>halide group</td>
</tr>
<tr>
<td>Z</td>
<td>number of formula units in the unit cell</td>
</tr>
</tbody>
</table>
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I would like to thank Professor Mike Fryzuk for giving me the opportunity to work in this group, and inspiring me with dinitrogen chemistry. His patience, encouragement and support were instrumental throughout my time at U.B.C.

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Dedication

For my family - mom, dad, grandma, grandpa, Agnes and Domina - I am truly blessed to have such a loving family.
Chapter One

The Chemistry of Dinitrogen.

1.1 Introduction.

The earth's atmosphere is composed of about 78% \( \text{N}_2 \). Reduced nitrogen is found in many biologically relevant compounds such as amines, nucleic acids and proteins, and nitrogen is an essential element for all life forms. However, despite its abundance, \( \text{N}_2 \) is extremely inert, and the challenge in trying to use transition-metal complexes to catalytically activate and functionalize \( \text{N}_2 \) still remains.

Using \( \text{N}_2 \) as a reagent industrially is appealing because it is abundant, accessible, and inexpensive; the development of a transition-metal catalyst that can convert \( \text{N}_2 \) into nitrogen-containing compounds such as amines or N-heterocycles would be ideal. However, the intrinsic properties of \( \text{N}_2 \) are a barrier to attaining such a cycle, so far. In contrast to isoelectronic carbon monoxide, which is a reactive molecule and an excellent ligand, \( \text{N}_2 \) is incredibly stable and a poor ligand. The reasons for its stability are: it is non polar, it has a high bond dissociation enthalpy (945 kJ mol\(^{-1}\)), as well as a large HOMO-LUMO gap. All of these properties make it difficult for \( \text{N}_2 \) to bind to transition metals, and to be oxidized or reduced.

When dinitrogen does bind to a metal complex it may become activated, and the degree of activation can be correlated from the N-N bond length (typically determined by X-ray diffraction), or by the stretching frequency of \( \text{N}_2 \) in the complex (determined by infrared or Raman spectroscopy). A comparison of N-N bond lengths of some organic compounds,
along with some examples of dinitrogen complexes is given in Table 1.1. Stretching frequencies determined by IR and Raman are also included, if data was available.

Table 1.1. N-N bond lengths and stretching frequencies (R = Raman, IR = Infrared) for some simple molecules, as well as for some dinitrogen metal complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>N-N bond Length (Å)</th>
<th>N-N Stretching Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂⁵</td>
<td>1.0975</td>
<td>2331 (R)</td>
</tr>
<tr>
<td>PhN=NPh⁶</td>
<td>1.255</td>
<td>1442 (R)</td>
</tr>
<tr>
<td>H₂N-NH₂⁷</td>
<td>1.449</td>
<td>1111 (R)</td>
</tr>
<tr>
<td>CpFe(dippe)(N₂)⁺⁸</td>
<td>1.13(1)</td>
<td>2112 (IR)</td>
</tr>
<tr>
<td>[([Pr₂PCH₂SiMe₂]N)Zr(Cl)]₂[η⁵:η²:N₂]</td>
<td>1.548(7)</td>
<td>731 (R)</td>
</tr>
<tr>
<td>[(η²:-C₅H₂-1,2,4-Me₃]₂Ti]₂[μ-η²:η²:N₂]¹⁹</td>
<td>1.216(3)</td>
<td></td>
</tr>
<tr>
<td>{[(Me₃Si)₂N]₂(THF)Y}₂[μ-η²:η²:N₂]¹¹</td>
<td>1.268(3)</td>
<td></td>
</tr>
<tr>
<td>[Cp°Ta[N(Pr)C(Me)N('Pr)]²(N₂)]¹²</td>
<td>1.288(10)</td>
<td></td>
</tr>
<tr>
<td>[(BuNSiMe₂N(CH₂CH₂PPr₂)₂Mn)₂[μ-η¹:η¹:N₂]¹³</td>
<td>1.208(6)</td>
<td>1685 (R)</td>
</tr>
<tr>
<td>[Ir(C₆H₃-2,6-(CH₂PBu₂)₂)]₂[μ-η¹:η¹:N₂]¹⁴</td>
<td>1.176(13)</td>
<td></td>
</tr>
<tr>
<td>{[(η²:C₅Me₄H]Zr]}₂[μ-η²:η²:N₂]¹⁵</td>
<td>1.377(3)</td>
<td></td>
</tr>
<tr>
<td>{[[(CH₂)₃C(ο-C₅H₅)]₄}Sm₃Li²[(μ-η²:η²:N₂)]Li(THF)₂₋(THF)₂¹⁶</td>
<td>1.502(5)</td>
<td></td>
</tr>
<tr>
<td>{[(η¹:C₅Me₄H)₂Hf]₂[μ-η²:η²:N₂]}¹⁷</td>
<td>1.423(11)</td>
<td></td>
</tr>
</tbody>
</table>

The degree of N₂ activation in a complex depends on the identity of the metal, and its oxidation state, as well as on the nature of the ligands in the complex.¹⁵ Early transition metal N₂ complexes typically display a greater degree of activation, while late transition metal N₂ complexes usually contain weakly activated nitrogen.⁴ Some examples¹⁹⁻²³ of
activated early transition metal N₂ complexes, along with their bond lengths (measured by single crystal X-ray diffraction) are shown in Figure 1.1.

Figure 1.1. Some examples of activated early transition metal N₂ complexes and their N-N bond lengths. For comparison, the bond lengths of dinitrogen and hydrazine are provided in the inset.

In Figure 1.1, N₂ activation is evident from the increased length of the N-N bond, which either approaches or exceeds the N-N single bond in hydrazine. The various complexes from structure D show even more dramatic lengthening of the N₂ bond;²² end-on hafnium and zirconium complexes have N-N bond lengths that range from 1.518(2) to
1.635(5) Å (structures Di - Dvi in Figure 1.1). Complex Di has an N₂ bond length that is 1.635(5) Å, and is the longest N-N bond measured to date for an N₂ complex.²²

The various binding modes of dinitrogen for both monometallic and bimetallic complexes, and the degree of N₂ activation are summarized in Table 1.2. The common bonding mode for transition metal dinitrogen complexes is end-on in both bimetallic and monometallic N₂ complexes.²⁴ It was not until 1988 when the first planar side-on bound N₂ complex (Cp*:₃Sm)₂(μ-η¹-η²-N₂) was communicated.²⁵ Since 1988, many other side-on bound dinitrogen complexes have been reported, all of which have been structurally characterized as dinuclear metal systems, with the exception of one side-on monometallic N₂ complex, [Os(NH₃)₅N₂][PF₆]₂.²⁶

**Table 1.2.** The different bonding modes of N₂ in mono- or bimetallic transition metal (M) complexes. Only connectivity is indicated, with approximations in bond order and N₂ activation (N-N triple bond = weak activation, N-N single bond = strong activation).

<table>
<thead>
<tr>
<th>Weak Activation</th>
<th>Strong Activation</th>
<th>End-on Mononuclear</th>
<th>End-on Dinuclear</th>
<th>Side-on Mononuclear</th>
<th>Side-on Dinuclear</th>
<th>Side-on End-on Dinuclear</th>
</tr>
</thead>
<tbody>
<tr>
<td>M=N≡N</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M=N=N=M</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M[N=N]M</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M[N=N]N=N=M</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4
1.2 Nitrogen Fixation and the Haber-Bosch Process.

In 1965, Allen and Senoff reported the first transition metal dinitrogen complex, \([\text{Ru(NH}_3\text{)}_2\text{N}_2]^2^+\), which resulted from the reaction of RuCl_3 with hydrazine hydrate, as shown in Equation 1.1.\(^\text{27}\)

\[
\text{RuCl}_3 \cdot x\text{H}_2\text{O} \rightarrow \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \\
\begin{array}{c}
\text{RuCl}_3 \cdot x\text{H}_2\text{O} \rightarrow \begin{array}{c}
\text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \\
\text{N}_2 \text{Ru(NH}_3\text{)}_2 \text{N}_2 \text{Cl}_2
\end{array}^2^+ \\
\end{array}
\]

Equation 1.1.

Since this discovery, the coordination chemistry of N\(_2\) has flourished. Some of this chemistry focused on modeling the active site in the nitrogenase enzyme, which converts N\(_2\) into ammonia, in a process known as nitrogen fixation (Equation 1.2).\(^\text{4}\)

\[
\text{N}_2(g) + 8\text{H}^+ + 8\text{e}^- + 16\text{MgATP} \rightarrow 2\text{NH}_3(g) + \text{H}_2(g) + 16\text{MgADP} + 16\text{P}_i
\]

Equation 1.2

Nitrogen fixation is carried out by certain bacteria, including \textit{Azotobacter vinelandii} and \textit{Clostridium pasteurianum},\(^\text{18}\) and produces thousands of tons of ammonia every day worldwide, (an estimated 170 x 10^6 tons/year) under ambient conditions (20°c, 1 atm).\(^\text{29}\)

The active site in nitrogenase, where N\(_2\) is reduced to NH\(_3\), is an iron-sulfur-molybdenum cofactor, or FeMoco.\(^\text{4}\) A high-resolution crystallographic analysis of nitrogenase determined
at 1.16 Å was performed in 2002, and revealed a light atom (X) in the centre of FeMoco (shown in Figure 1.2), that is compatible with being C, N, or O.

Figure 1.2. Structure of the FeMo cofactor extracted from the nitrogenase enzyme in *Azotobacter vinelandii.*

The identity of atom X in the centre of the cofactor remains elusive. Although theoretical investigations suggested that X is a nitrogen atom, recent experimental evidence does not support these claims. Despite the fact that the structure of FeMoco has been scrutinized in great detail, the mechanism by which it transforms N₂ to NH₃ is still unclear.

N₂ is converted into ammonia industrially via the Haber-Bosch process. In this process, N₂ reacts with three equivalents of H₂ to yield NH₃ under high temperature (400-550 °C) and pressure (270 atm) in the presence of an activated iron or ruthenium catalyst (Equation 1.3). This process yields millions of tons of ammonia annually, and fertilizer that is made from this ammonia is responsible for sustaining approximately 40% of the world's
Two Nobel Prizes were given for the discovery of the Haber-Bosch Process: the first was awarded to Fritz Haber in 1918, for discovering the nitrogen fixation reaction, and the second was awarded to Carl Bosch in 1931, for developing the high-pressure techniques that made this process industrially feasible.

\[ \text{Fe or Ru Catalyst} \quad \text{N}_2(g) + 3\text{H}_2(g) \xrightarrow{400-550 \degree \text{C}} 2\text{NH}_3(g) \]

Equation 1.3

1.3 The Chemistry of Side-on End-on Dinitrogen.

This thesis will focus on the chemistry of the side-on end-on N\(_2\) complex ([NPN]Ta\(_2\)(µ-H)\(_2\)(µ-η\(^1\)·η\(^2\)-N\(_2\)) (where [NPN] = [(PhNSiMe\(_2\)CH\(_2\)PPh\(_2\))]\(^2\)'), which will be noted as 1 below. Complex 1 contains two tridentate [NPN] ligands that are each bound to two formally Ta(V) metal centers.

The two Ta(V) centers are also bound η\(^1\)-η\(^2\) to the nitrogen molecule. The ligand synthesis is outlined in Scheme 1.1. The reaction of 2 equivalents of ClCH\(_2\)SiMe\(_2\)NHPH with 4
equivalents of n-BuLi and 1 equivalent of PhPH₂ produces Li₂[NPN], which in turn reacts with Me₃TaCl₂ to form [NPN]TaMe₃ via a metathesis reaction.

Scheme 1.1

Upon exposure of [NPN]TaMe₃ to 4 atm of H₂, the purple, diamagnetic Ta(IV)-Ta(IV) complex, ([NPN]Ta₂(μ-H)₄, 2, is produced (Equation 1.4). An ORTEP depiction of the solid-state molecular structure of this tetrahydride complex, along with selected bond lengths and bond angles is shown in Figure 1.3.

