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entitled

Group V Imido Complexes Bearing Mono-Anionic Acetophenone Imine Ligands

by

Abdollah Neshat

Submitted to the Graduate Faculty as partial fulfillment of the requirements

for the Doctor of Philosophy Degree in Chemistry

________________________________________________________________________

Dr. Joseph A. R. Schmidt, Committee Chair

________________________________________________________________________

Dr. Mark R. Mason, Committee Memebr

________________________________________________________________________

Dr. Viranga L. M. Tillekeratne, Committee Memebr

________________________________________________________________________

Dr. Dean M. Giolando, Committee Memebr

________________________________________________________________________

Dr. Patricia R. Komuniecki, Dean
College of Graduate Studies

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Ortho-metalation through C-H bond activation has been widely used as a means
to generate bidentate ligands that support metal complexes with catalytic activities in
hydroamination and alkyne hydroalkoxylation reactions. For this reason, many ligand
systems based on α,β-unsaturated ketones, esters and acetophenones have been the topic
of intense research in recent years. With late transition metals, chelation of the
acetophenone type ligands can be easily achieved through oxidative addition of the ortho
C-H bond. However, due to the high oxidation states of early transition metals, this route
cannot be utilized to successfully coordinate and synthesize analogous early transition
metal complexes. As discussed in Chapter Two, to achieve site-specific activation,
acetophenone imines were treated with n-BuLi.

The major goal of the research presented in this dissertation involved the
synthesis and characterization of a series of niobium and tantalum imido complexes with
these mono-anionic ortho-metalated acetophenone imine ligands. The products were
characterized using NMR spectroscopy, mass spectrometry, and elemental analysis.
These low symmetry complexes are produced with only one or two isomers in all cases and display interesting correlations between the steric bulk of the ligands employed and the isomers isolated. Crystal structures of several new niobium and tantalum complexes are presented as confirmation of the structural isomers produced. The reactions of the activated acetophenone imine ligands with several group V imido precursors demonstrate a few trends. For example, depending on the steric bulk of the imido group, more than one structural isomer was frequently generated and the ratio of these structural isomers varied depending upon the reaction temperature employed. In order to fully understand the steric and electronic effects of the acetophenone imine ligands on the structure and properties of the resulting metal complexes, more detailed studies were undertaken through the synthesis of a series of niobium and tantalum complexes by varying the size of the substituents on both imine and imido groups. Full details on this study are presented in Chapter Three.

To delineate the reactivity of these new metal complexes and to obtain potential catalyst precursors, we also undertook an investigation of the substitution chemistry accessible by derivatization of the metal halogen bond. Each derivatized complex was produced as a single isomer and fully characterized using NMR spectroscopy, elemental analysis, and X-ray crystallography. The successful isolation and characterization of derivatization reaction products of the niobium imido complex $L_2\text{NbCl(NAr)}$ ($L = \text{ortho-metalated acetophenone imine}$, $\text{Ar} = 2,6-\text{Pr}_2\text{C}_6\text{H}_3$) with carbon and oxygen donor ligands such as Me, Me$_3$SiCH$_2$, PhC≡C, Me$_3$SiC≡C, CF$_3$SO$_3$, and MeO are described. These more reactive $\sigma$-donor ligands were readily installed in place of the chloride ligand through salt metathesis reactions. The trimethylsilylmethyl complex showed significant
α-agnostic interactions between the methylene group and the niobium center. Similar strategies to derivatize the chloride complex utilizing lithiated amides (LiNMe₂, LiNEt₂, LiN₄Pr₂, and LiNC₃H₁₀) resulted in the production of a niobium-hydride species due to β-hydrogen elimination processes. All of the resulting C₁ symmetric complexes were formed as predominantly a single isomer and fully characterized using a combination of ¹H and ¹³C NMR spectroscopy, elemental analyses, and X-ray crystallography, when possible.
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Finally, it is time to close another important chapter in academic life before opening a new one and starting a new career. The past five years has been very challenging and rewarding times of my life. As it is hard to imagine the formation of any molecule without atoms (some sort of Chemistry rule, I guess), I can’t imagine earning a PhD degree from UT without the support and guidance of the following people.

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Chapter 1

A Brief Introduction to Bidentate Ligands, Ortho-Metalation, Hydroamination Reactions, and Group V Metal Imido Complexes

1.1 Bidentate Ligands in Organometallic Chemistry

The development of cyclopentadienyl-type ligands and the subsequent synthesis and isolation of ferrocene and titanocene complexes helped to construct the basis of modern organometallic chemistry about six decades ago.\textsuperscript{1-3} The theoretical and practical perspectives of this newer branch of chemistry are multifarious. On an academic level, curiosity in understanding the nature of metal-carbon bonds and their interactions not only has helped theoretical chemists to add more quantitative insights to the metal-ligand bonding theory, but also has expanded the technical knowledge of the synthesis of organometallic compounds to almost all metals and metalloids across the periodic table.\textsuperscript{4-7} Moreover, the development of organometallic compounds such as Grignard reagents and Ziegler-Natta polymerization catalysts has resulted in a host of efficient and cost-effective methodologies for the synthesis of organic and polymeric compounds with a broad range of applications.\textsuperscript{8-12} Undoubtedly, the careful selection of a metal and ligand
pair plays an important role in the utility of the resulting metal complexes as stoichiometric or catalytic reagents in organic reactions. This motif has led to the development of important classes of organometallic compounds for use in polymerization,\textsuperscript{13-17} hydroamination,\textsuperscript{18-20} hydrosilylation,\textsuperscript{21-25} and olefin metathesis reactions.\textsuperscript{26-30}

In simple terms, a ligand is an atom or a molecule that binds to a metal atom or ion. Depending on the type of binding atom, the resulting metal complex can be referred to as a coordination complex or an organometallic complex. In this regard, according to the general classification of compounds among chemists, a molecule is considered an organometallic compound if it contains at least one direct, single or multiple, metal-carbon bond. Moreover, two or more atoms of a ligand can participate in binding to the central metal, in which case the ligand system is referred to as bidentate or polydentate, respectively.

In 1925, Chugaev reported the first example of a platinum(II) complex bearing a bidentate ligand, generated by the addition of hydrazine to a platinum(II) isocyanide complex in the presence of a strong acid (Scheme 1-1).\textsuperscript{31} Although detailed information about the structure of this metal complex and its remarkable applications were revealed later, studies on the relative stability of such molecules introduced the chelate effect, which is caused by an overall increase in entropy when two monodentate ligands in a metal complex are replaced by one bidentate ligand.\textsuperscript{32-33}
Scheme 1-1. First example of a metal complex supported by a bidentate ligand.

Since such discoveries, bidentate ligands, as the first class of polydentate ligand, have played an important role in the development of homogeneous catalysts, especially with the main group elements and the late transition metals. Undoubtedly, compared to ligands with higher denticity, the simplicity of their synthesis, as well as the ease of their steric and electronic modification, has been one of the key factors in the extensive research on metal complexes bearing bidentate ligands.\textsuperscript{34-36}

One general approach to construct an organometallic complex bearing a bidentate ligand, especially with d-block elements, employs a cyclometalation reaction. This approach requires the presence of a heteroatom close to a C-R bond (R = H, C, N, O, Si, P). Initial coordination of the metal to the heteroatom and subsequent C-R bond activation are the necessary steps for the effectiveness of this procedure.\textsuperscript{37} An alternative method, often used to construct early transition metal complexes with C-N donor ligands, begins with a pre-functionalization step, such as \textit{ortho}-lithiation of an organic compound, followed by subsequent salt metathesis between the pre-functionalized organic molecule and the early transition metal salt.\textsuperscript{38} This approach is often utilized to construct organometallic complexes with the elements of group IV and V.
1.2 Ortho-metalation

Ortho-metalation is defined as the ability of certain substituents in an aromatic or heterocyclic ring to cause metalation to occur exclusively in the position ortho to that substituent. The early independent works by Gilman and Wittig on aromatic ethers, such as anisole, or on a variety of cyclic ethers using strong bases, such as alkyllithium reagents, showed that the presence of a heteroatom induces substitution of the hydrogen atom ortho to that heteroatom (Scheme 1-2). This simple yet remarkable discovery provided the basis for the concept of ortho-metalation, which now functions as a powerful tool to functionalize aromatic compounds. Subsequently, it also attracted extensive research on related aromatic and cyclic systems containing different functional groups with heteroatoms such as oxygen, sulfur, and nitrogen.

![Scheme 1-2](image)

**Scheme 1-2.** ortho-Metalation and subsequent functionalization of an aromatic ring.

Mechanistically, as depicted in Scheme 1-3, ortho-metalation occurs in two steps. The first step involves coordination of the metalloreagent to the heteroatom. In the second step, the ortho position is deprotonated, likely via an agostic intermediate to yield the ortho-metalated species shown. The addition of an electrophile allows for replacement of the metal atom to form a substituted aromatic compound.
In the early 1960’s, Hauser et al. reported the lithiation of benzyldimethylamine and similar tertiary amines. They also briefly discussed the mechanism of these reactions. Based on evidence from deuterium labeling studies, IR and $^1$H NMR spectroscopy, metalation of benzyldimethylamine I resulted in ring deuterated benzylamine IIa, not IIb (Figure 1-1).

Figure 1-1. ortho-Metalation of benzyldimethylamine.

Although many ortho directors have been identified, a good ortho director must possess certain characteristics in order to successfully promote the ortho-metalation process. For example, it should be inert to nucleophilic attack by the deprotonating reagents, and it also should coordinate well to the metal alkyls used, often alkyl lithium
reagents. Therefore, the type of heteroatom, size and overall charge of the ortho directing group plays an important role in determining its ortho directing ability. Factors determining ortho directing power become even more complicated in systems containing two ortho directors. In such cases, other chemical aspects of an ortho director, such as its inductive effect or even the metalation conditions used dramatically influence the outcome of the ortho-metallation reaction. For example, Slocum and Jennings have reported the ortho directing strengths of various groups in the ortho-metallation of para-substituted anisoles under a variety of reaction conditions (Figure 1-2).

\[
\text{DMG = SO}_2\text{NR}_2, \text{SO}_2\text{N}^-, \text{CON}^-, \text{CH}_2\text{NR}_2 > \text{OMe}, \text{CH}_2\text{CH}_2\text{NR}_2, \text{NR}_2, \text{CF}_3, \text{F}
\]

**Figure 1-2.** Ortho directing power of different functional groups.

Further studies on the substitution patterns of similar systems by Beak and Brown demonstrated that the order of ortho directing ability was substantially affected by the degree of intramolecular interactions (Figure 1-3).

\[
\text{DMG = CON}^-, \text{CONR}_2 > \text{C}_6\text{H}_5\text{NO} > \text{SO}_2\text{NR}_2, \text{SO}_2\text{N}^-, \text{CH}_2\text{NR}_2, \text{OMe}, \text{Cl}
\]

**Figure 1-3.** Ortho directing power of different functional groups with intramolecular interactions.
For practical utilization of the ortho-metalation phenomenon, especially in large-scale reactions, in addition to the proper choice of ortho directing group, parameters such as the type of alkylating reagent, reaction temperature, type of complexing reagents, and the choice of solvent play an important role. For example, studies by Gschwend\textsuperscript{52} on the lithiation of complex molecules such as aryloxazolines have shown that simple changes in reaction conditions such as ice-bath controlled temperature, the use of anhydrous ether, and the use of \(^n\)BuLi could improve upon the harsh reaction conditions involving Grignard reagents previously reported by Meyers et al.\textsuperscript{53} Additionally, as shown in Scheme 1-4, this method was utilized as an effective tool for the derivatization and transformations of aryloxazolines.

\begin{center}
\includegraphics[width=\textwidth]{Scheme_1-4.png}
\end{center}

**Scheme 1-4.** ortho-Metalation and derivatization of an oxazoline.

### 1.3 Hydroamination

Hydroamination is a chemical process involving the addition of a primary or secondary amine’s N-H bond across an unsaturated C-C bond in alkyne, alkene, allene, and diene substrates. Considering the fact that the majority of pharmaceuticals and biologically active molecules contain at least one C-N bond, it is important to develop catalytically viable reactions to facilitate C-N bond-forming reactions in order to satisfy growing industrial and academic demands for bioactive organic molecules. Early
attempts to address this demand involved complicated organic chemistry, which often
required harsh reaction conditions or the use of radical species to promote C-N bond
formation. For example, in 1954, Howk discovered that in the presence of alkali metals,
primary amines reacted with alkenes.\textsuperscript{54} According to this report, even at high
temperatures near 200 °C and reaction pressures around 800 atm, product yields were
typically poor. A plausible atom-efficient route to address this problem involves catalytic
hydroamination utilizing transition metal complexes.

\textbf{Scheme 1-5.} Addition of a primary amine to an alkene and alkyne.\textsuperscript{55}

Reaction products of the addition of an amine to alkene and alkyne substrates are
shown in Scheme 1-5. Major factors limiting the scope of this procedure are proposed to
be the electrostatic repulsion between the electron lone pair of the amine nitrogen atom
and the \(\pi\) electrons of the unsaturated substrate, as well as the energy mismatch between
the N-H \(\sigma\) bond and the unsaturated C-C bond energy level. Combination of these two
factors raises the activation energy barrier for direct amine addition to an unsaturated substrate.\textsuperscript{56}

Early attempts to overcome these large activation energy barriers included the use of catalysts based on lanthanide metal complexes.\textsuperscript{57} Although a great deal of success has been achieved using lanthanide catalysts, especially for intramolecular hydroamination, the limited scope and significant oxophilicity of lanthanide complexes has provided an impetus for the development of more robust systems, especially for intermolecular hydroamination reactions.\textsuperscript{18,59-60} As shown in Chart 1-1, there has been a growing interest in designing early and late transition metal complexes for intermolecular hydroamination. Despite great successes during the past 25 years, there are still lingering problems associated with hydroamination that remain an open area of research for scientists. According to a recent survey of the scientific community, some of these current challenges include functional group tolerance of the early transition metal catalysts, enantioselectivity in intramolecular hydroamination, and regioselectivity associated with alkene and alkyne substrates.\textsuperscript{61}
General mechanisms for the hydroamination of alkenes and alkynes are shown in Schemes 1-6 through 1-9. With late transition metal catalysts, the initial step of hydroamination often involves coordination of the alkene substrate. Subsequent nucleophilic attack of the amine on the activated olefin results in an aminoalkyl species, which, depending on the reaction conditions, can produce hydroamination or oxidative amination products (Scheme 1-6).^{56}

**Scheme 1-6.** Late metal assisted alkene oxidative amination (upper) and hydroamination (lower).^{56}
As mentioned previously, primary amines can be added to alkenes in the presence of alkali metals. Deprotonation of the amine by the metal yields a highly nucleophilic amido species that can attack the olefins more effectively (Scheme 1-7). However, this method has not gained much popularity for the hydroamination of alkenes due to the lack of control of the reaction products, poor reaction yields, and the necessity for stoichiometric amounts of alkali metal reagents.\(^{54, 62-64}\)

\[
\begin{align*}
\text{H-NR}_2 + \text{MR}^+ \rightarrow \text{M-NR}_2 & \rightarrow \text{M-} \text{NR}_2 \rightarrow \text{NR}_2 + \text{M}^+ \\
\text{e.g. } M = \text{Li, Na}
\end{align*}
\]

**Scheme 1-7.** Alkali metal assisted alkene hydroamination.\(^{56}\)

Zirconium and uranium amides effect catalytic hydroamination through similar mechanisms. As shown in Scheme 1-8, the active catalysts are actually the metal imido complexes, which result from amine elimination from metal bisamide catalyst precursors. Cycloaddition of these metal imido complexes with olefins and subsequent release of hydroamination products in the presence of excess amine substrate regenerates the metal imido catalyst while yielding the hydroamination reaction product.\(^{64-66}\)

\[
\begin{align*}
\text{H}_2\text{NR} + \text{L}_n\text{MR}^+ \rightarrow \text{L}_n\text{M=NR} & \rightarrow \text{L}_n\text{M-}\text{NR} \rightarrow \text{NHR} + \text{L}_n\text{M}=\text{NR} \\
\text{e.g. } M = \text{Zr, U}
\end{align*}
\]

**Scheme 1-8.** Early transition metal assisted alkene hydroamination.\(^{56}\)
Although less explored than other late transition metals, rhodium and iridium complexes have shown good catalytic activity for both intramolecular and intermolecular hydroamination reactions. Catalysts based on these metals can also participate in multi-step one-pot catalytic processes. Unlike most other transition metals, in these processes the rhodium or iridium complex catalyzes a hydroamination reaction and then a subsequent hydrosilylation reaction of the resulting hydroamination product in sequence. This process has been especially useful in generating a chiral center in the second step of the catalytic process when the product of the hydroamination reaction does not include a chiral center. The hydroamination reaction utilizing rhodium and iridium metal complexes is thought to involve oxidative addition of the amine substrate followed by subsequent insertion of the olefin (Scheme 1-9). Depending on the olefin employed, olefin insertion into the metal hydride or metal nitrogen bond can produce different hydroamination regioisomers.

![Scheme 1-9. Alkene hydroamination utilizing rhodium and iridium metals.](image)

1.4 Hydroamination Catalysts Based on Early Transition Metals

The first early transition metal hydroamination catalyst that showed a rich chemistry and compelling activity for the intermolecular hydroamination of alkynes and
dienes was reported by Bergman in the early 1990s.\textsuperscript{64} According to his report, when catalytic amounts of \( \text{Cp}_2\text{Zr}(\text{NHAr})_2 \) (\( \text{Cp} = \text{cyclopentadienyl}, \text{Ar} = 2,6-\text{Me}_2\text{C}_6\text{H}_3 \)) were heated to 90-120 °C in the presence of aniline and 2-butyne or diphenylacetylene, the enamine products shown in Scheme 1-10 were formed in high yields.

\[
\text{H}_2\text{NAr} + \text{R} = \text{R} \xrightarrow{\text{Cp}_2\text{Zr}(\text{NHAr})_2, 3 \text{ mol}\%} \text{NHAr}
\]

\( \text{Ar} = 2,6-\text{Me}_2\text{C}_6\text{H}_3 \)
\( \text{R} = \text{Ph}, \text{Me} \)

**Scheme 1-10.** Zirconium bisamide as intermolecular hydroamination catalyst.\textsuperscript{64}

According to the proposed mechanism for the alkyne and diene hydroamination reaction (Scheme 1-11), the active species in this catalytic reaction is a transient zirconium imido complex, \( \text{Cp}_2\text{Zr}=\text{NAr} \) (\( \text{Ar} = 2,6-\text{Me}_2\text{C}_6\text{H}_3 \)). This imido complex is formed when the starting bisamide complex undergoes a slow and reversible \( \alpha \)-elimination upon thermolysis. Although, the zirconium imidos have never been isolated from these catalytic reactions, they can be trapped by the addition of an unsaturated substrate such as 2-butyne, which subsequently forms an azametallacyclobutene. Notably, the presence of excess amine substrate competes with azametallacycle formation, regenerating the starting bisamide zirconium metal complex and hindering catalysis. The last step in the mechanistic cycle involves the addition of a second equivalent of amine to the metallacyclic intermediate, liberating the enamine and regenerating the zirconium imido complex.
Scheme 1-11. Catalytic cycle of intermolecular hydroamination utilizing a bisamide zirconium complex.\textsuperscript{64}

Despite these promising results, the zirconium bisamide catalyst system is limited in scope and application. For example, the slow and reversible $\alpha$-elimination step in the catalytic cycle is suggested to proceed to release the steric congestion of the amide ligands around the metal center.\textsuperscript{64} Based on this theory, it is reasonable to assume that this step will proceed faster with larger bisamide ligands in comparison to smaller bisamide ligands. However, zirconium complexes with bulky amide ligands, such as NHSiMe\textsubscript{2}(\textsuperscript{t}Bu), show no reactivity in the hydroamination of alkynes, even at elevated temperatures and prolonged reaction times. Further studies on this system revealed that even though the bulky zirconium bisamide complex undergoes $\alpha$-elimination and forms
the desired imido complex, the reactivity of its diphenylacetylene metallacyclic adduct is dramatically decreased when the second amine molecule is added to protonate the metallacycle and release the enamine product. This observation suggests that the bulkier ligand enhances the rate of the α-elimination step, but at the same time it reduces the overall rate of the reaction by lowering the rate of protonolysis of the metallacyclic adduct. Further complicating matters, with less bulky amides or smaller ancillary ligands surrounding the zirconium metal center, the analogous zirconium imido complexes are in equilibrium with non-catalytically active dimers that further limit the efficiency of these metal complexes as catalysts.

Despite mechanistic similarities, an analogous titanium amido hydroamination catalyst revealed major differences in reaction kinetics. Specifically, with the titanium bisamide complex, protonation of the azametallacycle is shown to be the slowest step, while with the corresponding zirconium bisamides, α-elimination of amine from the bisamide zirconium complex was proposed to be the rate-determining step.

Even with great successes in the hydroamination of a variety of alkyne, diene and allene substrates, to date there is no report of a generally successful alkene hydroamination catalyst using group IV metal imido complexes. Bergman attributes this issue to the inadequate electron density on the alkene substrates compared to alkyne and diene substrates.

In contrast, a number of neutral and cationic group IV metal complexes have been shown to catalyze the intramolecular hydroamination of primary and secondary aminoalkene substrates in a manner similar to the organolanthanide hydroamination
catalysts first reported by Marks. Intramolecular hydroamination is thermodynamically less challenging compared to intermolecular hydroamination of alkene and alkyne substrates. Overall, the majority of the catalytic systems for intramolecular aminoalkene hydroamination still suffer from a lack of enantioselectivity. The general mechanism for the hydroamination of a secondary aminoalkene utilizing cationic group IV metal complexes is shown in Scheme 1-12. Similar to the metal imido catalysts described above, the steric bulk of the amine substrate greatly affects the overall performance of these catalyst systems. For example, some dimeric or metal imido species are observed with the less bulky aminoalkene substrates, both of which reduce the yield of these catalysts.

**Scheme 1-12.** Secondary aminoalkene hydroamination in the presence of a cationic group IV metal complex.

According to the mechanism shown in Scheme 1-12, olefin insertion into the metal-amido bond is a critical step in the catalytic cycle. Therefore, the presence of a
functional group close to the olefin moiety in the aminoalkene substrate that enables olefin activation can greatly impact the success of these hydroamination catalysts. In a report by Scott et al.,\textsuperscript{71} a cationic zirconium complex employing a bulky ancillary chiral ligand effectively hydroaminated various inactive aminoalkenes. In this case, the Lewis acidity of the metal enhances the metal-olefin interaction and the bulky chiral ancillary ligand encourages better expression of the ligand chirality in the metal olefin interaction step (Figure 1-4). Furthermore, the enhanced Lewis acidity of the cationic metal center not only allows for a stronger interaction of the aminoalkene substrate, but it also adds to the rigidity of the metal-ligand bond, as compared to the more labile lanthanide-ligand bonds in other catalysts, which ultimately results in higher activity and better enantioselectivity.\textsuperscript{72}

![Figure 1-4. Chiral zirconium hydroamination catalyst.\textsuperscript{71}](image)

In addition to the cationic group IV metal complexes, many neutral group IV imido complexes also function as active catalysts for the hydroamination of primary aminoalkenes (Scheme 1-13).\textsuperscript{73-76} These catalysts employ a mechanism quite similar to
that observed by Bergman in the initial report of zirconium imido catalysts, as discussed above.

Scheme 1-13. Primary aminoalkene hydroamination in the presence of a neutral group IV metal complex.\textsuperscript{73}

There have also been a few examples of group V metal imido complexes with applications in intermolecular hydroamination catalysis.\textsuperscript{77} The most recent report by Bergman et al. demonstrated that the tantalum alkyl imido complex shown in Figure 1-5 effectively catalyzes the intermolecular hydroamination of alkynes, dienes, and allenes, following a similar catalytic pathway to its group IV counterparts. Interestingly, in this report it was shown that this newly developed highly electron deficient catalyst not only catalyzed the hydroamination reaction of the usual substrates, but was also successful in the hydroamination of unusual substrates, such as the reaction of norbornene with aniline.
1.5 The Importance of Group (V) Metal Imido Complexes

Studies by Gibson on bonding patterns in tetrahedral transition metal complexes indicate that the relative $\pi$-bonding strength of a metal-ligand bond can be deduced from the electronegativity of the main group element present. Therefore, he arranged the $\pi$-bonding strength of some important ligand classes as: $\text{RC}_3^3 > \text{N}_3^3 > \text{RN}_2^2 > \text{O}_2^2 > \text{RO}^- > \text{F}^-$ (R = alkyl, aryl). To verify this relative order, the stretching frequency of CO ligands has been measured in a series of octahedral tungsten complexes where the above $\pi$-bonding ligands were oriented trans to the CO ligand. A decrease in the CO stretching frequency was observed with strong $\pi$ donor ligands, such as the imido ligand, when oriented trans to the CO ligand.

As an extension to the isolobal relationship model developed by Hoffmann, Gibson has also shown that the imido group can be used as an alternative to the Cp ligand. This isolobal relationship is derived from a comparison of the energy levels and the symmetries of the frontier orbitals of the two ligands. The frontier orbital energy levels of Cp and imido ligands are shown in Figure 1-6.
The relatively low electronegativity of nitrogen, as well as the availability of one \( \sigma \) and two \( \pi \) orbitals in the imido ligand (with the same number of electrons) causes this ligand to be considered a very close alternative to the Cp ligand. Figure 1-7 illustrates how the isolobal relationship between Cp and imido ligands is used to construct alternatives to the bis-Cp zirconium complex using higher oxidation state metals such as niobium and molybdenum.\(^7\) Therefore, the construction and classification of ligands based on isolobal concepts may well serve as a useful basis for the development of new generations of functional transition metal complexes.

The imido ligand, being a strong \( \pi \)-donor ligand with ample opportunities for steric and electronic modification, provides a strong coordination environment for a metal center. For this reason, a significant amount of research has utilized the imido ligand (RN\(^2-\); R = alkyl, aryl) in the areas of thin films, coordination chemistry and...
organometallic chemistry. In the thin films industry, tantalum imido coordination complexes have served as precursors for the deposition of tantalum nitride (TaN) films. The major utility of the tantalum nitride films is in the area of microelectronics, where they serve as gate metal electrode materials in metal oxide semiconductors. Among the well-known techniques for thin film deposition, metal organic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD) techniques both utilize the volatility and high vapor pressure of metal organic precursors, such as tantalum complexes with mixed imido/amido, imido/alkoxo, or imido/bidentate N-donor ligands. It has been shown that the steric and electronic properties of the supporting ligands of these tantalum complexes can dramatically influence the quality of the deposited thin film. For example, when the supporting ligands are mixed imido/bidentate N-donor ligands, the carbon content of the resulting metal nitride film is greatly reduced, resulting in more homogeneous and higher quality thin films. This ligand effect has been attributed to the higher stability of the metal complex in the vapor phase during the deposition process. Specifically, the tantalum complex shown in Figure 1-8 has been reported as one successful precursor for the deposition of low carbon content tantalum nitride thin films at relatively low temperatures.
In the areas of organometallic and coordination chemistry, early metal imido bonds are more reactive than those involving the middle transition elements. Some examples of the broad range of reactivity supported by metal-imido complexes include C-H bond activation,\textsuperscript{83-86} cyclometallation with unsaturated substrates,\textsuperscript{87-89} H\textsubscript{2} activation,\textsuperscript{90} imine metathesis,\textsuperscript{91-93} and catalytic hydroamination reactions.\textsuperscript{64-67} Group IV neutral and cationic imido complexes have been a specific focus area, primarily because of observations of useful reactivity and good selectivity. Since similar mechanistic pathways are often followed by both group IV and V metal imido species, as noted in the area of catalytic hydroamination, in recent years the quantity and quality of research works published on the group V metal imidos has increased rapidly. This is partly due to the development of new ligand systems, which together with the imido ligand can provide robust metal complexes for catalytic and stoichiometric reactions.
1.6 The Aim and Outline of the Work Presented Herein

The importance of bidentate ligands and information about some strong \( \pi \)-donors, such as imido-type ligands, has been presented briefly in Sections 1-1 and 1-5 of this chapter. A survey of known group V metal imido species shows that the majority of these complexes take advantage of the presence of a second ligand system, such as cyclopentadienyl, alkoxy, amido, or bidentate ligands with N, N or O, N donor groups.\(^{94-98}\) As a contribution to this field of chemistry and to test the stability, reactivity and potential catalytic utility of the resulting metal complexes, we aimed to synthesize a series of group V metal imido complexes supported by activated acetophenone imine ligands.

