Synthesis of early transition metal complexes supported by pyrrolyl and indolyl based ligands

Christopher R. Yeisley
The University of Toledo
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Synthesis of Early Transition Metal Complexes Supported by Pyrrolyl and Indolyl Based Ligands

by

Christopher R. Yeisley

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Dr. Mark Mason, Committee Chair

Dr. Joseph Schmidt, Committee Member

Dr. Viranga Tillekeratne, Committee Member

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

The University of Toledo

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High oxidation state early transition metal complexes are Lewis acidic and electrophilic. The electrophilic center promotes the coordination and insertion of electron-rich substrates; such as alkenes, alkynes, and epoxides. Anionic ligands enable the metal center to retain Lewis acidity for catalytic applications and chelating ligands increase stability due to the chelate effect. Frequently, Constrained Geometry Catalysts (CGC) are comprised of early transition metals supported by chelating ligands. The chelating CGC ligands usually contain an $\eta^5$-dienyl moiety tethered to anionic donor. The pendent donor conventionally is an amide or alkoxide derivative which in turn quenches some of the Lewis acidity of the transition metal through $E \rightarrow M \pi$-donation ($E = O, N$) of lone pair electrons. Substituting heterocyclic nitrogen moiety (pyrrole or indole) for the pendent donor will reduce the $N \rightarrow M \pi$-donation due to lone pair delocalization within the aromatic ring. This thesis reports further developments of the cyclopentadienyl derivative of constrained geometry ligands featuring indolyl- and pyrrolyl- donor moieties and indolyl- and pyrrolyl- supported group 5 imido complexes.
In chapter 2, the synthesis and characterization of a series of dipyrrolyl- and diindolylmethane precursors envisioned to produce the Cp-based trianionic ligand are reported. Three new methanes are described, 5-(chloromethyl)dipyrrolylmethane, 2,2’-di(5-mesityl-1H-pyrrol-2-yl) ethyl chloride, and ethyl 2-(2,2’-di-3-methylindolyl)propionate, along with attempts to react with sodium cyclopentadienyl. In additional, tetramethylcyclopentadienyl acetaldehyde diethyl acetyl was synthesized and reactivity with pyrrole and 3-methylindole is discussed.

Chapter 3 reports synthesis and characterization of a series of elementary Group 5 imido complexes supported by pyrrolyl- and indolyl- ligands. A total of six compounds were synthesized by amine elimination and characterization included $^1$H and $^{13}$C NMR spectroscopy. The structure of ($^1$BuN)Nb{di(3-methylindolyl)phenylmethane}(NEt$_2$)(NHEt$_2$) was further characterized by X-ray crystallography to confirm connectivity. These complexes are envisioned to have broad application to catalytic processes.
For Jessica Gahr and my family whose support guided me through these years.

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<table>
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<tr>
<td>CDCl$_3$</td>
<td>chloroform-$d$</td>
</tr>
<tr>
<td>C$_6$D$_6$</td>
<td>benzene-$d_6$</td>
</tr>
<tr>
<td>CGC</td>
<td>constrained geometry catalyst</td>
</tr>
<tr>
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<td>cyclopentadienyl</td>
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<tr>
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<td>methylaluminoxanes</td>
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<tr>
<td>Mes</td>
<td>2,4,6-trimethylphenyl</td>
</tr>
<tr>
<td>NMR</td>
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<tr>
<td>ORTEP</td>
<td>Oak-Ridge Thermal Ellipsoid Plot</td>
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<td>pyridine</td>
</tr>
<tr>
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<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TsO$^-$</td>
<td>tosyl anion</td>
</tr>
<tr>
<td>SSC</td>
<td>single-site catalyst</td>
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Chapter 1

Applications of Group IV and V Transition Metal Complexes to Specific Organic Transformations

1.1 Introduction

Development of diverse methodologies for the synthesis of organic molecules has led to the production of a varied range of compounds. These compounds represent potential building blocks and final products with utility in pharmaceutical, fine, and bulk chemicals industries. Three specific organic transformations of interest within the Mason group related to the present work are single-site polymerization, \(^1, 2\) hydroamination, \(^3-5\) and hydroaminoalkylation.\(^6\)

The polymerization of low molecular weight olefins such as ethylene and propylene produce two of the most common plastics. Ziegler-Natta\(^7-10\) and Phillips-type\(^11\) heterogeneous catalyst systems represent the first commercialized processes for production of plastics. These systems are still used on industrial scales, over 60 years after their discovery. Heterogeneous catalytic systems have inherit disadvantages over homogeneous systems. The two most noteworthy being a lack of mechanistic understanding related to polymer formation and characterization of the active catalytic species. Homogeneous systems, such as single-site catalysts (described in section 1.2)
overcome these limitations through uniformity of all active catalytic species making these systems amenable to study the mechanism of olefin polymerization.

Hydroamination is formation of a new C-N bond via the addition of a primary or secondary amine N-H across an unsaturated C-C bond and represents a 100% atom efficient way to form amines, enamines, and imines.\(^3\) These nitrogen containing molecules are of interest in fine chemicals and pharmaceutical industries. Although the reaction is thermodynamically favored, the high reaction barrier along with equilibrium results in low yields without the use of a catalyst. Numerous metal catalyst systems have been studied over the past 40 years and every metallic group (transition, main, and rare earth) is represented within the extant literature. Hydroamination has garnered increased research effort within the last two decades and during the latter half of that time a shift towards early transition metal complexes was observed (described in section 1.3).\(^3\)-\(^5\),\(^12\)

Hydroaminoalkylation is a closely related reaction to hydroamination and differs by creating a new C-C bond between an amine and alkene.\(^6\) These systems represent one of the few ways for catalytic C-H bond activation. This was first highlighted over 30 years ago\(^13\) but remained largely ignored until seminal work in 2007\(^14\) demonstrated the potential of this reaction and created an interest in this catalytic transformation (described in section 1.4).\(^6\)

### 1.2 Single-Site Polymerization Catalysts

The first generation of single-site catalysts were bent metallocones of titanium, zirconium, and, to a lesser extent, hafnium.\(^15\) These complexes are exceptionally active and activities of more recent polymerization catalysts are still compared to these
complexes. The reason for this high activity is the stable intermediate formed during polymerization via an α-agostic interaction between the metal center and alkyl ligand (Figure 1.1).\textsuperscript{15}

Figure 1.1. Interaction of alkyl ligand with metal center.

Further developments within the field led to the discovery of \textit{ansa}-metallocenes, aptly named, where the two cyclopentadienyl moieties are tethered together. Benefits of this tethering included increased metal exposure and increased symmetries for the metal complexes. The increased accessibility to the metal allowed for longer chain alkenes, for example 1-hexene, to be incorporated into the polymer chain and increased catalytic activity of these systems. The new symmetries allowed for control of polymer tacticity (Figure 1.2). The tacticities influence the way the polymer chains interact with each other and directly affect the polymer properties (further discussed in section 2.1).

Figure 1.2. Common tacticities for polymers produced from propylene.
The first constrained-geometry catalyst (CGC) was synthesized by Shapiro and Bercaw\textsuperscript{16} (1), then later in 1990 Okuda\textsuperscript{17} published a titanium complex (2). Stevens et al.\textsuperscript{18} coined the term CGC due to the reduced angle formed between the centroid of the $\pi$-moiety and the additional donor bound to the metal center. This reduced angle allows for greater metal exposure. Dow Chemical\textsuperscript{18} and Exxon\textsuperscript{19} have published patents covering various derivatives of the first CGCs including various bridging groups, dienyl moieties, and pendent donor groups. Since these early reports extensive academic and industrial research has been performed to explore variants of the initial CGC’s.

CGC ligands are comprised of three main parts: i) a dienyl moiety, ii) pendent donor either anionic or neutral, and iii) bridge connecting the dienyl and pendent donor (Figure 1.3).\textsuperscript{20} The majority of research has focused on polymerization of alkenes, both short (ethylene, propylene) and long chain (1-butene, 1-hexene), but other catalytic process such as hydroboration\textsuperscript{21} and hydrogenation\textsuperscript{22} can be completed with correct derivatization.
CGC complexes supported by trianionic ligands are underrepresented within the extant literature. Seo and co-workers\textsuperscript{23} have synthesized and characterized mono and di-pyrrolyl cyclopentadienyl ligands along with their titanium complexes (Figure 1.4, 3). These complexes represent the only known CGC complexes to incorporate a pyrrole moiety, but no polymerization studies were completed. A handful of other group 4 complexes with trianionic ligands have been synthesized and characterized and contain the framework of CGC ligands with inclusion of an additional anionic donor. A few of these complexes (4, 5, 6)\textsuperscript{24-26} have been studied for their polymerization ability. These complexes challenge the traditional idea of needing a methyl group for initiation of polymerization. Early transition metal complexes, supported by a similar framework to our ligands, (e.g. 7) have been explored for their catalytic activity in polymerizing lactones. Niobium and tantalum complexes with the cyclopentadienyl tert-butyl amine ligand have also been published, but again no polymerization studies have been completed (8, 9).\textsuperscript{27} The under-representation of trianionic ligands and group 5 metal polymerization complexes presented an opportunity for us to explore a novel trianionic
ligand set while expanding the number of group 5 metal complexes within the extant literature.

![Chemical Structures](3-9)

**Figure 1.4.** CGC complexes supported by trianionic ligands and related complexes.

### 1.3 Hydroamination Catalysts

The production of amines, imines, and enamines has been accomplished through various methodologies since the early 1900s. The 100% atom efficiency of hydroamination provides an unmistakable advantage over other methodologies. Heterogeneous catalysts of late transition metals are among the earliest complexes employed and various systems were used: metal oxides (reduced by hydrogen), Pt and Pd black, and a late transition metal supported on Al₂O₃. Drawbacks for each system varied, but low yield and limited scope were observed in all three systems. Concurrent developments in homogeneous catalyst systems also employed late transition metals usually as chloride salts such as RhCl₃ · H₂O. In addition, catalyst systems of phosphine or phosphine oxides and pentacarbonyliron were investigated. These systems did have
higher yields than heterogeneous systems mentioned above, but still have limited application. Reactions of a secondary amine, diethylamine, with ethylene resulted in dealkylation of the amine and redistribution of the alkyl group. The only aromatic system investigated involved aniline.

