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Early Transition Metal CCC-NHC Pincer Complexes: Synthesis, Characterization, and Catalysis

Theodore Rudy Helgert

University of Mississippi

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EARLY TRANSITION METAL CCC-NHC PINCER COMPLEXES: SYNTHESIS, CHARACTERIZATION, AND CATALYSIS

A Dissertation presented in partial fulfillment of the requirements for the degree Doctor of Philosophy in the Department of Chemistry and Biochemistry The University of Mississippi

by

THEODORE R. HELGERT JR.

ADVISOR: PROFESSOR T. KEITH HOLLIS

December 2013
ABSTRACT

The previously reported amine elimination methodology for the metalation of CCC-NHC pincer ligand precursors has been extended to other early-transition metals and ligands. Specifically, synthetic results for the preparation of imidazole based CCC-NHC pincer Ti (IV), CCC-NHC pincer Ta (V) will be discussed. In addition, the synthesis of a new triazole based CCC-NHC pincer ligand precursor and its metalation with Ta (V) will be presented. Coordination sphere manipulation of the new pincer complexes using TMSCl for the Ti complex and lithium t-butylamide for the Ta complexes is also discussed. The reaction of the initial Ta CCC-NHC complex with lithium t-butylamide is of particular interest as it is the first X-ray crystallographically determined molecular structure of an early-transition metal anionic N-heterocyclic carbine complex. Catalytic results in hydroamination/cyclization with the Ti complexes and oxidative amination using the Ta complexes will also be reported.
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<thead>
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<th>Abbreviation</th>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>NHC</td>
<td>N-</td>
<td>Heterocyclic Carbene</td>
</tr>
<tr>
<td>MIC</td>
<td>Mesoionic Carbene</td>
<td></td>
</tr>
<tr>
<td>NHDC</td>
<td>Anionic N-Heterocyclic Dicarbene</td>
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<tr>
<td>CCC</td>
<td>Carbon, Carbon, Carbon (denotes which atoms of the pincer ligand are bonded to the metal)</td>
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<tr>
<td>Ta</td>
<td>Tantalum</td>
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<tr>
<td>Ti</td>
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<tr>
<td>Zr</td>
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<tr>
<td>Bu</td>
<td>Butyl</td>
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<td>t-Bu</td>
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<td>δ</td>
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<td>J</td>
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<td>TMSCl</td>
<td>Trimethylsilyl chloride</td>
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<td>Ti(NMe₂)₄</td>
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<td>Tetrakis(dimethylamino)zirconium(IV)</td>
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<td>t-BuN=Ta(NMe₂)₃</td>
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<td>Toluene</td>
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<td>Et$_2$O</td>
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<td>Methylene Chloride</td>
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<tr>
<td>DMSO</td>
<td>Dimethyl Sulfoxide</td>
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<td>CD$_2$Cl$_2$</td>
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<td>C$_6$D$_6$</td>
<td>Deuterated Benzene</td>
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<td>(3-butylimidazol-1-yl-2-idene)phenylene)(chloro)bis(dimethylamido)</td>
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Table A4-5. Bond Lengths for (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (15).

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Scheme 3.2.2.1 Synthesis of 1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene)(t-butylimido)(dimethylamido)iodotantalum(V) (15).

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7, $^1$H NMR, 300MHz, CD$_2$Cl$_2$

7, $^{13}$C NMR, 300MHz, CD$_2$Cl$_2$

8, $^1$H NMR, 300MHz, CD$_2$Cl$_2$

8, $^{13}$C NMR, 500MHz, CD$_2$Cl$_2$

8, 9, 9’, $^1$H NMR, 300MHz, CD$_2$Cl$_2$

8, 9, 9’, $^1$H NMR, 300MHz, CD$_2$Cl$_2$

8, 9, 9’, $^{13}$C NMR, 300MHz, CD$_2$Cl$_2$

8, 9, 9’, $^1$H NMR, 300MHz, CD$_2$Cl$_2$, NMR tube reaction

11, $^1$H NMR, 300MHz, CD$_2$Cl$_2$

11, $^{13}$C NMR, 300MHz, CD$_2$Cl$_2$

12, $^1$H NMR, 300MHz, CD$_2$Cl$_2$

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13, $^{13}$C NMR, 300MHz, CD$_2$Cl$_2$
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CHAPTER 1