The synthesis, characterization, and the site-specific lithiation of a series of acetophenone imines using strong alkyl lithium reagents such as \(^{8}\)BuLi, are presented in Chapter 2. The site-specific lithiation of these imines was achieved because of electronic effects due to the presence of a methylenedioxy moiety. Some details about the imine substituent’s influence on the clustering of the lithiated products are also presented in this chapter. In Chapter 3, a series of niobium and tantalum imido complexes with activated mono-anionic ortho-metalated acetophenone imine ligands are presented. They were characterized using NMR spectroscopy, mass spectrometry, and elemental analysis. These low symmetry complexes are produced with only one or two isomers in all cases and display interesting correlations between the steric bulk of the ligands employed and the isomers isolated. Finally, in Chapter 4, the successful isolation and characterization of derivatization reaction products of the niobium imido complex \( \text{L}_2\text{NbCl(NAr)} \) (\( \text{L} = \text{ortho-} \)
metalated acetophenone imine, Ar = 2,6-iPr₂C₆H₃) with carbon and oxygen donor ligands such as Me, Me₃SiCH₂, PhCC, Me₃SiCC, CF₃SO₃, and MeO are described. These more reactive σ-donor ligands were readily installed in place of the chloride ligand through salt metathesis reactions. Similar strategies to derivatize the chloride complex utilizing lithiated amides (LiNMe₂, LiNEt₂, LiNPr₂, and LiNC₅H₁₀) resulted in the production of a niobium-hydride species due to β-hydrogen elimination processes. All of the resulting \( C \)-symmetric complexes were formed as predominantly a single isomer and fully characterized using a combination of \(^1\)H and \(^{13}\)C NMR spectroscopy, elemental analyses, and X-ray crystallography, when possible.
Chapter 2

Mono-Anionic Acetophenone Imine Ligands: Synthesis, Ortho-Lithiation and Spectroscopic Studies

2.1 Introduction

Bidentate ligands have contributed vastly to the development of coordination and organometallic compounds.\textsuperscript{99-103} The need to better control a metal center’s electronic and steric properties by tuning the structure of the supporting ligands and the desire to achieve a higher selectivity for specific reaction products, especially with asymmetric catalysts, has made bidentate ligands a preferred choice over monodentate ligands.\textsuperscript{104-108} Among this class of ligands, the chemistry of C, N donor bidentate ligands is less explored. This limitation is largely attributed to the additional synthetic steps in their development that require, in some cases, non-trivial procedures.\textsuperscript{109} This limitation in the development of bidentate ligands is more pronounced when a diverse library of bidentate ligands or a large scale synthesis of them is planned. For example, one route to generate an anionic carbon donor ligand requires the activation of a C-H bond through oxidative addition by a metal atom, preferably in its medium to low oxidation state. Using this method, a number of useful catalysts with late transition metals and ligand systems such as \(\alpha,\beta\)-unsaturated ketones, esters and acetophenones have been developed.\textsuperscript{110-113}
However, due to the high oxidation states of early transition metals, this route cannot be utilized to successfully coordinate and synthesize analogous early transition metal complexes. As discussed in Chapter One, an alternative method to construct early transition metal complexes with carbon donor ligands begins with a pre-functionalization step such as ortho-lithiation of an organic compound, followed by subsequent salt metathesis between the pre-functionalized organic molecule and the early transition metal halide salt.\textsuperscript{38}

In addition to supporting metal centers as ancillary ligand systems, many bidentate ligands with C, N and C, C donor atoms can also participate in C-C bond-forming reactions, especially with group IV metals.\textsuperscript{114-116} This process is believed to proceed through a variety of pathways including reductive elimination,\textsuperscript{117-118} oxidative coupling,\textsuperscript{119-121} and migratory insertion.\textsuperscript{122-123} Therefore, the development of new metal complexes capable of C-C bond-forming reactions might help to further understand mechanistic aspects of the coupling reactions and also assist in the development of more reactive metal catalysts for organic molecule production.

\textit{ortho}-Lithiated imines provide an exciting new entry to C, N donor bidentate ligands.\textsuperscript{124} The lithiation of these imines can be directed by the incorporation of \textit{ortho}-directing functional groups, such as the methoxy group. In 1975, Ziegler and Fowler successfully \textit{ortho}-lithiated piperonal cyclohexylimine using n-butyllithium (\textit{n}BuLi) and isolated the subsequent product of its reaction with iodine.\textsuperscript{47} Given its electronic similarities to the methoxy group, the methylenedioxy functionality pioneered by Ziegler and Fowler undoubtedly has an \textit{ortho}-directing effect. Indeed, several \textit{ortho}-lithiated
compounds have been isolated incorporating the methylenedioxy group, including amides$^{125}$, amines$^{126}$ and thioethers$^{127}$.

Although the original work on the synthesis and characterization of most of the ancillary ligands represented in Scheme 2-1 has been initiated by our previous group members$^{25}$, continued research on similar ligands was also undertaken by the author of this dissertation in tandem with another group member$^{124,128}$. The main goal was to modify the reaction conditions and to complete the spectroscopic characterization of the ortho-lithiated imine ligand series in order to further investigate their ability as supporting ligands for main group and early transition metals. Details of the synthesis and spectroscopic characterization of some of the ligands ($\text{Li-L}_1^2$, $\text{Li-L}_4^4$, $\text{Li-L}_{6-8}$; Scheme 2-1) utilized in this study for the synthesis of group V metal imido complexes are presented herein.

**Scheme 2-1.** The synthesis and ortho-lithiation of imines.$^{124}$
2.2 Results and Discussion

**Imine Synthesis and *ortho*-Lithiation.** In the initial communication, our group showed that the acetophenone imine (H-L<sub>6</sub>) produced by the Schiff-base condensation reaction between 3,4-methylenedioxyacetophenone and 2,6-diethylaniline could be regioselectively deprotonated to produce a new mono-anionic bidentate ligand (Li-L<sub>6</sub>).<sup>38</sup> This new ligand was then successfully utilized in the synthesis of a series of titanium and zirconium complexes.<sup>38</sup> In an effort to lend steric and electronic diversity to this new ligand class, we have expanded the synthesis of these imines to include a much broader array of substituents (Scheme 2-2). Two new ketimines were formed by the Schiff-base condensation of 3,4-methylenedioxyacetophenone with 2,6-dimethylaniline (H-L<sub>4</sub>) and 2,6-diisopropylaniline (H-L<sub>8</sub>). Additionally, a related aldimine was produced by the Schiff-base condensation of piperonal with 2,6-diisopropylaniline (H-L<sub>7</sub>). Each of these imines was readily synthesized in refluxing toluene using a Dean-Stark trap to drive the reaction to high yield, and purification was effected by vacuum distillation.

![Scheme 2-2](image)

**Scheme 2-2.** Imine synthesis proceeds through a Schiff-base condensation reaction (R = Me; R' = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (H-L<sub>4</sub>), 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (H-L<sub>6</sub>), or R = H; R' = 2,6-′Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (H-L<sub>7</sub>), R' = 2,6-′Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (H-L<sub>8</sub>)).

In contrast, the Schiff-base condensation of 3,4-methylenedioxyacetophenone with tert-butylamine (′BuNH<sub>2</sub>) was not successful under any of the conditions tested. One possible explanation for this result is the formation of an ammonium salt when the
\( \text{tBuNH}_2 \) is mixed with the acid catalyst \((p\text{-toluene sulfonic acid})\), hindering its reactivity rather than activating the ketone to nucleophilic attack. Another possible explanation concerns the low boiling point of \( \text{tBuNH}_2 \); it may escape the Dean-Stark apparatus at the elevated temperature required to bring benzene or toluene to reflux. In order to overcome these synthetic challenges, the desired imine was produced by an alternative synthetic pathway involving the use of an imido titanium complex as the imine source. Thus, \( \text{H-L}^2 \) was synthesized in moderate yield by the reaction of 3,4-methylenedioxyacetophenone with one equivalent of \((\text{py})_3\text{Cl}_2\text{Ti(N}^\text{tBu}),\) with the poorly soluble titanium oxo byproduct readily removed by filtration (Scheme 2-3). The strong driving force of metal oxide formation promotes this reaction, yielding the desired imine.

\[
\text{Scheme 2-3. Synthesis of imine } \text{H-L}^2 \text{ utilizes an imido titanium reagent.}
\]

The imines \((\text{H-L}^2, \text{H-L}^4, \text{H-L}^{6-8})\) were lithiated with \( \text{nBuLi} \) to produce a series of mono-anionic bidentate ligands (Scheme 2-4). The electron-withdrawing methylenedioxy moiety (-OCH\(_2\)O-) helps to activate the adjacent aryl protons toward deprotonation by strong bases. Additionally, the electron pair on the nitrogen atom coordinatively directs the lithiating agent to deprotonate the aromatic ring in an ortho position. The combination of these effects allows for regiospecific lithiation of these imines by \( \text{nBuLi} \) at the carbon atom ortho to both groups. The steric bulk at the imine position has proven to be important in the stability of the lithiated acetophenone imines. For most of these imines \((\text{H-L}^4, \text{H-L}^{6-8})\), the product lithiated species were produced by
straightforward room-temperature ortho-lithiation using \textsuperscript{\textsubscript{n}}BuLi; however, in the case of \textbf{H-L\textsuperscript{2}}, these reaction conditions led to substantial formation of byproducts. The observed unwanted products included lithiation at other positions on the aryl ring and addition products resulting from attack at the carbon of the imine moiety. The very bulky aryl groups sterically shield the imine carbon atom in acetophenone imines \textbf{H-L\textsuperscript{4}}, \textbf{H-L\textsuperscript{6}}, \textbf{H-L\textsuperscript{7}} and \textbf{H-L\textsuperscript{8}}, which helps to prevent the formation of unwanted byproducts during lithiation. In contrast, \textbf{H-L\textsuperscript{2}} has a smaller nitrogen substituent (tert-butyl). This less bulky group does not protect the imine as well, allowing the undesirable byproducts to readily form. In order to circumvent this problem, lithiation of \textbf{H-L\textsuperscript{2}} was accomplished by using lower reaction temperatures (-78 °C) for longer periods, in addition to more dilute reaction concentrations.

\textbf{Scheme 2-4.} ortho-Lithiation of the acetophenone imines.

The full range of lithiated products (\textbf{Li-L\textsuperscript{2}}, \textbf{Li-L\textsuperscript{4}}, \textbf{Li-L\textsuperscript{6-8}}) has been characterized by \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectroscopy, as well as by elemental analysis or high-resolution mass spectrometry. One notable feature of these materials is that the hydrogen atoms of the -OCH\textsubscript{2}O- moiety display very large changes in their chemical shifts upon lithiation. For each of the aryl imines (\textbf{Li-L\textsuperscript{4}}, \textbf{Li-L\textsuperscript{6-8}}), the two protons of this group remained equivalent and shifted to higher field, while the \textsuperscript{1}H NMR spectrum of \textbf{Li-L\textsuperscript{2}} (derived from an alkyl imine) showed that these two protons had become inequivalent,
with one shifting to higher field and one to lower field. The $^1$H NMR spectra of both H-L$_2^2$ and Li-L$_2^2$ are shown in Figure 2-1 to demonstrate this effect.

![Figure 2-1. $^1$H NMR spectra of H-L$_2^2$ (top) and Li-L$_2^2$ (bottom); methyl groups omitted for clarity.](image)

Note that in the spectrum of H-L$_2^2$ the -OCH$_2$O- protons are equivalent, appearing at 5.28 ppm. After lithiation, the two protons are no longer equivalent and now appear as two resonances at 5.48 and 4.51 ppm. The $^1$H NMR signals derived from the methylenedioxy moiety prove to be quite diagnostic in this ligand set. In fact, these protons are indicative of the ligand’s environment in its transition metal complexes, as discussed below for the group V metal complexes. It is postulated that upon lithiation, the acetophenone imine ligands form either large clusters or polymerized species in which
the ligands gather around groups of lithium ions.\cite{130-133} The formation of aggregates of this type can result in superstructures with lower overall symmetry, explaining the inequivalence of the two $^1$H NMR resonances for the -OCH$_2$O- moiety. To further understand the clustering pattern of the lithiated products and to explain the changes in the spectroscopic properties of the lithiated products, our group undertook a detailed study of these lithiated compounds.\cite{124} Lithiated aryl and alkyl imines showed a significant difference in their $^1$H NMR spectra and X-ray structures. For example, the structure of Li-L$_2$ was determined to be a tetramer in the solid state when recrystallized from ether. The four lithium atoms are in a pseudo-tetrahedral arrangement, where each lithium in the tetramer is four-coordinate, bound to a nitrogen atom of one ligand, two bridging aryl carbons from two different ligands and the oxygen of a fourth ligand (Figure 2-2).

![Crystal structure of Li-L$_2$.](image)

**Figure 2-2.** Crystal structure of Li-L$_2$.  

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The crystal structure of \textbf{Li-L}^2 also shows that one methylene proton of the methylenedioxy ring is oriented towards the imine alkyl group, while the other points toward the aryl backbone. Because of this dissymmetry, in the \textsuperscript{1}H NMR spectrum of \textbf{Li-L}^2, the two methylene protons of the five-membered ring are observed as singlets at 5.47 and 4.74 ppm. The pronounced upfield chemical shift of one of these singlets can be attributed to ring current effects due to the close proximity of the proton to the centroid of the adjacent aryl backbone (~3.96 Å in the solid state).\textsuperscript{134-136}

This observation is in remarkable contrast to the \textsuperscript{1}H NMR observed for the lithiated aryl imines (\textbf{Li-L}^4, \textbf{Li-L}^6-8). For the lithiated aryl imines, in all cases the two protons of the methylenedioxy unit were found to be equivalent on the solution NMR timescale. Also, spectra of these ortho-lithiated aryl imines showed reasonably upfield shifted methylenedioxy protons. For the initial imine, these protons appeared at approximately 5.2 ppm, while they shifted to approximately 4.9 ppm in the lithium complexes. These methylene protons were observed to be chemically equivalent, although they do appear slightly broadened in the \textsuperscript{1}H NMR spectra. Thus, based on the differences in NMR spectra, a different clustering motif must be present in solution for the ortho-lithiated aryl imines. Based on crystallographic studies, \textbf{Li-L}^8 crystallizes as a polymer chain of dimer units in non-coordinating solvents such as benzene. As shown in Figure 2-3, lithium atoms in each dimeric chain are bound to the bridging ortho-carbon atoms of two ligands, as well as a nitrogen atom from one ligand and an oxygen atom from the methylenedioxy ring of the other ligand. The methylenedioxy oxygen atom not involved in bonding within the dimer forms a dative bond to a lithium center on an adjacent dimer to link the chain. Thus, two different types of dimers exist within the
polymeric chain: “donor” dimers that provide electron density from the oxygen donor atom and “acceptor” dimers with lithium atoms coordinated by this oxygen donation. The two types of dimers give rise to two chemically inequivalent lithium centers in the solid state. The lithium centers of the “donor” dimer are square-planar and the lithium centers of the “acceptor” dimer are square-pyramidal.

Figure 2-3. ORTEP diagram of \((\text{Li-Li})_2^b\) with thermal ellipsoids drawn at 50% probability; hydrogen atoms and benzene solvent molecule have been omitted for clarity. Note the presence of the square-planar lithium atom Li1 in the “donor” dimer and the square-pyramidal lithium atom Li2 in the “acceptor” dimer. Atoms labeled with “i” and “ii” are generated by the following symmetry operators: \(-x + 1, -y, -z; -x + 1, -y, -z + 1\).
When lithiated aryl imines are crystallized from a coordinating solvent such as ether a disruption in the formation of the polymeric chain is observed. For example, \( \text{Li-L}^4 \) was crystallized from ether as a dimer (Figure 2-4). Each lithium atom within the dimer adopts a distorted square-pyramidal geometry. Similar to the lithium atoms of the dimeric units in the \( \text{Li-L}^8 \) polymeric chain, each lithium atom in \( \text{Li-L}^4 \) is coordinated to two bridging ortho-carbon atoms, as well as nitrogen and oxygen atoms from the separate ligands. The coordination environment of each lithium atom is completed by a dative bond from an ether molecule.

Figure 2-4. ORTEP diagram of \( (\text{Li-L}^4\cdot\text{Et}_2\text{O})_2 \) with thermal ellipsoids drawn at 50% probability, crystallized from diethyl ether. Hydrogen atoms removed for clarity.

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2.3 Experimental

2.3.1. Ligand Synthesis

All ligands except H-L\textsuperscript{2} were synthesized according to the procedure described below:

To a solution of 3,4-methylenedioxyacetophenone (5.00 g, 30.4 mmol) or piperonal (5.00 g, 33.3 mmol) in toluene (300 mL) was added the appropriate amine (45.6 mmol) along with \textit{p}-toluenesulfonic acid monohydrate (1.50 g). After heating the solution to 110 °C in a Dean-Stark trap for 2 d, the solution was neutralized with saturated NaHCO\textsubscript{3}(aq), washed with deionized water (2 x 30 mL) and the organic portion dried over anhydrous MgSO\textsubscript{4}(s). Volatiles were distilled under reduced pressure (120 °C, 200 mtorr), leaving the desired product behind. Each oil was recrystallized from methanol at -25 °C, yielding a pale yellow crystalline solid (H-L\textsuperscript{4}: 6.8 g, 84%; H-L\textsuperscript{7}: 8.0 g, 85%; H-L\textsuperscript{8}: 8.0 g, 81%).

Lithiation of the ligands was accomplished following the general procedure:

To a solution of the ligand (10 mmol) in pentane (100 mL) at 0 °C, \textsuperscript{n}BuLi (7.0 mL, 1.4 M in hexanes, 9.8 mmol) was added dropwise via syringe. Upon addition of the \textsuperscript{n}BuLi, the solution turned red. The solution was stirred for 1 h at -78 °C and brought to room temperature and stirred for 3 h. The solution was filtered and the solid was dried under vacuum, yielding a dark orange solid. The solid was washed with copious amounts of pentane to give analytically pure material.

H-L\textsuperscript{2}: 3,4-Methylenedioxyacetophenone (2.0 g, 12 mmol) and (py)\textsubscript{3}Cl\textsubscript{2}Ti(N\textsuperscript{t}Bu\textsuperscript{10} (5.0 g, 12 mmol) were dissolved separately in toluene (50 mL). Then, the reactants were mixed at 0 °C and stirred for 1 h. The solution was brought to room temperature and stirred for
24 h, forming a red slurry. The slurry was filtered and the liquid portion dried under vacuum. The yellowish oil was dissolved in pentane (30 mL), filtered and concentrated, yielding a light green oil (3.5 g, 52%); \(^1\)H NMR (C\(_6\)D\(_6\), 400 MHz): 7.825 (s, 1H), 7.189 (d, 1H, J= 8.4 Hz), 6.652 (d, 1H, J= 8.4 Hz), 5.281 (s, 2H), 1.899 (s, 3H), 1.328 (s, 9H); \(^{13}\)C\(^{\{1\}H}\) NMR (C\(_6\)D\(_6\), 150 MHz): 159.77, 149.34, 148.57, 138.10, 121.40, 108.06, 107.64, 101.45, 55.27, 31.20, 18.64; IR: 3078 (s), 2965 (m), 2780 (m), 2359 (m), 2050 (w), 1963 (w), 1845 (m), 1640 (s), 1609 (s), 1491 (s), 1434 (s), 1362 (s), 1275 (s), 1111 (m), 1039 (s), 936 (m), 884 (m), 813 (m). HRMS\(_{\text{calc}}\): 219.1259 for C\(_{13}\)H\(_{17}\)NO\(_2\). HRMS\(_{\text{meas}}\): 219.1263.

Li-L\(^2\): (0.9 g, 40%); \(^1\)H NMR (C\(_6\)D\(_6\), 400 MHz): 6.744 (d, 1H, J= 7.8 Hz), 6.591 (d, 1H, J= 7.8 Hz), 5.485 (d, 1H, \(^2\)J\(_{HH}\)= 1.8 Hz), 4.520 (d, 1H, \(^2\)J\(_{HH}\)= 1.8 Hz), 2.185 (s, 3H), 1.001 (s, 9H); \(^{13}\)C\(^{\{1\}H}\) NMR (C\(_6\)D\(_6\), 150 MHz): 178.21, 157.18, 151.80, 142.47, 120.82, 107.96, 97.28, 55.57, 33.49, 30.66, 22.86; \(^7\)Li\(^{\{1\}H}\) NMR (C\(_6\)D\(_6\), 155 MHz): \(\delta\) 2.820; IR: 2924 (s), 2855 (s), 2723 (w), 2361 (m), 1618 (m), 1559 (m), 1460 (s), 1375 (s), 1302 (s), 1268 (m), 1042 (s), 942 (m), 799 (w), 721 (w). Melting point: 125 °C (dec.).

H-L\(^4\): (6.8 g, 84%); \(^1\)H NMR (C\(_6\)D\(_6\), 600 MHz): 7.993 (s, 1H), 7.246 (d, 1H, J= 8.0 Hz), 7.050 (d, 2H, J= 8.0 Hz), 6.953 (t, 1H, J= 8.0 Hz), 6.638 (d, 1H, J= 8.0 Hz), 5.300 (s, 2H), 1.985 (s, 6H), 1.659 (s, 3H); \(^{13}\)C\(^{\{1\}H}\) NMR (CDCl\(_3\), 150 MHz): 159.23, 145.32, 143.11, 142.74, 129.31, 128.42, 126.09, 122.84, 122.17, 108.32, 101.65, 98.11, 18.42, 17.21; IR: 3069 (w), 3015 (w), 2941 (m), 2901 (m), 1639 (s), 1607 (s), 1593 (s), 1504 (s), 1488 (s), 1472 (s), 1440 (s), 1365 (s), 1344 (s), 1291 (s), 1251 (s), 1222 (s), 1203 (s), 1156 (w), 1113 (m), 1092 (m), 1039 (s), 936 (m), 899 (m), 881 (m), 858 (w), 820 (m),
810 (m), 778 (m), 764 (m). Anal. Calcd. for C_{17}H_{17}NO_2: C, 76.38; H, 6.41; N, 5.24.
Found: C, 76.27; H, 6.18; N, 4.90; Melting point: 85-92 °C.

**Li-L^4:** (1.8 g, 67%); \(^1^H\) NMR (C_6D_6, 600 MHz): 7.228 (d, 1H, J= 8.0 Hz), 7.059 (d, 2H, J= 7.2 Hz), 6.963 (t, 1H, J= 7.2 Hz), 6.856 (d, 1H, J= 8.0 Hz), 4.810 (s, 2H), 1.801 (s, 6H), 1.645 (s, 3H); \(^{13}C\}^{1}H\) NMR (C_6D_6, 150 MHz): 144.03, 143.52, 129.33, 128.57, 125.92, 125.09, 123.64, 123.01, 122.38, 107.76, 107.73, 104.89, 101.38, 97.79, 18.20, 17.33, 16.91; \(^7Li\}^{1}H\) NMR (C_6D_6, 155 MHz): \(\delta\) 3.671; IR: 3150 (m), 2 875 (s), 1913 (w), 1837 (w), 1611 (s), 1561 (s), 1381 (s), 1321 (s), 1280 (s), 1236 (s), 1200 (s), 1164 (w), 1131 (m), 1082 (s), 1037 (s), 986 (w), 932 (s), 866 (w), 837 (m), 805 (m), 787 (s), 761 (s), 730 (w). Melting point: 136 °C (dec.).

**H-L^7:** (8.0 g, 85%); \(^1^H\) NMR (C_6D_6, 600 MHz): 7.901 (s, 1H), 7.741 (s, 1H), 7.191-7.154 (m, 3H), 6.942 (d, 1H, J= 7.2 Hz), 6.570 (d, 1H, J= 7.2 Hz), 5.201 (s, 2H), 3.15 (sept, 2H, J= 8.0 Hz), 1.18 (d, 12H, J= 8.0 Hz); \(^{13}C\}^{1}H\) NMR (C_6D_6, 150 MHz): 161.21, 151.10, 150.31, 149.23, 138.11, 131.83, 125.82, 124.74, 123.62, 108.53, 107.12, 101.75, 28.64, 23.82; IR: 2904 (s), 2729 (w), 1845 (w), 1765 (w), 1625 (m), 1597 (m), 1452 (s), 1375 (s), 1251 (s), 1194 (m), 1173 (m), 1091 (m), 1039 (s), 933 (m), 887 (w), 853 (w), 807 (m), 783 (m), 750 (m), 722 (m). Anal. Calcd. for C_{20}H_{23}NO_2: C, 77.64; H, 7.50; N, 4.53.
Found: C, 77.40; H, 7.59; N, 4.52. Melting point: 88-94 °C.

**Li-L^7:** (2.1 g, 68%); \(^1^H\) NMR (C_6D_6, 600 MHz): 8.036 (s, 1H), 7.045 (m, 3H), 6.899 (d, 1H, J= 7.2 Hz), 6.616 (d, 1H, J= 7.2 Hz), 4.975 (s, 2H), 2.953 (sept, 2H, J= 8.0 Hz), 0.990 (d, 12H, J= 8.0 Hz); \(^{13}C\}^{1}H\) NMR (C_6D_6, 150 MHz): 175.22, 161.21, 155.53, 149.34, 139.12, 129.53, 126.01, 124.32, 123.53, 105.91, 102.01, 98.84, 28.94, 24.14;
\(^7\text{Li}\{^1\text{H}\} \text{ NMR (C}_6\text{D}_6, 155 \text{ MHz)}: \delta 3.897; \text{ IR: 3061 (w), 2854 (s), 2725 (w), 2361 (w), 1622 (s), 1588 (m), 1553 (s), 1504 (w), 1486 (m), 1460 (s), 1382 (s), 1369 (s), 1323 (s), 1254 (s), 1174 (s), 1134 (w), 1114 (w), 1094 (s), 1046 (s), 934 (m), 861 (m), 788 (s).\)

Anal. Calcd for C\(_{20}\)H\(_{22}\)LiNO\(_2\): C 76.18, H 7.03, N 4.44. Found: C 76.64, H 7.06, N 4.73.

Melting point: 143 °C (dec.).

**H-L\(^8\): (8.0 g, 81%); \(^1\text{H} \text{ NMR (CDCl}_3, 400 \text{ MHz): } \delta 7.691 \text{ (d, 1H, } \text{J}_{\text{HH}} = 2.0 \text{ Hz), 7.482 (dd, 1H, } \text{J} = 8.0 \text{ Hz, } \text{J}_{\text{HH}} = 2.0 \text{ Hz), 7.21-7.00 (m, 3H), 6.891 (d, 1H, } \text{J} = 8.0 \text{ Hz), 6.042 (s, 2H), 2.732 (sept, 2H, } \text{J} = 7.0 \text{ Hz), 2.051 (s, 3H), 1.145 (d, 6H, } \text{J} = 7.0 \text{ Hz), 1.135 (d, 6H, } \text{J} = 7.0 \text{ Hz); } \text{^{13}C\{^1\text{H}\} NMR (CDCl}_3, 100 \text{ MHz): } \delta 149.61, 148.12, 136.65, 133.77, 129.12, 128.62, 124.16, 123.73, 122.72, 108.17, 107.94, 101.72, 29.09, 23.76, 23.28, 17.95; \text{ IR: 2952 (s), 2924 (s), 2854 (s), 2722 (w), 1859 (w), 1625 (m), 1604 (s), 1590 (m), 1506 (m), 1488 (s), 1460 (s), 1459 (s), 1438 (s), 1378 (s), 1363 (s), 1328 (w), 1288 (s), 1254 (s), 1221 (m), 1188 (m), 1039 (s), 933 (m), 898 (m), 881 (m), 817 (m), 808 (m), 775 (m), 726 (w), 690 (w), 635 (m). Anal. Calcd for C\(_{21}\)H\(_{25}\)NO\(_2\): C, 77.98; H, 7.79; N, 4.33. Found: C, 77.41; H, 8.05; N, 4.14. Melting point: 82-85 °C.**

**Li-L\(^8\): (2.6 g, 80%); \(^1\text{H} \text{ NMR (C}_6\text{D}_6, 400 \text{ MHz): } \delta 7.257 \text{ (d, 1H, } \text{J} = 8.4 \text{ Hz), 7.030-6.984 (m, 3H), 6.652 (d, 1H, } \text{J} = 8.4 \text{ Hz), 4.799 (s, 2H), 2.753 (sept, 2H, } \text{J} = 6.6 \text{ Hz), 1.900 (s, 3H), 0.978 (d, 6H, } \text{J} = 6.6 \text{ Hz), 0.882 (d, 6H, } \text{J} = 6.6 \text{ Hz); } \text{^{13}C\{^1\text{H}\} NMR (C}_6\text{D}_6, 100 \text{ MHz): } \delta 177.41, 155.65, 146.32, 144.11, 143.67, 138.30, 125.12, 124.56, 123.54, 105.50, 97.73, 28.54, 23.52, 18.37; \text{^{7}Li\{^1\text{H}\} NMR (C}_6\text{D}_6, 155 \text{ MHz): } \delta 4.121; \text{ IR: 2955 (s), 2921 (s), 2854 (s), 1614 (m), 1588 (w), 1558 (m), 1464 (s), 1459 (s), 1380 (s), 1320 (m), 1283 (m), 1278 (m), 1242 (s), 1186 (w), 1140 (w), 1129 (w), 1109 (w), 1094 (w), 1086 (w).
(w), 1055 (w), 1037 (m), 981 (w), 933 (w), 923 (w), 873 (w), 836 (w), 800 (w), 788 (w),
778 (w), 773 (w), 721 (w). Anal. Calcd for C\textsubscript{21}H\textsubscript{24}LiNO\textsubscript{2}: C, 76.58; H, 7.34; N, 4.25.
Found: C, 76.34; H, 7.56; N, 4.39. Melting point: 130-135 °C.