Activation of the amine prior to alkylation with the alkene increases reactivity and expands the scope. While there are various ways to activate the amine with amino radical and acylamino radicals being two examples, metal amides, which create a nucleophilic nature of the amine, have garnered intense interest and research over the last four decades. Metal amides of alkali metals, alkaline earth metals, early and late transition metals, and organic amides have all been studied. Only early transition metal catalyst development for hydroamination reaction will be discussed in this section. The reader is directed to Mueller et al. for a comprehensive review of hydroamination catalysts across the periodic table.

In the early 1990s, Bergman and Livinghouse published the initial reports utilizing homogeneous group 4 metal (titanium and zirconium) complexes as catalyst for hydroamination of alkynes. The catalysts shared a bisamido framework, but differed in the ancillary ligands. The mechanism for hydroamination of alkynes with primary amines using Bergman’s original catalyst is shown in Figure 1.5. The bisamido complex can be formed \textit{in situ} or isolated prior to catalysis.

In the proposed mechanism, the bisamido complex undergoes intramolecular proton transfer to form an imido complex (A). Alkyne is then added via a [2+2] cycloaddition (B) followed by protonolysis forming a new bisamido complex (C). A second intramolecular proton transfer occurs to reform the active imido species (A) and
the final product. The enamine (D) product can tautomerize to form an imine (E) and the R group influences the D:E ratio.

**Figure 1.5.** Proposed catalytic cycle for hydroamination of alkynes with primary amines.

Following the reports by Bergman and Livinghouse, intense research focused on development of group 4 hydroamination catalysts resulting in numerous catalyst and exploring important issues, such as regioselectivity. A handful of examples are shown in Figure 1.6 (10-17) with a special eye on the pyrrolyl-based complex 15 from Odom and co-workers. A number of group 3 metal hydroamination catalysts have also been disclosed within the open literature based on both scandium and yttrium, but group 5 metals (vanadium, niobium and tantalum) have generally been overlooked. The vast
majority of vanadium hydroamination catalysts reside in the oxidation state +4 and mimic
the group 4 metals. Bergman has moved along the periodic table publishing tantalum
catalysts, and a cationic group 5 catalyst was also studied to explore similarities to group
4 catalysts.

Figure 1.6. Representative examples of group 4 hydroamination catalysts.

To date, no hydroamination catalyst employing indolyl based ligands has been
reported and only Odom and co-workers have explored pyrrolyl based ligands. This
provides plenty of opportunities for novel and diverse catalysts based upon indolyl and
pyrrolyl frameworks.

1.4 Hydroaminoalkylation Catalysts

In 1972, Benedetti reported an unusual palladium-catalyzed reaction between
secondary amines and ethylene that resulted in formation of a new C-C bond between the
$\alpha$ carbon of the amine and the alkene. Later Maspero and Clerici expanded competent
hydroaminoalkylation catalysts to include transition metal amides of zirconium, niobium,
and tantalum. This reaction is now known as hydroaminoalkylation. Holmes and co-workers\textsuperscript{46} published a labeling study and proposed an azametallocyclopropane intermediate. Newer mechanistic studies by Doye\textsuperscript{47} and Hultzsch\textsuperscript{48} also concluded azametallocyclopropane to be the key intermediate. Although interest in activation of an \spthree C-H bond alpha to nitrogen is of interest to various groups,\textsuperscript{49} this route was largely ignored\textsuperscript{50, 51} until 2007 when Hartwig and Herzon\textsuperscript{14} published a study with catalyst 18 (Figure 1.7) that dramatically improved the yield from 38\% to 96\%.

![Image](image-url)

**Figure 1.7.** Hydroaminoalkylation catalysts

Despite the myriad of hydroamination catalysts which span the periodic table, hydroaminoalkylation catalysts are so far limited to early transition metals. Doye and co-workers have expanded this chemistry to include primary amines and produce cyclic products from intramolecular coupling employing compounds 19 and 20.\textsuperscript{47, 52-54} The disadvantage is the specificity of the reaction to only form six-member rings. The groups of Schafer\textsuperscript{55, 56} and Song\textsuperscript{57} utilize bisamidate ligands to produce chiral pre-catalyst
complexes (21-23). These catalysts are able to form chiral products in varying ratio (Figure 1.7). To date, no group 5 catalyst with indolyl or pyrrolyl ligand has been described.

The mechanism is similar to that for hydroamination, but the lack of a proton on the secondary amine results in the azametallocyclopropane intermediate (B) and not metal imido. The addition of the unsaturated hydrocarbon then forms an azametallocyclopentane intermediate (C) and subsequent protonolysis steps reform the bisamido (A) (Figure 1.8).

**Figure 1.8.** Proposed mechanism for hydroaminoalkylation of secondary amines with alkenes
1.5 Research Statement

As described throughout this chapter, group 4 and 5 complexes are instrumental in performing various organic transformations. Constrained geometry catalysts of group 4 metals have dominated the literature although examples of group 5 metals are known. Group 5 metal complexes employed in polymerization studies have demonstrated tolerance toward polar functionalized monomers. Interest in polymers incorporating or comprised of biomass derived monomers has grown within the last 5 years and typically those monomers have polar groups. In addition, the limited diversity in ligand sets for both group 4 and 5 complexes allows for exploration into varying electronic and steric demands around the metal center.

Previously, early transition metal complexes supported by bisindolylmethanes\textsuperscript{58,59} were studied for their capacity to polymerize ethylene\textsuperscript{60} within the Mason group (Figure 1.9). Indole based ligands were initially chosen due to reduced metal-nitrogen-metal bridging and reduced N\rightarrow M \pi donation. The activity of these systems was lower when compared to traditional metallocenes.

![Reaction Scheme](image)

**Figure 1.9.** Bisindolylmethane complexes previously synthesized by the Mason group.
A publication by Johnston and co-workers\textsuperscript{61} demonstrated transfer of nitrogen ligand from a zirconium complex to the aluminum activator. Although this transfer was not proven for the bisindolylmethane ligands, this could explain the low activity. Therefore a ligand based upon the bisindolylmethanes and the CGC ligands was conceived and initial research started by Dr. Ryan Rondo. The framework included a cyclopentadienyl moiety tethered to the bisindolylethane resulting in a trianionic ligand (Figure 1.10).

![Figure 1.10. Proposed ligand framework.](image)

This framework is also structurally similar to a monoanionic ligand set developed by the Otero group.\textsuperscript{62} Other trianionic ligand sets, trispyrrolyl-\textsuperscript{63} and trisindolylmethanes,\textsuperscript{64} have long standing interest within the Mason group. Their coordination to aluminum to produce Lewis acidic metal centers for catalytic purposes remains a lively area of research.\textsuperscript{65,66}

This thesis reports further attempts to synthesize the cyclopentadienyl trianionic ligand along with transition metal complexes for group 5 metals with potential applications in alkene polymerization, hydroamination, and hydroaminoalkylation. Chapter two discusses the two synthetic schemes proposed for 24 and 25 along with synthesis and characterization of intermediate compounds. Chapter three discusses
synthesis of group 5 complexes supported by pyrrolyl and indolyl ligands envisioned to have potential broad applications in the aforementioned organic transformations.
Chapter 2

Cyclopentadiene Derivatives of Trianionic Diindolyl Ethane Constrained Geometry Ligands

2.1 Introduction:

Cyclopentadienyl is undoubtedly the most utilized moiety in single-site olefin polymerization catalysts,\textsuperscript{67} and one of the most common ligands in all of organometallic chemistry. Group 4 metallocenes,\textsuperscript{68} ansa-metallocenes,\textsuperscript{69} and CGCs\textsuperscript{70} are unparalleled in terms of polymerization activity and number of studies when compared to other single-site catalysts. These complexes are commonly $C_{2v}$, $C_2$, $C_s$, or $C_1$ in their symmetry. The polyolefin’s tacticity, orientation of adjacent chiral centers, can be influenced by the symmetry of the precatalyst. Higher symmetry, $C_{2v}$, $C_2$, $C_s$ catalysts, generally result in production of one tacticity while $C_1$ symmetric complexes propagate various microstructures. Homopolymerization of 1-alkenes by a $C_{2v}$ symmetric complex\textsuperscript{71} (Figure 2.1, 26) results in atactic polymer. Isotactic polymer is generated from complexes with $C_2$ symmetry\textsuperscript{72} (e.g. 27), while $C_s$ symmetric\textsuperscript{73} (e.g. 28) complexes produce syndiotactic polymers. Atactic,\textsuperscript{74} syndiotactic,\textsuperscript{75} and hemiisotactic\textsuperscript{76} microstructures have all been produced from $C_1$ symmetric complexes 29, 30, and 31, respectively.
Figure 2.1. Ansα-metallocene complexes displaying $C_{2v}$ (26), $C_2$ (27), $C_s$ (28), and $C_1$ (29-31) symmetry.

The majority of $C_2$ symmetric constrained geometry catalysts generate atactic microstructure. An early patent by Canich\textsuperscript{19} explored non-$C_2$ symmetric CGC catalysts (32, Figure 2.2) for polymerization of propylene, and isotactic-enriched microstructures resulted. Waymouth and co-workers\textsuperscript{77} found contradicting results for complex 32 producing mostly atactic polymer. Based on the symmetry consideration of metallocenes, complex 32 should produce syndiospecific polymer which was not produced in either study. Turner and co-workers\textsuperscript{78} produced syndiotactic polymer after altering the activator from methylaluminoxane to $[B(C_6F_5)_3]$. These results demonstrate the diminished influence of symmetry in CGC complexes, compared to metallocenes, for generating a specific microstructure.
While symmetry is an inherent difference between cyclopentadienyl and indenyl, a second difference is their binding modes to metal centers with numerous binding modes\textsuperscript{79} being documented throughout the literature. The binding mode plays a critical role since it directly affects coordination number and electronic nature of the metal center. These differences are borne out in faster ligand substitution reactions\textsuperscript{79, 80} for indenyl complexes versus analogous cyclopentadienyl complexes. The reduction of dienyl hapticity via ring slippage facilitates the faster substitution reactions by providing an open coordination site. The stability gained from reforming the aromatic benzene ring within indenyl or fluorenly moieties helps promote ring slippage. Normally the $\eta^3$ binding mode is invoked under reaction conditions while the ground state complexes share the same binding mode, $\eta^5$. However, Jordan and co-workers isolated an ansa-hafnocene diamido complex, $[\text{Me}_2\text{Si}(\eta^5-1-\text{C}_9\text{H}_6)(\eta^3-2-\text{C}_9\text{H}_6)]\text{Hf(NMe}_2)_2$, (eq 1) displaying ring slippage in the ground state. Although this compound does not perform olefin polymerization, it does demonstrate that ring slippage can occur in formally unsaturated complexes.