Equation 1.4
Figure 1.3 ORTEP depiction of the solid state molecular structure of ([NPN]Ta)₂(μ-H)₄, 2 (ellipsoids at 50% probability). Hydrides were located on a difference map and refined isotropically, and tantalum hydride bond lengths were determined by PARST. All hydrogen atoms and phenyl ring carbons other than ipso carbons have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ta₁-Ta₁' 2.5602(8), Ta₁-H₁ 1.8471(290), Ta₁-H₂ 1.8542(258), Ta₁-N₁ 2.093(2), Ta₁-N₂ 2.058(2), Ta₁-P₁ 2.5741(10), H₁-Ta₁-H₂ 59.98(4), N₁-Ta₁-H₁ 90.81(8), N₁-Ta₁-H₂ 148.27(4), N₂-Ta₁-H₁ 155.17(1), N₂-Ta₁-H₂ 96.03(7), P₁-Ta₁-H₁ 86.65(7), P₁-Ta₁-H₂ 83.45(8) N₁-Ta₁-N₂ 110.69(10), N₁-Ta₁-Ta₁' 119.66(7), N₂-Ta₁-Ta₁' 123.26(7), N₁-Ta₁-P₁ 82.65(7), N₂-Ta₁-P₁ 84.08(8), P₁-Ta₁-Ta₁' 125.06(3).

The solid-state structure of 2 is C₄ symmetric, and the ¹H and ³¹P[¹H] NMR spectra indicate that 2 is also C₄ symmetric in solution; this is in contrast to that observed
for 1, which is C₂ symmetric in solution. Selected bond lengths for 1 and 2 are shown in Table 1.3.

Table 1.3. A comparison of selected bond lengths (Å) for 1 and 2.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta1</td>
<td>Ta2</td>
<td>2.5602(8)</td>
<td>Ta1</td>
<td>Ta2</td>
<td>2.8311(3)</td>
</tr>
<tr>
<td>Ta1</td>
<td>N1</td>
<td>2.093(2)</td>
<td>Ta1</td>
<td>N1</td>
<td>2.066(5)</td>
</tr>
<tr>
<td>Ta1</td>
<td>N2</td>
<td>2.058(3)</td>
<td>Ta1</td>
<td>N2</td>
<td>2.040(5)</td>
</tr>
<tr>
<td>Ta1</td>
<td>P1</td>
<td>2.5741(10)</td>
<td>Ta1</td>
<td>P1</td>
<td>2.625(2)</td>
</tr>
</tbody>
</table>

The Ta1-Ta1' bond length in 2 is 2.5602(8) Å, which is considerably shorter than the Ta1-Ta2 separation for 1 (2.8311(3) Å). A slightly smaller difference is observed with the Ta-N and Ta-P bonds. The Ta1-N1 and Ta1-N2 bond lengths for 2 (2.093(2) and 2.058(2) Å, respectively) are slightly longer than that of 1 (Ta1-N1 = 2.066(5), Ta1-N2 = 2.040(5)), and the Ta1-P1 for 2 (2.5741(10) Å) is slightly shorter than that for 1 (Ta1-P1 = 2.625(2) Å).

([NPN]Ta)₂(μ-H)₄ reacts with N₂ gas to form 1, (N-N bond: 1.319(4) Å), as shown in Equation 1.5. The yield of the reaction is improved if a mixture of 90% N₂ and 10% H₂ gases are used, although the precise mechanism of this is unknown.⁴⁰
The formation of 1 from 2 is interesting for many reasons. Firstly, the use of alkali metal reducing agents, (such as Na and KC₆), which are commonly used to form dinitrogen complexes, are avoided. Secondly, this is a rare example of forming an activated early transition metal dinitrogen complex by displacing H₂, although this reaction is known for late transition metals.

Complex 1 is also impressive in its wide scale of reactivity. In some cases, the side-on end-on N₂ can act as a nucleophile (Equation 1.6); for instance, 1 reacts with benzyl bromide to give the N-benzyl derivative, ([NPN]Ta(Br)₂(μ-H)(μ-η¹-η²-NN(CH₂-C₆H₅))(Ta[NPN]), 3, (N-N bond: 1.353(4) Å).
The reaction of 1 with simple hydride reagents E-H (E-H = 9-BBN (HBR₂), DIBAL (HAlR₂) and H₂SiBu") results in the functionalization of N₂. The first step is formation 4 via E-H addition across the Ta-N bond (Scheme 1.3). Complex 4 has been characterized in the solid-state for E = BR₂ or SiH₂Bu", and in solution by NMR spectroscopy for E = AlBu'₂. Second, H₂ elimination and cleavage of the N-N bond is common to these processes to form intermediate 5, (Scheme 1.2).

Intermediate 5 will yield different products depending on the hydride source (Scheme 1.3). Hydroboration of 1 (where E = BC₈H₁₄) degrades the [NPN] ligand and eliminates H₂ from the bridging hydrides to form to form [(PhNSiMe₂CH₂P(Ph)CH₂-SiMe₃µ-N)Ta(=NBC₈H₁₄)](µ-N)(Ta[NPN]), 6, along with one equivalent of benzene from the N-Ph of [NPN]. In this process, N₂ is cleaved and functionalized. ⁴⁵
Hydroalumination of 1 (where E = Al' Bu₂) produces ([NPN]TaH)(μ-H)(μ-η¹:η²-N₂Al(μ-H)Bu)(Ta[NPN]), 7.⁴⁶ In this process, one equivalent of isobutene is eliminated, and N₂ is cleaved and functionalized; however, although ligand degradation is not observed, one amide donor of [NPN] migrates from Ta to Al.

Hydrosilylation of 1 produces ([NPN]Ta₂(μ-NSiH₂Bu⁺)₂, 8, a symmetrical disilylimide complex that has a cleaved and functionalized N₂; in this complex, [NPN] remains intact.⁴⁷
1.4 Scope and Prospectus.

The central goal of this thesis is to explore new types of reactivity that lead to the cleavage and functionalization of N₂ in ([NPN]Ta(μ-H))₂(μ-η¹:η²-N₂), 1. In Chapter Two, the reactivity of 1 with several alkene reagents is investigated. Migratory insertion with primary alkenes occurs to form an activated end-on N₂ alkyl complex. The synthesis and characterization of these complexes is discussed.

The focus of Chapter Three is the reactivity of 1 with group IV and V metallocenes. With group IV metallocenes, N₂ is cleaved and functionalized. In contrast, group V metallocenes did not react with 1, and the reasons for this will be explained in this chapter.

In Chapter Four, the reactivity of 1 with GaCp* forms a new complex, 18, that was characterized using NMR spectroscopy. Complex 18 decomposes into a number of different P-containing species over the course of several days, as evident in the ³¹P{¹H} NMR spectrum. One of these species, 19, was isolated and characterized using X-ray diffraction. The solid-state structure showed evidence of ligand rearrangement, a process that was previously observed with hydroboration reactions of 1. The mechanism and characterization of 18 will be discussed in this chapter, along with a general summary of this thesis, and some suggested future work.
Chapter Two

Olefin Insertion Reactions of the Side-on End-on Dinitrogen Complex

2.1 Introduction.

Olefin insertion of M-H bonds is an important elementary step in many catalytic reactions. In its simplest terms, an olefin-hydride insertion is the addition of a metal-hydride bond across the π bond of an unsaturated hydrocarbon. This addition is a concerted process that occurs via the formation of a four-centered transition state (Figure 2.1).

![Figure 2.1](image)

**Figure 2.1.** An illustration of the four-centered transition state formed in an olefin-hydride insertion.

Molecular orbital studies have contributed to a better understanding of this process. These studies describe the key orbital interactions involved in olefin-hydride insertion: first, the alkene π orbital donates electrons to the LUMO antibonding $\sigma^*_{\text{MH}}$ orbital; second, back donation from the HOMO $\sigma_{\text{MH}}$ orbital to the olefin π* orbital creates a cyclic transition state that activates the insertion of the olefin into the metal hydride, to generate an alkyl transition-metal complex.
For a concerted reaction, the activation energy is typically lower than the bond dissociation energies of the weakest bonds to be broken. Some examples of hydride complexes and the activation energies for insertion of ethylene are provided in Figure 2.2. An explanation of the factors that affect the energy barrier for hydride-olefin insertion is beyond the scope of this chapter; however, the repulsion between non-bonding metal electrons and the electrons in the olefin, the type of ligands and metals that are used, and the electronic state of the olefin, have all shown to be factors in the activation barrier.

![Figure 2.2](image-url)  
**Figure 2.2.** Examples of hydride-olefin complexes and the activation energies (kcal/mol) associated with the hydride-insertion into ethylene. For comparison, the C=C bond energy for ethylene is shown in the inset.
The orientation of the olefin relative to the M-H bond is also important for the concerted reaction. The olefin must coordinate cis to the M-H bond in order to form a coplanar M-C-C-H fragment upon reaction (see Figure 2.3). Although A and B in Figure 2.3 both have a cis arrangement of the alkene and the M-H bond, A undergoes insertion at least 40 times faster than B because the M-C-C-H moiety can be coplanar.

![Figure 2.3. Two complexes in which the hydride and olefin ligands are cis. Complex A undergoes insertion faster than B.](image)

2.2 Olefin Insertion Reactions.

Olefin-insertion is a crucial step in many reactions, and is commonly explored with terminal transition metal-hydrides. There are only a few reported cases of olefin insertion into bridging transition metal-hydrides, some of which will be discussed in section 2.2.1. Hydrozirconation also features an olefin-hydride insertion to generate new organic products; this process, along with the reaction of 1 with propene, will be described in sections 2.2.2, and 2.2.3, respectively.
2.2.1. Olefin Insertion Reactions of Bridging Hydride Complexes.

The few reported cases of olefin-insertion reactions with bridging-hydride complexes have been limited to group 3 metal-hydrides. A kinetic study with (Cp*₂YH)₂ revealed that this process can occur via an associative or dissociative mechanism (Scheme 2.1). The associative mechanism involves the attack of the olefin on the metal-hydride, to generate two intermediates: an olefin-coordinated intermediate that undergoes insertion, and a second mono-hydride intermediate, which binds to an olefin and undergoes insertion. In the dissociative mechanism, the bridged-hydride complex forms two mono-hydride intermediates, and then coordinates an olefin, which undergoes insertion. Both processes depend on several factors, including the rate of dissociation of the hydride-dimer, the steric environment of the olefin, and of the metal-alkyl complex. For instance, the reaction of (Cp*₂YH)₂ with unhindered olefins, such as propene, butene and hexene, forms mono- or double-inserted products through an associative process. On the other hand, the reaction of (Cp*₂YH)₂ with sterically hindered olefins, such as 3-methyl butene, 2-methyl propene, occurs through a dissociative process and only forms mono-inserted products.
In some instances, olefin-insertion with group 3 bridged-hydride complexes can form bridging-alkyl complexes. For example, yttrium and scandium (Scheme 2.2) hydride dimers can react with primary olefins to form η¹- and η²- alkyl-bridged complexes.⁶¹,⁶²
2.2.2. Hydrozirconation of Olefins.

Hydrozirconation is the reaction of Cp₂ZrHCl (Schwartz's reagent) and an unactivated* alkene to generate the alkylzirconium(IV) product, Cp₂Zr(R)Cl. This process involves either the regiospecific addition of Zr-H to a terminal double bond, or Zr-H addition to an internal double bond, followed by rearrangement via Zr-H elimination and readdition to place the metal at the least hindered position of the alkyl chain. Subsequent reactions of Cp₂Zr(R)Cl produce a wide range of organic compounds, depending on the reagent that is used. For example, electrophilic halogenation reagents, such as Br₂, I₂, N-bromo-(NBS) or N-chloro-succinimide (NCS), to Cp₂Zr(R)Cl affords organic halides (RX)

* The term 'unactivated' refers to olefins that are substituted with alkyl or proton substituents only.
and Cp₂Zr(X)Cl.⁶⁵,⁶⁶ The reaction of Cp₂Zr(R)Cl with oxidizing reagents such as basic hydrogen peroxide, tert-butyl hydroperoxide, and m-chloro-perbenzoic acid yields alcohols.⁶⁷ Cp₂Zr(R)Cl undergoes an insertion reaction with carbon monoxide to yield an acylzirconium(IV) species that reacts subsequently with acids, Br₂/CH₃OH, hydrogen peroxide and NBS to generate aldehydes, esters, carboxylic acids, and acyl halides, respectively.⁶⁸ These reactions are illustrated in Figure 2.4.