INTRODUCTION TO CCC-NHC PINCER LIGANDS

1.1 Carbenes

Carbenes are defined as reactive, uncharged, divalent carbon species with six electrons in their valence shell.\(^1\) The seminal work on carbene was first published by Buchner over a century ago.\(^2,3\) Carbenes can have either a singlet or triplet spin state and adopt a linear or bent geometry (Figure 1.1.1). The spin state of a carbene is determined by the difference in energy between promoting one of the electrons of the non-bonding pair to a higher energy orbital and the energy required to pair both non-bonding electrons in the same orbital. For example, linear carbenes are triplet carbenes. Linear carbenes have an sp hybridization and two non-bonding degenerate orbitals (\(p_x\) and \(p_y\)). Consequently, the energy to promote one of the non-bonding electrons from the \(p_x\) orbital to the \(p_y\) orbital is less than the energy needed to pair both electrons \(p_x\) orbital (Figure 1.1.2). Thus, the non-bonding electrons occupy different orbitals with the same spin, yielding a triplet carbene.
The degeneracy of the frontier orbitals in carbenes is broken in the more common bent geometry. In a bent geometry the hybridization of the carbene carbon is sp². The p_y orbital remains essentially unchanged and is designated as the p_x orbital in a bent carbene. The formally pure p_x orbital in the linear carbene is stabilized from the s character it acquires in the bent geometry and is now designated the σ orbital. Depending on how stabilized the σ orbital is on the spin state of a bent carbene may be triplet or singlet. In the example of a bent carbene with an H-C-H bond angle of 136°, the σ orbital is not stabilized enough for the energy gap between the σ and p_x orbitals to be greater than the energy to pair both electrons in the same orbital. Thus both non-bonding electrons occupy different orbitals, adopt parallel spins yielding a triplet carbene (Figure 1.1.2). Conversely, in the example of a bent carbene where the H-C-H bond angle is 105°, the σ orbital is stabilized enough for the energy gap between the σ and p_x orbitals to be greater than the energy to pair both electrons in the same orbital and the frontier orbitals are designated as p_x and σ. Accordingly, the non-bonding electrons will both occupy the σ orbital with opposite spins, yielding a singlet carbene (Figure 1.1.2).
Figure 1.1.2 Singlet vs. Triplet Carbenes.

The spin state of carbenes is important, as it affects the reactivity of the carbene. The reaction of carbenes with alkenes to form cyclopropanes is well known and demonstrates how the spin state effects reactivity of the carbene.¹ Singlet carbenes react in a concerted manner with alkenes to form only one stereospecific product. Triplet carbenes react via a diradical type mechanism, where one of the non-bonding electron reacts with the one of the electrons of the π bond. This breaks the π bond and allows former double bond to rotate, prior to reacting with the second electron of the carbene, yielding diaesteromeric products (Scheme 1.1.1).⁴ From here only singlet carbenes will be discussed in the work, as the N-Heterocyclic carbenes (NHCs) are singlet carbenes.
1.2 N-Heterocyclic Carbenes (NHCs) and N-Heterocyclic Carbene Variants

N-Heterocyclic carbene (NHC) complexes were first synthesized by Öfele and Wanzlik in the 1960s.\(^5\)\(^6\) Although the first free carbene was reported in 1988 by Bertrand,\(^7\) it was not until 1991 that Arduengo published the first crystal structure of a free carbene.\(^8\) The crystal structure published by Arduengo was that of an NHC. The stability of NHCs was first attributed to the bulky adamantyl group bonded to the nitrogens of the NHC. However, following the publication of a methyl substituted NHC X-ray crystal structure in 1992, it was accepted that the electronic configuration of the NHC is the cause of its stability.\(^9\) The non-bonding electrons in the \(\sigma\) orbital of the carbene carbon are stabilized by the electron withdrawing effect of the adjacent nitrogen atoms (Figure 1.2.2). The empty \(p_\pi\) orbital is stabilized by the lone pairs on the
adjacent nitrogen atoms, which can delocalize into the empty orbital (Figure 1.2.2).