\textbf{Figure 2.2.} Indenyl and fluorenly GCG complexes.
Co-ligands also help promote ring slippage within SSC complexes as represented below. Okuda and co-workers\textsuperscript{81} synthesized complex 35 concluding, based on X-ray crystal data, that the fluorenyl moiety was bound between $\eta^5$ and $\eta^3$. In complex 36, the carbon ring distances are 0.058 or 0.038 Å longer than the 2.400 and 2.708 Å reported for 35. This elongation leads Shiono and co-workers\textsuperscript{82} to assert strictly an $\eta^3$ binding mode.

Figure 2.3. $\eta^5$–Fluorenyl (left) and $\eta^3$–fluorenyl (right) complexes of zirconium.

The above examples display complexes containing indenyl and fluorenyl ligands with hapticity below $\eta^5$ in the ground state complex. Monohapticity is also observed and facilitated by strongly donating ligands or introducing additional ligands.\textsuperscript{83,84} Ring slippage is also very prevalent in late transition metal complexes, Groups 7 through 10.\textsuperscript{85} Hapticity is not limited to five for indenyl and fluorenyl due to additional fused ring(s).
Hexahapto coordination through the benzene ring or nonahapto coordination through all the carbon atoms have been documented within the extant literature and represents common hapticities above five. Chirik and co-workers\textsuperscript{86} have synthesized a series of 1,3-disubstituted indenyl ligands which coordinate $\eta^9$ to low-valent zirconium. These complexes demonstrate ring slippage from $\eta^9$ to $\eta^6$ upon coordination of additional donors. The limited examples of symmetry and coordination mode difference between cyclopentadiene, indene, and fluorene above are not intended to be an exhaustive list, but merely to highlight and give representative examples.

The close relationship between cyclopentadiene and tetramethylcyclopentadiene causes substitution between moieties within ligand sets. A limited number of alkyl bridged ligands with either moiety are known. Silylated bridges are almost exclusively utilized for SSC ligand sets. The two main drawbacks for alkyl derivatives is formation of multiple isomers (eq 2), and longer reaction times.\textsuperscript{87}

\[ \text{Li}^+ \text{ Chattanooga} \rightarrow \text{Cl} \]

\[ \text{Et}_3\text{O} \]

\[ X = \text{OTs, Br} \]

\[ \text{50\%} \quad \text{Cl} \quad \text{Combined 50\%} \]

The isomers of alkyl-substituted tetramethylcyclopentadiene ligands, unlike cyclopentadiene ligands, do not become equivalent upon deprotonation for coordination to a metal center. Therefore the ratio of isomers of the alkyl compounds becomes important. Gruter and van Deek\textsuperscript{88} found solvents with conjugate acid’s pK\textsubscript{a} in the range of -2.5 to -10 produced the largest geminal isomer ratio with that isomer being the desired
product. A number of simple ether solvents fall within the pKₐ range: dimethoxyethane, methoxymethane, and isopropoxyisopropane. This approach does not alleviate the longer reaction times of up to a month,⁸⁷ and never leads to formation of a single isomer. An alternative route is to install the functionality prior to cyclization (eq 3).⁸⁹ This route overcomes both limitations encountered with alkyl derivatives, but suffers from being a more complex reaction.

Cyclopentadienyl and imido moieties are isolobal⁹⁰ which leads to an interest in Group 5 half-sandwich imido complexes as SSC. Gibson and co-workers carried out polymerization studies with catalyst 37 and 38 (Figure 2.4) using Et₂AlCl and [PhNMe₂H][B(C₆F₅)₄] as activators.⁹¹ Extremely low activity for polymerization was observed for these systems; therefore, interest became fleeting, leaving few studies of Group 5 half-sandwich complexes. The majority of studies carried out with this class of compounds involved homopolymerization of ethylene and norbornene; therefore, comparison between symmetry of catalyst and tacticity of the polymer is unattainable.
The Mason group became interested in synthesizing trianionic ligands for the purpose of expanding CGC compounds to include Group 5 metals. This work would be a hybrid of earlier work on CGC complexes and half-sandwich complexes. Dr. Ryan Rondo started the work by synthesizing indenyl- and fluorenyldiindolylethane and dipyrrrolylethane ligands (Figure 2.5) along with Group 4 and 5 complexes (Figure 2.5). The cyclopentadienyl ligand derivative was not produced by Dr. Rondo. 

Figure 2.5. Ligands and compounds synthesized by Dr. Ryan Rondo.
The highlighted differences between cyclopentadienyl, indenyl, and fluorenyl symmetries and coordination modes fueled the continued interest within the group for the cyclopentadiene-substituted ligand, and in this chapter the synthesis and partial characterization of compounds envisioned to produce cyclopentadienyl based trianionic constrained geometry ligands will be discussed. Specifically, the synthesis and characterization of the following compounds are reported: tetramethylcyclopentadienyl acetaldehyde diethylacetal (39), ethyl 2-(2,2’-di(3-methylindolyl))propionate (40), 2-(2,2’-di-(3-methylindolyl))propanol (41), 1,2-di-(3-methyl-2-indolyl)propene (42), 1,1’-di-tert-butoxycarbonyl-2,2’-dipyrrolylmethane (43), 5-(chloromethyl)dipyrrolylmethane (44), and 2,2’-di(5-mesityl-1H-pyrrol-2-yl)ethyl chloride (45). These compounds represent the group’s further attempts to synthesize cyclopentadienyl based trianionic ligands for use in Group 4 and 5 constrained geometry complexes.
2.2 Experimental

General Procedures

All air- and moisture-sensitive reactions were carried out under an inert atmosphere of purified argon or nitrogen using standard inert atmosphere techniques and an Innovative Technologies dry box. Chloroform-\textit{d} and benzene-\textit{d}$_6$ were dried by storage over activated molecular sieves. Solution NMR ($^1$H, $^{13}$C{$^1$H}) spectra were recorded on an Inova 600 or Varian Unity 400 spectrometer using a deuterated solvent as an internal lock. Chemical shifts are reported relative to TMS. Reagent grade tetrahydrofuran, ethyl acetate, hexanes, methylene chloride, diethyl ether, and absolute ethanol were used as received. Pyrrole was purchased from Aldrich Chemical Co. and distilled from calcium hydride prior to use. 3-Methylindole, bromoacetaldehyde diethylacetal, chloroacetaldehyde dimethylacetal, and pyridinium $p$-toluenesulfonate were purchased from Aldrich Chemical Co. and used as received. Sodium hydroxide and sulfuric acid were purchased from Fisher Scientific and used as received. Dipyrrolmethane$^{93}$ and 2-mesitylpyrrole$^{94}$ were synthesized by literature procedures. Boc$_2$O and ethyl pyruvate were borrowed from the Dr. L.M. Viranga Tillekeratne group and used without further purification. We thank Mr. Scott Birmingham of Boulder Scientific Company for a generous donation of tetramethylcyclopentadiene.

**Preparation of tetramethylcyclopentadienyl acetaldehyde diethylacetal (39)**

A 50 mL round bottom flask was charged with tetramethylcyclopentadiene (1.03 g, 8.44 mmol) and dimethoxyethane (25 mL). The solution was cooled to 0 °C and $^9$BuLi
(5.28 mL, 1.6 M, 8.45 mmol) was added via syringe. The solution was allowed to warm to room temperature and stirred overnight. After 12 h, the solution turned yellow and bromoacetaldehyde diethylacetal (1.66 g, 8.44 mmol) was added via cannula. The solution was stirred at room temperature for 5 days. After this time, water (10 mL) was added and the product was extracted in ether (3 × 25 mL). The ether was removed in vacuo and a yellow oil was obtained. Yield: 0.205 g, 0.844 mmol, 20%. The $^1$H NMR spectrum indicated a severe mixture of isomers and starting material.

**Preparation of ethyl 2-(2,2’-di-3-methylindolyl)propionate (40)**

A 50 mL round bottom flask was charged with 3-methylindole (1.23 g, 9.39 mmol) and ethyl pyruvate (0.550 g, 4.74 mmol). Ethanol (7 mL) was added and the solution stirred for 5 min at which time, a catalytic amount of sulfuric acid (4 drops) was added. Stirring continued for 12 h. Volatiles were removed in vacuo, and the residue was dissolved in diethyl ether (25 mL) and water (10 mL). The layers were separated and the aqueous layer extracted with ether (2 × 25 mL). The organic layers were combined, dried over anhydrous Na$_2$SO$_4$, and solvent removed in vacuo. The resulting tan solid was washed with hot hexanes and dried in vacuo. Yield: 1.20 g, 3.33 mmol, 71%. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.38 (br, 2H, NH), 7.57 (d, $^3$J$_{HH}$ = 7.6 Hz, 2H, indo-H7), 7.31 (d, $^3$J$_{HH}$ = 7.6 Hz, 2H, indo-H4), 7.20 (t, $^3$J$_{HH}$ = 7.6 Hz, 2H), 7.14 (t, $^3$J$_{HH}$ = 7.6 Hz, 2H), 4.26 (q, $^3$J$_{HH}$ = 7.2 Hz, 2H, OCH$_2$CH$_3$), 2.14 (s, 3H, CH$_3$), 2.12 (s, 6H, indo CH$_3$), 1.27 (t, $^3$J$_{HH}$ = 7.2 Hz, 3H, OCH$_2$CH$_3$). $^{13}$C($^1$H) NMR (CDCl$_3$, 100.6 MHz): $\delta$ 173.24, 134.69, 133.24, 129.93, 122.32, 119.59, 118.73, 111.10, 109.24, 62.43, 48.73, 24.58, 14.33, 9.57.
Preparation of 2-(2,2′-di-3-methylindolyl)propanol (41)

A 100 mL Schlenk flask, equipped with a dropping funnel, was charged with LiAlH₄ (0.247 g, 6.52 mmol) and THF (10 mL) to create a slurry. The slurry was cooled in an ice bath to ~5 °C. A degassed solution of compound 40 (1.17 g, 3.25 mmol) in THF (10 mL) was transferred via cannula into the dropping funnel, and compound 40 was added dropwise to the slurry over 10 minutes. The solution was allowed to warm to room temperature and stirred an additional 2 h. The reaction was quenched with water (2 × 10 mL) and the product extracted with diethyl ether (3 × 20 mL). Removal of solvent in vacuo produced an off white solid. Yield: 0.723 g, 2.28 mmol, 70%. ¹H NMR (CDCl₃, 400 MHz): δ 8.55 (s br, 2H, NH), 7.57 (d, 2H, ³JHH = 7.6 Hz, indo-H7), 7.31 (d, ³JHH = 7.6 Hz, 2H, indo-H4), 7.20 (t, ³JHH = 7.6 Hz, 2H), 7.15 (t, ³JHH = 7.6 Hz, 2H), 4.23 (d, ³JHH = 6.4 Hz, 2H, CH₂), 2.17 (s, 6H, indo-CH₃), 1.81 (s, 3H, CH₃).