**Figure 2.4.** Subsequent reactions of Cp₂Zr(R)Cl.
2.2.3. Olefin Insertion with ([NPN]Ta(μ-H)_2(μ-η^1:η^1-N_2)).

The formation of dark red ([NPN]Ta(CH_2)_{2}CH_3)_2(μ-η^1:η^1-N_2), 9, from 1 and propene over two weeks in toluene was described in 2001 (Equation 2.1). In 9, N_2 bridges the two tantalums end-on, and is moderately activated (N-N bond: 1.289(6) Å). This was the first report of olefin insertion via hydride migration using 1.

\[ \text{Equation 2.1} \]

It is likely that the bridging hydrides in 1 force N_2 into the side-on end-on configuration. Thus, the hydride migration reaction of 1 with olefins is likely to provide products in which the bonding mode of N_2 has been transformed, and the extension of this reaction to other alkenes is of interest. The reaction of 1 with 1-pentene and 1-hexene was investigated to see if it would affect the activation of coordinated dinitrogen in 1.
2.3 Results and Discussion.

2.3.1. Reaction of 1 with 1-pentene.

Given that hydride migration was observed with propene for the formation of 9, a similar reaction was attempted with 1-pentene. Stirring a brown mixture of 1-pentene and 1 in benzene overnight at 65°C generated a yellow-red solution, from which red ([NPN]Ta(CH$_2$)$_2$C$_5$H$_3$)$_2$(μ-η$^1$:η$^1$-N$_2$), 10, was isolated in 82% yield (Equation 2.2).

![Equation 2.2](image)

The $^{31}$P-$^1$H NMR spectrum of 10 reveals two singlets at δ 4.69 and 20.0 (Figure 2.5), which indicate two different $^{31}$P environments. The $^1$H NMR spectrum of 10 is C$_s$ symmetric, with inequivalent pentyl and silyl methyl resonances (Figure 2.6). The presence of two different ligand and alkyl environments was determined using $^1$H-COSY and $^1$H, $^{13}$C-HSQC spectroscopy. The absence of a peak attributable to a bridging or terminal hydride and the presence of alkyl ligand resonances in the $^1$H NMR spectrum, indicate that olefin insertion into the metal hydride has occurred in the formation of 10.
Figure 2.5. $^{31}$P$^{[1]}$H NMR spectrum of 10 in C$_6$D$_6$.

Figure 2.6. 300 MHz $^1$H NMR spectrum of 10 in C$_6$D$_6$. 
The $^{15}\text{N}_2$ labeled species ($[\text{NPN}]\text{Ta(CH_2)_4CH}_3)_2(\mu-\eta^1\eta^1-^{15}\text{N}_2$), 10-$^{15}\text{N}_2$, was prepared from the reaction of 1-$^{15}\text{N}_2$ and 1-pentene. The $^{31}\text{P}[\cdot\text{H}]$ NMR spectrum of 10-$^{15}\text{N}_2$ shows two resonances, a singlet at $\delta$ 20.0, and a resonance at $\delta$ 4.69 coupled to two different $^{15}\text{N}_2$ environments, with coupling constants of 30.5 and 6.5 Hz (Figure 2.7).

![Figure 2.7 $^{13}\text{P}[\cdot\text{H}]$ NMR spectrum of 10-$^{15}\text{N}_2$ in C$_6$D$_6$.](image)

The $^{15}\text{N}[\cdot\text{H}]$ NMR spectrum of 10-$^{15}\text{N}_2$ has two doublets of doublets at $\delta$ 14.1 and 25.9 (Figure 2.8). The resonance at $\delta$ 14.1 is coupled to one $^{15}\text{N}$ with a $^{31}\text{J}_{\text{NN}}$ value of 11.5 Hz, and also to one $^{31}\text{P}$ with $^{31}\text{J}_{\text{PN}} = 30.5$ Hz. The second resonance at $\delta$ 25.9 exhibits the same one-bond coupling to $^{15}\text{N}$ where $^{31}\text{J}_{\text{NN}} = 11.5$ Hz, and a three-bond coupling to $^{31}\text{P}$ with a coupling constant of 6.5 Hz. The coupling constants are similar to those observed in the $^{15}\text{N}[\cdot\text{H}]$ NMR spectrum of 9: $^{31}\text{J}_{\text{NN}} = 11.3$ Hz, and a two- and three-bond N-P coupling at 30.5 and 6.6 Hz respectively. X-ray quality crystals could not be obtained for 10, but the
NMR data suggests that in solution, 10 is C_6 symmetric and has two chemically different tantalum centers, like 9.

![NMR spectrum of 10 in C_6D_6](image)

**Figure 2.8.** ^15^N{^1^H} NMR spectrum of 10 in C_6D_6.

### 2.3.2. Reaction of 1 with 1-hexene.

Complex ([NPN]Ta(CH_2)_3CH_3)_(2)(\mu-\eta^1:\eta^1\cdot N_2), 11, was prepared in the same manner as 10, except 1-hexene was used instead of 1-pentene. Upon heating the mixture, the solution changed from brown to dark red, and a red precipitate ([NPN]Ta(CH_2)_3CH_3)_(2)(\mu-\eta^1:\eta^1\cdot N_2), 11, was collected in 86% yield (Equation 2.3).

![Reaction diagram](image)

**Equation 2.3**
$^1$H NMR spectroscopy, in conjunction with $^1$H-COSY and $^1$H, $^{13}$C-HSQC spectroscopy, showed the absence of upfield resonances attributable to hydride ligands, and the presence of two chemically inequivalent ligand and alkyl environments. The $^{31}$P-$^1$H NMR spectrum of 11 in C$_6$D$_6$ shows two singlets δ 6.46 and 21.75. The $^1$H NMR spectra of 11 shows four inequivalent silyl methyl resonances, and two chemically different ligand and alkyl environments. ($[\text{NPN}](\text{CH}_3)_5\text{Ta}(\mu-\eta^1:\eta^1-15\text{N}_2)_2$), 11-15N$_2$ was also prepared, and the $^{31}$P-$^1$H NMR spectrum of 11-15N$_2$ shows two resonances - a singlet at δ 22.0, and a doublet of doublets δ 6.93 with $^2$J$_{PN}$ = 29.5 Hz, and $^3$J$_{PN}$ = 6.5 Hz. $^{15}$N NMR spectroscopy for 11 showed two doublets of doublets at δ 14.15 and 25.94 (Figure 2.9). The resonance at δ 14.15 has a one-bond $^{15}$N coupling of $^1$J$_{NN}$ = 11.3 Hz, and a two-bond coupling to $^{31}$P at $^2$J$_{PN}$ = 29.5 Hz. The peak at δ 25.94 showed the identical one-bond coupling to $^{15}$N of $^1$J$_{NN}$ = 11.3 Hz, and a three-bond coupling to $^{31}$P of 6.5 Hz. X-ray quality crystals were formed from benzene by slow evaporation, and the solid state molecular structure of 11 was determined by X-ray diffraction. An ORTEP depiction of 11 with selected bond lengths and bond angles is shown in Figure 2.10.

![Figure 2.9](image_url) $^{15}$N-$^1$H NMR spectrum of 11 in C$_6$D$_6$. 

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Figure 2.10. ORTEP depiction of the solid state molecular structure 11, (ellipsoids at 50% probability). All hydrogen atoms and phenyl ring carbons other than ipso carbons have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ta1-N1 2.043(3), Ta1-N2 2.042(3), Ta1-N3 1.820(3), Ta1-C1 2.200(4), Ta1-P1 2.6851(10), N3-N3' 1.272(6), N1-Ta1-N2 115.42(13), N1-Ta1-N3 100.06(14), N2-Ta1-N3 104.37(13), N1-Ta1-P1 75.50(9), N1-Ta1-C1 121.68(17), C1-Ta1-N2 113.94(17), C1-Ta1-N3 95.95(16), P1-Ta1-N3 175.20(10), P1-Ta1-N2 79.41(9), Cl-Ta1-P1 85.05(12).

The solid-state structure of 11 has an N-N bond distance of 1.272(6) Å, which is similar to the N-N bond length found in 9 (N-N = 1.289(6) Å). The stereochemistry about the tantalum metal is distorted trigonal bipyramidal, where atoms P1 and N3 occupy the
axial positions, and atoms C1, N1 and N2 occupy the equatorial. In contrast to its C$_s$ symmetry in solution (C$_6$D$_6$, rt), the solid-state structure of 11 is C$_i$ symmetric. A possible explanation for this anomaly is that 11 exists as an equilibrium (see Equation 2.4) between the predominant cis-trans isomer (11A) at room temperature, and the minor trans-trans isomer (11B).

\[ \text{Equation 2.4} \]

The possibility that the equilibrium in Equation 2.4 could occur suggested that a $^{31}$P{$^1$H} VT-NMR study would be informative for this process. Figure 2.11 shows a low-temperature stack-plot of $^{31}$P{$^1$H} spectra of 11 in toluene acquired every 30 minutes with 10 K degree intervals, from 273 K (bottom) to 203 K (top). Integration of the peaks in Figure 2.11 with respect to temperature (K) shows an inverse relationship between 11A (δ 6.46 and δ 21.75) and 11B (δ 4.96); at lower temperatures, the resonance for 11B (δ 4.96, purple) begins to emerge, and the resonances at δ 21.75 (green) and δ 6.46 (pink) assigned to the cis- and trans- phosphorus atoms of 11A respectively, begin to decrease. The new resonance at δ 4.96 is a singlet (consistent with a symmetric phosphine complex) and close
in range to the trans-phosphorus resonance of 11A at δ 6.46, supporting the formation of 11B.

![Chemical structures of 11A and 11B](image)

**Figure 2.11.** $^{31}$P{H} spectra of 11 in toluene from 273 K (bottom) to 203 K (top) in -10 K increments.

A Van't Hoff graph of ln($K_{eq}$) vs 1/T (K$^{-1}$) shows the correlation of $K_{eq}$ as a function of temperature (Figure 2.12). $K_{eq}$ was taken at each temperature as the integral of 11B divided by the average integral of 11A, according to Equation 2.5 (below). The graph shows a positive linear correlation in the formation of 11B with decreasing temperature.

$$K_{eq} = \text{Integration of 11B (T)}/ \text{Average Integration of 11A (T)}$$

**Equation 2.5**
From the Van't Hoff plot of $\ln(K_{eq})$ vs $1/T$ (Figure 2.12), the enthalpy (\(\Delta H^\circ\)) and entropy (\(\Delta S^\circ\)) were determined using the slope of the line and the y-intercept (Equation 2.6 and Equation 2.7). The thermodynamic parameters for the equilibrium are $\Delta H^\circ = -1.4$ kJ/mol and $\Delta S^\circ = -9.8$ J/K, which are relatively small and consistent with an equilibrium between two very similar species. Although the data supports the existence of an equilibrium, the reason as to why 11B is preferred over 11A in the solid-state is unknown, and it is presumed that packing effects of the alkyl groups in the crystal favour the $C_\gamma$ symmetric conformer.

\[
y = 172.8x - 1.2 \quad \text{(Equation 2.6)}
\]

\[
\ln(K_{eq}) = -\frac{\Delta H^\circ}{R}(1/T) + \frac{\Delta S^\circ}{R} \quad \text{(Equation 2.7)}
\]

\[
\Delta H^\circ: \quad 172.8 = -\frac{\Delta H^\circ}{R}; \quad \text{therefore}, \quad \Delta H^\circ = -1.4 \text{ kJ/mol}
\]

\[
\Delta S^\circ: \quad -1.2 = \frac{\Delta S^\circ}{R}; \quad \text{therefore}, \quad \Delta S^\circ = -9.8 \text{ J/mol·K}
\]
A proposed mechanism for the olefin-insertion of 1 is shown in Scheme 2.3. The initial step is the attack of the olefin on the metal-hydride, followed by hydride-migration (i). In step two, the remaining bridging hydride is transformed into a terminal hydride, and the nitrogen moiety is rearranged from side-on end-on, to end-on (ii). In the third step, a concerted reaction occurs at the terminal hydride: a second alkene donates electrons from its \( \pi \) orbital into the \( \sigma^*_{Ta-H} \) orbital; back donation from the \( \sigma_{Ta-H} \) orbital into the \( \pi^* \) orbital of the alkene creates a four-centered four-electron transition state (iii). The final step is the insertion of the hydride into the beta position of the alkene, to form an alkyl-transition metal complex (v).
2.4 Conclusions.

The olefin-insertion of 1 with the primary alkenes pentene and hexene produces the pentyl and hexyl complexes 10 and 11, respectively. The insertion of pentene and hexene with 1 occurs almost immediately and is completed overnight; this is evident from the change in colour of the solution, which turns from dark brown to red.