2.4 Crystallography\textsuperscript{124}

A summary of crystal data and collection parameters for crystal structures of (Li-L\textsubscript{2})\textsubscript{4} and
(Li-L\textsubscript{4})\textsubscript{2}-Et\textsubscript{2}O are provided in Table 2.1. Detailed descriptions of data collection and data
solution are provided below. ORTEP diagrams were generated with the ORTEP-3 software package.\textsuperscript{137} For each sample, a suitable crystal was mounted on a glass fiber by
using Paratone-N hydrocarbon oil. The crystal was transferred to a Siemens SMART\textsuperscript{138} diffractometer with a CCD area detector, centered in the X-ray beam, and cooled to 140
K by using a nitrogen-flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. An arbitrary hemisphere of data was collected by using 0.3° ω-scans, and the data were integrated by
the program SAINT.\textsuperscript{139} The final unit-cell parameters were determined by a least-squares refinement of the reflections with I >2σ(I). Data analysis by using Siemens XPREP\textsuperscript{140} and the successful solution and refinement of the structure determined the space group.
Empirical absorption corrections were applied for (Li-L\textsubscript{2})\textsubscript{4} and (Li-L\textsubscript{4})\textsubscript{2}-Et\textsubscript{2}O by using
SADABS.\textsuperscript{141} Equivalent reflections were averaged, and the structures were solved by
direct methods using the SHELXTL software package.\textsuperscript{142} Unless otherwise noted, all non-hydrogen atoms were refined anisotropically.

(Li-L\textsubscript{2})\textsubscript{4}: X-ray quality crystals were grown from a saturated diethyl ether solution at -25 °C. The final cycle of full-matrix least-squares refinement was based on 1529 observed
reflections and 155 variable parameters and converged yielding final residuals: R = 0.0612, R_{all} = 0.1438, and GOF = 1.001.

(Li-L^4\cdot Et_2O)_2: X-ray quality crystals were grown from a saturated diethyl ether solution at -25 °C. The final cycle of full-matrix least-squares refinement was based on 4074 observed reflections and 236 variable parameters and converged yielding final residuals: R = 0.0456, R_{all} = 0.0517, and GOF = 1.027.
Table 2.1. Crystallographic data for compounds \((\text{Li-L}_2)^4\) and \((\text{Li-L}_4)^2\cdot \text{Et}_2\text{O}\).\textsuperscript{124}

<table>
<thead>
<tr>
<th>Compound</th>
<th>((\text{Li-L}_2)^4)</th>
<th>((\text{Li-L}_4)^2\cdot \text{Et}_2\text{O})</th>
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<tr>
<td>Empirical formula</td>
<td>(\text{C}<em>{13}\text{H}</em>{16}\text{LiNO}_2)</td>
<td>(\text{C}<em>{21}\text{H}</em>{26}\text{LiNO}_3)</td>
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<td>Space group</td>
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<td>(P2_1/n)</td>
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<tr>
<td>Temperature [K]</td>
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<td>140</td>
</tr>
<tr>
<td>(a) [Å]</td>
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<td>11.5286(4)</td>
</tr>
<tr>
<td>(b) [Å]</td>
<td>14.671(2)</td>
<td>13.1880(4)</td>
</tr>
<tr>
<td>(c) [Å]</td>
<td>11.476(2)</td>
<td>12.3759(4)</td>
</tr>
<tr>
<td>(\alpha) [°]</td>
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<td>90</td>
</tr>
<tr>
<td>(\beta) [°]</td>
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</tr>
<tr>
<td>(\gamma) [°]</td>
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<td>90</td>
</tr>
<tr>
<td>(V) [Å(^3)]</td>
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<td>1875.0(1)</td>
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<tr>
<td>(Z)</td>
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<td>4</td>
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<tr>
<td>Density\textsubscript{calcd.} [g/cm(^3)]</td>
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<td>1.231</td>
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<td>Siemens SMART</td>
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<td>Mo-(K\alpha) (0.71073)</td>
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<td>CCD area detector</td>
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<td>2θ range [°]</td>
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<td>4.52–56.64</td>
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<td>236</td>
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<td>0.0456</td>
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<tr>
<td>(R\textsubscript{w})</td>
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<td>(R\textsubscript{all})</td>
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<td>0.0517</td>
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<tr>
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<td>1.027</td>
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2.6 Conclusions

Several ortho-lithiated alkyl and aryl imines were synthesized by the Schiff-base condensation reaction of 3,4-methylenedioxyacetophenone or piperonal with alkyl and aryl amines. X-ray crystallography and multi-nuclear NMR spectroscopy studies showed that solvent polarity played an important role in the clustering motif of the lithiated products. A second important factor in determining the clustering of these lithiated salts involved the size and type of the substituents on the imine moiety. For example, crystallization of these products from noncoordinating solvents such as toluene led to the formation of coordination polymers. On the other hand, crystallization from diethyl ether led to the formation of discrete dimeric lithium complexes with square-pyramidal lithium centers when the nitrogen substituent was 2,6-Me$_2$C$_6$H$_3$. Lithiated alkyl imines, such as the tert-butyl imine, formed tetrameric units upon crystallization from ether. These ortho-lithiated imines offer an entry to bidentate C, N donor ligands to support a variety of main group and transition metals.\textsuperscript{38,128,237}
Chapter 3

Synthesis and Characterization of Niobium and Tantalum Imido Complexes Bearing Mono-Anionic Acetophenone Imine Ligands

3.1 Introduction

Among nitrogen donor ligand systems, imido groups (RN$^{2-}$; R = aryl, alkyl) have proven to be extremely important in early transition metal chemistry.$^{79}$ The strong bonding observed between the doubly anionic nitrogen donor atom and a highly charged early metal lends excellent stability, while broad tuning of the alkyl or aryl substituent provides for control of steric bulk.$^{79}$ In addition to supporting a range of interesting reaction chemistry, early work on imido complexes of group (V) metals was driven by their useful luminescence properties.$^{143-145}$ The first niobium and tantalum imido complexes, reported by Finn and co-workers in 1980, were synthesized by the reduction of acetonitrile with zinc or through the metathesis reaction of tantalum neopentylidenes with imines.$^{146}$ Later, a more economical route to tantalum and niobium imido complexes was reported, utilizing the reaction of silylated alkylamines with MCl$_5$. $^{147-149}$ A similar reaction of metal halides with silylanilines in the presence of 1,2-dimethoxyethane (dme) afforded a more stable series of metal imido precursors with the general formula of
M(NAr)Cl₃(dme) (M = Nb, Ta). The lability of DME and halide ligands in these imido complexes has provided for a variety of intriguing niobium and tantalum metal complexes. Herein, we describe their use as precursors in the synthesis of mono-anionic acetophenone imine group (V) complexes.

The broad use of bidentate ligands in transition metal chemistry derives from the stability garnered from the chelate effect, with the option of using two chemically different donor groups available as a means to more rigidly control the reactivity at the metal center. One way to generate a bidentate ligand system is through the regioselective ortho-metalation of an aryl group covalently attached to a second donor moiety. This process leads to an anionic ligand framework with two dissimilar donor atoms, yielding electronic asymmetry in the resulting complexes that can lead to unique reactivity. Ortho-metalation is commonly effected by the direct activation of an aryl C-H bond, through either oxidative addition or direct deprotonation by a strong base. With late transition metals, oxidative addition of the ortho C-H bond proves to be a very effective pathway to ortho-metalated complexes and to catalytically functionalize aryl groups in this position. In recent work, Crabtree has utilized this methodology to produce iridium complexes by the ortho-metalation of α,β-unsaturated ketones, esters and acetophenone, which have served as useful catalyst precursors for hydroamination and alkyne hydroalkoxylation reactions. Given this useful reactivity, many ligand systems based on α,β-unsaturated ketones, esters and acetophenones have been explored in recent years.

Our research group has been interested in the reactivity of related ortho-metalated imines. Ortho-metalation of acetophenone imines with late metals is readily accessible by
C-H activation of the aryl moiety, and this type of reaction allows for the synthesis of metal hydrides with potential applications in C-C bond coupling reactions. Unfortunately, this route has proven to be generally inaccessible for early transition metals. Many common early metal starting materials are in their maximum oxidation state, making ortho-metalation through oxidative addition of C-H bonds impossible. Alternate routes utilizing lower oxidation state metal centers have been shown to suffer from deleterious side reactions attributed to redox processes linked to ligand reduction, rather than the desired C-H activation. Due to these limitations, reports regarding the use of ortho-metalated acetophenone imine ligands with early metals are rare. We recently published an effective synthetic route to group (IV) transition metal complexes of mono-anionic ortho-metalated acetophenone imine ligands. Prior methods for the synthesis of early-metal complexes of ortho-metalated acetophenone imines had been limited to the insertion of cyano groups into metal-benzyne bonds, a reaction that yields dianionic versions of these ligands with very little substitutional flexibility. Herein, we report the synthesis of acetophenone imines with a variety of alkyl and aryl substituents that undergo site-specific lithiation upon treatment with n-BuLi. These activated ligands have been reacted with niobium and tantalum imido precursors to generate a series of thirteen new metal imido complexes. The structure and bonding in these complexes was determined by NMR and X-ray analyses. We believe that through the combination of the imido moiety and the new mono-anionic ortho-metalated acetophenone imine ligand system, a series of niobium and tantalum complexes with exceptional stoichiometric and catalytic reactivity will be uncovered.
3.2 Results and Discussion

3.2.1. Formation of Niobium and Tantalum Complexes. Direct metalation of the lithiated acetophenone imine ligands (see Chapter 2) through salt metathesis with group V metal halides (MCl$_5$) was problematic, resulting in intractable mixtures that rapidly decomposed to give insoluble brown materials. Because of these difficulties, attention was turned to the synthesis of niobium and tantalum complexes containing the imido moiety. Various aryl and alkyl imido complexes of the form L$_2$MCl$_3$(NR) (L = neutral donor ligand; M = Nb, Ta; R = aryl, alkyl) are known and thus function as excellent starting materials.$^{144, 149-151, 190-192}$ Use of the imido group allowed access to high-valent (M$^{5+}$) tantalum and niobium centers that were more stable than the native pentahalides; the strong metal-imido bond gives these species good thermal stability.$^79$ Furthermore, the substituent on the imido group helped to solubilize the metal precursors, such that low polarity solvents could be used.

Synthesis of the niobium and tantalum imido starting materials was based on previous literature reports. We primarily investigated niobium complexes utilizing (dme)NbCl$_3$(NR) where R = 2,6-$^t$Pr$_2$C$_6$H$_3$ (9), 2,6-Et$_2$C$_6$H$_3$ (10), 2,6-Me$_2$C$_6$H$_3$ (11), Ph (12), or $^t$Bu (13).$^{144,190}$ To show the applicability of these reactions with tantalum, we also explored complexes derived from (dme)TaCl$_3$(N-2,6-$^t$Pr$_2$C$_6$H$_3$) (14).$^{150}$ In general, a series of thirteen niobium and tantalum imido complexes (15 – 26, 20$^7$) were synthesized by reacting the group V starting materials (9 – 14) with 2 eq. of the lithiated ligand (Li-Li$^2$, Li-L$^4$, Li-L$^6$-8; Scheme 3-1). The best results were observed when using pentane as solvent, in which case the reaction occurs as a slurry throughout. In all cases, products of the form (L)$_2$MCl(NR) (L = ortho-metalated acetophenone imine) were produced. With
the bidentate anionic acetophenone imine ligands present, these species were characterized as six-coordinate, pseudo-octahedral complexes.

Scheme 3-1. Synthesis of niobium and tantalum complexes (see Table 3.1 for definitions of M, R, R’, and R”).

An analysis of the ligands utilized to produce the L₂MCl(NR) complexes (15 – 26, 20*) indicates that a number of possible structural isomers exist. The acetophenone imine ligand does not have a large enough bite angle to span trans positions around the metal center. Thus, there are only two structural isomers possible where the imido group is oriented trans to the chloride ligand. These isomers would necessitate either a two-fold rotation axis (trans acetophenone imine ligands) or a mirror plane (cis acetophenone imine ligands). In all cases, NMR spectroscopy revealed that no such symmetry operation existed within the observed complexes-that is, in each of these metal complexes, C₁ symmetry was observed. This was best indicated by the methylenedioxy resonances of the ligand backbone, where the presence of four inequivalent signals from the four protons (on the two ligands) indicated a complete lack of symmetry within the molecule. Thus, we deduced that the imido ligand was oriented cis to the chloride ligand in all complexes formed, while noting that this still left four possible structural isomers.
(present as racemates). The final important consideration in the analysis of the 
$L_2MCl(NR)$ complexes involved electronic parameters. Because of the very strong metal-imido bonding, the imido group exerts a significant $trans$ influence on the metal center. Thus, very weak bonding $trans$ to the imido ligand is expected, favoring dative bonding of the neutral imine donor, rather than the more strongly bound anionic aryl moiety of the facetophenone imine ligand. Thus, by constraining the complexes to those containing a chloride $cis$ to the imido group and a neutral imine donor $trans$ to the imido group, only two structural isomers are possible (Scheme 3-1). This was confirmed by the resonances observed in the $^1$H NMR for the $-OCH_2O-$ groups, as each of the thirteen new metal complexes exist as either one or two structural isomers. As an example of one structural isomer case, $^1$H NMR of the metal complex 15 is shown in Figure 3-1.

![Figure 3-1. $^1$H NMR spectrum of 15.](image-url)
In an effort to understand the factors controlling product distribution in the salt metathesis reactions, we investigated two steric aspects in relation to the isomers formed. In complexes 15-18 (Nb) and 23-26 (Ta), the bulkiest imido group (N-iPr₂C₆H₃) was used and the size of the ligand substituents was varied. Only one structural isomer was formed when the steric bulk of the ligand was very large (15, 23, 26) or quite small (18). Somewhat surprisingly, based on the X-ray crystal structures of complexes 17, 18 and 23, we found that the same isomer was present in both cases (Figures 3-3, 3-4, and 3-5). Specifically, this is the structural isomer with the acetophenone imine carbon donor atom oriented trans to the chloride ligand. The X-ray structure corresponded well with the solution NMR data. For example, in complex 23, the only equivalent proton resonances observed by ¹H NMR spectroscopy are those resulting from freely spinning methyl groups. The isopropyl groups show diastereotopic methyls and the methylenedioxy moieties yield a total of four inequivalent resonances. Moreover, through analysis of the methylenedioxy chemical shifts, while considering the relevant spatial locations in the solid-state structure, it is clear that the significant shielding of these protons is an effect of their location 3.7 – 4.2 Å above the aryl rings of the imido and acetophenone imine groups.¹³⁴, ¹³⁵ The shielding of these protons can be readily attributed to ring current effects from these aromatic systems and their approximate distances parallel their chemical shifts.¹³⁴, ¹³⁵

In contrast, complexes formed from the intermediate sized ligands (Nb: 16, 17; Ta: 24, 25) yielded a mixture of two structural isomers. Given the preference for the same isomer with both sterically large and sterically small ligands described previously, we were surprised by this result. By carrying out the syntheses of these complexes at various
reaction temperatures, we found that different ratios of the two isomers were produced as kinetic products that did not equilibrate in solution. That is, when examining the room temperature NMR spectra of complexes produced under different reaction temperatures, substantially differing product ratios were observed. Variable temperature NMR showed no change in isomeric ratios upon cooling, although the onset of some equilibration between the isomers was commonly observed near 60 °C for most isomers. The high temperature coalescence point was not reached at 100 °C for any of these four complexes. To demonstrate this effect, the $^1$H NMR of complex 16 at room temperature and at 80 °C (only methylenedioxy region peaks) is shown in Figure 3-2.

![Figure 3-2. $^1$H NMR spectrum of 16.](image)

In the cases of complexes 16 and 24, we were able to grow X-ray quality crystals and
determine the solid-state structures of these complexes (Figures 3-6 and 3-7). Subsequent NMR of these crystals revealed the presence of only a single isomer (no equilibration observed), confirming that the major isomer in 16 and 24 is the same structural isomer that we observed in the previous cases. We postulate that the second isomer was observed because of the steric congestion at the metal center in the case of intermediate steric bulk. With the reduced steric bulk, we suggest that isomerization pathways in the reaction intermediates are lower in energy and under the reaction conditions employed, small amounts of the minor product are formed that are unable to thermally equilibrate at room temperature. Investigations into alkylation of these complexes are presented in chapter 4.

In a second series of experiments, the bulkiest ligand was used and the imido group on the niobium was varied in size (15, 19-22). Similar to the previous set of experiments, each of these complexes was formed as either one or two structural isomers. The number of structural isomers produced during each reaction was entirely dependent upon the size of the imido group used. Complexes 15, 19 and 20 had very bulky arylimido moieties (2,6-R₂C₆H₃; R = iPr, Et, Me), resulting in the formation of only one structural isomer, while two isomers were formed when smaller imido moieties were used, as evidenced by 21 and 22. The preferred isomer had the same relative configuration as that observed in the earlier cases, as confirmed by the X-ray crystal structure of complex 20 (Figure 3-8). For reactions where two isomers were observed, the synthesis was carried out a second time at 0 °C, rather than room temperature. This did not prevent the formation of two isomers, but changed the ratios of the two isomers present. For example, the room temperature synthesis of 21 results in a 1:1 ratio of the two isomers, while low temperature synthesis (0 °C) of the same complex results in a 5:2
ratio. Thus, again we conclude that the structural isomers are not interconverting in solution at room temperature. Rather, their formation reflects the kinetic control of the products of these reactions at the employed temperatures. The major isomer for complexes 21 and 22 is the same as that described previously with the chloride ligand located trans to the anionic carbon of an acetophenone imine ligand, while the minor isomer contains the nitrogen atom of an acetophenone imine trans to the chloride. Overall, the synthesis of complexes 15-26 reveals that the salt metathesis reactions are controlled by more than just the steric size of the ligands, including such factors as reaction temperature, type of imido moiety, and the steric bulk of the ligand system.
Table 3.1. Metal complexes and selected physical properties.

<table>
<thead>
<tr>
<th>Complex</th>
<th>M</th>
<th>R</th>
<th>R'</th>
<th>R''</th>
<th>-OCH₂O- Resonances (δ, ppm)</th>
<th>Number of isomers</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>Nb</td>
<td>CH₃</td>
<td>2,6-iPr₂C₆H₃</td>
<td>2,6-iPr₂C₆H₃</td>
<td>5.141, 5.079, 5.033, 4.950, 5.143, 5.103, 5.056, 4.921</td>
<td>1</td>
<td>93%</td>
</tr>
<tr>
<td>23</td>
<td>Ta</td>
<td>CH₃</td>
<td>2,6-iPr₂C₆H₃</td>
<td>2,6-iPr₂C₆H₃</td>
<td>5.226, 5.211, 5.133, 5.038 (16), 5.580, 5.248, 5.083, 4.953 (16a), 5.246, 5.218, 5.162, 5.051 (24), 5.638, 5.270, 5.145, 5.019 (24a)</td>
<td>2</td>
<td>83%</td>
</tr>
<tr>
<td>16</td>
<td>Nb</td>
<td>CH₃</td>
<td>2,6-Et₂C₆H₃</td>
<td>2,6-iPr₂C₆H₃</td>
<td>5.226, 5.211, 5.133, 5.038 (16), 5.580, 5.248, 5.083, 4.953 (16a), 5.246, 5.218, 5.162, 5.051 (24), 5.638, 5.270, 5.145, 5.019 (24a)</td>
<td>2</td>
<td>80%</td>
</tr>
<tr>
<td>24</td>
<td>Ta</td>
<td>CH₃</td>
<td>2,6-Et₂C₆H₃</td>
<td>2,6-iPr₂C₆H₃</td>
<td>5.226, 5.211, 5.133, 5.038 (16), 5.580, 5.248, 5.083, 4.953 (16a), 5.246, 5.218, 5.162, 5.051 (24), 5.638, 5.270, 5.145, 5.019 (24a)</td>
<td>2</td>
<td>80%</td>
</tr>
<tr>
<td>17</td>
<td>Nb</td>
<td>CH₃</td>
<td>2,6-Me₂C₆H₃</td>
<td>2,6-iPr₂C₆H₃</td>
<td>5.391, 5.137, 4.812, 4.728 (17), 5.365, 5.107, 5.017, 4.843 (17a), 5.250, 5.240, 5.147, 5.077 (25), 5.658, 5.293, 5.217, 5.060 (25a)</td>
<td>2</td>
<td>75%</td>
</tr>
<tr>
<td>25</td>
<td>Ta</td>
<td>CH₃</td>
<td>2,6-Me₂C₆H₃</td>
<td>2,6-iPr₂C₆H₃</td>
<td>5.391, 5.137, 4.812, 4.728 (17), 5.365, 5.107, 5.017, 4.843 (17a), 5.250, 5.240, 5.147, 5.077 (25), 5.658, 5.293, 5.217, 5.060 (25a)</td>
<td>2</td>
<td>80%</td>
</tr>
<tr>
<td>18</td>
<td>Nb</td>
<td>CH₃</td>
<td>CMe₃ ('Bu)</td>
<td>2,6-iPr₂C₆H₃</td>
<td>5.223, 5.210, 5.009, 4.856</td>
<td>1</td>
<td>62%</td>
</tr>
<tr>
<td>19</td>
<td>Nb</td>
<td>CH₃</td>
<td>2,6-iPr₂C₆H₃</td>
<td>2,6-Et₂C₆H₃</td>
<td>5.132, 5.100, 4.980, 4.957</td>
<td>1</td>
<td>75%</td>
</tr>
<tr>
<td>20</td>
<td>Nb</td>
<td>CH₃</td>
<td>2,6-iPr₂C₆H₃</td>
<td>2,6-Me₂C₆H₃</td>
<td>5.132, 5.100, 4.980, 4.957</td>
<td>1</td>
<td>75%</td>
</tr>
<tr>
<td>20Ⅰ</td>
<td>Nb</td>
<td>H</td>
<td>2,6-iPr₂C₆H₃</td>
<td>2,6-Me₂C₆H₃</td>
<td>5.125, 5.092, 4.959, 4.932</td>
<td>1</td>
<td>72%</td>
</tr>
<tr>
<td>21</td>
<td>Nb</td>
<td>CH₃</td>
<td>2,6-iPr₂C₆H₃</td>
<td>Ph</td>
<td>5.387, 5.351, 5.208, 5.169 (21), 5.295, 5.093, 4.775, 4.743 (21a)</td>
<td>2</td>
<td>33%</td>
</tr>
<tr>
<td>22</td>
<td>Nb</td>
<td>CH₃</td>
<td>2,6-iPr₂C₆H₃</td>
<td>CMe₃ ('Bu)</td>
<td>5.481, 4.832, 4.668, 4.581 (22), 5.356, 5.252, 4.730, 4.665 (22a)</td>
<td>2</td>
<td>20%</td>
</tr>
<tr>
<td>26</td>
<td>Ta</td>
<td>H</td>
<td>2,6-iPr₂C₆H₃</td>
<td>2,6-iPr₂C₆H₃</td>
<td>5.161, 5.078, 5.058, 4.953</td>
<td>1</td>
<td>75%</td>
</tr>
</tbody>
</table>
Figure 3-3. ORTEP diagram (50% thermal ellipsoids) of \((L^4)_2\text{Nb(N-2,6-}^2\text{Pr}_2\text{C}_6\text{H}_3)\text{Cl}\) (17). Hydrogen atoms omitted for clarity. Bond lengths (Å): Nb1-Cl1 = 2.3881(6), Nb1-N1 = 1.767(2), Nb1-N2 = 2.351(2), Nb1-N3 = 2.486(2), Nb1-C13 = 2.260(2), Nb1-C30 = 2.202(2). Bond angles (°): Nb1-N1-C1 = 174.8(2), N2-Nb1-C13 = 70.51(7), N3-Nb1-C30 = 70.18(7).
Figure 3-4. ORTEP diagram (50% thermal ellipsoids) of \((L^2)_2\text{Nb}(\text{N-2,6-}^\text{t}\text{Pr}_2\text{C}_6\text{H}_3)\text{Cl}\) (18). Hydrogen atoms omitted for clarity. Bond lengths (Å): Nb1–Cl1 = 2.4489(7), Nb1–N1 = 1.777(2), Nb1–N2 = 2.464(2), Nb1–N3 = 2.358(2), Nb1–C13 = 2.170(3), Nb1–C26 = 2.278(3). Bond angles (°): Nb1–N1–C1 = 177.8(2), N2–Nb1–C13 = 72.82(9), N3–Nb1–C26 = 71.68(9).
Figure 3-5. ORTEP diagram (50% thermal ellipsoids) of (L₈)₂Ta(N-2,6-iPr₂C₆H₃)Cl (23). Hydrogen atoms, disordered methyl group and toluene solvate molecules are omitted for clarity. Bond lengths (Å): Ta1-Cl1 = 2.3627(9), Ta1-N1 = 1.786(3), Ta1-N2 = 2.360(3), Ta1-N3 = 2.519(3), Ta1-C13 = 2.245(3), Ta1-C34 = 2.195(4). Bond angles (°): Ta1-N1-C1 = 172.7(3), N2-Ta1-C13 = 71.1(1), N3-Ta1-C34 = 70.4(1).
Figure 3-6. ORTEP diagram (50% thermal ellipsoids) of (L^6)\textsubscript{2}Nb(N-2,6-iPr\textsubscript{2}-C\textsubscript{6}H\textsubscript{3})Cl (16). Hydrogen atoms, disordered methyl group, and pentane molecule have been omitted for clarity. Bond lengths (in Å): Nb1-Cl1 = 2.389(1), Nb1-N1 = 1.759(4), Nb1-N2 = 2.329(3), Nb1-N3 = 2.528(4), Nb1-C13 = 2.262(4), Nb1-C32 = 2.198(4). Bond angles (in deg): Nb1-N1-C1 = 173.1(4), N2-Nb1-C13 = 70.7(2), N3-Nb1-C32 = 70.1(2).
Figure 3-7. ORTEP diagram (50% thermal ellipsoids) of \((\text{L}^6)_2\text{Ta(N-2,6-}^2\text{Pr}_2\text{C}_6\text{H}_3)\text{Cl}\) (24). Hydrogen atoms and ether solvate molecule omitted for clarity. Bond lengths (Å): Ta1-Cl1 = 2.377(1), Ta1-N1 = 1.783(4), Ta1-N2 = 2.513(4), Ta1-N3 = 2.315(3), Ta1-C13 = 2.191(4), Ta1-C32 = 2.243(4). Bond angles (°): Ta1-N1-C1 = 173.4(3), N2-Ta1-C13 = 70.1(2), N3-Ta1-C32 = 71.0(2).
Figure 3-8. ORTEP diagram (50% thermal ellipsoids) of one of the two independent molecules of \((L^8)_2\text{Nb}(\text{N-2,6-Me}_2\text{C}_6\text{H}_3)\text{Cl} \ (20)\) in the asymmetric unit. Hydrogen atoms and ether solvate molecules are omitted for clarity. Bond lengths (Å): \(\text{Nb1-Cl1} = 2.3989(8), \text{Nb1-N1} = 1.764(3), \text{Nb1-N2} = 2.389(3), \text{Nb1-N3} = 2.538(3), \text{Nb1-C9} = 2.250(3), \text{Nb1-C30} = 2.207(3).\) Bond angles (°): \(\text{Nb1-N1-C1} = 172.7(2), \text{N2-Nb1-C9} = 70.7(1), \text{N3-Nb1-C30} = 70.4(1).\)
3.4 The Chemistry of a Vanadium Phenyl-imido Complex with *Ortho*-lithiated Acetophenone Imine Ligands

Despite the existence of a few reports of the synthesis of vanadium imido complexes from 1960, a convenient method for the synthesis of stable vanadium imido complexes, characterization, and their derivatization chemistry was first introduced by Maatta et al. in 1984. The procedure described by this group employs a vanadium source such as vanadium oxo trichloride (VOCl₃) and *p*-tolyl isocyanate. Refluxing this mixture in n-octane and the subsequent sublimation of the resulting dark solid produced the desired vanadium imido complex in high yield (>80%). By utilizing a similar strategy, Teuben et al. expanded the scope of this chemistry to half-sandwich vanadium imido complexes utilizing phenyl imido and substituted aryl imido groups (Scheme 3-2). The viable entries to the vanadium organoimido compounds described by these groups have allowed the isolation of a variety of stable vanadium (III and V) imido complexes, opening up the possibility of their use in further catalytic and stoichiometric reactions.

\[
\begin{align*}
\text{VOCl}_3 + \text{ArNCO} & \rightarrow \text{V(NAr)Cl}_3, \\
\text{ArNClCl} + \text{CpSiMe}_3 & \rightarrow \text{V(NAr)Cl}_3
\end{align*}
\]

*Ar* = Ph, 2,6-*Me*₂*C₆*H₃

**Scheme 3-2.** Synthesis of vanadium imido complexes.

As in the case of the imido complexes of the metals of group IV and other group V elements, the structure of the ancillary ligands in vanadium imido complexes plays an important role in their utility. For example, because of the isolobal relationship with

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group IV metal imido complexes, the cationic half sandwich vanadium imido complexes have been used in catalytic hydroamination. More notably, the vanadium imido complexes with alkyl, alkoxy, alkylidene, and bidentate N, N donor ligands have also been used in ring opening metathesis polymerization (ROMP), and more recently in ethylene polymerization reactions.

To compare the properties of a vanadium imido metal complex analogous to the niobium and tantalum imido complexes, we examined the reactivity of an ortho-lithiated acetophenone imine ligand with the vanadium phenyl-imido precursor.

Scheme 3-3. Reaction of a vanadium phenyl-imido precursor with the ortho-lithiated acetophenone imine ligand results in reductive coupling.