Preparation of 1,2-di-(3-methyl-2-indolyl)propene (42)

Compound 41 (0.506 g, 1.59 mmol) was dissolved in pyridine (5 mL) and the solution was cooled in an ice bath (0 °C). 4-Toluenesulfonyl chloride (0.303 g, 1.59 mmol) was added dropwise to the stirring solution. The resulting solution was stirred at 0 °C for 12 h. The reaction was quenched by adding water (10 mL) and extracted with diethyl ether (3 × 10 mL). After removal of the ether in vacuo, a red solid was collected. Yield 0.273 g, 0.946 mmol, 60%. ¹H NMR (CDCl₃, 400 MHz): δ 8.06 (br, 1H, indo-NH), 8.00 (br, 1H, indo-NH), 7.58 (d, ³JHH = 7.6 Hz, 2H, indo-H7), 7.35 (t, ³JHH = 7.6 Hz, 2H, indo-H4), 7.19-7.13 (m, 4H, indo-H5 and H6), 6.81 (s, 1H, CH), 2.50 (s, 3H, indo-CH₃), 2.49 (s, 3H, indo-CH₃), 2.36 (s, 3H, CH₃).
Preparation of 1,1’-di-tert-butoxycarbonyl-2,2’-dipyrrolylmethane (43)

Dipyrrolylmethane (0.100 g, 0.684 mmol) and Boc₂O (0.300 g, 1.37 mmol) were dissolved in 20 mL of THF and the resulting solution was stirred for 5 minutes. A catalytic amount of dimethylaminopyridine was added and stirring continued for 1 h. The volatiles were removed in vacuo, and the resulting residue was purified by flash chromatography (silica, 5% ethylacetate in hexanes). Two fractions were collected, combined, and dried in vacuo, leaving a colorless oil. ¹H NMR (CDCl₃, 600 MHz): δ 7.18 (s, 2H, pyrr-H₂), 5.99 (s, 2H, pyrr-H₃), 5.66 (s, 2H, pyrr-H₄), 4.26 (s, 2H, CH₂), 1.39 (s, 18H, C(CH₃)₃).

Preparation of 5-(chloromethyl)dipyrrolylmethane (44)

A 50 mL round bottom flask was charged with pyrrole (25.0 mL, 0.386 mol) and degassed with nitrogen for 5 min. Chloroacetaldehyde dimethylacetal (1.19 g, 9.65 mmol) was added and the solution stirred for 5 min. Pyridinium p-toluenesulfonate (0.004 g, 0.965 mmol) was added and the solution was stirred 40 min at room temperature. During the course of the reaction the solution changed from colorless to green. The reaction was quenched with 10% NaOH and precipitate was isolated by filtration. The excess pyrrole was collected by double trapping. The product was then extracted from the crude solid with hot hexanes. After removal of the solvent in vacuo, the product was isolated as a white solid. Yield: 0.376 g, 1.90 mmol, 20%. ¹H NMR (CDCl₃, 600 MHz): δ 8.04 (br, 2H, NH), 6.70 (s, 2H, pyrr), 6.21 (s, 2H, pyrr), 6.15 (s, 2H, pyrr), 4.46 (t, 3JHH = 6.6 Hz, 1H, CH), 3.98 (d, 3JHH = 6.6 Hz, 2H, CH₂Cl).
Preparation of 2,2'-di(5-mesityl-1H-pyrrol-2-yl)ethylchloride (45)

A 50 mL round bottom flask was charged with 2-mesitylpyrrole (0.320 g, 1.73 mmol) and dissolved in CH$_2$Cl$_2$ (10 mL). Chloroacetaldehyde dimethylacetal (2.35 g, 19.0 mmol) was added, and the solution was stirred for 5 minutes. At this point, pyridinium $p$-toluenesulfonate (0.043 g, 0.173 mmol) was added, and the solution was stirred overnight at room temperature. Solvent and volatiles were removed in vacuo resulting in an off white solid. The residue was extracted into Et$_2$O and the extract was filtered through Celite to remove the PPTS. The solvent was removed from the filtrate in vacuo and the remaining residue was extracted into CH$_2$Cl$_2$. The solution was filtered over a silica plug (10 g) and dried in vacuo, resulting in a white solid. Yield. 0.170 g, 0.395 mmol, 23%. $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.85 (br, 2H, NH), 6.90 (s, 4H, aryl), 6.17 (t, $^3$J$_{HH}$ = 3 Hz, 2H, pyrr), 5.98 (t, $^3$J$_{HH}$ = 3 Hz, 2H, pyrr), 4.50 (t, $^3$J$_{HH}$ = 6 Hz, 1H, CH), 4.05 (d, $^3$J$_{HH}$ = 6 Hz, 2H, CHCH$_2$Cl), 2.30 (s, 12H, o-aryl), 2.10 (s, 6H, p-aryl).

2.3 Results and Discussion:

Initially, a four step synthetic procedure was devised for production of indole- and pyrrole-based constrained geometry ligands. The first step involved condensation of indole or pyrrole with bromoacetaldehyde diethylacetal (eq 4).
Attempts by Dr. Ryan Rondo to produce the diindolylethane (46) or the analogous dipyrrolylethane, proved unsuccessful. The initial attempts screened various reaction parameters: acid catalyst (sulfuric acid, zirconium tetrachloride, or trifluoroacetic acid), temperature (ambient and elevated), and solvent (ethanol, methanol, acetonitrile, pyrrole). Reversing the order of condensation and salt metathesis steps resulted in the successful production of indenyl and fluorenyl derivatives of both 3-methylindole and pyrrole (eq 5).

The preparation and isolation of the analogous cyclopentadienyl ligands with cyclopentadienyl diethyl acetal was unsuccessful by these approaches, and only intractable materials were recovered using the original and modified conditions (eq 6).

The reason(s) this synthetic scheme did not produce the desired ligands during the condensation reaction is not known. Clearly, side reaction(s) are occurring to produce a black solid. Therefore, two additional routes were explored for the synthesis of the...
cyclopentadiene ligands 24 and 25. The first was nucleophilic substitution of halide-substituted dipyrrrolyl- or diindolylethanes with sodium or lithium cyclopentadienide. The alternate route was condensation of tetramethylcyclopentadienyl acetaldehyde diethylacetal with pyrrole or 3-methylindole. The abundance of dipyrrrolyl- and diindolylmethanes throughout the open literature warranted additional effort. Employing tetramethylcyclopentadienyl was anticipated to help limit side reaction(s) by blocking reactivity around the cyclopentadienyl ring.

![Image of ligands 24 and 25]

Figure 2.6. Cyclopentadienyl derivatives of trianionic ligand set.

2.3.1 Synthesis of tetramethylcyclopentadienyl acetaldehyde diethylacetal

Tetramethylcyclopentadiene was dissolved in DME (conjugate acid pKₐ is -2.97) and one equivalent of ⁷BuLi was added to the solution. The solution (eq 7) was stirred for 24 h at room temperature. The bromoacetaldehyde diethylacetal was then added as a solution via cannula. The resulting solution was stirred an additional 5 days, and after work up the ¹H NMR spectrum obtained in CDCl₃ displayed three resonances within the range of 3.5 to 4.7 ppm. The starting acetal’s methine resonance was at 4.7 ppm. The
other two triplets are believed to represent other isomers (eq 7), although which ones was not determined.

\[ \text{Product} \xrightarrow{1) \text{BuLi/DME}} \xrightarrow{2) \text{BrCH}_2\text{CH(OEt)}_2} \text{Isomers} \]

\[ (7) \]

While definitive proof of the desired product was not obtained, a condensation reaction between the product and pyrrole was conducted with ZrCl\(_4\) as catalyst and acetonitrile as solvent. A crude \(^1\)H NMR spectrum in CDCl\(_3\) was collected, but no peaks corresponding to the pyrrole moiety were observed. When 3-methylindole was substituted for pyrrole, similar results were obtained under identical reaction conditions. Due to the above results, the tetramethylcyclopentadienyl approach was discarded, and nucleophilic substitution reactions of dipyrrolyl- and diindolylmethanes became the focus.

2.3.2 Synthesis of 3-methylindole based methanes

Acid catalyzed condensation between indole and ketones, aldehydes, or acetals is well established.\(^96\) Previously, the Mason group has employed this methodology for synthesis of di(3-methylindol-2-yl)phenylmethane,\(^58\) 2-methoxyphenyldi(3-methylindol-2-yl)methane, and 2-pyridyldi(3-methylindol-2-yl)methane\(^59\) using a procedure similar to that reported by V. Dobeneck.\(^97\) Following that procedure but replacing benzaldehyde with ethyl pyruvate results in formation of ethyl 2-(2,2’-di-3-methylindolyl)propionate (40) in modest yield, 70%.
The $^1$H NMR spectrum of 40 in CDCl$_3$ indicates a symmetrical molecule with two doublets at 7.57 and 7.31 ppm, and two triplets at 7.20 and 7.14 ppm, for the aryl ring of indole. In addition, only one resonance is observed for the protons on nitrogens (8.38 ppm) and a singlet is observed for the methyl groups (2.12 ppm) of the indole ring. The remaining protons also resonate within expected ranges and display splitting patterns consistent with the proposed structure.

The reduction of the ethyl carboxylate moiety in 40 by excess LiAlH$_4$ cleanly formed 2-(2,2’-di-3-methylindolyl)propanol (41) in excellent yield. The indole moieties are still equivalent as expected and display minimal peak shift from the carboxylate. The loss of the resonances for the ethyl group in the $^1$H NMR spectrum in CDCl$_3$ and appearance of a doublet at 4.23 ppm for the methylene is indicative of the reduced product.