The NMR spectra of 10 and 11 suggest that they are structurally analogous in solution, with C₃ symmetry. The $^{31}P\{	ext{^1}H\}$ NMR spectra of the $^{15}$N₂ labeled species shows two distinct phosphorus resonances, where only one resonance is coupled to the end-on bound N₂ moiety. The solid-state structure of 11 was analyzed using X-ray diffraction and revealed an end-on bound N₂ unit with an N-N bond length of 1.272(6) Å. In contrast to its symmetry in solution, the solid-state structure of 11 is C₃ symmetric. A VT NMR study in conjunction with a Van't Hoff plot revealed that 11 forms an equilibrium between isomers 11A and 11B in solution, and that the solid-state structure of 11 was isomer 11B; however, it is still undetermined as to why this particular isomer is favoured in the solid-state.

2.5 Experimental.

2.5.1. General Procedure.

Unless otherwise stated, all manipulations were performed under an atmosphere of dry, oxygen-free argon or nitrogen by standard Schlenk or glovebox techniques (Vacuum Atmospheres HE-553-2 glovebox equipped with a MO-40-2H purification system and a -35 °C freezer). Ar and N₂ were dried through passage of a column with activated molecular
sieves and MnO. Hexanes, toluene, tetrahydrofuran, pentane, benzene and diethyl ether were purchased anhydrous from Aldrich, sparged with N₂ and passed through columns containing activated alumina and Ridox catalyst. THF-d₈, C₆D₆, and toluene-d₈ were dried over Na/K alloy under partial pressure, trap-to-trap distilled, and freeze-pump-thaw degassed three times. ¹H, ³¹P[¹H], ¹³C, ¹H/¹³C-HSQC and ¹H/¹H-COSY spectra were performed on a Bruker AV-300, Bruker AV-400 or Bruker AV-600 spectrometer, operating at 300.1, 400.0 and 600 MHz respectively. The ¹⁵N[¹H] spectra were performed on a Bruker 600 MHz spectrometer by Dr. Andrew Lewis and Colin Yilin Zhang at the Department of Chemistry at Simon Fraser University. Unless otherwise noted, all spectra were recorded at room temperature. The ¹H, ¹³C NMR spectra were referenced with C₆D₆ at δ 7.16 and 128.0, respectively. The ³¹P[¹H] NMR spectra were referenced to external P(OMe)₃ (δ 141.0 with respect to 85% H₃PO₄ at δ 0.0), and the ¹⁵N[¹H] spectra was referenced to an external solution of 100mM NH₄Cl in 90:10 H₂O:D₂O at δ -352.9. Chemical shifts (δ) listed are in ppm, and absolute values of the coupling constants are in Hz. Elemental Analyses were performed by David Wong at the Department of Chemistry at the University of British Columbia.

2.5.2. Materials and Reagents.

Reagents 1-pentene and 1-hexene were purchased from Aldrich and distilled before use. Complexes 1 and ¹⁵N₂-1 were prepared using literature methods.⁶⁵
2.5.3. Synthesis, Characterization, and Reactivity of Complexes.

Synthesis of \([\text{NPN}]\text{Ta(CH}_2\text{)}_4\text{CH}_3\)_2(\(\mu-\eta^1:\eta^1\)N\(_2\)), 10.

A solution of 1 (0.80 g, 0.634 mmol) and 1-pentene (2 mL, 18.28 mmol) in 50 mL benzene was sealed in a glass vessel equipped with a Teflon valve and stirred overnight at 65°C, at which time the colour of the solution changed from dark brown to yellow-red.

The vessel was brought into a glovebox where the solvent was removed by vacuum to leave a red residue. The residue was triturated three times with hexanes and decanted. The red solid was collected on a frit 82% yield (0.73 g).

\(^1H\) NMR (\(\text{C}_6\text{D}_6\), 400 MHz): δ 0.08, 0.31, 0.42, and -0.21 (s, 24H total, SiCH\(_3\)), 0.0 (br m, 2H, Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_1\)CH\(_3\)), 0.92 (t, 3H, Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.08 (t, 3H, Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.16 and 1.24 (m, 4H, SiCH\(_3\)P), 1.24 and 1.36 (m, 4H, SiCH\(_3\)P), 1.42 (m, 2H, Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.45 (m, 2H, Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.51 (m, 2H, Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.58 (m, 2H, Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.75 (m, 2H, Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.83 (m, 2H, Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 2.38 (m, 2H, Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 6.67, 6.98 (t, 4H, p-NC\(_6\)H\(_5\)), 6.74, 7.32 (m, 8H, m-NC\(_6\)H\(_5\)), 6.91, 7.08 (d, 8H, o-NC\(_6\)H\(_5\)), 7.13, 7.23 (m, 2H, p-PC\(_6\)H\(_5\)), 7.31, 7.48 (m, 4H, m-PC\(_6\)H\(_5\)), 7.74, 7.91 (dd, 4H, o-PC\(_6\)H\(_5\)).

\(^{31}P\)\(^1H\) NMR (\(\text{C}_6\text{D}_6\)): δ 4.69 (s), 20.0 (s).

\(^{13}C\)\(^1H\) NMR (\(\text{C}_6\text{D}_6\)): δ 0.54, 2.16, 4.33, and 6.13 (SiCH\(_3\)), 14.96, and 17.67 (SiCH\(_3\)P), 15.06 (Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 15.13 (Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 23.33 (Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 23.69 (Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 27.87 (Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 32.22 (Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 39.95 (Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 40.91 (Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 56.20 (Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 73.50 (Ta\(_5\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)),
CH₂CH₂CH₃, 122.15, 122.17 (p-NC₆H₅), 128.23, 128.39 (m-NC₆H₅), 126.63, 127.77 (o-NC₆H₅), 131.01, 130.48 (p-PC₆H₅), 129.40, 129.30 (m-PC₆H₅), 132.10, 134.53 (o-PC₆F₁₅).

HSQC NMR (C₆D₆): δ ('H; '¹³C) (-0.21; 0.54), (0.0; 73.5), (0.8; 2.16), (0.31; 4.33), (0.42; 6.13), (0.92; 15.06), (1.08; 15.13), (1.16; 17.67), (1.24; 17.67), (1.24; 14.96), (1.36; 14.96), (1.42; 27.87), (1.45; 23.33), (1.51; 23.69), (1.58; 32.22), (1.75; 39.95), (1.83; 56.20), (2.38; 40.91), (6.67; 122.15), (6.74; 128.23), (6.91; 126.63), (6.98; 122.17), (7.08; 127.77), (7.13; 131.01), (7.23; 130.48), (7.31; 129.40), (7.32; 128.39), (7.48; 129.30), (7.74; 132.10), (7.91; 134.53).

Analytical Calc'd for C₅₈H₈₄N₁₀Si₄Ta₂: C 49.20; N 6.00; H 6.04; Found: C 45.46%; C 6.13; H 6.10.

*All carbon analysis were found to be low, possibly due to the formation of tantalum carbide (TaC).

Synthesis of ([NPN]Ta(CH₂)₅CH₃)₂(R-1:1-1:15N₂), 10-¹⁵N₂.

By the method outlined above, 1-¹⁵N₂ (0.83 g, 0.658 mmol) and 1-pentene (2 mL, 18.28 mmol) were reacted to obtain 0.70 g of the red product (76% yield).

¹³P [¹H] NMR (C₆D₆): δ 6.81 (dd, ²JₚN = 30.4 Hz, ³JₚN = 6.5 Hz), 22.1 (s).

¹⁵N NMR (C₆D₆): δ 14.13 (dd, ¹JₚN = 11.5 Hz, ²JₚN = 6.5 Hz), 25.92 (dd, ³JₚN = 30.4 Hz, ⁴JₚN = 11.5 Hz).

Synthesis of ([NPNTa(CH₂)₃CH₃)₂(μ-η¹:η¹-¹⁵N₂), 11.

A mixture of 11 (0.9 g, 0.714 mmol) and 1-hexene (1.5 mL, 12.14 mmol) was stirred in 45 mL of benzene. The dark brown solution was stirred overnight at 65°C and
turned red. The vessel was brought into the glovebox, where the solvent was removed via vacuum and left a red residue that was triturated three times with hexanes, filtered and collected on a glass frit in 86% yield (0.88 g).

\(^1\)H NMR (C\(_6\)D\(_6\), 400 MHz): \(\delta -0.11, 0.10, 0.26, \) and 0.39 (s, 24H total, SiCH\(_3\)), 0.97 and 1.12 (m, 4H, SiCH\(_2\)P), 1.12 and 1.37 (m, 4H, SiCH\(_2\)P), -0.02 (br m, 2H, TaBCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 0.81 (m, 2H, Ta\(_6\)CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 0.87 (t, 3H, Ta\(_6\)CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.14 (m, 2H, Ta\(_6\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.28 (t, 3H, Ta\(_6\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.35 (m, 2H, Ta\(_6\)CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.61 (m, 2H, Ta\(_6\)CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.75 (m, 2H, Ta\(_6\)CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.86 (m, 2H, Ta\(_6\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.93 (m, 2H, Ta\(_6\)CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.96 (m, 2H, Ta\(_6\)CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 2.39 (m, 2H, Ta\(_6\)CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 6.68, 6.96 (t, 4H, p-NC\(_6\)H\(_5\)), 6.75, 7.34 (m, 8H, m-NC\(_6\)H\(_5\)), 6.93, 7.09 (d, 8H, o-NC\(_6\)H\(_5\)), 7.12, 7.28 (m, 2H, p-PC\(_6\)H\(_5\)), 7.36, 7.51 (m, 4H, m-PC\(_6\)H\(_5\)), 7.78, 7.93 (dd, 4H, o-PC\(_6\)H\(_5\)).

\(^{31}\)P\(^{\prime\text{H}}\) NMR (C\(_6\)D\(_6\)): \(\delta 6.46, 21.75\)

\(^{13}\)C\(^{\prime\text{H}}\) NMR (C\(_6\)D\(_6\)): \(\delta 0.46, 1.73, 4.34, 6.17\) (SiCH\(_3\)), 14.31, 17.75 (SiCH\(_2\)P), 14.68 (Ta\(_6\)CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 15.06 (Ta\(_6\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 15.93 (Ta\(_6\)CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 24.00 (Ta\(_6\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 28.21 (Ta\(_6\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 30.55 (Ta\(_6\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 32.07 (Ta\(_6\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 32.30 (Ta\(_6\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 38.47 (Ta\(_6\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 32.63 (Ta\(_6\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 63.16 (Ta\(_6\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 74.31 (Ta\(_6\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 117.12, 118.56
(p-NC\textsubscript{6}H\textsubscript{5}), 122.19, 123.01 (m-NC\textsubscript{6}H\textsubscript{5}), 126.67, 127.02 (o-NC\textsubscript{6}H\textsubscript{5}), 129.94, 130.76 (p-P\textsubscript{6}H\textsubscript{5}), 129.23, 129.37 (m-P\textsubscript{6}H\textsubscript{5}), 133.01, 134.23 (o-P\textsubscript{6}H\textsubscript{5}).

**HSQC NMR (C\textsubscript{6}D\textsubscript{6}):** δ (\textsuperscript{1}H; \textsuperscript{13}C) (-0.11; 0.46), (1.73; 0.10), (4.34; 0.26), (6.17; 0.39), (0.97; 14.31), (1.12; 14.31), (1.12; 17.75), (1.37; 17.75), (1.28; 14.68), (0.87; 15.06), (1.14; 15.93), (1.35; 24.00), (1.86; 28.21), (0.81; 30.55), (1.93; 32.07), (1.96; 32.30), (1.61; 38.47), (2.39; 32.63), (1.75; 63.16), (-0.02; 74.31), (6.68; 117.12), (6.96; 118.56), (6.75; 122.19), (7.34; 123.01), (6.93; 126.67), (7.09; 127.02), (7.12; 129.94), (7.28; 130.76), (7.36; 129.23), (7.51; 129.37), (7.78; 133.01), (7.93; 134.23).

**Synthesis of ([NPN]Ta(CH\textsubscript{2})\textsubscript{5}CH\textsubscript{3})\textsubscript{2}(1\textsuperscript{i}-TV\textsuperscript{-15}N\textsubscript{2}), 1\textsuperscript{15}N\textsubscript{2}.**

By the method outlined above, 1\textsuperscript{-15}N\textsubscript{2} (0.77 g, 0.610 mmol) and 1-hexene (1.5 mL, 12.14 mmol) were reacted to give 0.63 g (72% yield) of 1\textsuperscript{15}N\textsubscript{2}.