Consequently, NHCs are more stable than other carbene species.

**Figure 1.2.1** First Carbenes by Arduengo.

![Figure 1.2.1](image1)

**Figure 1.2.2** Electronic structure of NHCs, Nitrogen Lone Pair Donation, and Electron withdrawing Effect.

![Figure 1.2.2](image2)

Because of their strong $\sigma$-donating ability, lack of dissociation, and neutral charge, NHCs are considered phosphine complements.\textsuperscript{10,11} NHCs have become ubiquitous in late-transition metal complexes and catalysis.\textsuperscript{12} They have been successfully applied to a large range of catalytic reactions such as olefin metathesis,\textsuperscript{13} C-C coupling,\textsuperscript{14} and hydrosilylation.\textsuperscript{15} In contrast, early-transition metal NHC complexes, particularly in their highest oxidation state,\textsuperscript{12} have yet to be studied in the same depth.\textsuperscript{16-39} Group 5 NHC metal complexes are particularly scarce. Fryzuk has reported four, and to date the only, crystal structures of Ta complexes bearing an NHC
ligand. Reports of Ta NHC chemistry remain sparse despite significant reactivity with Ta which includes N$_2$ activation,$^{40-48}$ CO$_2$ activation,$^{49-51}$ chiral hydroaminoalkylation,$^{52}$ and C-N bond activation.$^{53,54}$

Although imidazole-based NHCs constitute the majority of NHC research, new NHC variants have also been synthesized. Noteworthy NHC variants are triazole-based NHCs, C-4 or C-5 bound “abnormal carbenes,” and anionic N-heterocyclic dicarbenes (NHDC). Triazole-based NHCs are similar to imidazole-based NHCs; however a methine group is replaced in the cyclic structure with a nitrogen. Depending on the location of the nitrogen in the cyclic structure a 1,2,3-triazole-based or a 1,2,4-triazole-based complex can be synthesized. In this work we will discuss the 1,2,4-triazole-based NHCs. Triazole-based NHCs are less $\sigma$-donating than the imidazole-based NHC due to the electron withdrawing effect of the extra nitrogen. Research into late-transition-metal triazole-based-NHC has been established,$^{55-63}$ yet no early-transition-metal (group 3, 4, or 5) triazole-based-NHC complexes have been reported.

Imidazole-based-NHCs bound by the C-4 or C-5 carbon are known as “abnormal carbenes” or Mesoionic Carbenes (MICs). The term mesoionic carbene is used to describe an NHC ring system where one must assign formal positive and negative charges. No resonance structure with all neutral formal charges can be written in a mesoionic carbene. The first report of abnormal binding to an NHC was in 2001 by Crabtree.$^{64}$ It was only just recently that the crystal structure of the first free abnormal carbene was reported by Bertrand.$^{65}$ Abnormal Carbenes/MICs are more electron donating than C-2 bound NHCs since they lack a second adjacent electron withdrawing nitrogen.$^{66}$ Research into late-transition-metal MICs have been established,$^{67}$ yet no reports of early-transition-metal MICs have been reported. In 2010,
Robinson published the first crystal structure of a free anionic N-heterocyclic dicarbene (NHDC) and has subsequently published the Zn complexes bearing the NHDC ligand.\textsuperscript{68,69} No X-ray crystal structures of early-transition-metal NHDC have been published to date.