As shown in Scheme 3-3, the intended reaction to synthesize a six-coordinate vanadium complex with imido and acetophenone imine ligands yielded a vanadium (III) species and reductively coupled bidentate ligands. Attempts involving changing the reaction solvent to more polar ether or less polar pentane or changing the reaction temperature did not prevent the reductive elimination process in this reaction. Considering the relatively small size of the vanadium ionic radius compared to niobium and tantalum and the bulky acetophenone imine ligand, the very favorable reductive elimination process in this reaction is not surprising. Additionally, as evidenced by the synthesis of a variety of
neutral and cationic vanadium complexes, vanadium is the most favorable element of the group V metals for access to chemistry in lower oxidation states.\textsuperscript{207,208}

The crystal structure of the main organic product of the reaction depicted in Scheme 3-3 is shown in Figure 3-9.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure39.png}
\caption{ORTEP diagram (50\% thermal ellipsoids) of (L\textsuperscript{8}-L\textsuperscript{8}). Hydrogen atoms omitted for clarity.}
\end{figure}
3.4 Experimental

3.4.1. General Considerations

All moisture and air sensitive manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques and dried glassware. Diethyl ether was dried by passage through an activated alumina column. Toluene, dichloromethane and pentane were dried over 4 Å activated molecular sieves. The dried solvents were sparged with nitrogen. 1,2-Dimethoxyethane (dme), tert-butylamine, cyclohexylamine, and triethylamine were vacuum transferred under nitrogen from anhydrous CaH$_2(s)$ and degassed with 3 freeze-evacuate-thaw cycles. Aniline, 2,6-diisopropylaniline, 2,6-diethylaniline and 2,6-dimethylaniline were distilled and stored over 4 Å molecular sieves. NbCl$_5$, TaCl$_5$, ZnCl$_2$, CDCl$_3$, chlorotrimethylsilane, piperonal, 3,4-methylenedioxyacetophenone and $^n$BuLi (1.5 M in hexanes) were used as purchased. Benzene-$d_6$ and toluene-$d_8$ were vacuum transferred under nitrogen from purple Na/benzophenone ketyl and degassed with 3 freeze-evacuate-thaw cycles. Me$_3$SiNH(2,6-$^i$Pr$_2$C$_6$H$_3$) (6), Me$_3$SiNH(2,6-Et$_2$C$_6$H$_3$) (7), Me$_3$SiNH(2,6-Me$_2$C$_6$H$_3$) (8), Nb(N-2,6-$^i$Pr$_2$C$_6$H$_3$)Cl$_3$(dme) (9), Nb(N-C$_6$H$_5$)$_2$Cl$_3$(dme) (12), Nb(NCMe$_3$)$_2$Cl$_3$(dme) (13), Ta(N-2,6-$^i$Pr$_2$C$_6$H$_3$)Cl$_3$(dme) (14), (py)$_3$Cl$_2$Ti(N$^n$Bu)$_2$, (H-L$_6$)$_3$ and (Li-L$_6$)$_3$ were prepared as previously described. The $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded in benzene-$d_6$, CDCl$_3$, or toluene-$d_8$ at ambient temperature on a VXRS 400 or an Inova 600 MHz spectrometer and referenced internally to residual proton peaks at $\delta$ 7.16 ppm (C$_6$D$_6$), 2.09 ppm (C$_7$D$_8$), or 7.27 ppm (CDCl$_3$) and $\delta$ 128.0 ppm (C$_6$D$_6$), 20.4 ppm (C$_7$D$_8$), or 77.23 ppm (CDCl$_3$) for $^{13}$C. Unless otherwise specified, given coupling constants are for $^3$J$_{HH}$. IR samples were prepared as Nujol mulls between KBr plates.
Melting points were performed on a Mel-Temp; those compounds that were air sensitive were taken in a capillary tube sealed under a nitrogen atmosphere and are uncorrected. Elemental analysis was performed by Columbia Analytics, Tucson, Arizona or Galbraith Laboratories, Knoxville, Tennessee. X-ray structure determinations were performed at the Ohio Crystallographic Consortium housed at the University of Toledo. High resolution mass spectra were obtained using electron impact ionization by the Mass Spectrometry Laboratory at the University of Illinois, Urbana, IL.

3.4.2. Metal Precursor Synthesis

**Nb(N-2,6-Et₂C₆H₃)Cl₃(dme) (10):**\(^{195}\) Toluene (40 mL) was added to NbCl₅ (5.0 g, 19 mmol) and the solution was cooled to 0 °C. Dimethoxyethane (2.0 mL) was added to 7 (4.20 g, 19.0 mmol). The 7/dme solution was slowly added to the NbCl₅/tol forming a purple solution and stirred for 1 h at 0 °C. After stirring overnight at room temperature, the solution was filtered, concentrated to half volume, and cooled to -30 °C. The purple precipitate was washed with pentane to yield a purple powder (5.7 g, 69%); \(^1\)H NMR (C₆D₆, 600 MHz): 7.031 (d, 2H, \(J = 8 \) Hz), 6.952 (t, 1H, \(J = 8 \) Hz), 4.164-4.092 (m, 4H), 3.493 (s, 3H), 3.162 (s, 3H), 2.655 (q, 4H, \(J = 8 \) Hz), 1.354 (t, 6H, \(J = 8 \) Hz); \(^{13}\)C\(_{\{\text{1}H\}}\) NMR (C₆D₆, 100 MHz): 145.40, 128.07, 126.98, 75.43, 70.67, 68.37, 62.62, 26.40, 17.60.

**Nb(N-2,6-Me₂C₆H₃)Cl₃(dme) (11):**\(^{195}\) Toluene (40 mL) was added to NbCl₅ (5.0 g, 19 mmol) and the solution was cooled to 0 °C. Dimethoxyethane (2.0 mL) was added to 8 (7.3 g, 38 mmol). The 8/dme solution was slowly added to the NbCl₅/tol forming a red solution and stirred for 1 h at 0 °C. After stirring overnight at room temperature, the
solution was filtered, concentrated to half volume, and cooled to -30 °C. The red precipitate was washed with pentane to yield a red powder (3.8 g, 49%); \(^1\)H NMR (C\(_6\)D\(_6\), 600 MHz): 6.730 (d, 2H, \(J = 7\) Hz), 6.595 (t, 1H, \(J = 7\) Hz), 3.430 (s, 3H), 3.090 (s, 3H), 3.019-2.996 (m, 4H), 2.941 (s, 6H); \(^{13}\)C\{\(^1\)H\} NMR (C\(_6\)D\(_6\), 100 MHz): 138.75, 128.25, 127.29, 75.20, 70.55, 68.40, 62.40, 20.08.

### 3.4.3. Metal Complex Synthesis

\((L^8)_2\text{Nb(N-2,6-iPr}_2\text{C}_6\text{H}_3)\text{Cl (15)}\): To a flask containing both 9 (2.0 g, 4.3 mmol) and Li-L\(^8\) (2.8 g, 8.6 mmol), pentane (100 mL) was added. The mixture was stirred overnight at ambient temperature. Then, the orange precipitate was filtered and remaining ligand was removed by washing with pentane (3 x 30 mL). Lithium chloride was readily removed by extracting the product into toluene (100 mL) and filtering. The solution was then dried under vacuum. The resulting oil was recrystallized from ether at -25 °C, yielding an orange crystalline solid (3.8 g, 93%). \(^1\)H NMR (C\(_6\)D\(_6\), 600 MHz): 7.208 (dd, 1H, \(J = 7.8\) Hz, \(4J_{HH} = 1.2\) Hz), 7.145 (d, 1H, \(J = 7.8\) Hz), 7.069-7.049 (m, 4H), 7.017 (d, 1H, \(J = 7.8\) Hz), 7.005 (d, 1H, \(J = 7.8\) Hz), 6.931 (t, 1H, \(J = 7.8\) Hz), 6.883 (d, 1H, \(J = 8.0\) Hz), 6.819 (d, 1H, \(J = 8.0\) Hz), 6.607 (d, 1H, \(J = 8.0\) Hz), 6.498 (d, 1H, \(J = 8.0\) Hz), 5.141 (s, 1H), 5.079 (s, 1H), 5.033 (s, 1H), 4.950 (s, 1H), 4.731 (sept, 1H, \(J = 7.2\) Hz), 3.951 (sept, 1H, \(J = 6.6\) Hz), 3.330 (sept, 1H, \(J = 6.6\) Hz), 3.280 (sept, 1H, \(J = 6.6\) Hz), 2.816 (sept, 1H, \(J = 6.6\) Hz), 2.452 (sept, 1H, \(J = 6.6\) Hz), 1.783 (s, 3H), 1.690 (s, 3H), 1.427 (d, 3H, \(J = 6.6\) Hz), 1.339 (d, 3H, \(J = 6.6\) Hz), 1.185 (d, 3H, \(J = 6.6\) Hz), 1.073 (d, 3H, \(J = 6.6\) Hz), 1.038 (d, 3H, \(J = 7.2\) Hz), 0.930 (d, 3H, \(J = 6.6\) Hz), 0.844-0.804 (m, 12H), 0.703 (d, 3H, \(J = 6.6\) Hz), 0.631 (d, 3H, \(J = 6.6\) Hz); \(^{13}\)C\{\(^1\)H\} NMR (C\(_6\)D\(_6\), 150 MHz): 183.12, 180.20, 156.76, 152.44, 150.10, 149.23, 148.36, 148.07, 148.05, 146.78, 143.60, 143.59, 143.41,
143.40, 142.25, 142.24, 141.69, 141.68, 140.81, 140.59, 127.32, 126.89, 126.80, 125.48, 125.00, 124.76, 123.64, 123.07, 122.36, 122.11, 108.38, 106.15, 99.82, 99.62, 29.90, 28.92, 28.46, 28.37, 27.95, 26.98, 26.74, 26.21, 25.49, 25.41, 25.25, 25.15, 25.11, 25.08, 24.53, 23.78, 23.29, 22.11, 21.51; IR: 3403 (m), 2854 (s), 2726 (w), 1635 (w), 1549 (w), 1463 (s), 1406 (m), 1367 (s), 1298 (m), 1250 (m), 1243 (m), 1172 (w), 1150 (w), 1122 (w), 1092 (w), 1052 (w), 985 (w), 952 (w), 860 (w). Anal. Calcd. for C$_{54}$H$_{65}$ClN$_3$NbO$_4$: C, 65.85; H, 6.91; N, 4.43. Found: C, 66.21; H, 6.51; N, 4.22.

Melting point: >250 ºC.

(L$_6$)$_2$Nb(N-2,6-$^1$Pr$_2$C$_6$H$_3$)Cl (16): To a flask containing both 9 (0.500 g, 1.07 mmol) and Li-L$_6$ (0.736 g, 2.44 mmol), pentane (50 mL) was added. The mixture was stirred at room temperature for 30 h forming an orange slurry. Volatiles were removed under vacuum, and the resulting solid was washed with pentane (2 x 50 mL) and extracted into toluene (50 mL). After filtration, drying under vacuum yielded a fine orange solid (0.80 g, 83%). $^1$H NMR spectroscopic data of this product revealed an equilibrium mixture of two isomers in a 1:1 ratio. The separation of $^1$H NMR and $^{13}$C NMR peaks was possible by variable temperature NMR studies of the product at 80 ºC in toluene-$d_8$ which leads to 3:1 peak ratios assignable as major and minor isomers. $^1$H NMR (C$_7$D$_8$, 400 MHz): Major isomer: 7.193 (d, 2H, $J = 7.8$ Hz), 7.123 (s, 2H), 7.045 (d, 2H, $J = 7.8$ Hz), 6.991-6.940 (m, 5H), 6.523 (d, 1H, $J = 7.8$ Hz), 6.490 (d, 1H, $J = 7.8$ Hz), 5.226 (s, 1H), 5.211 (s, 1H), 5.133 (s, 1H), 5.038 (s, 1H), 4.586 (sept, 1H, $J = 6.8$ Hz), 4.217 (sept, 1H, $J = 6.8$ Hz), 2.179 (dq, 2H, $^2$J$_{HH} = 15$ Hz, $J = 7.0$ Hz), 2.105 (s, 3H), 2.083 (d, 6H, $J = 6.8$ Hz), 1.815 (dq, 2H, $^2$J$_{HH} = 15$ Hz, $J = 7.0$ Hz), 1.738 (s, 3H), 1.731 (d, 3H, $J = 7.0$ Hz), 1.699 (dq, 2H, $^2$J$_{HH} = 15$ Hz, $J = 7.0$ Hz), 1.577 (dq, 2H, $^2$J$_{HH} = 15$ Hz, $J = 7.0$ Hz), 1.238 (d,
3H, \(J = 7.0\) Hz), 1.201 (d, 3H, 7.0 Hz), 1.107 (d, 3H, \(J = 7.0\) Hz), 1.092 (d, 6H, \(J = 6.8\) Hz); **Minor Isomer:** 6.930-6.872 (m, 8H), 6.836 (d, 1H, \(J = 7.6\) Hz), 6.785 (d, 1H, \(J = 7.6\) Hz), 6.545 (d, 1H, \(J = 7.6\) Hz), 6.417 (d, 1H, \(J = 7.6\) Hz), 6.278 (d, 1H, \(J = 7.6\) Hz), 5.580 (s, 1H), 5.248 (s, 1H), 5.083 (s, 1H), 4.953 (s, 1H), 4.493 (sept, 1H, \(J = 6.4\) Hz), 3.816 (sept, 1H, \(J = 6.4\) Hz), 3.166 (dq, 2H, \(J_{HH} = 15\) Hz, \(J = 7.0\) Hz), 2.547 (dq, 2H, \(J_{HH} = 15\) Hz, \(J = 7.0\) Hz), 2.430 (dq, 2H, \(J_{HH} = 15\) Hz, \(J = 7.0\) Hz), 2.374 (dq, 2H, \(J_{HH} = 15\) Hz, \(J = 7.0\) Hz), 2.101 (s, 3H), 1.897 (s, 3H), 1.405 (d, 3H, \(J = 7.0\) Hz), 1.261 (d, 3H, \(J = 6.4\) Hz), 1.141 (d, 3H, \(J = 7.0\) Hz), 1.040 (d, 3H, \(J = 7.0\) Hz), 0.839 (d, 3H, \(J = 7.0\) Hz), 0.730 (d, 3H, \(J = 6.4\) Hz), 0.683-0.646 (m, 6H); \(^{13}\)C\{\(^1\)H\} NMR (C\(_7\)D\(_8\), 100 MHz):

**Major Isomer:** 195.15, 182.70, 182.46, 180.36, 179.59, 156.21, 152.40, 150.07, 149.87, 148.23, 147.60, 143.15, 140.00, 138.04, 137.35, 135.89, 135.55, 129.15, 126.86, 126.45, 126.18, 126.00, 124.99, 124.69, 122.33, 121.93, 121.76, 107.97, 105.79, 99.81, 28.36, 27.58, 25.30, 24.62, 24.45, 24.30, 24.25, 24.08, 23.79, 23.64, 23.52, 19.18, 18.82, 18.52, 15.55, 15.35, 14.79, 12.85; **Minor Isomer:** 200.40, 152.27, 151.71, 149.69, 149.30, 149.25, 149.14, 148.58, 148.41, 147.45, 142.63, 138.90, 137.84, 137.25, 136.97, 136.88, 135.14, 126.31, 125.54, 124.82, 124.57, 124.25, 123.91, 123.75, 123.26, 123.08, 121.67, 106.83, 105.59, 100.99, 29.53, 28.73, 28.53, 26.30, 25.83, 24.16, 23.19, 21.58, 20.69, 20.48, 19.23, 18.05, 15.52, 14.55, 13.84, 12.19; IR: 1915 (s), 1549 (w), 1459 (s), 1375 (m), 1302 (w), 1244 (m), 1176 (w), 1147 (w), 1115 (w), 1046 (m), 941 (m), 860 (w), 804 (w), 778 (w), 725 (w). Anal. Calcd. for C\(_{50}\)H\(_{57}\)ClN\(_3\)NbO\(_4\): C, 67.30; H, 6.44; N, 4.71. Found: C, 66.58; H, 6.76; N, 4.33. Melting point: 205 °C (dec.).

(L\(^4\))\(_2\)Nb(N-2,6-\(^i\)Pr\(_2\)C\(_6\)H\(_3\))Cl (17): To a flask containing both 9 (0.500 g, 1.07 mmol) and Li-L\(^4\) (0.638 g, 2.44 mmol), pentane (50 mL) was added, forming a pale yellow slurry.
The mixture was stirred at room temperature for 30 h forming a brown slurry. Volatiles were removed under vacuum, and the resulting solid was washed with pentane (3 x 50 mL) and dried under vacuum leaving a fine orange solid. Lithium chloride was readily removed by extracting the product into toluene (50 mL) and filtering. The product was dried under vacuum. The resulting oil was recrystallized from ether at -25 ºC, yielding an orange crystalline solid (0.67, 75%). $^1$H NMR showed a non-interconverting mixture of two isomers with a 1:1 ratio of peak heights. $^1$H NMR signals assignable to each isomer was achieved by repetition of the above synthetic procedure at 0 ºC, which leads to a 3:1 ratio of the isomers. $^1$H NMR (C$_6$D$_6$, 400 MHz): **Major Isomer:** 7.194 (d, 1H, $J = 7.6$ Hz), 7.185 (d, 1H, $J = 7.6$ Hz), 6.998 (t, 1H, $J = 7.6$ Hz), 6.951 (t, 1H, $J = 7.6$ Hz), 6.814-6.775 (m, 6H), 6.673 (d, 1H, $J = 7.6$ Hz), 6.636 (d, 1H, $J = 7.6$ Hz), 6.441 (d, 1H, $J = 7.6$ Hz), 5.391 (d, 1H, $^2J_{HH} = 1.2$ Hz), 5.137 (d, 1H, $^2J_{HH} = 1.2$ Hz), 4.812 (d, 1H, $^2J_{HH} = 1.2$ Hz), 4.728 (d, 1H, $^2J_{HH} = 1.2$ Hz), 3.814 (sept, 1H, $J = 6.8$ Hz), 3.683 (sept, 1H, $J = 6.8$ Hz), 2.894 (s, 3H), 2.135 (s, 3H), 2.028 (s, 3H), 1.794 (s, 3H), 1.712 (d, 3H, $J = 6.8$ Hz), 1.172 (d, 3H, $J = 6.8$ Hz), 1.139 (s, 3H), 1.122 (s, 3H), 1.007 (d, 3H, $J = 6.8$ Hz), 0.741 (d, 3H, $J = 6.8$ Hz); **Minor Isomer:** 7.274 (d, 1H, $J = 7.6$ Hz), 7.079-7.051 (m, 3H), 6.966-6.941 (m, 5H), 6.746 (d, 1H, $J = 7.6$ Hz), 6.703 (d, 1H, $J = 7.6$ Hz), 6.595 (d, 1H, $J = 7.6$ Hz), 6.520 (d, 1H, $J = 7.6$ Hz), 5.365 (s, 1H), 5.107 (s, 1H), 5.017 (s, 1H), 4.843 (s, 1H), 3.376 (sept, 1H, $J = 6.8$ Hz), 2.952 (sept, 1H, $J = 6.8$ Hz), 2.802 (s, 3H), 2.236 (s, 3H), 1.885 (s, 3H), 1.760 (s, 3H), 1.614 (d, 3H, $J = 6.8$ Hz), 1.104 (s, 3H), 0.880 (s, 3H), 0.850 (d, 3H, $J = 6.8$ Hz), 0.587 (d, 3H, $J = 6.8$ Hz), 0.476 (d, 3H, $J = 6.8$ Hz); $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 150 MHz): **Major Isomer:** 182.90, 179.60, 156.35, 152.58, 150.32, 150.15, 150.07, 149.55, 149.36, 148.12, 147.67, 143.15, 140.03, 133.11, 132.09, 130.70, 130.50,
129.93, 129.52, 128.86, 128.02, 126.24, 125.67, 125.28, 125.09, 122.58, 122.19, 108.32, 106.23, 99.90, 28.68, 27.91, 25.22, 24.38, 24.31, 24.09, 20.49, 18.75, 18.27, 18.02, 17.81, 17.25; **Minor Isomer:** 183.23, 181.12, 152.90, 151.93, 150.25, 149.91, 149.63, 149.53, 147.31, 142.84, 138.86, 132.75, 132.16, 131.28, 129.76, 127.58, 125.38, 124.78, 124.32, 123.90, 123.64, 123.32, 122.72, 122.29, 108.07, 108.00, 107.29, 106.06, 101.70, 100.83, 29.91, 29.10, 29.01, 26.18, 24.74, 22.25, 21.09, 20.09, 19.67, 19.53, 18.86, 18.53; IR: 1923 (s), 1552 (m), 1459 (s), 1403 (m), 1377 (w), 1306 (m), 1242 (s), 1190 (w), 1147 (w), 1117 (w), 1091 (w), 1049 (w), 942 (w), 861 (w), 792 (w), 764 (w).

Anal. Calcd. for C_{46}H_{49}ClN_{3}NbO_{4}: C, 66.07; H, 5.91; N, 5.02. Found: C, 66.43; H, 6.82; N, 5.49. Melting point: 195-200 °C.

(L^{2})_{2}Nb(N-2,6-iPr_{2}C_{6}H_{3})Cl (18): A flask containing both 9 (0.321 g, 0.684 mmol) and Li-L^{2} (0.315 g, 1.38 mmol) was cooled to 0 °C. Then, pentane (50 mL) was added and the mixture was stirred cold for 30 minutes. After warming to room temperature and stirring for 24 h, a pale yellow slurry formed. The mixture was dried under vacuum and washed with pentane (3 x 50 mL), leaving a brown solid. Lithium chloride was readily removed by extracting the product into toluene (50 mL) and filtering. The product was then dried under vacuum. The resultant oil was recrystallized from ether at -25 °C, yielding a dark brown crystalline solid (0.32, 62%); $^1$H NMR (C_{6}D_{6}, 600 MHz): 7.134 (d, 1H, $\text{J} = 7.6$ Hz), 7.064 (d, 1H, $\text{J} = 7.6$ Hz), 7.024 (d, 1H, $\text{J} = 7.6$ Hz), 6.920 (t, 1H, $\text{J} = 7.6$ Hz), 6.801 (d, 1H, $\text{J} = 7.6$ Hz), 6.629 (d, 1H, $\text{J} = 7.6$ Hz), 6.543 (d, 1H, $\text{J} = 7.6$ Hz), 5.223 (d, 1H, $\text{J}_{\text{HH}} = 1.2$ Hz), 5.210 (d, 1H, $\text{J}_{\text{HH}} = 1.2$ Hz), 5.009 (d, 1H, $\text{J}_{\text{HH}} = 1.2$ Hz), 4.856 (d, 1H, $\text{J}_{\text{HH}} = 1.2$ Hz), 4.069 (sept, 1H, $\text{J} = 7.2$ Hz), 2.646 (sept, 1H, $\text{J} = 7.2$ Hz), 2.088 (s, 3H), 2.021 (s, 3H), 1.585 (d, 3H, $\text{J} = 7.2$ Hz), 1.519 (s, 9H), 1.390 (d, 3H, $\text{J} = 7.2$ Hz),
1.335 (s, 9H), 1.035 (d, 3H, \( J = 7.2 \) Hz), 1.018 (d, 3H, \( J = 7.2 \) Hz); \(^{13}\)C\{\(^{1}\)H\} NMR (C\(_6\)D\(_6\), 150 MHz): 179.80, 173.15, 149.63, 148.14, 147.87, 147.15, 141.49, 125.23, 123.75, 123.46, 122.97, 122.21, 120.13, 119.26, 107.27, 105.76, 101.95, 99.87, 99.20, 59.72, 58.07, 32.66, 32.15, 31.18, 28.49, 28.42, 27.94, 25.30, 25.07, 24.66, 23.67, 22.92, 22.56, 21.32; IR: 1683 (w), 1459 (s), 1375 (s), 1301 (w), 1256 (w), 1152 (w), 1043 (w), 941 (w), 804 (w), 724 (w); Anal. Calcd. for C\(_{38}\)H\(_{49}\)ClN\(_3\)NbO\(_4\): C, 61.66; H, 6.67; N, 5.68. Found: C, 61.98; H, 6.66; N, 5.62. Melting point: 150 ºC (dec.).

\((L^8)_{2}\)Nb(N-2,6-Et\(_2\)C\(_6\)H\(_3\))Cl (19): To a flask containing both 9 (0.40 g, 0.99 mmol) and Li-L\(^8\) (0.744 g, 1.82 mmol), pentane (50 mL) was added, forming an orange slurry. The mixture was stirred at room temperature for 30 h, forming a brown slurry. The mixture was dried under vacuum and washed with pentane (3 x 50 mL), leaving a fine orange solid. Lithium chloride was readily removed by extracting the product into toluene (50 mL) and filtering. The product was dried under vacuum. The resultant oil was recrystallized from ether at -25 ºC, yielding an orange crystalline solid (0.65 g, 75%); \(^1\)H NMR (C\(_6\)D\(_6\), 600 MHz): 7.208 (d, 1H, \( J = 8.0 \) Hz), 7.157 (t, 1H, \( J = 8.0 \) Hz), 7.065 (d, 1H, \( J = 8.0 \) Hz), 6.932 (d, 1H, \( J = 7.0 \) Hz), 6.909 (d, 1H, \( J = 7.0 \) Hz), 6.85 (d, 1H, \( J = 8.0 \) Hz), 6.85 (t, 1H, \( J = 7.0 \) Hz), 6.829 (d, 1H, \( J = 8.0 \) Hz), 6.610 (d, 1H, \( J = 8.0 \) Hz), 6.518 (d, 1H, \( J = 8.0 \) Hz), 6.518 (d, 1H, \( J = 8.0 \) Hz), 5.132 (d, 1H, \( J_{HH} = 1.0 \) Hz), 5.100 (d, 1H, \( J_{HH} = 1.0 \) Hz), 4.980 (d, 1H, \( J_{HH} = 1.0 \) Hz), 4.957 (d, 1H, \( J_{HH} = 1.0 \) Hz), 3.588 (sept, 1H, \( J = 7.0 \) Hz), 3.520 (dt, 1H, \( J_{HH} = 23 \) Hz, \( J = 8.0 \) Hz), 3.441 (dt, 1H, \( J_{HH} = 23 \) Hz, \( J = 8.0 \) Hz), 3.361 (sept, 1H, \( J = 7.0 \) Hz), 3.066 (dt, 1H, \( J_{HH} = 23 \) Hz, \( J = 8.0 \) Hz), 2.853 (sept, 1H, \( J = 7.0 \) Hz), 2.461 (dt, 1H, \( J_{HH} = 23 \) Hz, \( J = 8.0 \) Hz), 2.430 (sept, 1H, \( J = 7.0 \) Hz), 1.731 (s, 3H), 1.703 (s, 3H), 1.418 (d, 3H, \( J = 7.0 \) Hz), 1.190 (t, 3H, \( J = 8.0 \) Hz),
1.009 (t, 3H, J = 8.0 Hz), 0.893 (d, 3H, J = 7.0 Hz), 0.881 (d, 3H, J = 7.0 Hz), 0.869 (d, 3H, J = 7.0 Hz), 0.802 (d, 3H, J = 7.0 Hz), 0.791 (d, 3H, J = 7.0 Hz), 0.668 (d, 3H, J = 7.0 Hz), 0.656 (d, 3H, J = 7.0 Hz); $^{13}$C{${}^1$}H NMR ($C_6D_6$, 150 MHz): 183.30, 180.36, 156.97, 152.28, 150.02, 149.22, 148.55, 148.17 (x 2), 146.02, 143.66 (x 2), 143.39, 142.14, 141.99, 141.78 (x 2), 140.89, 140.27, 127.20, 126.95, 126.75, 125.75, 125.32, 124.96, 124.80, 124.45 (x 2), 123.65, 122.35, 108.42, 106.18, 99.90, 99.59, 29.72, 29.25, 28.50, 28.04, 26.75, 26.68, 26.09, 25.89, 25.50, 25.22 (x 2), 24.69 (x 2), 23.28, 21.93, 21.21, 15.62, 14.97; IR: 2854 (s), 1655 (m), 1635 (m), 1549 (m), 1462 (s), 1406 (m), 1377 (s), 1351 (w), 1298 (w), 1250 (w), 1172 (w), 1150 (w), 1092 (w), 1052 (w), 942 (w), 860 (w). Anal. Calcd. for $C_{52}H_{61}ClN_3NbO_4$: C, 67.86; H, 6.68; N, 4.57. Found: C, 67.28; H, 7.19; N, 4.26. Melting point: 180-187 ºC.