\textsuperscript{31}P\textsuperscript{[\textsuperscript{1}H]} NMR (C\textsubscript{6}D\textsubscript{6}): δ 6.93 ppm. (dd, \textsuperscript{3}J\textsuperscript{PN} = 6.5 Hz, \textsuperscript{3}J\textsuperscript{PN} = 29.5 Hz), 22.0 ppm.

\textsuperscript{15}N NMR (C\textsubscript{6}D\textsubscript{6}): δ 14.15 (dd, \textsuperscript{1}J\textsuperscript{NN} = 11.3 Hz, \textsuperscript{1}J\textsuperscript{NN} = 6.5 Hz), 25.94 (dd, \textsuperscript{3}J\textsuperscript{PN} = 30.4 Hz, \textsuperscript{1}J\textsuperscript{NN} = 11.3 Hz).
3.1 Introduction.

Metallocene dinitrogen complexes, and their reactivity patterns with other reagents have contributed to the current knowledge of $N_2$ activation and functionalization. Seminal discoveries involved the protonation of early metallocene $N_2$ complexes to form ammonia and hydrazine. For instance, in 1972, Shilov et al. reported the formation of ammonia from protonation of $(\text{Cp}_2\text{Ti})_2(\mu_2-\eta^1:\eta^1-N_2)$ with HCl. Similarly, Bercaw et al. discovered the formation of hydrazine from the reaction of $[(\text{C}_5\text{Me}_5)_2\text{ZrN}_2]_2(\mu_2-\eta^1:\eta^1-N_2)$ with excess HCl. Inspired by these discoveries, investigations for using metallocene complexes to transform $N_2$ into useful, organonitrogen products has emerged.

The extent of activation and the bonding mode of $N_2$ to group IV metallocenes is dictated by the nature of the substituents on the cyclopentadienyl (Cp) ligands (see Figure 3.1). For instance, the reduction of $(\eta^5-\text{C}_5\text{Me}_5)_2\text{ZrCl}_2$ with sodium amalgam (Na/Hg) in the presence of $N_2$ forms the end-on bridged dinitrogen complex with two terminal end-on bound dinitrogen units, $[(\eta^5-\text{C}_5\text{Me}_5)_2\text{ZrN}_2]_2(\mu^2-\eta^1:\eta^1-N_2)$, $A$; in contrast, when the Cp ring has only four methyl substituents, as in $(\eta^5-\text{C}_5\text{Me}_4\text{H})_2\text{ZrCl}_2$, and is reduced under similar conditions, the side-on $N_2$ bridged complex, $[(\eta^4\text{C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu_2-\eta^2:\eta^2-N_2)$, $B$, forms. The trend that is apparent in this example is that fewer methyl groups attached to the cyclopentadienyl ring seem to encourage an $\eta^2-N_2$ hapticity. This trend is also
observed with the titanocene derivative. $N_2$ is bound in the end-on bridging mode for both the penta- and tetramethylated Cp complexes $[(\eta^5-C_5Me_5)_2Ti](\mu^2-\eta^1:\eta^1-N_2)$ (C) and $[(\eta^5-C_5Me_5)_2Ti](\mu_2-\eta^1:\eta^1-N_2)$, (D),\textsuperscript{75,76} the side-on bridging $N_2$ is observed for the trimethylated Cp complex, $[(\eta^5-C_5H_5-1,2,4-Me_3)_2Ti](\mu_2-\eta^2:\eta^2-N_2)$ (E).\textsuperscript{77}

**Figure 3.1.** Side-on and end-on $N_2$ zirconocene and titanocene complexes.

Although there are several group IV metalloocene dinitrogen complexes, to date, only one example of a group V metalloocene-dinitrogen complex is known; the synthesis of complex $F$ is shown in Equation 3.1.\textsuperscript{78} The reaction of Cp*\textsubscript{2}TaCl\textsubscript{2} in THF with sodium amalgam under 1 atm $N_2$ forms $[(\eta^5-C_5Me_5)_2TaCl]_2(\mu_2-\eta^1:\eta^1-N_2)$, $F$, which has a moderately activated $N_2$ unit ($N=N = 1.235(13)$ Å).\textsuperscript{78}
Equation 3.1

Harsh alkali metal reducing agents, such as Na/Hg amalgam or KC₈ under an N₂ atmosphere, are typically employed to generate dinitrogen complexes from a metallocene halide, Cp₂MX₂ (X = Cl or I). In a few cases, dinitrogen complexes have been synthesized without the use of strong reductants via reductive elimination of H₂ from a dihydride complex; for example, [(η⁵-C₅Me₅H)₂Ti]₂(µ₂-η¹:η¹'-N₂) is formed from (η⁵-C₅Me₅H)₂TiH by elimination of H₂ under an N₂ atmosphere. A selection of group IV and V metallocene N₂ complexes, their precursors, and N-N bond lengths (Å) are listed in Table 3.1.
Table 3.1. Group IV and V metallocene dinitrogen complexes, their precursors and N-N bond lengths (Å) (measured via X-ray diffraction).

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Group IV and V metallocene N2 complexes</th>
<th>N-N bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(η²-C₅H₅-1,2,4-Me₃)₂TiH]₆ or [(η²-C₅H₅-1,2,4-Me₃)₂Ti]</td>
<td>[(η²-C₅H₅-1,2,4-Me₃)₂Ti]₂(μ₂-η²:η²-N₂)</td>
<td>1.216(3)²⁷</td>
</tr>
<tr>
<td>[(η²-C₅H₅-1,2,4-Me₃)₂Pr]</td>
<td>[(η²-C₅H₅-1,2,4-Me₃)₂Pr]₂(μ₂-η²:η²-N₂)</td>
<td>1.168(3)²⁷</td>
</tr>
<tr>
<td>rac-Me₂Si(η³-C₅H₅-2-SiMe₃-4-Bu)₂TiCl₂</td>
<td>rac-[Me₂Si-η³-C₅H₅-2-SiMe₃-4-Bu]₂Ti(μ₂-η²:η²-N₂)</td>
<td>1.174(3)²⁷</td>
</tr>
<tr>
<td>Me₂Si(η³-C₅Me₃)(η³-C₅H₅-3-Bu)₂TiCl₂</td>
<td>[Me₂Si(η³-C₅Me₃)(η³-C₅H₅-3-Bu)]₂(μ₂-η²:η²-N₂)</td>
<td>1.165(3)²⁷</td>
</tr>
<tr>
<td>(η³-C₅Me₃H₂)₂TiH</td>
<td>[(η³-C₅Me₃H₂)]₂(μ₂-η²:η²-N₂)</td>
<td>1.170(4)²⁵</td>
</tr>
<tr>
<td>(η³-C₅Me₃)₂TiCl₂</td>
<td>[(η³-C₅Me₃)]₂(μ₂-η²:η²-N₂)</td>
<td>1.160(14)²⁶</td>
</tr>
<tr>
<td>(η³-C₅Me₃)₂ZrCl₂</td>
<td>[(η³-C₅Me₃)]₂(μ₂-η²:η²-N₂)</td>
<td>1.182(5)²¹</td>
</tr>
<tr>
<td>Me₂Si(η³-C₅Me₃)(η³-C₅H₅-3-Bu)₂ZrCl₂</td>
<td>[Me₂Si(η³-C₅Me₃)(η³-C₅H₅-3-Bu)]₂(μ₂-η²:η²-N₂)</td>
<td>1.406(4)²⁴</td>
</tr>
<tr>
<td>(η³-C₅Me₃H₂)₂ZrCl₂</td>
<td>[(η³-C₅Me₃H₂)]₂(μ₂-η²:η²-N₂)</td>
<td>1.377(3)²⁴</td>
</tr>
<tr>
<td>Me₂Si(η³-C₅H₅-2-SiMe₃-4-CMe₃)₂ZrH₂</td>
<td>[Me₂Si(η³-C₅H₅-2-SiMe₃-4-CMe₃)]₂(μ₂-η²:η²-N₂)</td>
<td>1.2450(38)²⁶</td>
</tr>
<tr>
<td>(η³-C₅Me₃H₂)₂Hf₂</td>
<td>[(η³-C₅Me₃H₂)]₂(μ₂-η²:η²-N₂)</td>
<td>1.423(11)²⁵</td>
</tr>
<tr>
<td>(η³-C₅Me₃)₂TaCl₂</td>
<td>[(η³-C₅Me₃)]₂(μ₂-η²:η²-N₂)</td>
<td>1.235(13)²⁸</td>
</tr>
</tbody>
</table>

3.2 The Chemistry of Cp₂NbH₃ and Cp₂TaH₃.

In this chapter, the reactivity of 1 with group V metallocene hydrides, Cp₂TaH₃ and Cp₂NbH₃ is explored. Cp₂NbH₃ and Cp₂TaH₃ have similar chemical properties, but differ in their reactivity; the former is far more reactive than the latter. For example, in their reactions with HSiMe₂Ph, Cp₂TaH₃ requires a higher temperature and longer reaction time compared to Cp₂NbH₃. Structurally, these complexes exhibit a distorted trigonal bipyramidal structure; the two Cp rings are bent back, causing a mixing of the d, s, and p orbitals to form three hybrid orbitals in the equatorial plane (Figure 3.2).
Figure 3.2. An illustration of a group V metalloocene hydride.

Heating Cp₂MH₃ (M = Nb or Ta) in the presence of a ligand (L) is a common route to forming Cp₂MHL complexes,"it is believed that this process occurs via H₂ elimination from Cp₂MH₃ to generate a reactive intermediate, [Cp₂MH], although this intermediate has never been isolated or detected (Equation 3.2).

\[
\text{Cp₂MH₃} \quad \rightarrow \quad [\text{Cp₂MH}] + \text{H₂}
\]

Equation 3.2

Some reactions of Cp₂MH₃ are outlined in Scheme 3.1. Heating Cp₂NbH₃ or Cp₂TaH₃ in the presence of triethyl phosphine, carbon monoxide, alkenes and alkynes (L) gives Cp₂MHL.\(^8⁶\)\(^⁷\) The reaction of HSiMe₂Ph with niobocene and tantalocene hydrides oxidatively adds HSiMe₂Ph to afford the silyl derivatives.\(^8⁴\) When Cp₂NbH₃ or Cp₂TaH₃ are heated in absence of a ligand and eliminate a second equivalent of H₂, a cyclometallated dimer forms.\(^8⁶\)
3.3. The Reaction of 1 with Cp₂Zr(II) and Cp₂Ti(II).

As mentioned in Chapter 1, the reaction of 1 with main group hydride reagents (E-H) has previously been studied in the Fryzuk group. The extension of this type of E-H addition for metallocene hydrides was of particular interest. The zirconocene hydride reagent, [Cp₂ZrH₂]₂, reacts with 1 to give [N(μ-P=N)]Ta(μ-H)₂(μ-N(ZrCp₂))Ta[NPN], 12, along with the evolution of H₂ (¹H NMR (C₆D₆) = δ 4.47) (Equation 3.3). Complex 12 was characterized using X-ray analysis.
To determine the origin of liberated H₂, deuterium labeled 1, ([NPN]Ta)₂(μ-D)₄(μ-
η¹:η¹'-N₂) was reacted with [Cp₂ZrH₂]₂; the ¹H NMR spectrum revealed free H₂ (no HD),
and the formation of 12 with loss of the signal at δ 11.4 due to the two bridging tantalum
hydrides. This suggested that there was no HD exchange, and that the source of hydrogen
was from [Cp₂ZrH₂]₂ to provide a Cp₂Zr(II) species that was responsible for cleaving the N-
N bond in 1. To test this idea, 1 was reacted with a Cp₂Zr(II) precursor,
Cp₂Zr(py)Me₃SiCCSiMe₃. In this reaction, the formation of 12 was nearly quantitative
(90% yield), and strongly suggested that the hydrides of [Cp₂ZrH₂]₂ reductively eliminate
H₂ to form Cp₂Zr(II) before forming 12. The reaction of 1 with a Cp₂Ti(II) precursor,
Cp₂Ti(Me₃SiCCSiMe₃), was also explored, and produced the analogous complex, 13, which
was characterized by NMR spectroscopy. A proposed mechanism for the formation of 12
and 13 is shown in Scheme 3.2; this mechanism initially involves the formation of an adduct
(B), followed by an inner-sphere electron transfer to cleave the N-N bond to form a bridging
nitride species (C), one of which is transformed into a phosphinimide via nucleophilic attack
from the phosphine donor in [NPN] (D).
In this chapter, the reaction of 1 with a Cp₂Hf(II) precursor, Cp₂Hf(PMe₃)(η²-Me₃SiCCSiMe₃), was explored. In contrast to zirconium and titanium, hafnium has been infrequently used in N₂ activation because it is the most difficult group IV metal to reduce. Only recently has it shown the potential to form highly activated N₂ complexes; for example, extreme lengthening of the N-N bond is observed in hafnium guanidinate and amidinate complexes, also, hafnium N₂ complexes have the tendency to form the more reactive side-on N₂ complex as opposed to end-on. The reaction of 1 with Cp₂Hf(PMe₃)(η²-Me₃SiCCSiMe₃) will be described in section 3.4.1. In addition, the observation that Cp₂ZrH₂ is involved in the cleavage and functionalization of N₂ (described above), led us to investigate the reaction of group V metallocene hydrides, in particular Cp₂TaH₃ and Cp₂NbH₃. Would these metal hydrides undergo the same reductive elimination of H₂ to
generate a Cp₂MH(III) species that would be capable of cleaving and functionalizing N₂ in 1? These results will be described in section 3.4.2.