**Figure 2.7.** $^1$H NMR spectrum of compound 41. * denotes diethyl ether impurity.
The final step is nucleophilic substitution with the cyclopentadienyl anion mediated by the tosylate (TsO\(^-\)) group. Applying traditional reaction conditions for the tosylate formation,\(^9\) the alcohol was first dissolved in pyridine, and the solution was cooled to 0 °C, at which point tosyl chloride was added. The solution was maintained at this temperature and stirred overnight. During the course of the reaction a color change occurred - yellow to red - and the workup consisted of quenching with water, extracting with ether, and drying \textit{in vacuo}. The compound appears asymmetric by analyzing the \(^1\)H NMR spectrum in CDCl\(_3\). Two broad singlets at 8.05 and 7.94 ppm each integrate to one proton and are assigned as indole NH protons. In addition, there are three singlets at 2.49, 2.48, and 2.36 ppm which each integrate to three protons. If the tosylation had occurred, there would be three singlets in this region, but one should integrate to six protons for the methyls on the indole rings. The aromatic region displays only five resonances at 7.58, 7.35, 7.20, and 7.15 ppm. The resonance at 7.20 appears to be a quartet, but two doublets are resolved on the 200 MHz instrument. Finally, a peak at 6.80 ppm integrating to one proton is not expected at all in the final product. An ESI mass spectrum was obtained. The molecular peak at 408 \(m/z\) is not in line with a tosylated product but matches the structure for 42. The isomer formation for compound 42 was not investigated.
Figure 2.8. $^1$H NMR spectrum of compound 42.

The prevailing idea is that after tosylation a rearrangement occurs to alleviate steric strain around the quaternary carbon. The exact mechanism of the reaction is not known, and no literature precedent for this rearrangement was found. Attempts to grow X-ray quality crystals were unsuccessful.

An alternative route for the synthesis of the desired ligand from 41 involves replacement of the hydroxyl with a halogen. Iodine, imidazole, and triphenylphosphine were reacted with 41 following the procedure by Trost and Quancard, in which a hydroxyl on the β carbon of an indole ring was replaced with iodide. The reaction was tried three times, and during each run the reaction time was increased. After work-up, the $^1$H NMR spectra of products displayed only starting compound 41. This was confirmed by adding starting material, and the peak intensity increased compared to CDCl$_3$ resonance.
2.3.3 Synthesis of pyrrole based ethanes

Functionalized cyclopentadienyl ligands can be synthesized by reacting fulvenes with the appropriate lithiated compound. Otero and co-workers\textsuperscript{100} reacted lithiated bis(3,5-dimethylpyrazol-1-yl)methane with one equivalent of 6,6-diphenylfulvene or 6-\textit{tert}-butylfulvene.

![Chemical structure](image)

The acidic nature of the pyrrole nitrogen in our moiety requires protection prior to lithiation. The \textit{tert}-butyloxy (\textit{t}Boc) moiety was chosen as the protecting group due to the ease of removal under various conditions.\textsuperscript{101} The \textit{t}Boc moiety was introduced via reaction of di-\textit{tert}-butyldicarbonate (\textit{t}Boc\textsubscript{2}O) with dipyrrolylmethane following the procedure for \textit{t}Boc-pyrrole.\textsuperscript{102} Compound 43 was isolated as clear and colorless oil on small scale.

![Chemical structure](image)

The \textit{1}H NMR spectrum of 43 (Figure 2.9) in CDCl\textsubscript{3} is consistent with the pyrrole moieties being equivalent with a total of three resonances being observed. The methyl and methylene protons are singlets at 1.39 and 4.29 ppm, while pyrrolyl protons resonate at 5.66, 5.99, and 7.18 ppm, respectively.
Compound 43 was dissolved in THF and one equivalent of $^6$BuLi was added at -78 °C. The solution was warmed to room temperature and stirred an additional hour. At this time, one equivalent of D$_2$O was added, and a second proton NMR in CDCl$_3$ was taken. While the new NMR did not match the starting material, deprotonation on the methylene bridge was not confirmed. This fact, along with the low yield, required alternative routes to be explored. Numerous synthetic methodologies exist for the acid catalyzed condensation of pyrrole with various electrophiles. Employing the procedure disclosed by Betley, the reaction of pyrrole and chloroacetaldehyde dimethylacetal catalyzed by PPTS results in 5-(chloromethyl)dipyrrolylmethane (44) in approximately 20% yield. The formation of oligomers and polymeric compounds of pyrrole reduces the overall yield. The $^1$H NMR spectrum of 44 (Figure 2.10) in CDCl$_3$ indicates solely the 2,2' product with $C_{2v}$ symmetry with one broad nitrogen proton resonance at 8.04 ppm. In addition, only three pyrrole resonances are observed at 6.70, 6.21, and 6.15 ppm. The methane and methylene display resonances at 4.46 and 3.98 ppm.
ppm with the expected splitting pattern. After trying a few alternative reaction conditions, no improvement in yield was observed; therefore, aryl substituted pyrroles were employed.

Figure 2.10. $^1$H NMR spectrum of compound 44. * CH$_2$Cl$_2$ impurity.

Odom$^{104}$ and Betley$^{103}$ have observed the ability to switch the ratio between pyrrole and the electrophile when 2-arylp Yrroles are used. Substitution at the other $\alpha$ position was the only observed product. The reaction of 2-mesitylpyrrole$^{94}$ with excess chloroacetaldehyde dimethylacetal using PPTS as the acid catalyst produces 2,2'-di(5-mesityl-1H-pyrrol-2-yl) ethyl chloride (45). The $^1$H NMR spectrum indicates a symmetrical structure for the product and exhibits a broad singlet at 7.85 ppm for the nitrogen protons. Also two resonances for the pyrrole are observed at 6.17 and 5.98 ppm and four aryls protons resonance is observed at 6.91 ppm. The methine and methylene resonances are both shifted downfield to 4.50 and 4.05 ppm, respectively, while the methyl groups of the mesityl resonate at 2.30 (ortho) and 2.10 (para) ppm.
These two compounds were envisioned to produce the cyclopentadienyl ligand with the final step being a salt metathesis with sodium cyclopentadienyl; however, nucleophilic substitution did not produce the desired ligand. The $^1$H NMR spectra of the crude reaction mixtures show mostly starting material along with other resonances that do not match the predicted spectrum for the product. Increasing equivalents of sodium cyclopentadienyl to 10 and a more polar solvent did not produce the desired result. After trying the above routes it appears that the cyclopentadienyl based ligand will continue its elusive nature.

### 2.4 Conclusions

The synthesis and partial characterization of novel bis-pyrrolyl and indolyl ethanes are reported. Acid catalyzed condensation was employed in all cases to form the ethanes for further functionalization. In the case of compound 40, reduction of the carboxylate to an alcohol followed by an S$_{N}$2 substitution did not result in formation of the desired product. Halo substituted pyrrolyl ethanes, compounds 44 and 45, were also envisioned to form the desired product through an S$_{N}$2 reaction. In neither case was the desired product formed, either a proposed rearrangement occurred or starting material was observed.
Chapter 3

Early Transition Metal Complexes Coordinated by Pyrrolyl and Indolyl Based Ligands

3.1 Introduction

Group 4 hydroamination catalysts 11 and 12 (Figure 3.1) were published in the early 1990s by Bergman\textsuperscript{35} and Livinghouse\textsuperscript{36} for reactions of alkynes with primary amines. Bergman’s system was intermolecular while Livinghouse studied intramolecular reactions. Subsequent early transition metal complexes were based upon metalloocene complexes with either amido or methyl donors (Figure 3.1).\textsuperscript{37-40, 105} Only the Odom\textsuperscript{42} group has examined a pyrolyl-based ligand set (e.g. 15).
While the above is only a representative collection of group 4 catalysts and many more are known, group 5 complexes known to catalyze hydroamination are rare. The groups of Arnold\textsuperscript{44} and Lorber\textsuperscript{43} published the first reports of group 5 complexes for hydroamination. Arnold studied trialkyl imido tantalum (V) complexes and Lorber studied mixed imido/amido vanadium (IV) complexes. Lorber also studied a vanadium (IV) complex with carbazole as the ancillary ligand.\textsuperscript{43} This is the only known group 5 metal supported by an N-heterocycle that catalyzes hydroamination of alkynes. Both studies examined a highly reactive system for hydroamination, aryl amine with alkyne, leaving the scope of group 5 metals unexplored. Johnson and co-workers recently reported reactivity of bidentate sulfonamide alcohol ligands with both group 4 and 5 metals.\textsuperscript{106}

*Figure 3.1. Group 4 hydroamination catalysts.*
Group 5 complexes supported by pyrrolyl, indolyl, and carbazolyl based ligands are rare (Figure 3.2), potentially explaining their limited application in hydroamination. The syntheses of N-heterocyclic complexes are conducted through amine elimination (e.g. 48, 49, 50, and 51) or salt metathesis (e.g. 52, 53). Although group 5 complexes haven’t found extensive use in hydroamination, they dominate hydroaminoalkylation.

![Figure 3.2. Niobium and tantalum complexes supported by pyrrolyl and indolyl based ligands.](image)

Although hydroaminoalkylation was first reported over 30 years ago, limited research was conducted until 2007 when Hartwig and Herzon\textsuperscript{14} employed compound 54 (Figure 3.3) and altered the amine from dialkylamines to N-aryl alkylamines. This caused a reduction in reaction time (24 h) and increased yield (>95%). Recent research has continued to focus on early transition metals with the Doye (55, 56) group.
exploring titanium while Schafer and co-workers examined both group 4 (57)\textsuperscript{56} and group 5 (58)\textsuperscript{55} complexes. Song (59)\textsuperscript{57} and Hultzsch (60a,b)\textsuperscript{48} have exclusively looked at niobium and tantalum complexes supported by binaphtholate ligands.

Figure 3.3. Group 4 and 5 hydroaminoalkylation catalysts.