$(L^8)_{2}Nb(N-2,6-Me_2C_6H_3)Cl$ (20): To a flask containing both 11 (0.40 g, 0.98 mmol) and Li-L$^8$ (0.796 g, 2.44 mmol), pentane (50 mL) was added, forming a pale yellow slurry. The mixture was stirred at room temperature for 30 h, forming a brown slurry. The mixture was dried under vacuum and washed with pentane (3 x 50 mL), leaving a fine orange solid. Lithium chloride was readily removed by extracting the product into toluene (50 mL) and filtering. The product was then dried under vacuum. The resultant oil was recrystallized from ether at -25 ºC, yielding an orange crystalline solid (0.58 g, 66%); $^1$H NMR ($C_6D_6$, 600 MHz): 7.208 (dd, 1H, J = 8.0 Hz, $^4$J$_{HH}$ = 1 Hz), 7.162 (t, 1H, J = 8.0 Hz), 7.08 - 7.04 (m, 4H), 6.868 (d, 1H, J = 8.0 Hz), 6.820 (d, 1H, J = 7.0 Hz), 6.819 (d, 1H, J = 8.0 Hz), 6.800 (d, 1H, J = 7.0 Hz), 6.695 (t, 1H, J = 7.0 Hz), 6.595 (d, 1H, J = 8.0 Hz), 6.521 (d, 1H, J = 8.0 Hz), 5.133 (d, 1H, $^2$J$_{HH}$ = 1.0 Hz), 5.108 (d, 1H, $^2$J$_{HH}$ = 1.0 Hz), 5.018 (d, 1H, $^2$J$_{HH}$ = 1.0 Hz), 4.845 (d, 1H, $^2$J$_{HH}$ = 1.0 Hz), 3.668 (sept,
1H, $J = 7.0$ Hz), 3.373 (sept, 1H, $J = 7.0$ Hz), 2.938 (sept, 1H, $J = 7.0$ Hz), 2.799 (s, 3H), 2.434 (sept, 1H, $J = 7.0$ Hz), 2.233 (s, 3H), 1.721 (s, 3H), 1.706 (s, 3H), 1.411 (d, 3H, $J = 7.0$ Hz), 0.923 (d, 3H, $J = 7.0$ Hz), 0.914 (d, 3H, $J = 7.0$ Hz), 0.874 (d, 3H, $J = 7.0$ Hz), 0.800 (d, 3H, $J = 7.0$ Hz), 0.788 (d, 3H, $J = 7.0$ Hz), 0.754 (d, 3H, $J = 7.0$ Hz), 0.677 (d, 3H, $J = 7.0$ Hz); $^{13}$C{$_1$H} NMR (C$_6$D$_6$, 150 MHz): 151.85, 149.90, 149.36 (x 2), 148.64 (x 2), 147.96, 143.68, 143.22, 142.03 (x 2), 141.70 (x 2), 141.00, 140.70, 139.85 (x 2), 136.23 (x 2), 127.48, 127.22, 127.11, 127.02, 126.70, 125.71, 124.85, 124.40, 123.89, 123.68, 122.39, 108.40, 106.27, 99.91, 99.64, 29.75, 29.26, 28.53, 28.02, 26.78, 26.60, 25.49, 25.29, 25.01, 24.77, 24.57, 23.20, 21.80, 21.08, 21.03, 19.63; IR: 2905 (s), 1650 (m), 1635 (m), 1509 (m), 1444 (s), 1401 (w), 1357 (m), 1345 (w), 1280 (m), 1238 (w), 1154 (w), 1144 (w), 1087 (w), 1052 (w), 938 (w), 802 (w). Anal. Calcd. for C$_{50}$H$_{57}$ClN$_3$NbO$_4$: C, 67.30; H, 6.44; N, 4.71. Found: C, 67.05; H, 6.69; N, 4.36. Melting point: 149 ºC (dec.).

(L$_7^7$)$_2$Nb(N-2,6-Me$_2$C$_6$H$_3$)(Cl) (20$^*$)

To a flask containing both 11 (0.50 g, 1.2 mmol) and Li-L$_7$ (0.76 g, 2.4 mmol), pentane (100 mL) was added. The mixture was stirred overnight at ambient temperature. Then, the orange precipitate was filtered and remaining ligand was removed by washing with pentane (3 x 30 mL). Lithium chloride was readily removed by extracting the product into toluene (50 mL) and filtering. The solution was then dried under vacuum (0.75 g, 72%). $^1$H NMR (C$_6$D$_6$, 600 MHz): 8.032 (s, 1H), 7.882 (s, 1H), 7.184 (d, 1H, $J = 7.8$ Hz), 7.083 (d, 2H, $J = 7.8$ Hz), 7.050-7.031 (m, 2H), 6.862 (d, 1H, $J = 7.8$ Hz), 6.840 (d, 1H, $J = 7.8$ Hz), 6.737 (t, 2H, $J = 7.8$ Hz), 6.452 (d, 1H, $J = 7.8$ Hz), 5.125 (s, 1H), 5.092 (s, 1H), 4.959
(s, 1H), 4.932 (s, 1H), 3.763 (sept, 1H, J = 7.2 Hz), 3.618 (sept, 1H, J = 7.2 Hz), 2.856 (s, 3H), 2.415 (d, 3H, J = 7.2 Hz), 2.324 (s, 3H), 1.256 (sept, 1H, J = 7.2 Hz), 0.964 (d, 3H, J = 7.2 Hz), 0.926 (d, 3H, J = 7.2 Hz), 0.882 (d, 3H, J = 7.2 Hz), 0.858 (d, 3H, J = 7.2 Hz), 0.723 (d, 3H, J = 7.2 Hz), 0.690 (d, 3H, J = 7.2 Hz); 13C{1H} NMR (C₆D₆, 150 MHz): 177.30, 176.28, 156.81, 152.69, 151.02, 150.76, 150.49, 149.74, 143.63, 142.40, 142.28, 141.08, 141.03, 140.81, 137.45, 137.19, 128.62, 127.53, 127.01, 126.18, 125.60, 124.53, 110.77, 109.16, 108.25, 106.80, 104.73, 100.32, 99.78, 98.44, 29.53, 28.58, 28.47, 27.95, 27.88, 27.46, 27.32, 26.61, 26.58, 25.67, 24.32, 23.30, 22.77, 19.67; IR: 3040 (w), 2924 (s), 1550 (m), 1461 (s), 1377 (m), 1247 (m), 1056 (m), 804 (m), 724 (m); Anal. Calcd. for C₄₈H₅₃N₃NbO₄Cl·Et₂O: C, 66.55; H, 6.77; N, 4.48. Found: C, 66.84; H, 7.06; N, 4.29. Melting point: 130-135 °C (dec.).

(L₈)₂Nb(N-C₆H₅)Cl (21): To a flask containing both 12 (2.0 g, 7.2 mmol) and Li-L₈ (2.4 g, 14 mmol) which had been cooled (0 °C), cold pentane (100 mL) was added, forming a yellow slurry. The mixture was kept at 0 °C for 1 h, brought to room temperature and stirred for 3 h. The mixture was filtered and washed with pentane (3 x 30 mL). Lithium chloride was readily removed by extracting the product into toluene (50 mL) and filtering. The product was concentrated under vacuum to precipitate a fine green solid with a 5: 2 ratio of the products (1.8 g, 33 %); ¹H NMR (C₆D₆, 600 MHz): Major Isomer: 7.261 (d, 1H, J = 8.0 Hz), 7.175 (t, 1H, J = 8.0 Hz), 7.09 - 7.02 (m, 3H), 7.042 (d, 1H, J = 8.0 Hz), 6.947 (d, 1H, J = 8.0 Hz), 6.837 (t, 2H, J = 7.0 Hz), 6.763 (d, 1H, J = 8.0 Hz), 6.697 (d, 1H, J = 8.0 Hz), 6.609 (t, 1H, J = 7.0 Hz), 6.476 (d, 1H, J = 7.0 Hz), 6.204 (d, 2H, J = 7.0 Hz), 5.387 (d, 1H, ²JHH = 1.0 Hz), 5.351 (d, 1H, ²JHH = 1.0 Hz), 5.208 (d, 1H, ²JHH = 1.0 Hz), 5.169 (d, 1H, ²JHH = 1.0 Hz), 3.726 (sept, 1H, J = 7.0 Hz),
3.442 (sept, 1H, J = 7.0 Hz), 3.281 (sept, 1H, J = 7.0 Hz), 3.187 (sept, 1H, J = 7.0 Hz), 1.828 (s, 3H), 1.796 (s, 3H), 1.444 (d, 3H, J = 7.0 Hz), 1.241 (d, 3H, J = 7.0 Hz), 1.139 (d, 3H, J = 7.0 Hz), 1.058 (d, 3H, J = 7.0 Hz), 1.004 (d, 3H, J = 7.0 Hz), 0.819 (d, 3H, J = 7.0 Hz), 0.783 (d, 3H, J = 7.0 Hz), 0.588 (d, 3H, J = 7.0 Hz); **Minor Isomer:** 7.277 (d, 1H, J = 8.0 Hz), 7.241 (d, 1H, J = 8.0 Hz), 7.191 (d, 1H, J = 8.0 Hz), 7.003 (d, 1H, J = 8.0 Hz), 6.981 (d, 1H, J = 8.0 Hz), 6.981 (t, 1H, J = 8.0 Hz), 6.960 (t, 1H, J = 8.0 Hz), 6.937 (t, 1H, J = 8.0 Hz), 6.896 (d, 1H, J = 8.0 Hz), 6.866 (d, 1H, J = 8.0 Hz), 6.845 (t, 1H, J = 8.0 Hz), 6.451 (d, 1H, J = 8.0 Hz), 5.295 (d, 1H, J = 2.0 Hz), 5.093 (d, 1H, J = 2.0 Hz), 4.775 (d, 1H, J = 2.0 Hz), 4.743 (d, 1H, J = 2.0 Hz), 3.761 (sept, 1H, J = 7.0 Hz), 3.645 (sept, 1H, J = 7.0 Hz), 2.932 (sept, 1H, J = 7.0 Hz), 2.804 (sept, 1H, J = 7.0 Hz), 2.054 (s, 3H), 1.919 (s, 3H), 1.597 (d, 3H, J = 7.0 Hz), 1.077 (d, 3H, J = 7.0 Hz), 1.029 (d, 3H, J = 7.0 Hz), 0.895 (d, 3H, J = 7.0 Hz), 0.878 (d, 3H, J = 7.0 Hz), 0.798 (d, 3H, J = 7.0 Hz), 0.599 (d, 3H, J = 7.0 Hz), 0.563 (d, 3H, J = 7.0 Hz); $^{13}$C $^1$H NMR (C$_6$D$_6$, 150 MHz): **Major Isomer:** 185.12, 184.48, 159.09, 152.14, 150.48, 149.33, 149.24 (x 2), 148.94, 142.13, 141.95, 141.79, 141.74, 141.02, 139.51, 127.90, 127.55, 127.28, 127.14, 125.18, 124.98, 124.61, 124.53, 124.48, 124.19, 123.86, 122.83, 122.74, 106.94, 105.67, 100.51, 100.39, 28.86, 28.67, 28.66, 26.96, 25.77, 25.35, 25.15, 24.79, 24.69, 24.65, 23.77, 23.32, 20.51, 20.11; **Minor Isomer:** 182.27, 180.46, 176.75, 169.34, 153.06, 151.40, 150.14, 149.94, 149.57, 147.17, 144.95, 143.43, 142.03, 141.74, 141.70, 138.76, 128.92, 128.68, 127.28, 126.67, 126.44, 125.55, 124.74, 124.63, 124.40, 124.23, 122.62, 122.06, 107.56, 106.23, 100.68, 100.09, 30.75, 29.90, 29.04, 28.20, 27.36, 26.78, 26.71, 25.59, 25.51 (x 2), 23.07, 22.72, 22.07, 21.73; IR: 1543 (m), 1460 (s), 1408 (m), 1377
(L^8)_2Nb(N-CMe_3)Cl (22): A flask containing both 13 (1.0 g, 3.9 mmol) and Li-L^8 (2.6 g, 7.8 mmol) was cooled to 0 °C, followed by the addition of cooled pentane (50 mL). A yellow slurry formed and was stirred at 0 °C for 1 h. The mixture was warmed to room temperature and stirred for an additional 3 h. The mixture was filtered and washed with pentane (3 x 20 mL). Lithium chloride was readily removed by extracting the product into toluene (50 mL) and filtering. The resulting solution was then dried under vacuum to yield a fine dark green solid (0.6 g, 20%). The ^1H NMR shows a mixture of two isomers in a 3:1 ratio. ^1H NMR (C_6D_6, 600 MHz): **Major isomer:** 7.290 (d, 1H, J = 7.8 Hz), 7.203 (d, 1H, J = 7.8 Hz), 7.086 (t, 2H, J = 7.8 Hz), 7.016 (d, 2H, J = 7.8 Hz), 6.691 (d, 1H, J = 7.8 Hz), 6.549 (d, 1H, J = 7.8 Hz), 6.489 (d, 1H, J = 7.8 Hz), 5.481 (d, 1H, J_HH = 1.2 Hz), 4.832 (d, 1H, J_HH = 1.2 Hz), 4.668 (s, 1H), 4.581 (s, 1H), 4.250 (sept, 2H, J = 7.2 Hz), 4.087 (sept, 2H, J = 7.2 Hz), 3.314 (s, 3H), 3.118 (s, 9H), 1.900 (s, 3H), 1.670 (d, 6H, J = 7.2 Hz), 1.615 (d, 6H, J = 7.2 Hz), 1.510 (d, 6H, J = 7.2 Hz), 0.932 (d, 6H, J = 7.2 Hz); **Minor Isomer:** 7.338 (d, 1H, J = 7.8 Hz), 7.257 (d, 1H, J = 7.8 Hz), 7.191 (d, 1H, J = 7.8 Hz), 7.092 (d, 2H, J = 7.8 Hz), 6.977 (t, 2H, J = 7.8 Hz), 6.921 (d, 1H, J = 7.8 Hz), 6.849 (d, 1H, J = 7.8 Hz), 6.646 (d, 1H, J = 7.8 Hz), 5.356 (d, 1H, J_HH = 1.2 Hz), 5.252 (d, 1H, J_HH = 1.2 Hz), 4.730 (s, 1H), 4.665 (s, 1H), 3.959 (sept, 2H, J = 6.6 Hz), 3.519 (sept, 2H, J = 6.6 Hz), 3.380 (s, 3H), 3.263 (s, 9H), 2.110 (s, 3H), 1.430 (d, 3H, J = 6.6 Hz), 1.405 (d, 3H, J = 6.6 Hz), 1.365 (d, 3H, J = 6.6 Hz), 1.301 (d, 3H, J = 6.6 Hz), 1.172 (d, 3H, J = 6.6 Hz), 1.002 (d, 3H, J = 6.6 Hz), 0.691 (d, 3H, J = 6.6 Hz).
6.6 Hz), 0.510 (d, 3H, J = 6.6 Hz); $^{13}$C{¹H} NMR (C₆D₆, 150 MHz): **Major Isomer:** 156.12, 151.65, 150.18, 139.39, 137.83, 130.08, 129.84, 128.39, 127.90, 127.20, 126.89, 126.35, 125.94, 125.34, 125.33, 125.30, 125.13, 124.90, 123.90, 109.33, 109.10, 107.37, 101.15, 34.54, 31.96, 30.30, 30.26, 29.95, 29.74, 29.31, 27.10, 26.86, 26.40, 26.29, 25.46, 24.93, 24.45, 22.93, 22.19, 22.09, 19.56; **Minor Isomer:** 153.41, 146.65, 142.93, 142.44, 140.79, 140.73, 135.61, 128.73, 128.30, 126.01, 125.07, 124.85, 124.55, 119.18, 108.71, 108.45, 106.90, 102.87, 102.61, 101.46, 101.40, 100.24, 85.45, 35.15, 32.70, 32.51, 32.42, 31.73, 29.86, 29.08, 28.34, 27.03, 26.96, 26.57, 26.21, 25.61, 24.75, 24.34, 24.23, 22.48, 19.11; IR: 2926 (s), 2853 (s), 2355 (s), 1555 (w), 1492 (m), 1456 (s), 1373 (m), 1243 (m), 1046 (m), 823 (w). Melting Point: 175 °C (dec.).

**($L^8$)$_2$Ta(N-2,6-iPr$_2$C$_6$H$_3$)Cl (23):** To a flask containing both 14 (0.30 g, 0.54 mmol) and Li-$L^8$ (0.352 g, 1.08 mmol), pentane (100 mL) was added, and the mixture was stirred at room temperature for 24 h, forming an orange slurry. The mixture was filtered, washed with pentane (2 x 50 mL), and dried under vacuum leaving a fine orange solid. Lithium chloride was readily removed by extracting the product into toluene (50 mL), filtering and removing solvent under vacuum (0.51, 85%). Crystals suitable for X-ray diffraction were recrystallized from a 1:1 ratio of toluene and n-pentane after two days at -18 °C. ¹H NMR (C₆D₆, 600 MHz): 7.195 (d, 1H, J = 7.2 Hz), 7.131 (d, 1H, J = 7.2 Hz), 7.114-7.064 (m, 4H), 7.057 (d, 1H, J = 7.8 Hz), 7.034 (t, 1H, J = 7.2 Hz), 6.913 (d, 1H, J = 7.8 Hz), 6.888 (d, 1H, J = 6.0 Hz), 6.875 (d, 1H, J = 6.0 Hz), 6.621 (d, 1H, J = 7.8 Hz), 6.497 (d, 1H, J = 7.8 Hz), 5.143 (s, 1H), 5.103 (s, 1H), 5.065 (s, 1H), 4.921 (s, 1H), 4.686 (sept, 1H, J = 6.6 Hz), 3.901 (sept, 1H, J = 6.6 Hz), 3.308 (sept, 1H, J = 6.6 Hz), 3.268 (sept, 1H, J = 6.6 Hz), 2.640 (sept, 1H, J = 6.6 Hz), 2.399 (sept, 1H, J = 6.6 Hz), 1.775 (s, 3H),
1.658 (s, 3H), 1.404 (d, 3H, J = 6.6 Hz), 1.359 (d, 3H, J = 6.6 Hz), 1.267 (d, 3H, J = 6.6 Hz), 1.091 (d, 3H, J = 6.6 Hz), 1.043 (d, 3H, J = 6.6 Hz), 0.913 (d, 3H, J = 6.6 Hz), 0.837-0.809 (m, 12H), 0.679 (d, 3H, J = 6.6 Hz), 0.578 (d, 3H, J = 6.6 Hz); ^13C{^1H} NMR (C₆D₆, 150 MHz): 183.93, 181.34, 179.63, 178.38, 154.52, 153.26, 150.73, 150.42, 150.09, 148.29, 147.26, 147.13, 143.85, 143.26, 142.61, 142.36, 141.98, 140.91, 127.57, 126.98, 126.92, 126.15, 124.91, 124.46, 124.26, 123.65, 123.36, 122.42, 121.38, 108.24, 106.14, 99.93, 99.78, 29.82, 29.28, 28.65, 28.45, 27.94, 27.10, 26.80, 26.29, 25.71, 25.56, 25.26, 25.22, 25.09, 25.02, 24.80, 23.51, 23.35, 22.64, 22.04; IR: 1547 (m), 1459 (s), 1408 (w), 1376 (w), 1303 (w), 1248 (m), 1150 (w), 1123 (w), 1094 (w), 1050 (w), 943 (w), 863 (w), 800 (w), 777 (w). Anal. Calcd. for C₅₄H₆₅ClN₃O₄Ta: C, 62.57; H, 6.32; N, 4.04. Found: C, 62.66; H, 6.11; N, 4.02. Melting point: 210 °C (dec.).

(L⁶)₂Ta(N-2,6-iPr₂C₆H₃)Cl (24): To a flask containing both 14 (0.20 g, 0.36 mmol) and Li-L⁶ (0.217 g, 0.723 mmol), pentane (100 mL) was added, and the mixture was stirred at room temperature for 24 h, forming an orange slurry. The mixture was filtered, washed with pentane (2 x 50 mL), and dried under vacuum leaving a fine orange solid. Lithium chloride was readily removed by extracting the product into toluene (30 mL) and filtering. ^1H NMR spectroscopic data of this product revealed an equilibrium mixture of two isomers in a 2:1 ratio. The separation of ^1H NMR and ^13C NMR peaks was possible by variable temperature NMR studies of the product at 42 °C in C₆D₆ which leads to 3:1 peak ratios assignable as major and minor isomers. Crystals suitable for X-ray diffraction were recrystallized from ether after a day at -25 °C (0.28 g, 80%); ^1H NMR (C₆D₆, 400 MHz): Major isomer: 7.216 (d, 2H, J = 8.0 Hz), 7.197 (d, 2H, J = 8.0 Hz), 7.052 (d, 1H, J = 8.0 Hz), 7.013-6.868 (m, 4H), 6.591 (dd, 2H, J = 8.0 Hz, ^4J_HH = 1.2 Hz), 6.534 (dd,
2H, \(J = 8.0\) Hz, \(^4J_{HH} = 1.2\) Hz), 5.246 (s, 1H), 5.218 (s, 1H), 5.162 (s, 1H), 5.051 (s, 1H), 4.573 (sept, 1H, \(J = 7.2\) Hz), 4.219 (sept, 1H, \(J = 7.2\) Hz), 3.149 (dq, 2H, \(^2J_{HH} = 16\) Hz, \(J = 7.2\) Hz), 2.620 (dq, 2H, \(^2J_{HH} = 16\) Hz, \(J = 7.2\) Hz), 1.720 (dq, 2H, \(^2J_{HH} = 16\) Hz, \(J = 7.2\) Hz), 1.622 (s, 3H), 1.592 (s, 3H), 1.372 (d, 3H, \(J = 7.2\) Hz), 1.319 (d, 3H, \(J = 7.2\) Hz), 1.139 (t, 3H, \(J = 7.2\) Hz), 1.108 (t, 3H, \(J = 7.2\) Hz), 0.869 (d, 3H, \(J = 7.2\) Hz), 0.813 (d, 3H, \(J = 7.2\) Hz), 0.784 (t, 3H, \(J = 7.2\) Hz), 0.753 (t, 3H, \(J = 7.2\) Hz); **Minor isomer:** 7.258 (d, 2H, \(J = 7.6\) Hz), 7.094-7.020 (m, 3H), 6.841 (d, 2H, \(J = 8.0\) Hz), 6.774 (d, 2H, \(J = 8.0\) Hz), 6.742 (d, 2H, 8.0 Hz), 6.466 (dd, 1H, \(J = 8.0\) Hz), 6.353 (dd, 1H, \(J = 8.0\) Hz, \(^4J_{HH} = 1.2\) Hz), 5.638 (s, 1H), 5.270 (s, 1H), 5.145 (s, 1H), 5.019 (s, 1H), 3.749 (sept, 1H, \(J = 6.8\) Hz), 3.412 (dq, \(^2J = 16\) Hz, \(J = 7.2\) Hz), 3.335 (sept, 1H, \(J = 6.8\) Hz), 2.364 (dq, \(^2J = 16\) Hz, \(J = 7.2\) Hz), 1.896 (dq, \(^2J = 16\) Hz, \(J = 7.2\) Hz), 1.695 (dq, \(^2J = 16\) Hz, \(J = 7.2\) Hz), 1.539 (s, 3H), 1.530 (d, 3H, \(J = 7.2\) Hz), 1.522 (s, 3H), 1.253 (d, 3H, \(J = 7.2\) Hz), 1.205 (d, 3H, \(J = 7.2\) Hz), 1.149 (t, 3H, \(J = 7.2\) Hz), 0.791 (t, 3H, \(J = 7.2\) Hz), 0.744 (t, 3H, \(J = 7.2\) Hz), 0.714 (d, 3H, \(J = 7.2\) Hz); \(^{13}C\{^1H\} \text{NMR (C}_6\text{D}_6, 150 MHz): **Major Isomer:** 183.59, 181.09, 178.95, 178.90, 158.18, 153.35, 150.76, 150.38, 149.62, 148.32, 148.18, 147.95, 143.19, 138.58, 137.94, 136.55, 136.36, 127.30, 126.97, 126.50, 126.30, 125.82, 125.59, 124.45, 123.25, 122.09, 121.58, 108.20, 106.14, 100.30, 100.08, 30.08, 28.33, 27.50, 25.21, 24.83, 24.77, 24.61, 24.33, 24.03, 23.98, 23.73, 19.35, 16.23, 15.30, 14.68, 13.43; **Minor isomer:** 182.22, 178.65, 175.98, 172.56, 150.20, 144.71, 149.62, 147.82, 143.04, 141.44, 140.21, 138.41, 137.72, 135.70, 128.40, 128.16, 126.73, 126.08 (x 2), 125.26, 124.87, 124.62, 124.55, 124.42, 123.83, 122.95, 107.25, 105.88, 100.93, 100.24, 66.24, 28.88, 28.46, 27.75, 26.74, 26.21, 25.77, 25.60, 23.49, 22.02, 20.03, 18.75, 16.28, 15.92,
15.01, 14.37, 12.82; IR: 2923 (s), 2856 (s), 1459 (m), 1248 (w), 1122 (w), 1050 (w), 943 (w), 805 (w), 723 (w). Anal. Calcd. for C$_{50}$H$_{57}$ClN$_3$O$_4$Ta: C, 61.25; H, 5.86; N, 4.29. Found: C, 61.58; H, 6.19; N, 4.17. Melting point: 190-195 °C.

(L$_4$)$_2$Ta(N-2,6-iPr$_2$C$_6$H$_3$)Cl (25): To a flask containing both 14 (0.133 g, 0.240 mmol) and Li-L$_4$ (0.125 g, 0.482 mmol), pentane (100 mL) was added, and the mixture was stirred at room temperature for 24 h, forming an orange slurry. The mixture was filtered, washed with pentane (2 x 50 mL), and dried under vacuum, leaving a fine orange solid. The fine powder was redissolved in toluene and the insoluble LiCl was filtered off. Removal of volatiles under vacuum left behind a brownish oil. The oil was recrystallized from ether at -25 °C, yielding an orange crystalline solid. $^1$H NMR showed a mixture of two isomers with a 1:1 ratio. Synthesis of this product at 0 °C results in the formation of major and minor isomers in a 3:1 ratio (0.18, 80%); $^1$H NMR (C$_6$D$_6$, 600 MHz): **Major isomer:** 7.258 (d, 1H, $J = 7.2$ Hz), 7.038 (d, 1H, $J = 7.2$ Hz), 6.990 (d, 1H, $J = 7.2$ Hz), 6.930-6.884 (m, 3H), 6.882 (d, 1H, $J = 7.8$ Hz), 6.862 (d, 1H, $J = 7.2$ Hz), 6.855 (d, 1H, $J = 7.8$ Hz), 6.815 (d, 1H, $J = 7.8$ Hz), 6.688 (t, 1H, $J = 7.8$ Hz), 6.588 (d, 1H, $J = 7.8$ Hz), 6.533 (d, 1H, $J = 7.8$ Hz), 5.250 (s, 1H), 5.240 (s, 1H), 5.147 (s, 1H), 5.077 (s, 1H), 4.616 (sept, 1H, $J = 6.6$ Hz), 4.318 (sept, 1H, $J = 6.6$ Hz), 2.354 (s, 3H), 1.869 (s, 3H), 1.593 (s, 3H), 1.481 (s, 3H), 1.466 (s, 3H), 1.435 (d, 3H, $J = 6.6$ Hz), 1.365 (d, 3H, $J = 6.6$ Hz), 1.331 (s, 3H), 1.222 (d, 3H, $J = 6.6$ Hz), 0.810 (d, 3H, $J = 6.6$ Hz); **Minor isomer:** 7.128 (d, 1H, $J = 7.8$ Hz), 7.085 (d, 1H, $J = 7.8$ Hz), 7.035 (d, 1H, $J = 7.8$ Hz), 6.962-6.930 (m, 6H), 6.741 (t, 1H, $J = 7.8$ Hz), 6.507 (d, 1H, $J = 8.4$ Hz), 6.481 (d, 1H, $J = 8.4$ Hz), 6.342 (d, 1H, $J = 7.8$ Hz), 5.658 (s, 1H), 5.293 (s, 1H), 5.217 (s, 1H), 5.060 (s, 1H), 3.760 (sept, 1H, $J = 6.6$ Hz), 3.576 (sept, 1H, $J = 6.6$ Hz), 2.403 (s, 3H), 2.189 (s, 3H), 2.139 (s, 3H),
1.897 (s, 3H), 1.663 (d, 3H, J = 6.6 Hz), 1.580 (s, 3H), 1.292 (d, 3H, J = 6.6 Hz), 1.199 (s, 3H), 1.157 (d, 3H, J = 6.6 Hz), 0.710 (d, 3H, J = 6.6 Hz); $^{13}$C$_{1}$H NMR (C$_6$D$_6$, 150 MHz): Major Isomer: 183.68, 180.74, 178.99, 178.90, 158.04, 150.94, 150.74, 150.43, 149.32, 149.10, 148.55, 142.95, 141.24, 133.38, 132.34, 131.34, 130.72, 129.97, 128.89, 128.75, 128.54, 126.44, 125.85, 125.79, 124.47, 123.22, 121.97, 121.53, 108.18, 106.25, 100.37, 100.13, 28.26, 27.58, 25.43, 24.58, 24.22, 24.19, 20.48, 18.64, 18.19, 18.01, 17.13; Minor Isomer: 184.30, 182.57, 178.01, 172.39, 150.36, 150.22, 149.68, 149.54, 147.80, 147.21, 133.02, 132.91, 131.71, 130.10, 129.46, 127.97, 127.49, 125.65, 125.42, 125.03, 124.59, 123.70, 123.30, 121.82, 108.06, 107.33, 106.01, 101.71, 100.92, 100.31, 29.96, 28.85, 28.51, 26.24, 24.82, 22.36, 21.16, 20.14, 19.75, 19.63, 19.23, 18.53, 18.05; IR: 3175 (w), 2926 (s), 2864 (s), 1550 (m), 1492 (w), 1456 (s), 1373 (s), 1347 (w), 1243 (m), 1119 (w), 1088 (w), 1046 (m), 937 (w), 823 (w), 761 (w). Anal. Calcd. for C$_{46}$H$_{49}$ClN$_3$O$_4$Ta: C, 59.77; H, 5.34; N, 4.55. Found: C, 59.63; H, 5.32; N, 4.33. Melting point: 150 ºC (dec.).