**Figure 1.2.3** NHC and NHC Variants.

![Imidazole-based NHC, Triazole-Based NHC, Abnormal Carbene/MIC, anionic N-Heterocyclic Dicarbene](image)

### 1.3 Pincer Ligands

The pincer ligand architecture is an important class of tridentate, meridional binding ligands that form robust metal complexes.\textsuperscript{70-72} Shaw first synthesized pincer complexes in the 1970s.\textsuperscript{73-76} Pincer ligands have application in a variety of reactions;\textsuperscript{77-80} noteworthy examples include C-F bond activation,\textsuperscript{81,82} alkane dehydrogenation,\textsuperscript{72} and catalytic C-C bond formation.\textsuperscript{71} The general architecture of a pincer ligand is a central, often aromatic, donor group flanked by two lateral donor groups (Figure 1.3.1). One of the reasons for the widespread use of pincer ligands is the ability to vary the lateral donor groups, providing an effective way to alter the properties of the metal center. Accordingly, incorporation of NHCs into pincer ligands has become of increasing interest.\textsuperscript{71,83-88}

**Figure 1.3.1** General Structure of a Pincer Complex.

![Structure of a Pincer Complex](image)
1.4 CCC-NHC Pincer Ligands

The incorporation of NHCs in a pincer ligand architecture is has become of increasing interest for many groups worldwide. Four major classes of bis(NHC) pincer ligands have been studied and are distinguished by two characteristics. The first characteristic is the central aryl donor group being a nitrogen or carbon. The second characteristic is whether there is a methylene spacer in-between between the aryl and NHC donor ligands. The Hollis group has pioneered work involving of Type B bis(NHC) pincer ligands (Figure 1.4.1), and several groups globally have continued developing this class of ligand. Use of early-transition metal amido starting materials for triple C-H bond activation of the ligand precursors, via amine elimination, is an effective route to synthesize complexes bearing multidentate ligands. In particular, this methodology has yielded a facile route for the synthesis of group 4 CCC-NHC pincer complexes. The electrophilicity of the d\(^0\) metal center, in conjunction with the basicity of the dimethylamido ligands, were exploited to facilitate the necessary triple C-H bond activation of the imidazolium salt precursor. An additional advantage that the amine elimination pathway has, in the synthesis of CCC-NHC group 4 pincer complexes, is the ability to vary the non pincer ligands by the amount of metal amido starting material used. It was discovered that use of excess Zr(NMe\(_2\))\(_4\) yielded CCC-NHC bis(dimethylamido)iodo Zr complex (Scheme 1.4.1). Using freshly sublimed Zr(NMe\(_2\))\(_4\) in a stoichiometric amount with the CCC-NHC ligand precursor in toluene at 160 °C yielded CCC-NHC (dimethylamido)bis(iodo) Zr complex (Scheme 1.4.2). This methodology has also been expanded to synthesize the analogous Hf pincer complexes as well (Scheme 1.4.2). These group 4 transition metal pincer NHC complexes were shown to catalyze the hydroamination/cyclization of unactivated alkene-
amines (Scheme 1.4.3), \(^{31,32}\) and to undergo transmetallation to late metal centers (Scheme 1.4.4). \(^{30-32,107}\)

**Figure 1.4.1.** Metal Complexes Derived from CCC-NHC Pincer Ligands.

![Metal Complexes Derived from CCC-NHC Pincer Ligands](image)

**Scheme 1.4.1** Triple C-H Bond Activation of CCC-NHC Ligand Precursor.

![Triple C-H Bond Activation of CCC-NHC Ligand Precursor](image)

**Scheme 1.4.2** Stoichiometric Synthesis of CCC-NHC Group 4 Metal Complexes.

![Stoichiometric Synthesis of CCC-NHC Group 4 Metal Complexes](image)
Scheme 1.4.3 Catalytic Hydroamination/Cyclization of Unactivated Alkene-Amines.

Scheme 1.4.4 Transmetallation to Late-Transition Metal Complexes.