The numerous nitrogen-based ligand sets used to support group 5 complexes lend credence to pyrrolyl or indolyl ligands being successful for synthesis of target compounds and potential application in hydroamination and hydroaminoalkylation. The paucity of pyrrolyl and indolyl based complexes of niobium and tantalum leave many opportunities to further this chemistry. This chapter will report the synthesis and characterization of niobium and tantalum compounds based upon pyrrolyl and indolyl ligands. The synthesis and characterization of novel group 5 imido complexes will be discussed, specifically, Nb(N\textsuperscript{i}Bu)(NC\textsubscript{4}H\textsubscript{4})\textsubscript{2}(NEt\textsubscript{2})(NHEt\textsubscript{2}) (61), Ta(N\textsuperscript{i}Bu)(NC\textsubscript{4}H\textsubscript{4})\textsubscript{2}(NEt\textsubscript{2})(NHEt\textsubscript{2})
(62), \( \text{Nb}({}^t\text{Bu})(\text{NC}_9\text{H}_8)_2(\text{NEt}_2)(\text{NHEt}_2) \) (63), \( ({}^t\text{Bu})\text{Nb}\{\text{di}(3\text{-methylinolyl})\text{phenylmethane}\}(\text{NEt}_2)(\text{NHEt}_2) \) (64), \( ({}^t\text{Bu})\text{Nb}\{\text{di}(3\text{-methylinolyl})\text{phenylmethane}\}(\text{NEt}_2)(4^t\text{Bupy}) \) (65), \( ({}^t\text{Bu})\text{Nb}\{\text{di}(3\text{-methylinolyl})-2\text{-pyridylmethane}\}\text{Cl}(\text{py}) \) (66).

3.2 Experimental

General Procedures

All air- and moisture- sensitive reactions were carried out under an inert atmosphere of purified argon using standard inert atmosphere techniques and an Innovative Technologies dry box. Chloroform-\(d\) and benzene-\(d_6\) were dried by storage over activated molecular sieves. Solution NMR (\(^1\text{H}\)) spectra were recorded on an Inova
600 or Varian Unity 400 MHz spectrometer using a deuterated solvent as an internal lock. Chemical shifts are reported relative to TMS. Reagent grade tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Hexanes and toluene were distilled from sodium prior to use. Methylene chloride and pyrrole were distilled from calcium hydride prior to use. 3-Methylindole, 2-bromomesitylene, and benzaldehyde were purchased from Aldrich Chemical Co. and used as received. NbCl$_5$ and TaCl$_5$ were purchased from Strem Chemical and used as received. Nb(N$_t$Bu)Cl$_3$(py)$_2$,$^{111}$ Nb(N$_t$Bu)(NEt$_2$)$_3$,$^{111}$ Ta(N$_t$Bu)(NEt$_2$)$_3$,$^{112}$ di(3-methylindolyl)phenylmethane,$^59$ and di(3-methylindolyl)-2-pyridylmethane$^{113}$ were synthesized by literature procedures.

**Synthesis of [Nb(N$_t$Bu)(NC$_4$H$_4$)$_2$(NEt$_2$)(HNEt$_2$)] (61)**

A 50 mL flask was charged with [Nb(N$_t$Bu)(NEt$_2$)$_3$] (0.100 g, 0.263 mmol) and toluene (10 mL). Neat pyrrole (0.100 g, 1.49 mmol) was added to the flask in the glovebox. The solution was stirred for ten minutes at room temperature during which time the solution color changed from light yellow to dark yellow. The solution was dried in vacuo resulting in a yellow oil. Yield: 0.105 g (91%). $^1$H NMR (benzene-$d_6$, 400 MHz): $\delta$ 7.08 (s, 4H, pyrr), 6.64 (s, 4H, pyrr), 3.62 (q, $^3$J$_{HH}$ = 6.6 Hz, 4H, CH$_2$CH$_3$), 2.05 (br, NHCH$_2$CH$_3$) 1.35 (s, 9H, C(CH$_3$)$_3$), 0.850 (t, $^3$J$_{HH}$ = 6.6 Hz, 6H, CH$_2$CH$_3$), 0.632 (br, NHCH$_2$CH$_3$).
**Synthesis of [Ta(N\text{t}Bu)(NC_4H_4)(NET_2)(HNET_2)] (62)**

A 50 mL flask was charged with [Ta(N\text{t}Bu)(NET_2)] (0.100 g, 0.214 mmol) and toluene (7 mL). Neat pyrrole (0.100 g, 1.49 mmol) was added to the flask in the glovebox. The solution was stirred for ten minutes at room temperature during which time the solution color changed from light yellow to dark yellow. The solution was dried *in vacuo* resulting in a yellow solid. Yield: 0.087 g (89%). ^1H NMR (benzene-\textit{d}_6, 400 MHz): \(\delta\) 7.07 (s, 4H, pyrr), 6.64 (s, 4H, pyrr), 3.61 (q, \(^3J_{HH} = 6.0\) Hz, 4H, \(CH_2CH_3\)), 2.13 (br, NH\text{CH}_2\text{CH}_3), 1.37 (s, 9H, C(C\text{H}_3)_3), 0.86 (t, \(^3J_{HH} = 6.6\) Hz, 6H, \(CH_2CH_3\)), 0.784 (br, NH\text{CH}_2\text{CH}_3).

**Synthesis of [Nb(N\text{t}Bu)(NC_9H_8)(NET_2)(HNET_2)] (63)**

A 50 mL flask was charged with [Nb(N\text{t}Bu)(NET_2)] (0.100 g, 0.263 mmol) and toluene (10 mL). 3-Methylindole (0.071 g, 0.541 mmol) was added as a solid. The solution changed from yellow to red and was heated for 2 h with stirring at 60 °C. After this time, the solution was dried *in vacuo* producing a red solid. The solid was then washed with cold hexanes and dried *in vacuo*. Yield: 0.124 g, 83%. ^1H NMR (benzene-\textit{d}_6, 600 MHz): \(\delta\) 7.88 (d, \(^3J_{HH} = 7.2\) Hz, 2H, indo-H7), 7.78 (d, \(^3J_{HH} = 7.2\) Hz, 2H, indo-H4), 7.35 (t, \(^3J_{HH} = 7.2\) Hz, 2H, indo-H5 or H6), 7.29 (t, \(^3J_{HH} = 7.2\) Hz, 2H, indo-H5 or H6), 7.15 (s, 2H, indo-H2), 3.72 (q, \(^3J_{HH} = 6.6\) Hz, 4H, \(CH_2CH_3\)), 3.50 (q, \(^3J_{HH} = 6.6\) Hz, HN\text{CH}_2\text{CH}_3), 2.47 (s, 6H, indo-CH_3), 1.99 (br, HN\text{CH}_2\text{CH}_3), 1.45 (s, C(CH_3)_3, 9H), 0.989 (t, \(^3J_{HH} = 6.6\) Hz, HN\text{CH}_2\text{CH}_3), 0.69 (t, \(^3J_{HH} = 6.6\) Hz, 6H, \(CH_2CH_3\)), 0.363 (br, NH\text{CH}_2\text{CH}_3).
**Synthesis of \((t^3\text{Bu}N)\text{Nb}\{\text{di}(3\text{-methylindolyl})\text{phenylmethane}\}(\text{NEt}_2)(\text{NHEt}_2)\) (64)**

A 50 mL flask was charged with \([\text{Nb}(t^3\text{Bu})(\text{NEt}_2)_3]\) (0.200 g, 0.526 mmol) and toluene (10 mL). A solution of \text{di}(3\text{-methylindolyl})\text{phenylmethane} (0.184 g, 0.526 mmol) dissolved in toluene (10 mL) was added via cannula. The resulting solution changed from yellow to red and was heated to 65 °C for 2.5 h. The solution was dried *in vacuo* leaving a red solid. The solid was re-dissolved in minimal toluene (7 mL) and hexanes (4 mL). This solution was placed in the freezer (-20 °C) overnight, and yellow crystals of X-ray quality formed.

\(1^H\) NMR (benzene-\(d_6\), 600 MHz): \(\delta\) 8.02 (d, \(^3J_{HH} = 8.4\) Hz, 1H, indo-H7), 7.88 (d, \(^3J_{HH} = 8.4\) Hz, 1H, indo-H4), 7.84 (d, \(^3J_{HH} = 8.4\) Hz, 1H, indo-H7), 7.76 (d, \(^3J_{HH} = 8.4\) Hz, 1H, indo-H4), 7.47 (t, \(^3J_{HH} = 8.4\) Hz, 1H, indo-H5 or H6), 7.41 (t, \(^3J_{HH} = 7.2\) Hz, 1H, indo-H5 or H6), 7.36 (m, \(^3J_{HH} = 7.2\) Hz, 3H, indo-H5 and H6), 7.41 (t, \(^3J_{HH} = 7.8\) Hz, 1H, phenyl), 7.01 (t, \(^3J_{HH} = 7.8\) Hz, 2H, phenyl), 6.96 (t, \(^3J_{HH} = 7.8\) Hz, 2H, phenyl), 6.22 (s, CH, 1H), 4.84 (q, \(^3J_{HH} = 6.6\) Hz, 1H, NCH\(_2\)CH\(_3\)), 4.47 (q, \(^3J_{HH} = 6.6\) Hz, 1H, NCH\(_2\)CH\(_3\)), 3.27 (q, \(^3J_{HH} = 6.6\) Hz, 1H, NCH\(_2\)CH\(_3\)), 2.77 (m, 1H, NCH\(_2\)CH\(_3\)), 2.55 (s, 3H, indo-CH\(_3\)), 2.51 (s, 3H, indo-CH\(_3\)), 2.46 (t, \(^3J_{HH} = 6.6\) Hz, 1H, HNCH\(_2\)CH\(_3\)), 2.33 (m, \(^3J_{HH} = 6.6\) Hz, 2H, HNCH\(_2\)CH\(_3\)), 1.67 (q, \(^3J_{HH} = 6.6\) Hz, 1H, HNCH\(_2\)CH\(_3\)), 1.21 (s, 9H, C(CH\(_3\))\(_3\)), 1.05 (t, 3H, \(^3J_{HH} = 6.6\) Hz, NCH\(_2\)CH\(_3\)), 0.940 (t, 3H, \(^3J_{HH} = 6.6\) Hz, HNCH\(_2\)CH\(_3\)), 0.30 (t, \(^3J_{HH} = 6.6\) Hz, 3H, HNCH\(_2\)CH\(_3\)), -0.10 (t, \(^3J_{HH} = 6.6\) Hz, 3H, NCH\(_2\)CH\(_3\)).
Synthesis of (′BuN)Nb{di(3-methylindolyl)phenylmethane}(NEt$_2$)(4-′Bupy) (65)