($L^7$)$_2$Ta(N-2,6-iPr$_2$C$_6$H$_3$)Cl (26): To a flask containing both 14 (0.60 g, 1.1 mmol) and Li-$L^7$ (0.813 g, 2.58 mmol), pentane (100 mL) was added, forming a yellow slurry. The mixture was stirred at room temperature for 24 h, forming an orange slurry. The mixture was filtered, washed with pentane (3 x 30 mL), and dried under vacuum, leaving a fine orange solid. The fine powder was redissolved in toluene and the insoluble LiCl was filtered off. Volatiles were removed under vacuum. The resulting oil was recrystallized from ether at -25 ºC, yielding an orange crystalline solid (0.74 g, 75%); $^1$H NMR (C$_6$D$_6$, 600 MHz): 8.050 (s, 1H), 7.957 (s, 1H), 7.281 (d, 1H, J = 7.8 Hz), 7.261 (d, 1H, J = 7.8 Hz), 7.188-6.906 (m, 8H), 6.639 (d, 1H, J = 7.8 Hz), 6.573 (d, 1H, J = 7.8 Hz), 6.440 (d,
1H, J = 7.8 Hz), 5.161 (s, 1H), 5.078 (s, 1H), 5.058 (s, 1H), 4.953 (s, 1H), 4.754 (sept, 1H, J = 6.6 Hz), 4.116 (sept, 1H, J = 6.6 Hz), 3.739 (sept, 1H, J = 6.6 Hz), 3.339 (sept, 1H, J = 6.6 Hz), 2.780 (sept, 1H, J = 6.6 Hz), 2.685 (sept, 1H, J = 6.6 Hz), 1.303 (d, 3H, J = 6.6 Hz), 1.260 (d, 3H, J = 6.6 Hz), 1.170 (d, 3H, J = 6.6 Hz), 0.991-0.862 (m, 18 H), 0.826 (d, 3H, J = 6.6 Hz), 0.721 (d, 3H, J = 6.6 Hz), 0.671 (d, 3H, J = 6.6 Hz); $^{13}$C{$_{^1}$H} NMR (C$_6$D$_6$, 150 MHz): 177.01, 176.35, 153.28, 151.03, 150.53, 150.52, 149.32, 143.78, 142.78, 142.27, 141.26, 141.03, 137.79, 128.93, 127.85, 127.68, 127.45, 126.95, 126.37, 125.94, 125.72, 124.00, 123.93, 123.65, 123.03, 122.86, 122.22, 109.26, 106.66, 100.36, 99.99, 29.88, 29.05, 28.61, 28.27, 28.04, 27.90, 27.78, 27.53, 25.78, 25.47, 25.26, 25.14, 24.58, 24.36, 23.45, 23.13, 23.08, 22.76, 21.89; IR: 2923 (s), 2856 (s), 1608 (w), 1552 (w), 1459 (s), 1410 (w), 1376 (m), 1250 (m), 1167 (w), 1111 (w), 1058 (w), 798 (w), 723 (w). Anal. Calcd. for C$_{52}$H$_{61}$ClN$_3$O$_4$Ta: C, 61.93; H, 6.10; N, 4.17. Found: C, 62.02; H, 5.96; N, 4.15. Melting point: 185 ºC (dec.).

L$_8$-L$_8$: A flask containing both V(=NPh)Cl$_3$ (0.50 g, 2.0 mmol) and Li-L$_8$ (1.33 g, 4.04 mmol) was cooled to -77 ºC. Then, toluene (20 mL) was added to the flask. The slurry was warmed to room temperature while stirring overnight. The resulting precipitate (LiCl) was filtered and the dark brown solution was concentrated under vacuum. The dark brown color of the resulting solid is due to contamination with paramagnetic V(=NPh)Cl species (see Scheme 3-3). A brown gooey solid was obtained from this crude product by extracting with pentane and concentrating under vacuum. Careful crystallization from concentrated pentane solution at room temperature or a 1:1 ratio of pentane and ether and storing overnight at -25 ºC resulted in the reductive coupling product as a white powder (0.33 g, 25%). $^1$H NMR (C$_6$D$_6$, 600 MHz): 7.226 (d, 2H, J =
8.4 Hz), 7.137-7.115 (m, 4H), 7.083 (d, 2H, J = 7.8 Hz), 6.649 (d, 2H, J = 7.8 Hz), 5.431 (s, 2H), 5.210 (s, 2H), 2.839 (sept, 2H, J = 6.6 Hz), 2.674 (sept, 2H, J = 6.6 Hz), 1.922 (s, 6H), 1.145 (d, 6H, J = 6.6 Hz), 1.109 (d, 6H, J = 6.6 Hz), 1.078 (d, 12H, J = 6.6 Hz);

\[^{13}\text{C}\{^{1}\text{H}\}\] NMR (C\textsubscript{6}D\textsubscript{6}, 150 MHz): 168.10, 163.68, 148.46, 147.39, 147.18, 136.87, 136.75, 136.69, 136.67, 129.67, 128.90, 126.03, 124.26, 124.18, 123.80, 123.75, 123.01, 122.74, 116.83, 108.28, 108.18, 107.95, 101.75, 101.72, 29.10, 28.41, 28.36, 24.27, 23.77, 23.72, 23.29, 21.45; IR: 2960 (s), 2857 (s), 1460 (s), 1378 (m), 1260 (m), 1097 (m), 1044 (m), 800 (m). Melting point: 80-85 °C.

3.5 Crystallography

Summaries of crystal data and collection parameters for crystal structures of 16, 17, 18, 20, 23, 24, and L\textsuperscript{8}-L\textsuperscript{8} are provided in Tables 3.2, 3.3, 3.4. Detailed descriptions of data collection, as well as data solution, are provided below. ORTEP diagrams were generated with the ORTEP-3 software package.\textsuperscript{137} For each sample, a suitable crystal was mounted on a pulled glass fiber using Paratone N hydrocarbon oil. The crystal was transferred to a Siemens SMART\textsuperscript{138} diffractometer with a CCD area detector, centered in the X-ray beam, and cooled to the indicated temperature using a nitrogen-flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. An arbitrary hemisphere of data was collected using 0.3° ω scans, and the data were integrated by the program SAINT.\textsuperscript{139} The final unit cell parameters were determined by a least-squares refinement of the reflections with I > 10σ(I). Data analysis using Siemens XPREP\textsuperscript{140} and the successful solution and refinement of the structure determined the space group. An empirical absorption correction was applied using SADABS.\textsuperscript{141} Equivalent reflections were averaged, and the structures were solved
by direct methods using the SHELXTL software package.\textsuperscript{142} Unless otherwise noted, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as fixed atoms but not refined.

16. X-ray quality crystals were grown from a saturated solution of diethyl ether at -20 °C. The asymmetric unit contains one half molecule of disordered solvent located at an inversion center. Additionally, one ligand methyl group is disordered over two positions. The disordered solvent molecule was refined isotropically. The final cycle of full-matrix least-squares refinement was based on 11698 observed reflections and 558 variable parameters and converged yielding final residuals: \( R = 0.0814, R_{\text{all}} = 0.1200 \) and \( \text{GOF} = 1.002 \).

17. X-ray quality crystals were grown from a saturated solution of diethyl ether at -20 °C. The final cycle of full-matrix least-squares refinement was based on 10183 observed reflections and 496 variable parameters and converged yielding final residuals: \( R = 0.0361, R_{\text{all}} = 0.0546 \) and \( \text{GOF} = 0.928 \).

18. X-ray quality crystals were grown from a saturated solution of diethyl ether at -20 °C. The final cycle of full-matrix least-squares refinement was based on 9101 observed reflections and 424 variable parameters and converged yielding final residuals: \( R = 0.0389, R_{\text{all}} = 0.0863 \) and \( \text{GOF} = 0.936 \).

20. X-ray quality crystals were grown from a saturated solution of diethyl ether at -20 °C. The asymmetric unit contained two independent molecules of compound 20, as well as two ordered diethyl ether solvent molecules. The final cycle of full-matrix least-squares refinement was based on 24814 observed reflections and 1153 variable parameters and converged yielding final residuals: \( R = 0.0586, R_{\text{all}} = 0.1117 \) and \( \text{GOF} = \)
23. X-ray quality crystals were grown from a layered solution of toluene and pentane at -20 °C. In addition to compound 23, the asymmetric unit contained two molecules of disordered toluene, located in three separate regions. Additionally, one isopropyl methyl group is disordered over two positions. The toluene molecules were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 14845 observed reflections and 669 variable parameters and converged yielding final residuals: R = 0.0406, R_all = 0.0545 and GOF 1.044.

24. X-ray quality crystals were grown from a saturated solution of diethyl ether at -20 °C. The asymmetric unit contained one half molecule of disordered diethyl ether located at an inversion center. The disordered solvent molecule was refined isotropically. The final cycle of full-matrix least-squares refinement was based on 11859 observed reflections and 549 variable parameters and converged yielding final residuals: R = 0.0451, R_all = 0.0623 and GOF = 1.028.

Li\textsuperscript{8}-L\textsuperscript{8}: X-ray quality crystals were grown from a saturated pentane solution at -25 °C. The final cycle of full-matrix least-squares refinement was based on 7192 observed reflections and 433 variable parameters and converged yielding final residuals: R = 0.0570, R_all = 0.1017, and GOF = 0.8850.
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Table 3.3. Crystal data and collection parameters

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<tr>
<td>γ [°]</td>
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<tr>
<td>V [Å³]</td>
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</tr>
<tr>
<td>R_all</td>
<td>0.1017</td>
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<tr>
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</table>
3.6 Conclusions

Mono-anionic acetophenone imine ligands with a wide diversity of imine substituents have proven to be strong chelating ligands for the synthesis of niobium and tantalum imido complexes of the form (L)\textsubscript{2}MCl(NR) (L = ortho-metalated acetophenone imine; M = Nb, Ta; R = aryl, alkyl). Primarily, the complexes are synthesized as only a single structural isomer (out of at least six possible isomers). Exceptions where two isomers are observed suggest the formation of kinetic products and careful fractional crystallization allowed for the isolation of a single major isomer in several cases. These complexes are quite robust–stable to temperatures of at least 150 °C in all cases. Chapter 4 discusses the substitution of the chloride ligand with alkyl and amido groups. Ongoing research in the Schmidt group involves the stoichiometric and catalytic chemistry of these new complexes.
Chapter 4

Derivatization of Niobium Complexes Bearing Imido and Acetophenone Imine Ligands

4.1 Introduction

The investigation of group V and VI complexes possessing metal-carbon multiple bonds has led to the development of numerous useful early transition metal alkylidene catalysts with applications in organic transformations such as olefin metathesis and ring opening polymerization. For niobium alkylidenes, it is believed that several key features are indispensible to provide good stability and high catalytic activity. First, the steric bulk of the ligands is important. In addition to satisfying the metal’s coordination sphere, the ligands must be small enough to allow substrates access to the metal center for catalysis, while having enough steric bulk to prevent catalyst decomposition through the formation of bimolecular species. Another important aspect of these catalysts involves the alkylidene substituents and their electronic properties. The presence of the alkylidene’s electron rich carbon moiety adjacent to the very electrophilic early metal center as a result of the formation of the metal-carbon multiple bond leaves both ends of this moiety highly susceptible to electrophilic and nucleophilic attacks, leading to catalytic or stoichiometric reactions of the metal complex. Thus, in the
development of these catalysts, it has been found that careful supporting ligand design is crucial for overall catalyst performance, while the alkylidene fragment present initially can have a dramatic effect on catalyst initiation rates.

The imido moiety (NR$_2$; R = alkyl, aryl) is somewhat similar to that of the alkylidene, in terms of overall charge and reactivity with various unsaturated substrates.$^{224}$ The additional lone pair on the nitrogen atom usually interacts with the metal center, making this a 6-electron donor fragment, as is often observed by a nearly linear M-N-R bond angle. This stronger bonding has hindered efforts to develop catalytic reactivity of the metal-imido fragment, although catalytic imine metathesis has met with some success.$^{224-226}$ Additionally, early transition metal imido complexes have been extensively applied to catalytic hydroamination reactions, especially after the emergence of Ti imido complexes exhibiting high activities for intermolecular hydroamination.$^{215,227-232}$

Also based on similarities to known group IV transition metal catalysts, several vanadium alkyl and aryl imido complexes have been shown to display good selectivity and functional group tolerance in the polymerization of smaller alkynes.$^{233,234}$ Undoubtedly, the continued investigation of metal imido reactivity utilizing new ligand platforms will help to extend the applications of these early transition metal imido complexes.$^{235}$

A focus of recent efforts in our research group has been the development of orthometallated aryl imines. Through the careful choice of imine substituents, direct lithiation reactions have led to ortho-lithiated acetophenone imine derivatives, as well as the related aldimines (see Chapter Two).$^{38,124,236}$ These have proven to be useful chelating ligands to support group IV and V metal chemistry.$^{38,237,128}$ In Chapter Three,
we described the synthesis of a series of niobium and tantalum imido complexes employing these structurally tunable bidentate, orthometallated acetophenone imine ligands. The overall strategy utilized salt metathesis reactions of a metal imido precursor \([M(NR)\text{Cl}_3(\text{dme})]; (M = \text{Nb, Ta})\] with the ortho-lithiated acetophenone imine ligands to yield new metal complexes with the general formula \(L_2M\text{Cl}(NR)\) \((M = \text{Nb, Ta}; L = \text{ortho-metalated acetophenone imine, } R = \text{substituted aryl or } ^{t}\text{Bu})\). The further derivatization of the metal-halogen bond in these complexes is the subject of the work presented in this Chapter, including details of the synthesis and structural characterization of several new complexes with more reactive \(\sigma\)-donor ligands bound to the group V metal center.

**Scheme 4-1.** Derivatization reactions of 15 \((R', R'' = 2,6-^{t}\text{Pr}_2C_6H_3)\).
4.2 Results and Discussion

The synthesis and characterization of a series of group V metal complexes with the general formula L₂MCl(NR) (M = Nb, Ta; L = ortho-metalated acetophenone imine; R = tBu or aryl) were described in Chapter Three.¹²⁸ These metal complexes were formed by the salt metathesis reactions of group V imido starting materials with lithiated acetophenone imine ligands. The thirteen reported derivatives were characterized as six-coordinate, pseudo-octahedral species. Because of the low symmetry of these complexes, six different structural isomers are possible (plus enantiomers, where appropriate), but due to the electronic effects of the different ligand donor atoms, each complex was isolated as only one or, in some cases, two isomers. Various trends were identified correlating the steric bulk of the acetophenone imine and imido ligands with the isolated structural isomers. In general, very sterically bulky or sterically small ligands generated only a single isomer of the metal complexes. As an example, complex 15 was isolated as a single isomer, as shown in Scheme 1.²³⁸ To delineate the reactivity of these new metal complexes and to obtain potential catalyst precursors, we undertook an investigation of the substitution chemistry accessible by derivatization of the metal halogen bond. Out of the many previously synthesized metal complexes, 15 was chosen as the substrate of interest in this study due to its robust structure and the fact that it exists as only one isomer. It was hypothesized that the large steric bulk in 15 would limit reaction products to single isomers, reducing the complexity inherent to these derivatization reactions. A general summary of the substitution reactions of 15 presented herein is shown in Scheme 4-1.
The primary focus of this study was to replace the chloride ligand of 15 with a variety of more reactive \( \sigma \) donor ligands, such as alkyls, aryls, or alkynyls, as well as oxygen, phosphorus and nitrogen donor ligands. The general approach employed for this chemistry was to react 15 with a reactive alkali metal salt of the desired \( \sigma \)-donor ligand in order to utilize a salt metathesis reaction to form the derivatized niobium complexes. In many cases, complex 15 was unreactive upon treatment with alkali or alkaline earth metal reagents, as exemplified by attempts at derivatization using PhLi, PhMgBr, LiNH\( t^\text{Bu} \), LiN(SiMe\( 3 \))\( 2 \), LiNHAr, NaOAr, Ph\( 2 \)PLi, \( n^\text{Bu} \)Li or \( t^\text{Bu} \)Li. Given the large steric bulk of many of these functional groups, we suspect that the failure of these reactions was due to the significant steric constraints of the very bulky ligands present in complex 15. However, in four cases, 15a-d, derivatization reactions successfully resulted in low to moderate yields of complexes containing new Nb-C bonds. Although much work has been accomplished using cyclopentadienyl supporting ligands, non-cyclopentadienyl niobium complexes of this type with both imido and alkyl groups, such as methyl and trimethylsilylmethyl, or alkynyl ligands, such as trimethylsilylacetylide and phenylacetylide, are quite rare and to date few examples of niobium complexes of this sort are reported in the literature.\(^ {215,238-247} \)

Treatment of 15 with MeLi in ether at \(-77^\circ\text{C}\) resulted in a red material that NMR spectroscopy revealed to be a complex mixture of products. Alternatively, the choice of MeLi·LiBr as the alkylating agent gave better control over the derivatization reaction, most likely due to the attenuated reactivity of the carbanion in this reagent. The \(^1\text{H}\) NMR spectrum of the orange powder resulting from the reaction of 15 and MeLi·LiBr confirmed that the methylated complex (15a) retains the same isomeric configuration as
found in the starting metal complex (see discussion below). The methyl group appeared at 1.353 ppm, while the –OCH2O– units showed four signals at 5.193, 5.162, 5.103, and 5.078 ppm. Successful alkylation of complex 15 was also achieved upon its treatment with trimethylsilylmethyl lithium. The bulky trimethylsilylmethyl ligand has seen broad use in early transition metal chemistry, and there are many previous reports of its application in niobium complexes.244-268 Its popularity is undoubtedly linked to current commercial availability and the kinetic stability provided by the sterically bulky trimethylsilyl group. Based on 1H NMR spectroscopy, it was clear that an alkylated product (15b) was produced as a single isomer in the reaction of 15 with LiCH2SiMe3. The NMR spectra of 15b were quite interesting, especially in terms of the resonances associated with the trimethylsilylmethyl group. In the 1H NMR spectrum, the methylene protons of this alkyl group were diastereotopic and appeared at vastly different chemical shifts (3.926 and -0.888 ppm; $^2J_{HH} = 9.2$ Hz). Most previous reports of niobium complexes with the trimethylsilylmethyl ligand do not display inequivalent methylene protons (even in chiral species where these protons are expected to be diastereotopic), although the chemical shifts reported for these protons span a wide spectral range (-1.5 to 3.6 ppm).245-259 A limited number of reports do show inequivalent proton signals for this methylene group, and in these cases, the two protons are generally widely separated in the spectrum (often ~3 ppm apart).244,264-268 Green and coworkers found a 1.5 ppm separation between these two diastereotopic protons in related hydrazido complexes and attributed the chemical shift difference to ring current effects from $\pi$-interactions with adjacent ligands.265 In contrast, for more extreme cases (~3 ppm chemical shift difference), this effect has been attributed to $\alpha$-agostic interactions between the
methylene group and the highly electrophilic metal center. Complex 15b has the largest difference yet observed for these two protons in a niobium species and we attribute the observed resonances in our $^1$H NMR spectrum to a combination of both effects: π-interactions with the aryl groups of the acetophenone imine ligands, as well as an α-agostic interaction between the trimethylsilylmethyl group and the niobium center in complex 15b. Further, we have determined the $^{13}$C-$^1$H coupling constant for this methylene carbon atom to be 104.74 Hz, a smaller value than typically observed for methylene groups, lending further evidence for an α-agostic interaction. For comparison, the $^1J_{C-H}$ coupling constant for the methyl complex (15a) was found to be much larger (120.54 Hz). X-ray quality crystals of 15b were grown from a saturated ether solution at ambient temperature. As expected based on the NMR spectroscopy, 15b is formed as a different isomer than the starting metal complex 15 (Figure 4-1). In 15b, the trimethylsilylmethyl ligand is positioned trans to an imine nitrogen, rather than a phenyl carbon atom. Bond distances and angles for 15b are summarized in Table 4.1. The hydrogen atoms of the methylene unit of the trimethylsilylmethyl ligand were located in the difference map and refined positionally, further confirming the strong agostic interaction present in this complex. One hydrogen atom of this unit interacts strongly with the metal center as noted by the acute Nb-C-H bond angle (73(6)$^\circ$ degrees). Additionally, the Nb-C-Si angle (140.9(5)$^\circ$ degrees) is much more obtuse than usual as a result of the Nb-H interaction. Overall, this agostic interaction, in addition to ring current effects from the phenyl ring coordinated to the niobium center cis to the trimethylsilylmethyl ligand account for its $^1$H NMR spectroscopic characteristics.
Figure 4-1. ORTEP diagram (50% thermal ellipsoids) of 15b. Hydrogen atoms (other than the agostic methylene unit) have been omitted for clarity.

Table 4.1. Selected bond distances (Å) and angles (deg) in crystal structures.

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<td>131.1(4)</td>
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We attribute the unsuccessful derivatization of 15 with bulkier σ donor ligands to the steric congestion at the metal center in this complex since no reaction was observed with the larger reagents. To confirm this hypothesis, we synthesized a slightly less
sterically constrained niobium complex (20*), in which the imido group from 15 (N-2,6-iPr2C6H3) was replaced by the smaller N-2,6-Me2C6H3 group and aldimine ligands were used in place of the ketimine ligands. As hoped, 20* reacted with excess phenyl lithium, giving the desired metathesis product after an overnight reaction period (Scheme 4-2). Like most of the derivatized metal complexes described in this work, further purification of the product was achieved by washing the crude material with pentane and concentrating an ether solution to give a light brown solid. Its 1H NMR spectrum shows only one isomer with the geometry denoted in Scheme 4-2 as confirmed by the appearance of new 1H NMR peaks for the diagnostic –OCH2O– moiety of the aldimine ligands at 5.224, 5.109, 5.077, and 4.944 ppm.

Scheme 4-2. The less sterically bulky 20* allows for derivatization with PhLi (R’= 2,6-iPr2C6H3, R”= 2,6-Me2C6H3).

Given the large steric bulk around niobium in 15, we felt that it might be an ideal precursor for the isolation of alkynyl complexes. Thus, derivatization with lithium phenylacetylide and lithium trimethylsilylacetylide was also tested. Very few niobium trimethylsilylacetylide complexes are known (none structurally characterized), and only one niobium phenylacetylide complex has been previously characterized by X-ray diffraction. Both reactions were performed in ether, resulting in brown solutions. In the
reaction of 15 with lithium phenylacetylide, the alkynyl complex (15c) was isolated as a single isomer upon crystallization from ether. The X-ray crystal structure of 15c shows a C1 symmetric molecule with distorted octahedral geometry around the metal center (Figure 4-2). Bond distances and angles for 15c are summarized in Table 4.1. In contrast, the trimethylsilylacetylide complex (15d) initially forms as only one isomer (major; as drawn in Scheme 4-1), as observed by 1H NMR spectroscopy, but upon extraction into pentane and cooling to -25 °C, it partially isomerized, resulting in a 1:1 ratio of two isomers. These two isomers are the same as observed in the chloride complexes discussed in Chapter Three128 and represent the two most favorable structures based on electronic considerations (minor isomer is analogous to 15b). This isomerization can be explained based upon the differing strengths of σ-donation of the anionic carbon on these two acetylide ligands. The σ-donation of the anionic carbon in the phenylacetylide ligand is weaker due to the poorer electron-releasing ability of the phenyl substituent, in turn making it a weaker trans effect ligand. Thus, upon derivatization of 15 with the weaker trans effect ligand, we expect the acetylide to orient trans to the stronger donor group of the orthometallated acetophenone ligand, namely the carbon atom. On the other hand, for the trimethylsilylacetylide ligand, the electron-releasing trimethylsilyl group enhances the terminal carbon’s negative charge so that it behaves as a stronger trans effect ligand. This results in less discrimination between the imine carbon and nitrogen donors, resulting in the formation of a mixture of both isomers.
The reactions of 15 with anionic oxygen donor ligands, such as triflate and methoxide, were found to proceed readily to give derivatized products. Treatment of 15 with silver triflate in toluene produces 15e as a brown powder upon workup. $^1$H and $^{13}$C NMR analyses of the resulting material confirmed the successful isolation of a new metal complex. Unfortunately, no crystals of 15e suitable for X-ray diffraction were obtained. The assignment of 15e as the simple metathesis product where an inner sphere triflate ligand takes the place of the chloride ligand was confirmed by the resonances observed in the $^1$H and $^{13}$C NMR spectra, as well as the elemental analysis of the isolated brown powder. Inner sphere triflate ligands are often observed in niobium complexes due to the very oxophilic nature of this early transition metal center. $^{273-277}$ The specific isomer where the triflate ligand is located trans to the carbon donor atom of an acetophenone imine ligand was assigned based on the $^1$H NMR resonances of the methylenedioxy groups, as discussed in detail below. A similar reaction of 15 with sodium methoxide in
ether and subsequent workup in pentane produced a red precipitate, which \(^1\)H NMR spectroscopy showed to be a single isomer of a new product. The most notable spectroscopic aspects of this compound (15f) were the resonances for the methoxy group: 4.711 (\(^1\)H) and 69.10 ppm (\(^{13}\)C). X-ray quality crystals of this compound were grown from pentane and its crystal structure is shown in Figure 4-3. Unlike the other crystal structures presented in this work, the asymmetric unit of 15f contains three complete niobium complexes, as well as two pentane molecules. The three independent molecules of 15f in the asymmetric unit are virtually identical, although not related by any crystallographic symmetry operations. Also notable is the structural isomer formed by complex 15f. The strongly \(\sigma\)-donating methoxy group is located trans to the nitrogen atom of the acetophenone imine ligand, meaning that this complex has completely isomerized compared to the starting complex (15), in which the chloride atom was trans to the carbon of the acetophenone imine.

![Figure 4-3. ORTEP diagram (50% thermal ellipsoids) of 15f. Other two metal complexes, hydrogen atoms and two pentane solvent molecules have been omitted for clarity.](image-url)
Previous studies on the chemistry of amide ligands with niobium(III) and tantalum(III) suggest that amides can be successfully utilized to support group V metals in that oxidation state.\textsuperscript{278} On the other hand, the use of amide ligands with a lower oxidation state group V metal such as niobium(II) results in alternate reaction pathways and the formation of highly reactive species.\textsuperscript{279} Gambarotta et al. have shown that C-N bond activation of the amide or oxidative addition of C-H bonds to the metal center are common processes, leading to the formation of reactive and unexpected products.\textsuperscript{280} Fascinated with the high activity of zirconium amides in catalytic hydroamination reactions\textsuperscript{281-288} and considering the high oxidation state of the metal center in 15, we attempted to extend the derivatization reactions of 15 to include nitrogen donor ligands, specifically amides. To that end, we treated complex 15 with various structurally simple dialkyl amide substrates, including LiNMe\textsubscript{2}, LiN\textsubscript{2}Et\textsubscript{2}, LiN\textsubscript{i}Pr\textsubscript{2}, and cyclic LiNC\textsubscript{5}H\textsubscript{10}. In all cases, a purple solid precipitated from solution soon after the reaction mixture had warmed to ambient temperature. NMR spectroscopy of the purple precipitate in benzene-\textit{d}_6 indicated the presence of one or more new metal complexes (with no evidence of paramagnetic species), although the spectra were quite complicated, preventing reliable determination of reaction products based on these crude materials. Since the purple materials had low solubility in benzene-\textit{d}_6, the NMR analyses were also performed in toluene-\textit{d}_8 and CDCl\textsubscript{3}, neither of which proved to be more interpretable. Quenching this material by exposure to excess water resulted in formation of the protio ligands as expected, implying that ligand activation processes were not present, in contrast to the results reported by Gambarotta. Further complicating matters, we found that drying this purple material under vacuum resulted in a slow transformation to a yellow solid.
Exposure to vacuum for a few hours resulted in complete conversion to the new yellow material. As such, we attempted to grow X-ray quality crystals of the purple material directly from the reaction mixture, but we were unsuccessful in all cases. Given the complexity of the NMR spectra of the purple materials, we hypothesize that this material is an equilibrium mixture of the desired niobium-amide complex and its subsequent seven-coordinate β-hydride elimination product (intermediate drawn in Scheme 4-1). Upon drying under vacuum, the somewhat volatile coordinated imine resulting from β-hydride elimination is slowly removed, thus forcing the equilibrium to the generation of exclusively the 6-coordinate niobium-hydride complex (15g). The ¹H NMR spectrum of the yellow solid (15g) shows a single isomer and a distinctive broad singlet at 9.98 ppm that integrates to one proton. The ¹H NMR spectrum of this yellow solid is always the same, no matter which of the amides is used to effect this reaction. Unfortunately, all attempts to generate X-ray quality crystals of this complex have led to yellow powders or microcrystalline material. In previous work, Cummins has shown that niobium-hydride complexes can be produced by β-hydride elimination reactions and that these are frequently found to be readily reversible reactions. Additionally, the hydride resonance is commonly found at low field for high-valent early transition metal complexes, and it is often broadened when bound to a quadrupolar niobium nucleus. Thus, the downfield chemical shift for our niobium(V)-hydride ¹H NMR signal and its characteristically broad signal at 9.98 ppm lend further support for our assignment of 15g as a 6-coordinate niobium-hydride complex.
Subsequent exposure of either the purple precipitate or the niobium-hydride (15g) to air rapidly results in the formation of a niobium hydroxide complex (15h). This complex was produced in the highest yield and purity by simply opening the Schlenk flask containing one of these materials and exposing it to ambient atmosphere for ten minutes. This was then resealed and workup under air-free conditions led to the isolation of 15h in high yield. The resulting 1H NMR spectrum shows the disappearance of the hydride resonance at 9.98 ppm and the appearance of a hydroxide signal at 8.79 ppm. Furthermore, 15h readily crystallizes from ether and its crystal structure is shown in Figure 4-4.