3.4. Results and Discussion.

3.4.1. Reaction of 1 with Cp₂Hf(PMe₃)(η²-Me₃SiCCSiMe₃).

A benzene solution of 1 and Cp₂Hf(PMe₃)(η²-Me₃SiCCSiMe₃) was heated for three days at 75°C. This generated a dark purple mixture, from which a purple solid, [N(µ-P=P=NP)]Ta(µ-H)₂(µ-N(HfCp₂))Ta[NPN], 14, was isolated in 73% yield (Equation 3.4).

\[
\text{Equation 3.4}
\]

The \(^{31}\)P{¹H} NMR (C₆D₆) spectrum of 14 (Figure 3.3) has two singlet resonances at δ 15.64 and 54.89, indicating that there are two different phosphorus environments. These resonances are similar to those observed for 12 (δ 7.3, 46.7) and 13 (δ 8.6, 46.4).
Figure 3.3. $^{31}\text{P}[^{1}\text{H}]$ NMR spectrum of 14 in C$_6$D$_6$.

The $^1$H NMR spectrum of 14 in C$_6$D$_6$ shows four inequivalent silyl methyl resonances, a single Cp resonance at $\delta$ 5.55, and a doublet for the bridging hydrides at $\delta$ 11.48. The $^{15}$N$_2$ labeled derivative, [N(µ-P=^{15}\text{N})N]Ta(µ-H)$_2$(u-^{15}\text{N}(\text{HfCp}_2))Ta[NPN], 14-^{15}\text{N}_2, was also prepared. The $^{15}$N$[^{1}\text{H}]$ NMR spectrum reveals a doublet at $\delta$ -194.3 ($J_{PN}$ = 31.6 Hz), and a doublet at 204.25 ($J_{PN}$ = 5.6 Hz); these two resonances are not mutually coupled, and implies that N-N cleavage has occurred. The $^{31}\text{P}[^{1}\text{H}]$ NMR spectrum of 14-^{15}\text{N}_2 also shows two resonances: a singlet at $\delta$ 11.15, and a doublet at $\delta$ 50.43, with a one-bond P-N coupling constant of 31.6 Hz.

Crystals of 14 were grown from an evaporated benzene solution, and analyzed using X-ray diffraction. The solid-state molecular structure of 14, along with selected bond lengths and bond angles, is shown in Figure 3.4.

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Figure 3.4. An ORTEP depiction of the solid-state molecular structure of 14 (ellipsoids at 50% probability). Hydrides were located on a difference map and refined isotropically. All hydrogen atoms and phenyl ring carbons other than ipso carbons have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ta1-Ta2 2.6819(4), Ta1-N1 2.094(4), Ta1-N2 2.133(4), Ta2-N2 1.941(4), N1-Hfl 2.110(4), N2-Hfl 2.020(4), N1-P1 1.594(4), Ta1-N3 2.094(4), Ta1-N4 2.057(4), Ta2-N5 2.122(4), Ta2-N6 2.114(4), Ta2-P2 2.6115(14), N1-Ta1-N2 85.95(15), Ta1-N2-Ta2 82.18(14), N1-Hfl-N2 88.47(16), P1-N1-Ta1 121.1(2), P1-N1-Hfl 146.8(3), N3-Ta1-N4 106.96(17), N5-Ta2-N6 105.10(17), Ta1-Ta2-N2 52.00(11).

The solid-state structure of 14 shows a cleaved N₂ unit with a bridging hafnocene fragment between two nitrogen atoms (N1 and N2). Complex 14 is structurally analogous...
to 12; both complexes have a cleaved and functionalized N₂ unit, and a phosphinimide bond (P₁=N₁). This can suggest that 14 was formed via the same mechanism that was proposed for 12 (Scheme 3.5). The bond lengths of 14 are nearly identical to those of 12. The Ta₁-Ta₂ distance is 2.6819(4) Å, similar to other Ta(IV)-Ta(IV) bond lengths that have been reported. The phosphinimide bond length (P₁-N₁) is 1.594(4) Å, and is within a range that is commonly found for groups 4 and 5 phosphinimide complexes. The Hf-N bond lengths (Hf₁-N₁ = 2.110(4), Hf₁-N₂ = 2.020(4) Å) are slightly shorter than the Zr-N bond lengths in 12, (Zr₁-N₁ = 2.146(9), Zr₁-N₂ = 2.040(9) Å), as expected.

3.4.2. Attempted Reaction of 1 with Cp₂TaH₃ and Cp₂NbH₃.

A 1:1 mixture of 1 and Cp₂TaH₃ was stirred in d₈-toluene at room temperature for 2 weeks. The reaction was monitored by ³¹P[¹H] and ¹H NMR spectroscopy, and no new species were observed by periodically monitoring the reaction over 2 weeks. To promote the loss of H₂ to generate a [Cp₂TaH] species, the same mixture was heated at 100°C for 2 weeks, but produced no visible change. The mixture was also heated under a flow of N₂ for 6 hours, but again there was no change. High-temperature ¹H NMR spectroscopy was also used to monitor the progress of the reaction at 100°C, however, no new products were observed using this technique. The more reactive Cp₂NbH₃ was also attempted. A 1:1 mixture of 1 and Cp₂NbH₃ was stirred in benzene at room temperature for 1 week. The progress of the reaction was monitored by ³¹P[¹H] and ¹H NMR spectroscopy in C₆D₆, but like the Cp₂TaH₃ reaction above, did not show the formation of any new products. The same mixture was heated and stirred at 90°C for 5 hours under a flow of N₂ to promote the loss of H₂ from Cp₂NbH₃ and form [Cp₂NbH]²⁺; however, this did not produce any visible
change. High-temperature $^1$H NMR spectroscopy at 90°C was also used to observe the progress of the reaction at this temperature, but did not show the formation of any new product.

As mentioned earlier in this chapter, Cp$_2$MHL complexes are formed by heating Cp$_2$MH$_3$ in the presence of a ligand, (L). It is believed that heating Cp$_2$MH$_3$ eliminates H$_2$ to form an equilibrium with a reactive intermediate, [Cp$_2$MH]; however this intermediate has never been isolated or detected. Therefore, a possible explanation for the lack of reactivity between 1 and Cp$_2$MH$_3$ might be because the reverse reaction of H$_2$ with [Cp$_2$MH] occurs quicker than the reaction between Cp$_2$MH$_3$ with 1 (Equation 3.5).

![Equation 3.5](image)

3.5 Conclusions.

The observation that Cp$_2$Zr(II) reacts with 1 to form 12 compelled us to investigate the reaction of 1 with other group IV and group V metalloocene complexes. The reaction of 1 and Cp$_2$Hf(PMe$_3$)$_2$(η$^2$-Me$_3$SiCSiMe$_3$) forms 14, which contains a cleaved and functionalized N$_2$ unit, and the formation of a new phosphinimide bond. Complexes 12 and 14 are structurally analogous, and it is strongly suggested that both complexes are formed via the same proposed mechanism for 12 (Scheme 3.5).
Unfortunately, the group V metallocene hydrides \(\text{Cp}_2\text{TaH}_3\) and \(\text{Cp}_2\text{NbH}_3\) do not react with 1. \(\text{Cp}_2\text{MH}_3\) \((M = \text{Ta}, \text{Nb})\) was heated to provide a reactive intermediate \([\text{Cp}_2\text{MH}]\), but no reaction was observed. Since the \([\text{Cp}_2\text{MH}]\) intermediate cannot be isolated or detected, a possible explanation for lack of reactivity between 1 and \(\text{Cp}_2\text{MH}_3\), might be because the reverse reaction of \(\text{H}_2\) and \([\text{Cp}_2\text{MH}]\) occurs quicker than the forward reaction of \([\text{Cp}_2\text{MH}]\) and 1.

3.6 Experimental.

3.6.1. General Procedure.

Unless otherwise stated, general procedures were performed as described in Section 2.4.1.

3.6.2. Materials and Reagents.

\(\text{Cp}_2\text{Hf}(\text{PMc}_3)(\eta^2-\text{Me}_3\text{SiC}_2\text{SiMe}_3)\)^{102} \(\text{C}_{10}^2\) and \(\text{N}_2\text{C}_{10}^2\) were prepared using literature methods.


Synthesis of \([\text{N}(\mu-\text{P=N})\text{N}]\text{Ta}(\mu-\text{H})_2(\mu-\text{N}(\text{HfCP}_2))\text{Ta}[\text{NPN}]\), 12.

\([(\text{NPN})\text{Ta}(\mu-\text{H})_2(\mu-\text{H}^1-\text{N}_2)\text{ (0.65 g, 0.515 mmol)} \text{ and \(\text{Cp}_2\text{Hf}(\eta^2-\text{Me}_3\text{SiC}_2\text{SiMe}_3)\text{ (0.29 g, 0.515 mmol)}\) was dissolved in 50 mL benzene at room temperature.}

The brown mixture was stirred for three days at 75°C, and the colour of the solution changed from brown to purple. The vessel was brought into a glovebox and the solvent was removed under vacuum, leaving a purple residue.
that was triturated with hexanes and filtered to collect a purple powder, 14 (Yield = 0.59 g, 73%).

$^1$H NMR (C$_6$D$_6$, 25°C, 400 MHz): -0.13, 0.12, 0.19, 0.28 (s, 6H each, SiCH$_3$), 1.32 (dd, $^3$J$^\text{HH}$ = 10.9 Hz, $^2$J$^\text{HH}$ = 22.5 Hz, 4H, SiCH$_2$P), 1.94 (dd, $^3$J$^\text{HH}$ = 14.0 Hz, $^2$J$^\text{HH}$ = 39.2 Hz, 4H, SiCH$_2$P), 5.54 (s, 10H, $^\eta^5$-C$_5$H$_5$), 6.52, 6.76, 6.99, 7.08, 7.29 (d, t, 20H total, NC$_6$H$_5$), 7.13, 7.21, 7.26, 7.38 (d, t, 6H total, PC$_6$H$_6$), 7.54, 7.88 (dd, 4H, PC$_6$H$_6$) 11.48 (d, 2H, $^3$J$^\text{TaN}$ = 16.6 Hz)

$^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 15.64 (s) 54.89 (s).

$^{13}$C{$^1$H} NMR (C$_6$D$_6$): 0.33, 3.75, 4.44, 5.18 (SiCH$_3$), 14.6, 20.33 (SiCH$_2$P), 108.63, ($^\eta^5$-C$_5$H$_5$), 117.10, 118.53, 120.56, 122.86, 126.67, 129.51 (NC$_6$H$_5$), 129.02, 129.27, 129.95, 131.30 (PC$_6$H$_6$), 131.83, 133.42 (o-PC$_6$H$_6$).

Analytical Calc'd for C$_{58}$H$_{74}$N$_6$P$_2$Si$_4$Ta$_2$Hf: C 44.37; H 4.75; N 5.35; Found: C 44.67; H 5.11; $^*$.N 4.81.

$^*$.Nitrogen analysis were found to be low, possibly due to the formation of HfN or TaN.

Synthesis of [N($\mu$-P=$^{15}$N)N]Ta($\mu$-H)$_2$($\mu$-$^{15}$N(HfCp$_2$))Ta[NPN], 12-$^{15}$N$_2$.