A 50 mL flask was charged with [Nb(N′Bu)(NEt)$_2$]$_3$ (0.200 g, 0.526 mmol) and toluene (10 mL). A solution of di(3-methylindolyl)phenylmethane (0.184 g, 0.526 mmol) and 4-′tert-butylpyridine (0.07 g, 0.526 mmol) dissolved in toluene (10 mL) was added via cannula. The resulting solution was heated to 65 ºC for 2.5 h during which time the solution became orange/yellow. The solution was cooled to room temperature and dried in vacuo leaving a yellow solid. $^1$H NMR (CDCl$_3$, 600 MHz): δ 8.46 (d, $^3$J$\text{HH} = 5.4$ Hz, 2H, 4′-Bu), 7.77 (d, $^3$J$\text{HH} = 7.8$ Hz, 1H, indo-H7), 7.52 (d, $^3$J$\text{HH} = 7.2$ Hz, 1H, indo-H7), 7.50 (d, $^3$J$\text{HH} = 7.8$ Hz, 1H), 7.29 (d, $^3$J$\text{HH} = 5.4$ Hz, 2H), 7.16 (m, 6H) 7.05 (t, $^3$J$\text{HH} = 7.2$ Hz, 2H, phenyl) 6.89 (t, $^3$J$\text{HH} = 7.2$ Hz, 1H, phenyl), 6.81 (d, $^3$J$\text{HH} = 7.8$ Hz ,1H, phenyl), 6.56 (t, $^3$J$\text{HH} = 7.8$ Hz, 1H, phenyl), 6.11 (s, 1H, CH), 4.63 (br, 1H, NCH$_2$CH$_3$), 4.42 (br, 1H, NCH$_2$CH$_3$), 2.54 (s, 3H, indo-CH$_3$), 2.51 (s, 3H, indo-CH$_3$), 2.07 (br, 1H, NCH$_2$CH$_3$), 1.74 (br, 1H, NCH$_2$CH$_3$), 1.36 (s, 9H, N′Bu), 1.27 (s, 9H, 4-C(CH$_3$)$_3$), 1.07 (br, 3H, NCH$_2$CH$_3$), -0.173 (br, 3H, NCH$_2$CH$_3$).

(′BuN)Nb{di(3-methylindolyl)-2-pyridylmethane}Cl(py) (66)

A 50 mL flask was charged with di(3-methylindolyl)-2-pyridylmethane (0.200 g, 0.586 mmol) and THF (10 mL). The solution was cooled to -78 ºC and n′BuLi (0.72 mL, 1.6 M in hexanes, 1.15 mmol) was added via syringe. After warming to room temperature, the solution was stirred for 30 min then dried in vacuo. The resulting solid was re-dissolved in toluene (10 mL) and transferred to a 50 mL flask charged with Nb(N′Bu)Cl$_3$(py)$_2$ (0.262 g, 0.610 mmol) and toluene (15 mL). After stirring for 24 h, the solution was filtered and concentrated in vacuo. Pentane (20 mL) was added and the
solution sat overnight at room temperature. A second filtration was performed and the purple solid was collected. Yield (48%). $^1$H NMR (benzene-$d_6$, 600 MHz): $\delta$ 8.17 (d, $^3J_{HH} = 4.8$ Hz, 1H, pyridyl), 7.94 (d, $^3J_{HH} = 7.8$ Hz, 1H, pyridyl), 7.81 (t, $^3J_{HH} = 7.8$ Hz, 1H, indo-H7), 7.66 (t, $^3J_{HH} = 7.8$ Hz, 1H, pyridyl), 7.56 (d, $^3J_{HH} = 7.8$ Hz, 1H, indo-H7), 7.33 (d, $^3J_{HH} = 7.2$ Hz, 1H, indo), 7.25 (m, 4H, indo-H5 and H6), 7.17 (d, $^3J_{HH} = 7.2$ Hz, 1H, py), 7.14 (t, $^3J_{HH} = 7.2$ Hz, 1H, py), 7.00 (t, $^3J_{HH} = 7.2$ Hz, 1H), 6.95 (m, 3H), 6.79 (t, $^3J_{HH} = 7.2$ Hz, 1H), 6.01 (s, 1H, C$_7$H), 2.49 (s, 3H, indo-CH$_3$), 2.44 (s, 3H, indo-CH$_3$), 1.53 (s, 9H, C(CH$_3$)$_3$).

Table 3.1. Crystal data and structure refinement details for compound 64.

<table>
<thead>
<tr>
<th>Formula</th>
<th>C$<em>{37}$H$</em>{50}$N$_5$Nb·C$_7$H$_8$</th>
<th>temp, °C</th>
<th>−133</th>
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<tr>
<td>Fw</td>
<td>749.8</td>
<td>$\mu$, mm$^{-1}$</td>
<td>2.707</td>
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<td>Cryst. Syst</td>
<td>Triclinic</td>
<td>$\lambda$, Å</td>
<td>1.54178</td>
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<td>Space group</td>
<td>$P1$</td>
<td>transm coeff</td>
<td>0.752-0.490</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>10.0458(3)</td>
<td>2$\theta$ limits, deg</td>
<td>25.36 to 65.01</td>
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<tr>
<td>$b$, Å</td>
<td>11.7279(4)</td>
<td>total no. of data</td>
<td>29,999</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>18.1181(5)</td>
<td>no. unique data</td>
<td>5757</td>
</tr>
<tr>
<td>$a$, deg</td>
<td>83.53(0)</td>
<td>no. obsd data$^a$</td>
<td>5721</td>
</tr>
<tr>
<td>$\beta$, deg</td>
<td>86.39(6)</td>
<td>no. of params</td>
<td>499</td>
</tr>
<tr>
<td>$\gamma$, deg</td>
<td>71.18(7)</td>
<td>$R_1 (I &gt; 2\sigma(I))$$^b$</td>
<td>0.0418</td>
</tr>
<tr>
<td>$V$, Å$^3$</td>
<td>2006.9(0)</td>
<td>$wR_2 (I^2, all data)^c$</td>
<td>0.1024</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
<td>max, min peaks, e/Å$^3$</td>
<td>0.671, −0.525</td>
</tr>
<tr>
<td>$D_{calcd}$, g cm$^{-3}$</td>
<td>1.241</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a I > 2\sigma(I)$. $^b R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|$. $^c wR_2 = [\Sigma (w(F_o^2 - F_c^2)^2)] \Sigma [w(F_o^2)]^{1/2}$. 

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3.3 Results and Discussion

The majority of group 5 complexes (48-51)\textsuperscript{107-109} supported by pyrrolyl or indolyl moieties were synthesized by amine elimination. Amine elimination within early transition metal complexes has two main advantages: ease of synthesis and removal of by-product \textit{in vacuo}.\textsuperscript{114-116} The main disadvantage is potential coordination of the liberated amine saturating the metal’s coordination sphere. Tris(diethylamido)\textit{tert}-butylimidoniobium and tantalum complexes are produced in excellent yield, 70\% over two steps, and present versatile access to new complexes. Our initial research aimed at converting \textit{t}Bu=Nb(NEt\textsubscript{2})\textsubscript{3} to pyrrolide and indolide complexes resulted in coordination of only two pyrroles or indoles as evidenced by \textsuperscript{1}H NMR spectroscopy. Based upon this observation, di(indolyl)methane ligands along with pyrrolyl and indolyl were studied.

3.3.1 Synthesis of pyrrole and indole based Group 5 complexes

Excess pyrrole was reacted with Nb(N\textit{t}Bu)(NEt\textsubscript{2})\textsubscript{3} in toluene at room temperature (eq. 12). Complete conversion was accomplished within ten minutes and a yellow oil was obtained after removal of solvent and by-products \textit{in vacuo}. Integration of \textsuperscript{1}H NMR resonances (Figure 3.4) suggests a coordination sphere of two symmetric pyrrolides (7.08 and 6.64 ppm), one amido (3.62 and 0.85 ppm), and one \textit{t}Bu imido (1.35 ppm) group. Also coordination of a free diethylamine appears to occur, however the peaks are broad and indicative of exchange. Under prolonged vacuum the amount of the amine is reduced based upon integration, although so far no spectrum without coordinated amine has been observed.
Two different approaches for coordination of a third pyrrolide were undertaken, first simply heating the mixture to 60 °C for 15 h and second, adding methyl iodide. Neither provided the desired product.

\[
M(N'^\text{Bu})(N\text{Et}_2)_3 + 5 \text{ eq.} \xrightarrow{\text{toluene}} M(N'^\text{Bu})(N\text{Et}_2)_3 - \text{HNEt}_2 \xrightarrow{\text{Et}^2\text{HN}} M \quad \text{(12)}
\]

\[
M = \text{Nb (61), Ta (62)}
\]

**Figure 3.4.** $^1$H NMR spectrum of compound 61. * residual solvent peak.

Compound 62 (eq. 12) was synthesized in an identical manner to compound 61. The tantalum congener was isolated as a yellow solid. The $^1$H NMR spectrum of compound 62 appears almost identical to that for compound 61. Pyrrolyl peaks are observed at 7.07 and 6.64 ppm while amido peaks are observed at 3.61 and 0.86 ppm. The $'^\text{Bu}$ imido peak resonates at 1.37 ppm with broad amine peaks at 2.13 and 0.78 ppm, respectively.
In an analogous reaction, two equivalents of 3-methylindole were substituted for pyrrole and reacted with Nb(N<sup>9</sup>Bu)(NEt<sub>2</sub>)<sub>3</sub> in toluene (eq 13). The reaction mixture initially turned slightly red and <sup>1</sup>H NMR spectra from scouting reactions showed incomplete conversion. Therefore heat was applied at 60 °C for two hours in the presence of a slight excess of 3-methylindole. The resulting solid was washed with cold hexanes to remove the excess 3-methylindole.

$$\text{Nb(N}^9\text{Bu)(NET}_2)_3 + 2 \text{H}_{\text{II}} \rightarrow \text{toluene 60 °C } \rightarrow \text{H}_{\text{NET}_2}$$  (13)

The <sup>1</sup>H NMR spectrum of compound 63 indicates the two indolyls are chemically equivalent with doublets at 7.88 and 7.78 ppm for indolyl H7 and H4, respectively. The H5 and H6 protons resonate at 7.35 and 7.29 ppm, both as triplets. Since the indolyls are untethered, H2 is observed at 7.15 ppm as a singlet. The methylene protons on the amido are observed at 3.72 ppm as a quartet while the indolyl methyl groups resonate at 2.47 ppm as a singlet. The <sup>1</sup>Bu imido protons are observed at 1.45 ppm as a singlet, and the triplet at 0.69 ppm was assigned as the methyl group on the amido. This upfield shift is discussed and explained later with the X-ray structure of compound 64. Similar to the pyrrolyl complex, a liberated diethyl amine is coordinated to niobium and the amount is reduced under prolonged vacuum. In addition, free, un-coordinated amine is observed in the <sup>1</sup>H NMR spectrum (Figure 3.5).
3.3.2 Synthesis of Group 5 complexes supported by di(3-methylin dolyl)methane

Diindolylmethanes were chosen due to coordination of only two pyrroles or indoles as discussed above. The di(3-methylin dolyl)phenylmethane has been studied within the Mason group and represented a logical starting point. Compound 64 was synthesized by heating one equivalent of ligand with one equivalent of Nb(N\textsuperscript{t}Bu)(NEt\textsubscript{2})\textsubscript{3} in toluene (eq 14). The resulting solution turned slightly red upon mixing and darker red during heating similar to compound 62.