The methylenedioxy resonances in the 1H NMR spectra of these complexes (Table 4.2) prove to be quite useful in determining the structural isomers of the products described herein (15, 15a-h, 20*, 20a*). In all cases, the two inequivalent, diastereotopic methylene groups yield a set of four resonances in the region near 5 ppm. It is clear that
two types of compounds exist based on these resonances: one where all four resonances are near 5.00 ppm with a narrow spectral distribution and a second type with lower field (~5.5 ppm) and higher field (~4.7 ppm) resonances with a much wider distribution of signals. Based on these observations, those from Chapter Three,\textsuperscript{128} and the X-ray crystal structures determined herein, we can conclude that the first type of methylene resonances (all four close to 5 ppm) denote the structural isomer with the imido group \textit{trans} to the nitrogen of an orthometallated acetophenone imine and the carbon atoms of the two acetophenone imine ligands arranged \textit{cis} to each other. Thus, the second set of resonances (spread across a spectral window from 5.5 to 4.7 ppm) indicates the other preferred isomer, with imido group \textit{trans} to the nitrogen of an orthometallated acetophenone imine and the carbon atoms of the two acetophenone imine ligands \textit{trans} to one another. Thus, a general trend in the geometry of the metal complexes resulting from the derivatization reactions of 15 relates to the donor strength of the ligands employed in these complexes. With weaker \textit{trans} effect ligands, such as phenylacetylide and triflate, the metal complex prefers a geometry such as the one shown in Figure 4-2, in which the new substituent is positioned \textit{trans} to the acetophenone imine ligand’s anionic carbon atom. On the other hand, with stronger \textit{trans} effect ligands such as hydride, methoxide and hydroxide, the entering ligand is oriented \textit{trans} to the imine nitrogen instead. As was the case in Chapter Three,\textsuperscript{128} the very strongly donating imido group is always found \textit{trans} to the weakly donating nitrogen atom of an orthometallated acetophenone imine, leaving only two isomers as possibilities for our derivatized complexes.
Table 4.2. Methyleneedioxy $^1$H NMR chemical shifts observed.

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<tr>
<td>15a</td>
<td>5.19 5.16 5.10 5.08</td>
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<tr>
<td>15b</td>
<td>5.52 5.36 4.79 4.67</td>
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<tr>
<td>15c</td>
<td>5.19 5.16 5.13 5.08</td>
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<tr>
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<tr>
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<td>15h</td>
<td>5.51 5.36 4.82 4.81</td>
</tr>
<tr>
<td>20*</td>
<td>5.13 5.09 4.96 4.93</td>
</tr>
<tr>
<td>20a*</td>
<td>5.22 5.11 5.08 4.94</td>
</tr>
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</table>

4.3 A Cationic Niobium Imido Complex

The majority of transition metal based catalysts are electronically unsaturated and the hypothesis is that the unsaturation causes a better catalyst-substrate interaction.$^{299}$ For example, group IV olefin polymerization catalysts show higher activities in the presence of Lewis acid cocatalysts, such as aluminum alkyls or methyl aluminoxane.$^{300}$ However, the use of Lewis acid cocatalysts is not limited to only group IV metal complexes.$^{77}$ Unsaturation in a metal complex can be achieved simply by the reaction of a metal halide or metal alkyl with alkali metals, such as sodium or potassium, and Lewis acidic borate compounds, such as B(C$_6$F$_5$)$_3$. $^{301}$ General pathways to generate cationic metal complexes using some potent Lewis acidic boron compounds are shown in Scheme 4-3.$^{302}$ While the use of congeners of B(C$_6$F$_5$)$_3$, such as [Ph$_3$C][B(C$_6$F$_5$)$_4$], and anilinium salts, such as
[PhNHMe₂][B(C₆F₅)₄], results in complete abstraction of an alkyl group, the use of B(C₆F₅)₃ often leaves the alkyl group in the proximity of the metal cation, although in many cases this weak interaction between the alkyl and the metal center does not adversely affect the reactivity of the cationic metal complex.

![Scheme 4-3](image)

Scheme 4-3. Known routes to form cationic metal complexes.

In order to prepare cationic niobium species isoelectronic to the group IV hydroamination catalysts, the reactivity of the niobium methyl complex (15a) was tested with B(C₆F₅)₃. Because of the high solubility of 15a and B(C₆F₅)₃ in C₆D₆, these reactions were performed in this solvent, instead of C₆D₅Br, which is often used to solubilize these cationic complexes. Upon mixing 15a with B(C₆F₅)₃ in an NMR tube, the initial orange solution changed to an intense red color. The ¹H and ¹¹B NMR spectra of the resulting solution were also noticeably different from that of the starting materials 15a and B(C₆F₅)₃. The ¹¹B NMR spectrum of the resulting mixture showed a high field shift for boron, which is indicative of the formation of a four coordinate borate compound due to the extra shielding effect of the methyl group in this anion. The equilibrium shown in
Scheme 4-4 is highly dependent on reaction temperature. At 45 °C and higher, the equilibrium favors the formation of 15a, as confirmed by comparison of the $^1$H NMR spectrum of the reaction mixture at 45 °C (or higher) with the $^1$H NMR spectrum of the isolated starting material (15a).

![Scheme 4-4](image)

**Scheme 4-4.** Formation of a cationic niobium imido complex.

The reactivity of the cationic niobium complex (27) was tested with a variety of unsaturated substrates, such as cyclooctene, phenyl isocyanate, and 2,3-dimethyl-1,3-butadiene. All reactions were performed in C$_6$D$_6$ and the $^1$H NMR spectroscopic analysis confirmed the formation of multiple products in each case. As discussed in Section 1-4, the formation of metallacyclic intermediates upon addition of unsaturated substrates to group IV metal imido species plays an important role in the catalytic cycle for hydroamination catalyzed by metal imido complexes. Ongoing studies include full characterization of the cationic orange solid (27; Scheme 4-4) and complete analyses of the multiple isomers obtained in the reactions of the cationic niobium complex with unsaturated substrates.
4.4 Experimental

All moisture and air sensitive manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques and dried glassware. Diethyl ether was dried by passage through an activated alumina column. Toluene and pentane were dried over 4 Å activated molecular sieves. The dried solvents were sparged with nitrogen. AgSO$_3$CF$_3$ (AgOTf), $^9$BuLi (1.5 M in hexanes), MeLi-LiBr (1.6 M in hexanes), Me$_3$SiCH$_2$Li (1.0 M in pentane), and LiNMe$_2$ were used as purchased. Benzene-$d_6$ was vacuum transferred under nitrogen from purple Na/benzophenone ketyl and degassed with 3 freeze-evacuate-thaw cycles. Nb(N-2,6-Me$_2$C$_6$H$_3$)Cl$_3$(dme) (11),$^{128}$ Li-L,$^{7,128}$ (L$_5$)$_2$Nb(N-2,6-Pr$_2$C$_6$H$_3$)(Cl) (15),$^{128}$ (L$_7$)$_2$Nb(N-2,6-Me$_2$C$_6$H$_3$)(Cl) (20a$^*$),$^{269}$ C$_6$H$_5$Li,$^{291}$ PhCCLi,$^{292}$ Me$_3$SiCCLi,$^{293}$ MeONa,$^{294}$ LiNEt$_2$,$^{295}$ LiNPr$_2$,$^{296}$ LiNC$_5$H$_10$,$^{297}$ and B(C$_6$F$_5$)$_3$,$^{298}$ were prepared following literature procedures. The $^1$H and $^{13}$C{$^1$H} NMR spectra was recorded in benzene-$d_6$ at ambient temperature on a VXRS 400 or an Inova 600 MHz spectrometer and referenced internally to residual peaks at δ 7.16 ($^1$H) and δ 128.0 ppm ($^{13}$C). IR samples were prepared as Nujol mulls between KBr plates and spectra were taken on a Perkin-Elmer XTL FTIR spectrophotometer. Melting points were performed on a Mel-Temp; those compounds that were air sensitive were taken in a capillary tube sealed under a nitrogen atmosphere and are uncorrected. Elemental analysis was performed by Galbraith Laboratories, Knoxville, Tennessee. X-ray structure determinations were performed at the Ohio Crystallographic Consortium housed at the University of Toledo.
(L\textsuperscript{8})\textsubscript{2}Nb(N-2,6-i-Pr\textsubscript{2}C\textsubscript{6}H\textsubscript{3})(CH\textsubscript{3}) (15a)

A flask containing 15 (0.20 g, 0.21 mmol) in ether (100 mL) was cooled to -77 °C. To this solution, MeLi-LiBr (0.13 ml, 1.6 M in hexanes, 0.21 mmol) was added dropwise. The mixture was stirred and its temperature was maintained at -77 °C for 2 hours. Then, it was warmed to room temperature overnight. The resulting precipitate (LiCl) was filtered and the orange colored supernatant was concentrated. Orange crystals were obtained after 24h upon cooling the concentrated solution to -25 °C (0.04 g, 20%). \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 600 MHz): 7.185-7.030 (m, 7H, Ar H), 6.983 (d, 1H, \textit{J} = 7.2 Hz, Ar H), 6.963 (d, 1H, \textit{J} = 7.2 Hz, Ar H), 6.898 (d, 1H, \textit{J} = 8.0 Hz, Ar H), 6.836 (d, 1H, \textit{J} = 8.0 Hz, Ar H), 6.591 (d, 1H, \textit{J} = 8.0 Hz, Ar H), 6.561 (d, 1H, \textit{J} = 8.0 Hz, Ar H), 5.193 (s, 1H, OCH\textsubscript{2}O), 5.162 (s, 1H, OCH\textsubscript{2}O), 5.103 (s, 1H, OCH\textsubscript{2}O), 5.078 (s, 1H, OCH\textsubscript{2}O), 4.442 (sept, 1H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}), 3.828 (sept, 1H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}), 3.331 (sept, 1H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}), 3.071 (sept, 1H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}), 2.252 (sept, 1H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}), 1.761 (s, 3H, MeC=N), 1.678 (s, 3H, MeC=N), 1.362 (d, 3H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}), 1.353 (s, 3H, Nb-Me), 1.220 (d, 3H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}), 1.210 (d, 3H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}), 1.087 (d, 3H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}), 1.075 (d, 3H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}), 0.930 (d, 3H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}), 0.843 (d, 3H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}), 0.783 (d, 3H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}), 0.751 (d, 3H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}), 0.745 (d, 3H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}), 0.736 (d, 3H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}), 0.689 (d, 3H, \textit{J} = 6.8 Hz, CHMe\textsubscript{2}); \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (C\textsubscript{6}D\textsubscript{6}, 150 MHz): 182.22, 180.62, 156.51, 152.62, 150.40, 148.52, 147.95, 147.87, 147.74, 145.70, 143.52, 142.55, 141.53, 141.35, 141.27, 128.44, 128.20, 127.12, 126.40, 126.33, 124.95, 124.21, 124.10, 123.80, 123.75, 123.35, 122.73, 121.10, 107.55, 106.10, 99.82, 29.47, 29.43, 29.06, 28.50, 28.40, 27.85, 26.72, 26.14,
26.10, 25.52, 25.34, 25.28, 25.20, 25.15, 25.10, 24.42, 23.20, 23.01, 21.70, 21.50; IR: 3044 (w), 2933 (s), 2853 (s), 1551 (m, C=N), 1461 (s), 1375 (s), 1300 (m), 1245 (m), 1089 (w), 1043 (w), 938 (w), 792 (m); Anal. Calcd. for C\(_{55}\)H\(_{68}\)N\(_3\)NbO\(_4\): C, 71.18; H, 7.39; N, 4.53. Found: C, 69.57; H, 7.17; N, 4.71. Melting point: 160-165 ºC (dec.).

\(\text{(L}^5\)_2\text{Nb(N-2,6-iPr}_2\text{C}_6\text{H}_3)(\text{CH}_2\text{SiMe}_3)\) (15b)

A flask containing 15 (0.20 g, 0.21 mmol) and LiCH\(_2\)SiMe\(_3\) (0.020 g, 0.25 mmol) was cooled to -77 ºC. Then, ether (50 mL) was added to the flask. The mixture was stirred and its temperature was maintained at -77 ºC for 2 hours. The slurry was warmed to room temperature overnight. The resulting precipitate (LiCl) was filtered and the brown colored solution was concentrated until a brown powder was obtained. The brown powder was washed with pentane (2 × 20mL). Red crystals were obtained after 24 hours upon dissolving clean product in ether and cooling the concentrated solution to -25 ºC (0.090 g, 45%). \(^1\)H NMR (C\(_6\)D\(_6\), 600 MHz): 7.195 (d, 1H, \(J = 7.8\) Hz, Ar H), 7.093 (d, 1H, \(J = 7.8\)Hz, Ar H), 7.049 (dd, 1H, \(J = 7.8\) Hz, \(^4\)\(J_{HH} = 1.2\) Hz, \(m\)-iPr\(_2\)C\(_6\)H\(_3\)), 7.021 (d, 1H, \(J = 7.8\) Hz, Ar H), 6.982 (m, 4H, Ar H), 6.920 (d, 1H, \(J = 7.8\) Hz, Ar H), 6.904 (d, 1H, \(J = 7.8\) Hz, Ar H), 6.786 (dd, 1H, \(J = 7.8\) Hz, \(^4\)\(J_{HH} = 1.2\) Hz, \(m\)-iPr\(_2\)C\(_6\)H\(_3\)), 6.447 (t, 1H, \(J = 7.8\) Hz, \(p\)-iPr\(_2\)C\(_6\)H\(_3\)), 6.417 (d, 1H, \(J = 7.8\) Hz, Ar H), 5.524 (s, 1H, OCH\(_2\)O), 5.355 (s, 1H, OCH\(_2\)O), 4.791 (s, 1H, OCH\(_2\)O), 4.667 (s, 1H, OCH\(_2\)O), 4.659 (sept, 1H, \(J = 6.4\) Hz, CHMe\(_2\)), 3.926 (d, 1H, \(\text{}^3\)\(J_{HH} = 9.2\) Hz, CH\(_2\)SiMe\(_3\)), 3.813 (sept, 1H, \(J = 6.4\) Hz, CHMe\(_2\)), 3.157 (sept, 1H, \(J = 6.4\) Hz, CHMe\(_2\)), 3.053 (sept, 1H, \(J = 6.4\) Hz, CHMe\(_2\)), 2.913 (sept, 1H, \(J = 6.4\) Hz, CHMe\(_2\)), 2.661 (sept, 1H, \(J = 6.4\) Hz, CHMe\(_2\)), 2.119 (s, 3H, MeC=N), 1.823 (s, 3H, MeC=N), 1.460 (d, 3H, \(J = 6.4\) Hz, CHMe\(_2\)), 1.340 (d, 3H, \(J = 6.4\) Hz, CHMe\(_2\)), 1.271 (d, 3H, \(J = 6.4\) Hz, CHMe\(_2\)), 1.103 (d, 3H, \(J = 6.4\) Hz, CHMe\(_2\)), 1.050
(d, 3H, J = 6.4 Hz, CHMe₂), 1.007 (d, 3H, J = 6.4 Hz, CHMe₂), 0.866 (d, 3H, J = 6.4 Hz, CHMe₂), 0.858 (d, 3H, J = 6.4 Hz, CHMe₂), 0.806 (d, 3H, J = 6.4 Hz, CHMe₂), 0.635 (d, 3H, J = 6.4 Hz, CHMe₂), 0.590 (d, 3H, J = 6.4 Hz, CHMe₂), 0.566 (d, 3H, J = 6.4 Hz, CHMe₂), -0.002 (s, 9H, SiMe₃), -0.888 (d, 1H, JHH = 9.2 Hz, CH₂SiMe₃); ¹³C{¹H} NMR (C₆D₆, 150 MHz): 180.13, 178.83, 152.78, 151.89, 149.90, 148.80, 147.70, 147.46, 146.60, 146.07, 143.43, 142.72, 142.60, 141.78, 141.70, 141.20, 139.80, 128.51, 128.27, 126.34, 125.95, 125.16, 125.13, 124.67, 124.62, 124.34, 123.84, 123.08, 122.68, 122.30, 106.99, 105.86, 100.08, 99.85, 30.87, 29.91, 29.62, 28.60, 28.56, 28.50, 27.93, 27.83, 27.19, 26.87, 26.70, 26.60, 26.50, 26.30, 26.10, 25.30, 25.20, 24.86, 23.73, 23.31, 22.96, 22.95, 22.33, 21.78, 5.23; IR: 3159 (w), 2919 (s), 1556 (m, C=N), 1460 (s), 1370 (s), 1249 (m), 1085 (m), 1042 (m), 792 (s), 720 (m); Anal. Calcd. for C₅₈H₇₆N₃NbO₄Si: C, 69.65; H, 7.66; N, 4.20. Found: C, 65.44; H, 6.69; N, 4.79. Melting point: 195-200 ºC (dec.).

(L⁸)₂Nb(N-2,6-iPr₂C₆H₃)(C₂Ph) (15c)

A flask containing 15 (0.20 g, 0.21 mmol) and LiC₂Ph (0.033 g, 0.32 mmol) was cooled to -77 ºC. Then, ether (50 mL) was added to the flask. The mixture was stirred and its temperature was maintained at -77 ºC for 2 hours. The slurry was warmed to room temperature overnight. The resulting white precipitate (LiCl) was filtered and the solution was concentrated until a dark red powder was obtained. The dark red powder was washed with pentane (2×20 mL). Light brown crystals were obtained after 48 hours upon dissolving clean product in ether and cooling the concentrated solution to -25 ºC (0.080 g, 40%). ¹H NMR (C₆D₆, 600 MHz): 7.205 (d, 1H, J = 7.2 Hz, Ar H), 7.187 (d, 1H, J = 7.2 Hz, Ar H), 7.152-7.142 (m, 2H, Ar H), 7.133 (d, 2H, J = 7.2 Hz, Ar H), 7.128 (d, 1H, J =
7.2 Hz, Ar H), 7.052-7.005 (m, 6H, Ar H), 6.932 (d, 1H, J = 7.2 Hz, Ar H), 6.912 (d, 1H, J = 7.2 Hz, Ar H), 6.865 (d, 1H, J = 8.0 Hz, Ar H), 6.583 (d, 1H, J = 7.2 Hz, Ar H), 6.517 (d, 1H, J = 7.2 Hz, Ar H), 5.190 (s, 1H, OCH₂O), 5.161 (sept, 1H, J = 6.8 Hz, CHMe₂), 5.134 (s, 1H, OCH₂O), 5.082 (s, 1H, OCH₂O), 5.016 (s, 1H, OCH₂O), 3.946 (sept, 1H, J = 6.8 Hz, CHMe₂), 3.834 (sept, 1H, J = 6.8 Hz, CHMe₂), 3.432 (sept, 1H, J = 6.8 Hz, CHMe₂), 2.906 (sept, 1H, J = 6.8 Hz, CHMe₂), 2.514 (sept, 1H, J = 6.8 Hz, CHMe₂), 1.735 (s, 3H, MeC=N), 1.674 (s, 3H, MeC=N), 1.313 (d, 3H, J = 6.8 Hz, CHMe₂), 1.298 (d, 3H, J = 6.8 Hz, CHMe₂), 1.140 (d, 3H, J = 6.8 Hz, CHMe₂), 1.129 (d, 3H, J = 6.8 Hz, CHMe₂), 1.088 (d, 3H, J = 6.8 Hz, CHMe₂), 1.025 (d, 3H, J = 6.8 Hz, CHMe₂), 0.952 (d, 3H, J = 6.8 Hz, CHMe₂), 0.937 (d, 3H, J = 6.8 Hz, CHMe₂), 0.846 (d, 3H, J = 6.8 Hz, CHMe₂), 0.819 (d, 3H, J = 6.8 Hz, CHMe₂), 0.740 (d, 3H, J = 6.8 Hz, CHMe₂), 0.715 (d, 3H, J = 6.8 Hz, CHMe₂); ¹³C{¹H} NMR (C₆D₆, 150 MHz): 182.60, 182.17, 161.82, 161.03, 152.06, 150.65, 150.15, 148.93, 148.73, 147.10, 143.59, 143.15, 142.14, 141.95, 141.05, 131.79, 127.76, 126.97, 126.80, 126.35, 125.02, 124.90, 124.45, 124.10, 124.03, 123.75, 123.46, 122.84, 122.23, 122.06, 108.32, 106.17, 99.90, 99.70, 29.82, 29.05, 28.80, 28.33, 28.00, 26.77, 26.69, 26.23, 26.00, 25.96, 25.63, 25.33, 24.56, 24.41, 23.80, 23.66, 23.53, 23.33, 22.96, 21.98, 21.36; IR: 3035 (m), 2950 (s), 2846 (s), 1562 (s, C=N), 1450 (s), 1398 (s), 1333 (s), 1285 (s), 1075 (s), 932 (s), 779 (s), 674 (m); Anal. Calcd. for C₆₂H₇₀N₃NbO₄: C, 73.43; H, 6.96; N, 4.14. Found: C, 68.32; H, 6.72; N, 4.56. Melting point: 185-190 °C (dec.).
(L^8)_{2}Nb(N-2,6-iPr_{2}C_{6}H_{3})(C_{2}SiMe_{3}) (15d)

A flask containing 15 (0.20 g, 0.21 mmol) and LiC_{2}SiMe_{3} (0.030 g, 0.31 mmol) was cooled to -77 °C. Then, ether (50 mL) was added to the flask. The mixture was stirred and its temperature was maintained at -77 °C for 2 hours. The slurry was warmed to room temperature overnight and was stirred for 48 hours. The resulting white precipitate (LiCl) was filtered and the solution was concentrated until a brown powder was obtained. The brown powder was washed with pentane (2 × 20 mL). Brown crystals were obtained upon dissolving clean product in ether and cooling the concentrated solution to -25 °C (0.080 g, 40%). **Major isomer:** \(^1\)H NMR (C_{6}D_{6}, 600 MHz): 7.211 (d, 1H, J = 7.8 Hz, Ar H), 7.086 (d, 1H, J = 7.8 Hz, Ar H), 7.068-7.023 (m, 5H, Ar H), 6.950 (t, 2H, J = 7.8 Hz, p-iPr_{2}C_{6}H_{3}), 6.848 (d, 1H, J = 7.8 Hz, Ar H), 6.766 (d, 1H, J = 7.8 Hz, Ar H), 6.585 (d, 1H, J = 7.8 Hz, Ar H), 6.489 (d, 1H, J = 7.8 Hz, Ar H), 5.153 (s, 1H, OCH_{2}O), 5.077 (sept, 1H, J = 6.6 Hz, CHMe), 5.067 (s, 1H, OCH_{2}O), 5.053 (s, 1H, OCH_{2}O), 4.948 (s, 1H, OCH_{2}O), 3.885 (sept, 1H, J = 6.6 Hz, CHMe), 3.607 (sept, 1H, J = 6.6 Hz, CHMe), 3.326 (sept, 1H, J = 6.6 Hz, CHMe), 2.828 (sept, 1H, J = 6.6 Hz, CHMe), 2.414 (sept, 1H, J = 6.6 Hz, CHMe), 1.704 (s, 3H, MeC=N), 1.623 (s, 3H, MeC=N), 1.535 (d, 3H, J = 6.6 Hz, CHMe), 1.460 (d, 3H, J = 6.6 Hz, CHMe), 1.303 (d, 3H, J = 6.6 Hz, CHMe), 1.032 (d, 3H, J = 6.6 Hz, CHMe), 1.012 (d, 3H, J = 6.6 Hz, CHMe), 0.940 (d, 3H, J = 6.6 Hz, CHMe), 0.866 (d, 3H, J = 6.6 Hz, CHMe), 0.851 (d, 3H, J = 6.6 Hz, CHMe), 0.797 (d, 3H, J = 6.6 Hz, CHMe), 0.732 (d, 6H, J = 6.6 Hz, CHMe), 0.654 (d, 3H, J = 6.6 Hz, CHMe), 0.161 (s, 9H, SiMe_{3}); **Minor isomer:** \(^1\)H NMR (C_{6}D_{6}, 600 MHz): 7.278 (d, 1H, J = 7.8 Hz, Ar H), 7.224 (d, 1H, J = 7.8 Hz, Ar H), 7.189 (d, 1H, J = 7.8 Hz, Ar H), 7.137 (d, 1H, J = 7.8 Hz, Ar H), 7.128-7.085 (m, 4H, Ar H), 7.015 (d, 1H, J = 7.8 Hz,
Ar H), 6.935 (d, 1H, \(J = 7.8\) Hz, Ar H), 6.629 (t, 1H, \(J = 7.8\) Hz, \(p^3\)Pr2C6H3), 6.461 (d, 1H, \(J = 7.8\) Hz, Ar H), 6.425 (d, 1H, \(J = 7.8\) Hz, Ar H), 5.483 (s, 1H, OCH2O), 5.475 (s, 1H, OCH2O), 4.703 (s, 1H, OCH2O), 4.637 (s, 1H, OCH2O), 4.469 (sept, 1H, \(J = 6.6\) Hz, CHMe2), 3.915 (sept, 1H, \(J = 6.6\) Hz, CHMe2), 3.320 (sept, 1H, \(J = 6.6\) Hz, CHMe2), 2.945 (sept, 1H, \(J = 6.6\) Hz, CHMe2), 2.643 (sept, 1H, \(J = 6.6\) Hz, CHMe2), 2.411 (sept, 1H, \(J = 6.6\) Hz, CHMe2), 1.944 (s, 3H, MeC=N), 1.865 (s, 3H, MeC=N), 1.780 (d, 3H, \(J = 6.6\) Hz, CHMe2), 1.766 (d, 3H, \(J = 6.6\) Hz, CHMe2), 1.704 (d, 3H, \(J = 6.6\) Hz, CHMe2), 1.622 (d, 3H, \(J = 6.6\) Hz, CHMe2), 1.615 (d, 3H, \(J = 6.6\) Hz, CHMe2), 1.448 (d, 3H, \(J = 6.6\) Hz, CHMe2), 1.398 (d, 3H, \(J = 6.6\) Hz, CHMe2), 1.391 (d, 3H, \(J = 6.6\) Hz, CHMe2), 1.225 (d, 3H, \(J = 6.6\) Hz, CHMe2), 1.168 (d, 3H, \(J = 6.6\) Hz, CHMe2), 1.131 (d, 3H, \(J = 6.6\) Hz, CHMe2), 1.075 (d, 3H, \(J = 6.6\) Hz, CHMe2), -0.019 (s, 9H, SiMe3); **Major isomer:** \(^{13}\)C\{\(^1\)H\} NMR (C\(_6\)D\(_6\), 150 MHz): 181.67, 180.80, 156.45, 153.23, 152.26, 152.10, 150.34, 150.14, 149.27, 147.20, 143.73, 141.73, 139.19, 128.68, 127.03, 126.52, 126.44, 125.28, 125.08, 124.68, 124.45, 124.15, 123.95, 123.82, 122.63, 121.93, 108.19, 107.79, 100.70, 100.50, 99.70, 99.50, 30.57, 30.03, 29.10, 28.95, 28.72, 28.46, 28.25, 28.17, 27.91, 27.65, 27.06, 26.91, 26.74, 26.54, 26.51, 25.86, 25.64, 25.44, 25.35, 24.16, 24.10, 23.65, 23.48, 0.75; **Minor isomer:** \(^{13}\)C\{\(^1\)H\} NMR (C\(_6\)D\(_6\), 150 MHz): 182.32, 180.70, 154.75, 154.60, 153.53, 152.79, 149.90, 149.00, 148.87, 147.85, 147.32, 143.62, 143.35, 142.38, 141.65, 141.54, 138.82, 136.57, 126.94, 126.42, 126.26, 126.17, 125.19, 124.99, 124.89, 124.60, 124.26, 124.06, 123.49, 122.84, 101.61, 100.71, 30.40, 29.94, 29.53, 28.84, 28.36, 27.98, 27.81, 26.90, 26.79, 25.71, 25.05, 23.88, 23.20, 22.55, 22.01, 21.21, 21.03, 20.97, 17.85, 17.50, 14.53, 2.02, 1.47, 0.65; IR: 3063 (m), 2938 (s), 2852 (s), 1552 (s, C=N), 1460 (s), 1408 (s), 1303 (s), 1261 (s), 1090 (s), 947 (s), 801 (s), 683
(m); Anal. Calcd. for C$_{59}$H$_{74}$N$_{3}$NbO$_{4}$Si: C, 70.14; H, 7.39; N, 4.16. Found: C, 69.79; H, 7.42; N, 4.14. Melting point: 230-235 $^\circ$C (dec.).

$(L^8)_{2}$Nb(N-2,6-$^i$Pr$_2$C$_6$H$_3$)(SO$_3$CF$_3$) (15e)

A flask containing 15 (0.20 g, 0.21 mmol) and AgSO$_3$CF$_3$ (AgOTf) (0.10 g, 0.42 mmol) was cooled to -77 $^\circ$C. Then, toluene (50 mL) was added to the flask. The mixture was stirred and its temperature was maintained at -77 $^\circ$C for 2 hours. Then, the slurry was warmed to room temperature and was stirred for 48 hours. The resulting grey precipitate (AgCl) was filtered and the brown solution was concentrated until a brown powder was obtained. The brown powder was washed with ether (20 mL) and filtered (0.050 g, 25%).