By the same method outlined above, 1-$^{15}$N$_2$ (0.88 g, 0.698 mmol) and Cp$_2$Hf($^\eta^2$-Me$_3$SiC$_5$SiMe$_3$) (0.393 g, 0.698 mmol) were reacted to give (0.84 g, 87% yield) of 12-$^{15}$N$_2$.

$^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 11.15 (s), 50.43 (d, $^3$J$^\text{PN}$ = 31.6 Hz).

$^{15}$N NMR (C$_6$D$_6$): $\delta$ -194.3 (d, $^3$J$^\text{PN}$ = 31.6 Hz), 204.25 (d, $^3$J$^\text{PN}$ = 5.6 Hz).
3.6.4. Attempted Reactions of 1 and Cp₂MH₃.

Complex 1 (102 mg, 0.08 mmol) and Cp₂MH₃ (1 equivalent) was dissolved in 1.5 ml in toluene and sealed in a J-Young tube and heated at 100°C (for M = Ta) and 90°C (for M = Nb).

Complex 1 (1 g, 0.8 mmol) and Cp₂MH₃ (1 equivalent) was dissolved in toluene and heated at 100°C for 6 hours (M = Ta) and 90°C for 5 hours (M = Nb) under a flow of N₂.
Chapter Four

The Reactivity of a Group 13 Complex with Side-on End-on coordinated N₂.

4.1 Introduction.

When nitrogen is activated in a transition-metal complex, the N₂ unit may be susceptible to electrophilic attack. The most common electrophilic addition reaction with coordinated dinitrogen is protonation.¹⁰⁴ Protonation of transition-metal N₂ complexes is of interest because it is invoked in biological nitrogen fixation.¹⁰⁵,¹⁰⁶ One example of a homogeneous catalyst that is capable reducing and protonating dinitrogen to ammonia is the mononuclear molybdenum complex, [HIPTN₂N]Mo(N₂), ([HIPTN₂N]³⁻ = [3,5-(2,4,6-i-Pr₃-C₆H₂)₂C₆H₃NCH₂CH₂]³⁻) shown below.¹⁰⁷ This complex contains a tetradentate triamidoamine ligand, and can reduce N₂ to NH₃ under ambient conditions (at room temperature and 1 atmospheric pressure).
The catalytic production of organonitrogen compounds from molecular nitrogen has become a "holy grail" in dinitrogen research; thus, in addition to protonation reactions, the reactions of coordinated N\textsubscript{2} with other electrophilic reagents have also been explored. Some reactions of N\textsubscript{2} complexes with group 13 electrophiles, afford new N-E bonds. For example, cis-[W(N\textsubscript{2})\textsubscript{2}(L)\textsubscript{3}L\textsubscript{1}L\textsubscript{1}] reacts with GaCl\textsubscript{3} and AlCl\textsubscript{3} to form trans,trans-[[WCl(PMe\textsubscript{2}Ph)\textsubscript{4}(μ\textsubscript{3}-N\textsubscript{2})\textsubscript{2}(GaCl\textsubscript{2})\textsubscript{2}](N-N = 1.32(2) Å) (B) and [WCl(Py)(PMe\textsubscript{2}Ph)\textsubscript{3}(μ\textsubscript{3}-N\textsubscript{2})\textsubscript{2}(AlCl\textsubscript{3})\textsubscript{2}] (N-N = 1.46(4) and 1.25(3) Å) (C), respectively; the reaction of trans-[NBu\textsubscript{4}][W(NCS)(N\textsubscript{2})(dppe)\textsubscript{2}] (D) with H\textsubscript{2}BCMe\textsubscript{2}CHMe\textsubscript{2} forms the boryldiazenido complex, trans-[W(NCS)(N=NBHCMe\textsubscript{2}CHMe\textsubscript{2})(dppe)\textsubscript{2}] (N-N = 1.262(7) Å) (E). These reactions are illustrated in Scheme 4.1.

![Scheme 4.1](image)

Electrophilic group 14 complexes can also react with coordinated dinitrogen (see Scheme 4.2). For instance, the reaction of trans-[W(N\textsubscript{2})\textsubscript{2}(dppe)\textsubscript{2}] (A) with alkyl bromides
and acyl chlorides forms new N-C bond complexes (B and C).\textsuperscript{112,113} Silicon electrophiles can react with coordinated N\textsubscript{2} to form N-Si bonds; the reaction of \textit{cis}-[W(N\textsubscript{2})\textsubscript{2}(dppe)\textsubscript{2}] (D) with Me\textsubscript{3}SiI affords a silyldiazenido complex, \textit{trans}-[WI(NMe\textsubscript{3})\textsubscript{2}(PMe\textsubscript{2}Ph)\textsubscript{4}] (E);\textsuperscript{114} similarly, the reduction of [N\textsubscript{3}N]MoCl ([N\textsubscript{3}N = N(CH\textsubscript{2}CH\textsubscript{2}NSiMe\textsubscript{3})\textsubscript{3}] (F) with magnesium generates ([N\textsubscript{3}N]Mo-N=N)\textsubscript{2}Mg(THF)\textsubscript{2}, which reacts with Me\textsubscript{3}SiCl to form [N\textsubscript{3}N]Mo-N=NSiMe\textsubscript{3} (G).\textsuperscript{115}

![Scheme 4.2](image)

4.2. Reaction of 1 with Lewis Acids.

Lewis acids XR\textsubscript{3}, (XR\textsubscript{3} = AlMe\textsubscript{3} (15), GaMe\textsubscript{3} (16), and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (17) react with 1 to form the adducts, [(NPN)Ta]\textsubscript{2}(µ-H)\textsubscript{2}(µ-η\textsuperscript{+}N\textsuperscript{3}NXR\textsubscript{3}) (see Equation 4.1).\textsuperscript{116} The solid-state structures of 15, 16, and 17 have N-N bond lengths longer than that of 1, at
1.363(7), 1.356(18), and 1.393(7) Å, respectively. In this chapter, the reactivity of 1 with GaCp* is explored.

Equation 4.1.

4.3. Results and Discussion.

4.3.1. Reaction of 1 with GaCp*.

The initial reaction of 1 and GaCp* (1:1 equivalent) at room temperature is immediate but incomplete, as indicated by $^{31}P{^1H}$ NMR spectroscopy (Figure 4.1); in addition to the resonances of 1 (δ 11.7 and 13.8), the $^{31}P{^1H}$ NMR spectrum shows two doublets at δ 14.3 and 22.3 (J$_{pp}$ = 14.67 Hz), that are reminiscent of the $^{31}P{^1H}$ NMR spectrum of the adduct complex [[(NPN)Ta$_2$(μ-H)$_2$(μ-η$^1$:η$^2$-NNGaMe$_3$)], 16.
Since the reaction is not complete after stirring for several days at room temperature, the same mixture was heated overnight at 65°C. This resulted in the conversion of 1 into a new complex, [NPN]Ta(μ-N(GaCp*))Ta(=NPh)[NPμ-N], 18. Attempts to isolate 18 were unsuccessful; however, the complex was characterized in situ using $^1$H/$^{13}$C-HSQC, $^{31}$C($^1$H), $^{31}$P($^1$H) and $^{15}$N($^1$H) NMR spectroscopy, and based on the data provided by these spectra, a proposed structure for 18 is shown in Equation 4.2.
The $^{31}\text{P}[{^1}\text{H}]$ NMR spectrum of 18 no longer shows the two mutually coupled doublets that were observed at the onset of the reaction (i.e. Figure 4.1), but reveal two new singlets at $\delta$ -2.65 and 20.38, indicative of two different $^{31}\text{P}$ environments (Figure 4.2). The $^1\text{H}$ NMR spectrum of 18 shows no peaks in the region where the resonances for the bridging hydrides typically occur (at $\delta$ 11), but show eight singlets assigned to silyl methyl protons, and a singlet at $\delta$ 1.89 assigned to GaCp* protons (Figure 4.3); these findings suggest that 18 is $C_1$ symmetric in solution. Since 1 does not decompose or eliminate H$_2$ even in refluxing in toluene, the loss of the bridging hydrides in the formation of 18 appears to require heating 1 in the presence of GaCp*.

![Figure 4.2. $^{31}\text{P}[{^1}\text{H}]$ NMR spectrum of 18 in C$_6$D$_6$.](image)

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Figure 4.3. 400 MHz $^1$H NMR ($C_6D_6$) spectrum of 18. The trace amount of $Et_2O$ is an impurity in the deuterated solvent.

The $^{15}$N$_2$ labeled derivative, $[NPN]Ta(\mu-^{15}$N(GaCp$^*)_2)Ta(=NPh)[NP\mu-^{15}$N]. 18-$^{15}$N$_2$, was also prepared and characterized by NMR spectroscopy, and supports the structure proposed for 18 in Equation 4.3. The $^{31}$P-$^1$H NMR spectrum of 18-$^{15}$N$_2$ shows two doublets at $\delta$ -0.97 ($^2J_{PN} = 19.27$ Hz) and 22.08 ($^2J_{PN} = 11.06$ Hz); these resonances are different from those reported for the metalloocene complexes 12, 13, and 14 in Chapter 3, which show only one $^3$P resonance coupled to an $^{15}$N nucleus and indicates that 18 is structurally different from these complexes. The $^{15}$N-$^1$H NMR spectrum (Figure 4.4) shows two doublet of doublets at $\delta$ -23.2 ($^2J_{PN} = 19.27$ Hz, $^1J_{NN} = 3.01$Hz) and at $\delta$ 291.2 ($^2J_{PN} = 11.06$ Hz, $^1J_{NN} = 2.01$ Hz); these values are in contrast to those reported for 1-$^{15}$N$_2$, at $\delta$ -20.4 ($J_{NN} = 6.6, 24.6$ Hz; $J_{NN} = 21.6$ Hz) and 163.6 ($J_{NN} = 3.5, 21.2$ Hz; $J_{NN} = 21.6$),
indicating that the side-on end-on N2 in 1 has changed in 18. Furthermore, the splitting in the $^{15}$N($^1$H) NMR resonances of 18 reveals two different nitrogen atoms that are not mutually coupled, but coupled to different phosphorus and silicon environments (the $^{2}$J$_{NP}$ and $^{4}$J$_{NS}$ values found herein are within the range of other [NPN] complexes that have a similar structure to 18 and exhibit a two-bond N-P and one-bond N-Si coupling) implying that N-N bond cleavage has occurred, and that each $^{15}$N atom has a unique chemical environment, thereby supporting the structure proposed for 18 in Equation 4.3.

![NMR resonances](image)

**Figure 4.4** $^{15}$N($^1$H) NMR resonances of 18 in C$_6$D$_6$.

Complex 18 is unstable in solution, and can be observed by $^{31}$P($^1$H) NMR spectroscopy to convert into a number of other P-containing species over several days. One of the products of this reaction was determined to be [(PhN)(NPµ-N)Ta]$_2$, 19. The solid-state molecular structure of 19 was established by X-ray crystallography (Figure 4.5), and can support the structure of 18 proposed in Equation 4.3.
Figure 4.5. An ORTEP depiction of the solid-state molecular structure of 19 (ellipsoids at 50% probability). All silyl methyl groups, hydrogen atoms and phenyl ring carbons other than ipso carbons have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Tal-Tal' 3.0878(5), Tal-N3 2.0264(15), Tal-N1 1.8006(16), Tal-N2 2.0686(16), Tal-P1 2.6172(6), N3-Si2 1.1776(16), N3-Tal-N3' 89.82(6), N3-Tal-N2 103.48(6), N1-Tal-N3 109.99(7), N3-Tal-P1 146.19(15), N1-Tal-P1 101.35(5), N1-Tal-N2 108.97(7), Si2-N3-Tal 129.06(9), Tal-N3-Tal' 99.18(6).

The geometry about the tantalum center is best described as distorted square pyramidal, with the axial position occupied by N1, and the base vertices occupied by P1, N2, N3 and N3'. Decomposition of the [NPN] ligand at the N-Si bond is evident from the
structure. A square $M_2N_2$ unit ($M = \text{Ta}$) is also apparent in the solid-state, and is a shape that has previously been observed with other group V $N_2$ complexes.$^{117,118}$

The solid-state structure of 19 has a center of inversion, and it is apparent that there is no GaCp* in the complex. It is possible that GaCp* is responsible for the different symmetry observed between complexes 18 and 19, and that complex 18 is merely a GaCp* adduct of 19. The solid-state structure of 19 shows a cleaved N-N bond where the bridging N atoms are each bound to an Si atom; the $^{15}$N[$^1$H] NMR spectrum of 18 shows two distinct $^{15}$N environments that each display J$_{NN}$ coupling, and support the formation of a N-Si bond, like 19. The $^1$H NMR spectrum of 18 also shows loss of the bridging hydride resonance at $\delta$ 11.4, and is in agreement with the solid-state structure of 19, which shows no bridging hydride atoms. Therefore, the bonding information provided by the solid-state structure of 19 further supports the structure of 18 proposed in Equation 4.3.