Figure 3.5. \textsuperscript{1}H NMR spectrum of compound 63.
The $^1$H NMR spectrum of the crude red product indicated an asymmetric nature to the complex. The four doublets at 8.02, 7.88, 7.84, and 7.76 ppm are assigned to H7 and H4 of the inequivalent indolyl rings. The additional two peaks from the indolyl aryl ring (H5 and H6) are observed at 7.47 and 7.41 ppm as multiplets. The three phenyl peaks are observed at 7.36, 7.01, and 6.96 ppm. The methine proton is observed as a singlet in the typical region, 6.22 ppm (Figure 3.6).

![Aromatic region of $^1$H NMR spectrum of compound 64.](image)

Figure 3.6. Aromatic region of $^1$H NMR spectrum of compound 64.

The methyl groups on the inequivalent indolyl rings resonate at 2.55 and 2.51 ppm, while the $^1$Bu protons are observed at 1.21 ppm (Figure 3.7). All three peaks are singlets and integration corresponds to expected values. The one set of amido methylene protons appear diastereotopic at 4.84 and 4.47 ppm. The other two protons resonate at 3.27 and
2.77 ppm. The peaks assigned to methylene protons of the coordinated amine also appear to be diastereotopic at 2.46 and 2.33 ppm. The methyl groups on the amido and amine also appear inequivalent with peaks at 1.05, 0.94, 0.30, and -0.10 ppm each integrating to three protons.

Based on the crystal structure (Figure 3.8) the reason for the upfield shift of the amido protons can be seen. The methyl group from one of the amido groups sits above the ring of the indolyl therefore the ring current causes the large downfield shift to 4.85 and 4.47 ppm.

![Figure 3.7. Aliphatic region of 1H NMR spectrum of compound 64.](image)

Compound 64 was re-dissolved in a minimal amount of toluene, hexanes were added to the flask, and then the sample stored at -35 °C overnight. Yellow crystals amenable to X-ray crystallography study formed. Crystallographic data confirmed the bidentate structure of 64 proposed by 1H NMR spectroscopy along with the presence of a coordinated amine to form a five coordinate niobium. Niobium-imido bond distance Nb1-N13 is 1.743(6) Å and within the range of reported niobium imido distances.\\textsuperscript{111, 117} The nearly linear angle for Nb1-N13-C130 of 165° is consistent with the imido being a
six electron donor. Niobium-amino bond distances for Nb1-N14 and Nb1-N15 are 2.119(1) Å and 2.134(7) Å, respectively, and within the range of reported niobium-amido bonds.\textsuperscript{111, 117, 118} A relatively short metal-amido bond distance, as well as trigonal planar geometry of the amido nitrogens, suggest $\pi$-donation of the nitrogen lone pair to the metal center. Niobium-indolyl bond distance for Nb1-N11 and Nb1-N12 are 2.180(7) Å and 2.173(3) Å, respectively. The niobium-indolyl bond distances are elongated compared to the Nb-N amido distances, as expected due to reduced $N\rightarrow M \pi$ donation since the nitrogen lone pair is delocalized within the aromatic ring.\textsuperscript{109}

\textbf{Figure 3.8.} ORTEP diagrams of 64. Thermal ellipsoids are drawn at the 30\% probability level. Hydrogen atoms are omitted for clarity.
Table 3.2. Selected bond distances and angles for complex 64.

<table>
<thead>
<tr>
<th>Bond distances (Å)</th>
<th>Bond angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb1–N11 2.180(7)</td>
<td>N11–Nb1–N12  81.9(4)</td>
</tr>
<tr>
<td>Nb1–N12 2.173(3)</td>
<td>N14–Nb1–N15  90.8(0)</td>
</tr>
<tr>
<td>Nb1–N13 1.743(6)</td>
<td>Nb1–N13–C130 165.6(1)</td>
</tr>
<tr>
<td>Nb1–N14 2.119(1)</td>
<td>N15–Nb1–N12  149.2(7)</td>
</tr>
<tr>
<td>Nb1–N15 2.134(7)</td>
<td>N13–Nb1–N11  104.2(7)</td>
</tr>
</tbody>
</table>

The synthesis of compound 65 was carried out in an analogous fashion to compound 64. The main difference is one equivalent of 4-tert-butylpyridine and one equivalent of ligand were mixed prior to addition of Nb(N¹Bu)(NEt₂)₃. The reaction was again heated to 65 °C for 2.5 h. A color change from the slight yellow to darker yellow/orange was observed (eq 15). The red color seen in both compound 63 and 64 was not observed during this reaction.

\[
\text{Nb(N¹Bu)(NEt₂)₃} \overset{\text{toluene, 60 °C}}{\rightarrow} \text{65}
\]

The aromatic region of the \(^1\)H NMR spectrum for compound 65 (Figure 3.9) appears similar to that for compound 64 with additional peaks for the 4-tert-
butylpyridine. The reduction of aliphatic resonances is due to loss of the coordinated amine. The aromatic region was not assigned using 2D techniques, but integration leads to 17 aromatic protons consistent with the proposed structure. The amido resonances are in the same region 4.63 and 4.42 ppm along with 2.07, 1.74, 1.07, and -0.17 ppm (Figure 3.10). The indolyl methyl peaks at 2.54 and 2.51 ppm leads to the conclusion that the complex is asymmetric. Therefore the $^1$H NMR spectrum lends credibility to a coordination sphere similar to that for compound 64 with a 4-tert-buty1pyridine in place of the amine.

**Figure 3.9.** Aromatic region of $^1$H NMR spectrum of compound 65. * unreacted ligand or free 4-t-Bupy
3.3.3 Synthesis of \( (^{t}BuN)Nb\{(2-py)di(3-methylindolyl)methane\}Cl(py) \)

Dr. Ryan Rondo has synthesized compound 67 and to further that chemistry an attempt to synthesis compound 68 was undertaken.

The salt metathesis method was employed for synthesis of compound 66 (eq 16). The first step was deprotonation of \( di(3\text{-methylindolyl})2\text{-pyridylmethane} \) with two equivalents of \(^tBuLi\) in THF. The solution was cooled prior to addition of \(^tBuLi\). After stirring for 30 min, the solvent was removed \( \text{in vacuo} \). The lithium salt of the ligand was then re-dissolved in toluene and added to a solution of \( Nb(N^{t}Bu)Cl_{3}(py)_{2} \). The solution’s color changed from a light yellow to a dark purple. The solution stirred for an additional 24 h at which point, the solution was filtered over Celite\textsuperscript{\textregistered} to remove LiCl. The volume
was reduced by a third and pentane was layered on top. The solution was kept at room temperature overnight during which purple crystals grew. An X-ray crystallography data set was collected but ultimately the data proved not to be of publication quality nor was the data set complete enough to display connectivity.

\[
\text{Nb} \left( \text{N}^\text{Bu} \right) \text{Cl}_3 \left( \text{py} \right)_2 + \begin{array}{c}
\text{2 } \text{t}^\text{BuLi/THF} \\
\text{-2 } \text{t}^\text{BuH} \\
\text{toluene} \\
\text{-2 LiCl} \\
\text{-py}
\end{array} \rightarrow \begin{array}{c}
\text{Cl} \\
\text{N}^\text{Bu}
\end{array}
\]

(16)

The $^1$H NMR spectrum for compound 66 shows an asymmetric nature to the complex again. The methyls on the indolyl are inequivalent and observed at 2.49 and 2.44 ppm (Figure 3.11). Based upon the proposed structure the aromatic region should contain 17 protons but the overlapping peaks with the solvent and free ligand makes integration difficult; however integration near 17 is obtained. The imido protons are observed within the normal region, 1.53 ppm. While the $^1$H NMR spectrum cannot conclusively determine the structure, the asymmetric nature of the ligand along with imido location when compared to analogous compounds lends credence to the proposed structure and not that of compound 68.
3.3.4 Synthesis of CpNb(N^tBu)(pyrrolyl)_2

Herrman and co-workers have synthesized compounds 69 and 70 through amine elimination starting with the homoleptic amido. This prompted investigation into an alternative synthesis for compound 51 through amine elimination. This route could then be applied to other compounds including the bisindolylmethanes used previously.

\[
\begin{align*}
M = \text{Nb (69) Ta (70)}
\end{align*}
\]
The first step was adding freshly cracked cyclopentadiene to Nb(N'Bu)(NEt₂)₃ and heating to 60 ºC for 2 h to drive the amine elimination. The solution was then dried in vacuo resulting in a yellow oil. The ¹H NMR spectrum was taken and compared with that of compound 69. The oil was re-dissolved in toluene and excess pyrrole was added and the solution was heated to 60 ºC again for 2 h. The solution was then dried in vacuo resulting in a yellow solid. A second ¹H NMR spectrum was taken matching Gibson’s characterization of compound 53. The pyrrole peaks are observed at 7.16 ppm and the second peak is not reported. The five protons for the cyclopentadienyl resonate at 5.91 ppm, while the imido protons are at 1.19 ppm. The reaction was done in an NMR tube therefore no yield was recorded. Herrman and co-workers report an 81% yield for compound 69 and compound 70 was produced in 91% yield therefore synthesis of compound 53 and derivatives by this route should result in moderate yields.

3.4 Conclusion

The synthesis and partial characterization of a series of niobium complexes is reported. Amine elimination produced the various complexes (13, 61-65) in moderate to excellent yield. X-ray crystallography confirmed the connectivity of compound 64. The bidentate indolyl ligand employed in compounds 64-66 mimics the bidentate binnaphtholate ligands Hultzsch and co-workers have used lending credence to potential applications in hydroamination and hydroaminoalkylation. In addition, compound 53 was synthesized via amine elimination and represents a model compound for exploring catalytic activity of the untethered form of our trianionic ligand.
References