$^1$H NMR (C$_6$D$_6$, 600 MHz): 7.406 (dd, 1H, $J = 7.8$ Hz, $^4J_{HH} = 1.2$ Hz, $^m$-Pr$_2$C$_6$H$_3$), 7.203 (dd, 1H, $J = 7.8$ Hz, $^4J_{HH} = 1.2$ Hz, $^m$-Pr$_2$C$_6$H$_3$), 7.141 (d, 1H, $J = 7.8$ Hz, Ar H), 7.068-7.037 (m, 3H, Ar H), 7.011 (d, 1H, $J = 7.8$ Hz, Ar H), 6.995 (t, 1H, $J = 7.8$ Hz, $^p$-Pr$_2$C$_6$H$_3$), 6.934 (d, 1H, $J = 7.8$ Hz, Ar H), 6.875 (d, 1H, $J = 7.8$ Hz, Ar H), 6.812 (d, 1H, $J = 7.8$ Hz, Ar H), 6.095 (t, 1H, $J = 7.8$ Hz, Ar H), 6.045 (s, 1H, OCH$_2$O), 5.045 (s, 1H, OCH$_2$O), 4.929 (s, 1H, OCH$_2$O), 4.710 (sept, 1H, $J = 6.6$ Hz, CHMe$_2$), 3.950 (sept, 1H, $J = 6.6$ Hz, CHMe$_2$), 3.318 (sept, 1H, $J = 6.6$ Hz, CHMe$_2$), 3.266 (sept, 1H, $J = 6.6$ Hz, CHMe$_2$), 2.787 (sept, 1H, $J = 6.6$ Hz, CHMe$_2$), 2.439 (sept, 1H, $J = 6.6$ Hz, CHMe$_2$), 1.780 (s, 3H, MeC=N), 1.684 (s, 3H, MeC=N), 1.435 (d, 3H, $J = 6.6$ Hz, CHMe$_2$), 1.330 (d, 3H, $J = 6.6$ Hz, CHMe$_2$), 1.203 (d, 3H, $J = 6.6$ Hz, CHMe$_2$), 1.063 (d, 3H, $J = 6.6$ Hz, CHMe$_2$), 1.025 (d, 3H, $J = 6.6$ Hz, CHMe$_2$), 0.923 (d, 3H, $J = 6.6$ Hz, CHMe$_2$), 0.861 (d, 3H, $J = 6.6$ Hz, CHMe$_2$), 0.832-0.804 (m, 9H, CHMe$_2$), 0.689 (d, 3H, $J = 6.6$ Hz, CHMe$_2$), 0.615 (d, 3H, $J = 6.6$ Hz, CHMe$_2$); $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 150 MHz): 183.17, 180.25, 150.11, 149.26, 148.32,
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\[ \text{IR: 2923 (s), 2852 (s), 1545 (w, C=N), 1460 (s), 1411 (w), 1376 (m), 1299 (w), 1247 (m), 1017 (w), 802 (w), 721 (w)} \]

\[ \text{Anal. Calcd. for C}_{55}\text{H}_{68}\text{F}_{3}\text{N}_{3}\text{NbSO}_{7}: \text{C, 62.20; H, 6.17; N, 3.96. Found: C, 62.14; H, 6.89; N, 3.51. Melting point: 130-135°C (dec.).} \]

\((L^8)_{2}\text{Nb(N-2,6-iPr}_{2}\text{C}_{6}\text{H}_{3})(\text{OCH}_{3})\) (15f)

A flask containing 15 (0.20 g, 0.21 mmol) and MeONa (0.017 g, 0.32 mmol) was cooled to -77 °C. Then, ether (50 mL) was added to the flask. The mixture was stirred and its temperature was maintained at -77 °C for 2 hours. Then, the slurry was warmed to room temperature and was stirred for 48 hours. The resulting white precipitate (NaCl) was filtered and the orange solution was concentrated under vacuum. The resultant orange powder was washed with pentane (20 mL) and filtered (0.12 g, 60%). $^1$H NMR (C$_6$D$_6$, 600 MHz): 7.156 (dd, 1H, $J = 7.2$ Hz, $^4J_{HH} = 1.2$ Hz, $m$-iPr$_2$C$_6$H$_3$), 7.060 (dd, 1H, $J = 7.2$ Hz, $^4J_{HH} = 1.2$ Hz, $m$-iPr$_2$C$_6$H$_3$), 7.015 (t, 2H, $J = 7.2$ Hz, $p$-iPr$_2$C$_6$H$_3$), 7.003 (dd, 1H, $J = 7.2$ Hz, $^4J_{HH} = 1.2$ Hz, $m$-iPr$_2$C$_6$H$_3$), 6.975 (t, 1H, $J = 7.8$ Hz, $p$-iPr$_2$C$_6$H$_3$), 6.916 (d, 1H, $J = 8.4$ Hz, Ar H), 6.909 (d, 1H, $J = 8.4$ Hz, Ar H), 6.865 (d, 1H, $J = 7.8$ Hz, Ar H), 6.862 (d, 1H, $J = 7.8$ Hz, Ar H), 6.829 (dd, 1H, $J = 7.2$ Hz, $^4J_{HH} = 1.2$ Hz, $m$-iPr$_2$C$_6$H$_3$), 6.485 (d, 1H, $J = 8.4$ Hz, Ar H), 6.463 (d, 1H, $J = 7.8$ Hz, Ar H), 5.563 (s, 1H, OCH$_2$O), 5.275 (s, 1H, OCH$_2$O), 4.711 (s, 3H, OMe), 4.690 (s, 1H, OCH$_2$O), 4.669 (s, 1H, OCH$_2$O), 4.421 (sept, 1H, $J = 7.2$ Hz, CHMe$_2$), 3.855 (sept, 1H, $J = 7.2$ Hz, CHMe$_2$), 3.597 (sept, 1H, $J = 7.2$ Hz, CHMe$_2$), 3.301 (sept, 1H, $J = 7.2$ Hz, CHMe$_2$), 2.680 (sept, 2H, $J = 7.2$ Hz, CHMe$_2$)
Hz, $\text{CHMe}_2$), 1.891 (s, 3H, $\text{MeC}=$N), 1.830 (s, 3H, $\text{MeC}=$N), 1.425 (d, 3H, $J = 7.2$ Hz, $\text{CHMe}_2$), 1.283 (d, 3H, $J = 7.2$ Hz, $\text{CHMe}_2$), 1.160 (d, 3H, $J = 7.2$ Hz, $\text{CHMe}_2$), 1.098 (d, 3H, $J = 7.2$ Hz, $\text{CHMe}_2$), 0.927 (d, 3H, $J = 7.2$ Hz, $\text{CHMe}_2$), 0.845 (d, 3H, $J = 7.2$ Hz, $\text{CHMe}_2$), 0.816 (d, 3H, $J = 7.2$ Hz, $\text{CHMe}_2$), 0.697 (d, 3H, $J = 7.2$ Hz, $\text{CHMe}_2$), 0.475 (d, 3H, $J = 7.2$ Hz, $\text{CHMe}_2$); $^{13}$C{\text{^1H}} \text{NMR (C}_6\text{D}_6, 150 \text{ MHz}): 180.68, 179.37, 154.04, 153.83, 149.32, 148.70, 147.25, 146.17, 145.78, 145.20, 143.48, 142.78, 142.00, 141.96, 141.90, 141.19, 128.68, 126.32, 125.97, 124.78, 124.67, 124.65, 124.58, 123.56, 123.36, 122.57, 122.25, 106.95, 105.95, 100.12, 99.90, 69.10, 30.25, 29.79, 28.51, 28.21, 27.96, 27.89, 26.93, 26.72, 26.67, 26.00, 25.94, 25.80, 25.42, 24.88, 23.77, 23.30, 22.85, 22.56, 21.84, 21.31; IR: 3020 (m), 2921 (s), 2870 (s), 1565 (m, C=N), 1460 (s), 1377 (s), 1248 (m), 1061 (m), 942 (m), 799 (m), 722 (m); Anal. Calcd. for C$_{55}$H$_{68}$N$_3$NbO$_5$: C, 69.96; H, 7.26; N, 4.45. Found: C, 63.70; H, 7.04; N, 3.83. Melting point: 170-175 °C (dec.).

$(\text{L}_8)^2\text{Nb(N-2,6-}^3\text{Pr}_2\text{C}_6\text{H}_3)(\text{H})$ (15g)

A flask containing 15 (0.20 g, 0.21 mmol) and LiNMe$_2$ (0.016 g, 0.32 mmol) was cooled to -77 °C. Then, ether (50 mL) was added to the flask. The mixture was stirred and its temperature was maintained at -77 °C for 2 hours. Then, the slurry was warmed to room temperature overnight. The resulting pale purple precipitate was filtered and washed with ether. Drying of the purple powder under vacuum overnight resulted in a yellow powder (0.080 g, 40%). The reaction of 15 with LiNEt$_2$, LiN$i^$Pr$_2$ and LiNC$_5$H$_{10}$ under similar conditions results in identical products. $^1$H NMR (C$_6$D$_6$, 600 MHz): 9.988 (s, 1H, Nb-H), 7.276 (dd, 1H, $J = 8.0$ Hz, $^4J_{HH} = 1.2$ Hz, $m$-$^3$Pr$_2$C$_6$H$_3$), 7.198 (dd, 1H, $J = 8.0$ Hz, $^4J_{HH} =$
1.2 Hz, $m^i$Pr$_2$C$_6$H$_3$), 7.065 (d, 1H, $J = 8.0$ Hz, Ar H), 7.010-6.942 (m, 5H, Ar H), 6.898 
(d, 2H, $J = 8.0$ Hz, Ar H), 6.841 (d, 1H, $J = 8.0$ Hz, Ar H), 6.522 (d, 1H, $J = 8.0$ Hz, Ar 
H), 6.461 (d, 1H, $J = 8.0$ Hz, Ar H), 5.453 (s, 1H, OCH$_2$O), 5.288 (s, 1H, OCH$_2$O), 4.836 
(s, 1H, OCH$_2$O), 4.763 (s, 1H, OCH$_2$O), 4.291 (sept, 1H, $J = 6.8$ Hz, CHMe$_2$), 3.508 
(sept, 1H, $J = 6.8$ Hz, CHMe$_2$), 3.081 (sept, 1H, $J = 6.8$ Hz, CHMe$_2$), 2.890 (sept, 1H, $J = 
6.8$ Hz, CHMe$_2$), 2.637 (sept, 2H, $J = 6.8$ Hz, CHMe$_2$), 1.898 (s, 3H, MeC=N), 1.887 (s, 
3H, MeC=N), 1.429 (d, 3H, $J = 6.8$ Hz, CHMe$_2$), 1.405 (d, 3H, $J = 6.8$ Hz, CHMe$_2$), 
1.172 (d, 3H, $J = 6.8$ Hz, CHMe$_2$), 1.105 (d, 3H, $J = 6.8$ Hz, CHMe$_2$), 1.076 (d, 6H, $J = 
6.8$ Hz, CHMe$_2$), 1.063 (d, 3H, $J = 6.8$ Hz, CHMe$_2$), 0.842 (d, 3H, $J = 6.8$ Hz, CHMe$_2$), 
0.787 (d, 3H, $J = 6.8$ Hz, CHMe$_2$), 0.766 (d, 3H, $J = 6.8$ Hz, CHMe$_2$), 0.560 (d, 3H, $J = 
6.8$ Hz, CHMe$_2$), 0.483 (d, 3H, $J = 6.8$ Hz, CHMe$_2$); $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 150 MHz): 
182.80, 181.67, 158.09, 155.33, 154.03, 149.70, 149.25, 147.27, 145.08, 145.00, 144.08, 
143.28, 141.66, 141.30, 141.19, 141.00, 128.08, 126.20, 124.97, 124.76, 124.17, 124.06, 
123.98, 123.76, 123.45, 122.66, 122.14, 106.25, 105.05, 101.02, 100.29, 33.15, 31.89, 
30.51, 28.41, 27.78, 27.09, 26.89, 26.62, 26.28, 26.07, 25.98, 25.95, 25.72, 24.37, 24.00, 
23.40, 22.97, 22.66, 21.54, 21.11; IR: 2926 (s), 2853 (s), 1586 (m, C=N), 1456 (s), 1373 
(s), 1337 (m), 1238 (m), 1093 (m), 1057 (m), 992 (m), 803 (m); Melting point: 190-195 
°C (dec.).
(L⁸)₂Nb(N-2,6-iPr₂C₆H₃)(OH) (15h)

With stirring, a flask containing dry 15g (0.10 g, 0.10 mmol) in the solid state was exposed to ambient atmosphere for 10 minutes, resulting in a light yellow powder. To obtain X-ray quality crystals of the resulting metal hydroxide complex, it was dissolved in pentane (10 mL), filtered and cooled to -25 °C (0.080 g, 80%). ¹H NMR (C₆D₆, 600 MHz): 8.787 (s, 1H, OH), 7.201 (dd, 1H, \( J_HH = 8.0 \) Hz, \( m-iPr_2C_6H_3 \)), 7.065 (t, 1H, \( J_HH = 8.0 \) Hz, \( p-iPr_2C_6H_3 \)), 7.055 (d, 1H, \( J_HH = 8.0 \) Hz, Ar H), 6.920 (d, 1H, \( J_HH = 8.0 \) Hz, Ar H), 6.910 (d, 1H, \( J_HH = 8.0 \) Hz, Ar H), 6.819 (dd, 1H, \( J_HH = 8.0 \) Hz, \( m-iPr_2C_6H_3 \)), 6.487 (d, 1H, \( J_HH = 8.0 \) Hz, Ar H), 6.460 (d, 1H, \( J_HH = 8.0 \) Hz, Ar H), 5.511 (s, 1H, OCH₂O), 5.362 (s, 1H, OCH₂O), 4.817 (s, 1H, OCH₂O), 4.810 (s, 1H, OCH₂O), 4.381 (sept, 1H, \( J_HH = 6.8 \) Hz, CHMe₂), 3.758 (sept, 1H, \( J_HH = 6.8 \) Hz, CHMe₂), 3.601 (sept, 1H, \( J_HH = 6.8 \) Hz, CHMe₂), 3.406 (sept, 1H, \( J_HH = 6.8 \) Hz, CHMe₂), 2.773 (sept, 1H, \( J_HH = 6.8 \) Hz, CHMe₂), 2.637 (sept, 1H, \( J_HH = 6.8 \) Hz, CHMe₂), 1.940 (s, 3H, MeC=N), 1.861 (s, 3H, MeC=N), 1.409 (d, 3H, \( J_HH = 6.8 \) Hz, CHMe₂), 1.173 (d, 3H, \( J_HH = 6.8 \) Hz, CHMe₂), 1.103 (d, 3H, \( J_HH = 6.8 \) Hz, CHMe₂), 1.097 (d, 3H, \( J_HH = 6.8 \) Hz, CHMe₂), 1.088 (d, 3H, \( J_HH = 6.8 \) Hz, CHMe₂), 0.970 (d, 3H, \( J_HH = 6.8 \) Hz, CHMe₂), 0.868 (d, 3H, \( J_HH = 6.8 \) Hz, CHMe₂), 0.856 (d, 3H, \( J_HH = 6.8 \) Hz, CHMe₂), 0.852 (d, 3H, \( J_HH = 6.8 \) Hz, CHMe₂), 0.805 (d, 3H, \( J_HH = 6.8 \) Hz, CHMe₂), 0.567 (d, 3H, \( J_HH = 6.8 \) Hz, CHMe₂), 0.545 (d, 3H, \( J_HH = 6.8 \) Hz, CHMe₂); ¹³C{¹H} NMR (C₆D₆, 150 MHz): 182.78, 179.52, 149.26, 148.80, 146.93, 143.20, 128.42, 128.23, 126.53, 126.32, 126.03, 125.07, 124.90, 124.76, 124.60, 123.75, 123.60, 123.50, 122.95, 122.65, 122.45, 122.35, 122.10, 121.90, 119.27, 106.78, 106.52, 105.90, 100.20, 30.31, 29.93, 29.13, 28.75, 28.70, 28.51, 28.18, 27.82, 26.54, 26.20, 25.90, 25.42, 25.17, 24.79, 24.07, 23.80, 23.32, 22.50, 21.34; IR: 3050 (m), 2916
(s), 2853 (s), 1565 (m, C=N), 1461 (s), 1415 (m), 1379 (s), 1306 (m), 1249 (m), 1051 (m), 948 (m), 797 (m), 725 (m); Anal. Calcd. for $C_{54}H_{66}N_3O_5$: C, 69.72; H, 7.16; N, 4.52. Found: C, 68.31; H, 7.34; N, 4.81. Melting point: 70-75 °C (dec.).

$(L^7)_{2}Nb(N-2,6-Me_2C_6H_3)(C_6H_5)$ ($20a$)

A flask containing $20^\circ$ (0.20 g, 0.23 mmol) and LiPh (0.040 g, 0.46 mmol) was cooled to -77 °C. Then, ether (50 mL) was added to the flask. The mixture was stirred and its temperature was maintained at -77 °C for 2 hours. The slurry was warmed to room temperature overnight. The resulting white precipitate (LiCl) was filtered and the solution was concentrated until a brown powder was obtained. The brown powder was washed with pentane (2×20 mL) and filtered (0.10 g, 40%). $^1H$ NMR ($C_6D_6$, 600 MHz): 8.186 (s, 1H, HC=N), 8.050 (s, 1H, HC=N), 7.890 (t, 3H, $J = 7.6$ Hz, Ar H), 7.459 (d, 2H, $J = 7.6$ Hz, Ar H), 7.290 (d, 1H, $J = 7.6$ Hz, Ar H), 7.271 (d, 1H, $J = 7.6$ Hz, Ar H), 7.199 (d, 1H, $J = 7.6$ Hz, Ar H), 6.950 (d, 1H, $J = 7.6$ Hz, Ar H), 6.930 (d, 1H, $J = 7.6$ Hz, Ar H), 6.840 (d, 1H, $J = 7.6$ Hz, Ar H), 6.766-6.717 (m, 4H, Ar H), 6.451 (d, 1H, $J = 7.6$ Hz, Ar H), 6.436 (d, 1H, $J = 7.6$ Hz, Ar H), 5.224 (s, 1H, OCH$_2$O), 5.109 (s, 1H, OCH$_2$O), 5.077 (s, 1H, OCH$_2$O), 4.944 (s, 1H, OCH$_2$O), 3.891 (sept, 1H, $J = 6.8$ Hz, CHMe$_2$), 3.767 (sept, 1H, $J = 6.8$ Hz, CHMe$_2$), 3.638 (sept, 1H, $J = 6.8$ Hz, CHMe$_2$), 3.014 (s, 3H, Me$_2$C$_6$H$_3$), 2.737 (sept, 1H, $J = 6.8$ Hz, CHMe$_2$), 2.111 (s, 3H, Me$_2$C$_6$H$_3$), 1.462 (d, 3H, $J = 6.8$ Hz, CHMe$_2$), 1.161 (d, 3H, $J = 6.8$ Hz, CHMe$_2$), 1.102 (d, 3H, $J = 6.8$ Hz, CHMe$_2$), 1.071 (d, 3H, $J = 6.8$ Hz, CHMe$_2$), 1.042 (d, 3H, $J = 6.8$ Hz, CHMe$_2$), 0.879 (d, 3H, $J = 6.8$ Hz, CHMe$_2$), 0.826 (d, 3H, $J = 6.8$ Hz, CHMe$_2$), 0.692 (d, 3H, $J = 6.8$ Hz, CHMe$_2$); $^{13}C{^1}H_1$ NMR ($C_6D_6$, 150 MHz): 177.41, 176.32, 161.28, 143.66, 142.13, 142.06, 141.17, 141.03, 137.56, 137.46, 136.67, 131.43, 129.29,
129.05, 128.65, 127.59, 127.47, 126.98, 126.92, 126.35, 126.26, 125.86, 125.69, 125.63, 124.53, 124.00, 123.64, 109.25, 109.18, 108.59, 107.17, 106.77, 106.74, 101.72, 100.35, 99.81, 29.58, 28.70, 28.53, 27.92, 27.46, 26.60, 26.40, 25.73, 25.70, 24.79, 23.83, 23.11, 22.78, 19.71; IR: 3053 (w), 2920 (s), 2857 (s), 1557 (m, C=N), 1463 (s), 1377 (s), 1252 (s), 1095 (m), 1056 (m), 938 (m), 797 (s), 727 (m); Anal. Calcd. for C_{54}H_{58}N_{3}NbO_{4} · C_{5}H_{12}: C, 72.45; H, 7.21; N, 4.30. Found: C, 69.18; H, 7.69; N, 4.15. Melting point: 115-120 °C (dec.).

[(L^8)_{2}Nb(N-2,6-^iPr_{2}C_{6}H_{3})][MeB(C_{6}F_{5})_{3}] (27): To a flask containing both 15a (0.50 g, 0.54 mmol) and B(C_{6}F_{5})_{3} (0.28 g, 0.54 mmol), benzene (20 mL) was added. The mixture was stirred for 5 min. Then, the solvent was removed under vacuum. The resulting orange solid was washed with pentane (10 mL) and filtered. The precipitate was dried under vacuum (0.58 g, 74%). $^1$H NMR (C_{6}D_{6}, 600 MHz): 7.108 (d, 2H, $J$ = 8.0 Hz), 7.070 (d, 1H, $J$ = 8.0 Hz), 7.009 (d, 1H, $J$ = 8.0 Hz), 6.930 (d, 1H, $J$ = 8.0 Hz), 6.865 (d, 1H, $J$ = 8.0 Hz), 6.782 (d, 1H, $J$ = 8.0 Hz), 6.725 (t, 1H, $J$ = 8.0 Hz), 6.693-6.654 (m, 3H), 6.498 (d, 1H, $J$ = 8.0 Hz), 3.998 (d, 1H, $J$ = 16.8 Hz), 5.910 (d, 1H, $J$ = 8.0 Hz), 5.667 (d, 1H, $J$ = 16.8 Hz), 5.125 (s, 1H), 5.078 (s, 1H), 3.999 (sept, 1H, $J$ = 7.2 Hz), 3.482 (sept, 1H, $J$ = 7.2 Hz), 3.277 (sept, 1H, $J$ = 7.2 Hz), 3.144 (sept, 1H, $J$ = 7.2 Hz), 2.551 (sept, 2H, $J$ = 7.2 Hz), 1.765 (s, 3H), 1.330 (s, 3H), 1.268 (d, 3H, $J$ = 7.2 Hz), 1.239 (d, 3H, $J$ = 7.2 Hz), 1.215 (d, 3H, $J$ = 7.2 Hz), 1.109 (d, 3H, $J$ = 7.2 Hz), 1.029 (d, 3H, $J$ = 7.2 Hz), 0.860 (d, 3H, $J$ = 7.2 Hz), 0.850 (d, 3H, $J$ = 7.2 Hz), 0.836 (d, 3H, $J$ = 7.2 Hz), 0.821 (d, 3H, $J$ = 7.2 Hz), 0.813 (s, 3H), 0.802 (d, 3H, $J$ = 7.2 Hz), 0.695 (d, 3H, $J$ = 7.2 Hz), 0.525 (d, 3H, $J$ = 7.2 Hz). $^{13}$C($^1$H) NMR (C_{6}D_{6}, 150 MHz): 197.50, 189.43, 158.44, 151.92, 149.09, 147.84, 147.02, 145.21, 144.30, 144.12, 142.52, 140.87, 140.68,
138.10, 136.30, 133.78, 131.98, 130.67, 127.28, 127.13, 126.87, 124.58, 124.20, 123.75, 122.83, 122.53, 119.56, 119.09, 118.70, 106.55, 102.60, 70.73, 68.30, 29.85, 29.66, 28.63, 27.91, 27.63, 27.33, 25.80, 25.63, 25.57, 25.30, 25.20, 24.03, 23.81, 23.77, 23.07, 23.00, 22.97, 20.72, 14.63. $^{19}$F{$^1$H} NMR (376 MHz, C$_6$D$_6$): -133.34 (o-F), -160.75 (p-F), -165.73 (m-F) (B(C$_6$F$_5$)$_3$: -132.25 (o-F), -149.50 (p-F), -161.10 (m-F)). $^{11}$B NMR (128 MHz): -2.540 (B(C$_6$F$_5$)$_3$: 40.20). IR: 2951 (s), 2851 (s), 1511 (m), 1461 (s), 1375 (m), 1090 (m), 1018 (m), 800 (s). Melting point: 110-115 °C.

4.5 Crystallography

Summaries of crystal data and collection parameters for crystal structures of 15b, 15c, 15f, and 15h are provided in Table 4.3 and 4.4. Detailed descriptions of data collection, as well as data solution, are provided below. ORTEP diagrams were generated with the ORTEP-3 software package. For each sample, a suitable crystal was mounted on a pulled glass fiber using Paratone-N hydrocarbon oil. The crystal was transferred to a Siemens SMART diffractometer with a CCD area detector, centered in the X-ray beam, and cooled to the indicated temperature using a nitrogen-flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. An arbitrary hemisphere of data was collected using 0.3° $\omega$ scans, and the data were integrated by the program SAINT. The final unit cell parameters were determined by a least-squares refinement of the reflections with $I > 10\sigma(I)$. Data analysis using Siemens XPREP and the successful solution and refinement of the structure determined the space group. An empirical absorption correction was applied using SADABS. Equivalent reflections were averaged, and the structures were solved by direct methods using the SHELXTL software package. Unless otherwise noted, all non-hydrogen
atoms were refined anisotropically, and hydrogen atoms were included as fixed atoms but not refined.

**15b.** X-ray quality crystals were grown from a saturated solution of diethyl ether at ambient temperature. The hydrogen atoms of the methylene unit of the trimethylsilylmethyl ligand were located in the difference map and refined positionally, while all other hydrogen atoms were included as fixed contributions. The final cycle of full-matrix least-squares refinement was based on 7925 observed reflections and 610 variable parameters and converged yielding final residuals: \( R = 0.0811, \ R_{all} = 0.0945, \) and \( \text{GOF} = 1.173. \)

**15c.** X-ray quality crystals were grown from a saturated solution of diethyl ether at -20 °C. The final cycle of full-matrix least-squares refinement was based on 4913 observed reflections and 631 variable parameters and converged yielding final residuals: \( R = 0.0744, \ R_{all} = 0.1704, \) and \( \text{GOF} = 1.001. \)

**15f.** X-ray quality crystals were grown from a saturated solution of pentane at -20 °C. The asymmetric unit contained three independent molecules of complex 15f with essentially equivalent metrical parameters, as well as two molecules of pentane. One carbon atom (C13B, ligand carbon atom bound to the niobium center) was refined with restrained thermal parameters to prevent it from adopting a non-positive definite thermal value. The final cycle of full-matrix least-squares refinement was based on 12831 observed reflections and 1819 variable parameters and converged yielding final residuals: \( R = 0.0646, \ R_{all} = 0.1641, \) and \( \text{GOF} = 0.987. \)

**15h.** X-ray quality crystals were grown from a saturated solution of diethyl ether at -20 °C. The structure was refined as a racemic twin. The final cycle of full-matrix
least-squares refinement was based on 7989 observed reflections and 614 variable parameters and converged yielding final residuals: $R = 0.0589$, $R_{\text{all}} = 0.1384$, and $\text{GOF} = 1.065$. 
Table 4.3. Crystal Data and Collection Parameters

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<th>Compound</th>
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<td>Siemens SMART</td>
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<td>Mo K\textsubscript{α} (λ = 0.71073)</td>
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<td>CCD area detector</td>
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### Table 4.4. Crystal Data and Collection Parameters

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<td>Mo $K_α$ ($\lambda = 0.71073$ Å)</td>
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<td>Graphite</td>
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<td>hemisphere</td>
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<td>7989</td>
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<td><strong>GoF</strong></td>
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4.6 Conclusions

We have shown that the \( \text{L}_2\text{NbCl(NAr)} \) (\( \text{L} = \text{ortho}-\text{metalated acetophenone imine} \)) complexes from Chapter Three can be successfully derivatized with a wide range of more reactive \( \sigma \)-donor ligands, such as alkyl, alkynyl, triflate, methoxy, and hydroxy groups. The main limitation to these reactions involves steric bulk, as larger substituent groups did not react in these salt metathesis reactions. Attempts to produce niobium-amide complexes led exclusively to the isolation of a niobium-hydride complex (15g), resulting from \( \beta \)-hydride elimination. Careful analysis of the \( ^1\text{H} \) NMR spectra of these various complexes indicate that the resulting structural isomer isolated from these reactions directly related to the chemical shifts observed for the ligand methylenedioxy protons and isomeric preference is dictated primarily by the \( \sigma \)-donor strength of the various ligands in these niobium complexes.
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289. Attempts to synthesize analogous complexes by protonolysis of compound 15a with diethylamine, tert-butylamine, or aniline were unsuccessful. Mixing of equimolar amounts of amine and 15a in diethylether or benzene at room temperature or 50 °C yielded no reaction products after extended reaction periods. Further, reaction of 15 with n-BuLi in diethylether failed under similar conditions,
precluding observation of similar $\beta$-hydride elimination processes from alkyl complexes. Finally, attempts to synthesize amide complexes by treatment of 15 with LiNHAr, LiNH$t$Bu, or LiN(SiMe$_3$)$_2$ (amides without $\beta$-hydrogens) produced less than 10% conversion to products in all cases, even after heating to 50 °C for extended reaction periods in diethylether.