Decomposition of the [NPN] ligand at the N-Si bond has previously been observed with hydroboration reactions of 1 (Equation 4.3) with HB(C$_6$H$_{11}$)$_2$ (20) and 9-BBN (21).$^{119}$ The mechanism for this process has been investigated by MacKay et al.;$^{119}$ the reaction of deuterium labeled 1, ([NPN]Ta)$_2$(µ-D)$_2$(µ-η$_1$$^2$-η$_2$-N$_2$), with 9-BBN and HB(C$_6$H$_6$) revealed that N-N bond cleavage in 1 was correlated to H$_2$ elimination from the bridging hydrides; $^{15}$N NMR studies revealed that the bridging nitrogen atoms in 20 and 21 originated from the side-on end-on N$_2$ in 1;$^{120}$Si NMR studies showed that the Si atom from [NPN] migrates to the bridging N atom.
4.4. Conclusions.

The reaction of 1 with GaCp* results in a cleaved and functionalized N2 complex, [NPN]Ta(μ-N(GaCp*))Ta(=NPh)[NPμ-N], 18. Although 18 could not be isolated, a possible solution structure was assigned by NMR spectroscopy and isotopic labeling. Complex 18 converts to 19, [(PhN)(NPμ-N)Ta]2, spontaneously in solution over several days. Both 18 and 19 have undergone ligand decomposition, most likely because of the reactivity of the N-Si bond in [NPN]; Si is bound to the bridging nitride, and a phenylamide group is bound to Ta. A similar decomposition of [NPN] has been observed upon hydroboration of 1, and it is presumed that the formation of complex 18 and 19 occurs through a similar mechanism.

4.5 Summary and Future Work.

This thesis investigates the reactivity of the tantalum dinitrogen complex, ([NPN]Ta)2(μ-H)2(μ-η1:η2-N2), 1, with primary alkenes, group IV and V metallocenes, and with GaCp*. In Chapter 2, the reaction of 1 with the 1-pentene and 1-hexene produced
([NPN]Ta(CH$_2$)$_2$CH$_3$)$_2$(µ-η':η'-N$_2$), 10, and ([NPN]Ta(CH$_2$)$_2$CH$_3$)$_2$(µ-η':η'-N$_2$), 11, each with two new Ta-C bonds, and a change to the bonding mode of N$_2$ in 1. This reaction likely occurs through the olefin-insertion of the primary alkene into the Ta-H bond. Complexes 10 and 11 were characterized by NMR spectroscopy, and the solid-state structure of 11 revealed that the N$_2$ unit is in the bridging end-on mode, with an N-N bond length of 1.272(6) Å. The symmetry of 11 in solution is different from its symmetry in the solid-state. Complex 11 forms two isomers in solution; 11A which is the C$_3$ isomer and the predominant isomer in solution at room temperature, and 11B, which is the minor C$_3$ isomer. Therefore, the solid-state structure represents isomer 11B, although it is unclear as to why this particular isomer is favoured in the solid-state.

In Chapter 3 the reactivity of 1 with group IV and V metallocenes was investigated. The reaction of 1 with Cp$_2$Hf(PMe$_3$)$_3$(η$_2$-Me$_3$SiCCSiMe$_3$) produces [N(µ-P=N)N]Ta(µ-H)$_2$(µ-N(HfCp$_2$))Ta[NPN], 14, in which N$_2$ is cleaved and new Hf-N and P=N bonds have formed. The cleavage of N$_2$ in 1 may be accomplished by the donation of two electrons from a Cp$_2$Hf(II) species. In addition, the reaction of 1 with group V metallocene hydrides Cp$_2$MH$_3$ (M = Nb, Ta) was attempted, however, no reaction was observed. It is believed that the 16 electron intermediate, [Cp$_2$MH(III)] reacts quicker with H$_2$ than with 1, and does not produce any useful result.

In Chapter Four, the reaction of 1 with GaCp$^*$ to produce [NPN]Ta(µ-N(GaCp*))Ta(=NPh)(NPµ-N), 18, was reported. Complex 18 decomposes over several days, and one product of decomposition that was isolated was [(PhN)(NPµ-N)Ta]$_2$, 19. The solid-state structure of 19 showed that the [NPN] ligand was cleaved at the N-Si bond, similar to that observed for the reaction of 1 with 9-BBN and HB(C$_6$H$_5$)$_2$. 

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This thesis has discussed the reaction of \( \text{I} \) with some early transition metal complexes in Chapter 4. In addition to many other reactions of \( \text{I} \) with early transition-metal complexes that remain to be explored, the reaction of \( \text{I} \) with certain late-transition metal complexes should be attempted. For example, \( \text{Pd}_2(\text{dba})_3 \) or \( \text{(COD)}_2\text{Ni} \) may form adduct complexes or cleave and functionalize \( \text{N}_2 \) in \( \text{I} \). The reaction of \( \text{I} \) with other organic reagents such as cyclic alkenes and allenes and is another area that can be explored, and may possibly result in the formation of a carbon-nitrogen bond.

4.6. Experimental.


Unless otherwise stated, general procedures were performed as described in Section 2.4.1.

4.6.2. Materials and Reagents.

\( \text{GaCp}^* \), \( \text{I}^{120} \) and \( \text{N}_2\text{-I}^{121} \) were prepared using literature methods.


Synthesis of \( [\text{NPN}]\text{Ta}(\mu-\text{N}(\text{GaCp}^*))\text{Ta}(=\text{NPh})[\text{NP} \mu-\text{N}] \), 18.

\( \text{GaCp}^* \) (16.5 mg, 0.081 mmol) was added dropwise to a solution of \( \text{I} \) (102 mg, 0.081 mmol) in 1.5 mL of \( \text{C}_6\text{D}_6 \) at room temperature. The mixture was sealed in a J-Young tube and heated overnight at 65°C.

\( ^1\text{H NMR (C}_6\text{D}_6, 400 \text{ MHz)}: -0.78, -0.34, -0.19, -0.16, 0.08, 0.27, 0.39, 0.51 (s, 3H each, Si\text{CH}_3), 0.78, 0.88, 1.05, 1.26 (m, 2H each, Si\text{CH}_2\text{P}), 1.98 (s, 15H, Ga\text{C}_{10}\text{H}_{15}), 6.81, \)

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6.84, 6.87, 6.92, 6.94, 6.96, 7.01, 7.05, 7.08, 7.23, 7.30, 7.38, 7.42 (d, t, 20H, NC₆H₅, 
7.53, 7.66, 8.15, 8.38 (m, dd, 10H, PC₆H₅).

³¹P{¹H} NMR (C₆D₆, 161 MHz): δ -2.65 (s) 20.38 (s).

¹³C{¹H} NMR (C₆D₆, 101 MHz): 0.05, 1.29, 2.11, 2.46, 3.12, 3.27, 5.28, 6.57 
(SiCH₃), 10.3 (GaC₅(C₅H₁₅)), 113.4 (GaC₅(C₅H₁₅)), 13.6, 15.8, 20.4, 21.8 (SiCH₂P), 
119.6, 121.8, 121.3, 121.9, 122.1, 123.5, 124.1, 125.7, 125.9, 129.1, 129.4, 129.8, 131.3 
(phenyl ring carbons), 131.8, 133.7, 134.3 and 135.2 (PC₆H₅). *Note some proton and 
carbon resonances were eclipsed by solvent.

¹H/¹³C HSQC NMR (C₆D₆): δ (¹H; ¹³C) (-0.78; 2.11), (-0.34; 1.29), (-0.16; 2.46), 
(0.08; 0.05), (0.27; 3.12), (0.39; 5.38), (0.51; 6.57); (0.78; 13.6), (0.33; 20.4), (1.05; 21.8), 
(1.26; 15.8); (1.98; 10.3); (6.81; 121.8), (6.84; 122.1), (6.87; 119.6), (6.92; 123.5), (6.94; 
119.6), (6.96; 124.1), (7.01; 121.9), (7.05; 125.9), (7.08; 129.1), (7.23; 129.4), (7.30; 
131.3), (7.38; 129.8), (7.53; 131.8), (7.66; 133.7), (8.15; 134.3), (8.38; 135.2).

Synthesis of [NPN]Ta(μ-¹⁵N(GaCp*))Ta(=NPh)[N¹⁵N], 18⁻¹⁵N₂.

By the method outlined above, 1⁻¹⁵N₂ (0.93 g, 0.737 mmol) and GaCp* (0.151 g, 
0.737 mmol) were reacted in 1.5 mL C₆D₆.

³¹P{¹H} NMR (C₆D₆, 161 MHz): δ -0.97 (d, ²JPN = 19.27 Hz) and 22.08 (d, ³JPN = 
11.06 Hz).

¹⁵N NMR (C₆D₆, 60 MHz): δ -23.2 (²JPN = 19.27 Hz, ¹JNS = 3.01 Hz) and at δ 291.2 
(²JPN = 11.06 Hz, ¹JNS = 2.01 Hz).
4.7 References.


Chpt 2


Okuda, J.; Voth, P.; Arndt, S.; Spaniol, T. P.; Green, M. L.; Ackerman, L. J. *Organometallics*, 2003, 22, 63.


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116 Studt, F.; MacKay, B. A.; Johnson, S. A.; Patrick, B. O.; Fryzuk, M. D.; Tuckzek, F.


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120 Jutzi, P.; Neumann, B.; Reumann, G.; Stammler, H. G. Organometallics, 1998, 17,
1305.

121 Fryzuk, M. D.; Johnson, S. A.; Patrick, B. O.; Albinati, A.; Mason, S. A.; Koetzle, T. F. J.
## Appendix

Table A-1. Crystallographic Data and Structure Refinement for ([NPN]Ta)₂(μ-H)₄ (2) and ([NPN]Ta(CH₂)₅CH₃)₂(μ-η¹:η¹-N₂) (11).

<table>
<thead>
<tr>
<th></th>
<th>([NPN]Ta)₂(μ-H)₄ (2)</th>
<th>([NPN]Ta(CH₂)₅CH₃)₂(μ-η¹:η¹-N₂) (11)</th>
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<tr>
<td>Empirical formula</td>
<td>C₄₈H₆₆N₄P₄Si₄Ta₂</td>
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<td>red, prism</td>
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<td>triclinic</td>
</tr>
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<td>P-1</td>
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</tr>
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</tr>
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<td>R (F², all data)</td>
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\[
R_1 (F^2, I>2\sigma(I)) = \frac{\sum |F_{\text{calc}}| - |F_{\text{obs}}|}{\sum |F_{\text{obs}}|} R_w (\text{all data}) = \left( \sum w(F_{\text{calc}}^2 - |F_{\text{obs}}|^2)^2 / \sum w|F_{\text{obs}}|^2 \right)^{1/2}
\]
Table A-2. Crystallographic Data and Structure Refinement for $[N(µ-P=N)Ta(µ-H)\text{2}(µ-N(N\text{HcP}_2))Ta[NPN]}$ (14) and $[(\text{PhNH})(N\text{Pµ-N})Ta_2]$ (19).

<table>
<thead>
<tr>
<th></th>
<th>$[N(µ-P=N)Ta(µ-H)\text{2}(µ-N(N\text{HcP}_2))Ta[NPN]}$ (14)</th>
<th>$[(\text{PhNH})(N\text{Pµ-N})Ta_2]$ (19)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>$C_{70}H_{86}Hf,N_6P_2Si_4Ta_2$</td>
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<td>$P1$</td>
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<tr>
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<td><strong>β, deg</strong></td>
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<td><strong>no. of parameters</strong></td>
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<td><strong>R (F², all data)</strong></td>
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<tr>
<td><strong>Rw (F², all data)</strong></td>
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</tr>
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<td><strong>R (F, I&gt;σ(I))</strong></td>
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</table>

$R_1 (F^2, I>2σ(I)) = \Sigma |F_o - F_c|/\Sigma F_c; \quad R_w (\text{all data}) = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_c^2)^{1/2}$