The work herein focuses on the extension of the amine elimination methodology to synthesize new early-transition-metal CCC-NHC pincer complexes. Specifically, new Ti and Ta CCC-NHC pincer complexes were synthesized and characterized. Use of Ti(NMe₂)₄ as a metalating reagent for the imidazolium salt ligand precursors yielded CCC-NHC pincer Ti dimethylamido halide complexes in good yields. The CCC-NHC pincer Ti bis(dimethylamido)
halide complexes were found to be good catalysts for the hydroamination/cyclization of alken-
amines. Manipulation of the coordination sphere of the CCC-NHC pincer Ti dimethylamine
halide complexes was achieved with TMSCl to yield the appropriate CCC-NHC pincer Ti
tris(halide) complex. CCC-NHC pincer Ta (t-butylimido)(dimethylamido)(iodo) complexes
using imidazolyl and triazolyl based ligands were synthesized with Ta(=NtBu(NMe$_2$)$_3$ as a
metalation reagent. The triazole Ta complex is of particular importance as it is, to the best of our
knowledge, the first report of an early-transition-metal (group 3, 4, and 5) triazole based NHC
complex. Treatment of the CCC-NHC pincer Ta (t-butyrimido)(dimethylamido)(iodo) with
lithium t-butyramide synthesized the CCC-NHC pincer Ta bis(t-butylimido) complex, which was
found to be a great catalyst for oxidative amination/cyclization of alkenyl amines. This reaction
is rare as there are only a few reports of the transformation of unactivated amino-alkenes to
cyclic imines.$^{108,109}$ Upon heating the reaction, during the synthesis of the Ta CCC-NHC pincer
bis(t-butylimido) complex, a NHDC carbene was formed. The NHDC ligand was bonded to Ta
via the C-4 carbon and is the first example of an early-transition-metal MIC and NHDC.
LIST OF REFERENCES
References


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2.1 Research Background

Since the discovery of isolable push-pull and N-heterocyclic carbenes,\textsuperscript{1,2} stable carbenes have been the focus of intense research.\textsuperscript{3} Because of their strong $\sigma$-donating ability and lack of dissociation, they are considered phosphine complements.\textsuperscript{4,5} N-heterocyclic carbenes (NHCs), in particular, have become ubiquitous in late-transition metal complexes and catalysis.\textsuperscript{6} They have been successfully applied to a large range of catalytic reactions such as olefin metathesis,\textsuperscript{7} C-C coupling,\textsuperscript{8} and hydrosilylation.\textsuperscript{9} In contrast, early-transition metal NHC complexes, particularly in their highest oxidation state,\textsuperscript{6} have yet to be studied in the same depth.\textsuperscript{10-33} Only a small number of Ti NHC complexes have been reported.\textsuperscript{14,16,18,20,27,28,31,32,34-38} Successful applications
of Ti NHC complexes were as efficient catalysts for ethylene and rac-lactide polymerization.\textsuperscript{20,27,31,34,38}

Pincer ligands are another important class that has been studied extensively.\textsuperscript{39} Pincer ligands have been known since the 1970’s and have been used to efficiently catalyze a variety of reactions.\textsuperscript{40,41} The development of pincer Ir complexes for efficient, catalytic alkane dehydrogenation highlights the importance of pincer ligands in organometallic chemistry.\textsuperscript{42} The meridional, tridentate nature of pincer ligands makes them a favored motif for ligand design as the resulting complexes have been demonstrated to be robust.\textsuperscript{39} Many research groups have applied stability through chelation in the design of bidentate and tridentate NHC ligands featuring anionic tethers, typically aryloxide or amido functionalities, to overcome the tendency of ligand dissociation from the hard Lewis acidic metal center.\textsuperscript{15,23,29,43} Incorporation of NHCs into pincer ligands has become of increasing interest.\textsuperscript{40,44,45} Yet, only a few examples of early-transition metal pincer NHC complexes have been reported.\textsuperscript{23,46,47}

The Hollis group has previously reported Zr and Hf complexes of a pincer ligand architecture with an anionic phenyl group tethering two NHC groups.\textsuperscript{24-26} By exploiting two characteristics of the early-transition metal amido starting material, the electrophilicity of the $d^0$ metal center and the basicity of the dimethylamido ligands, the desired triple C-H bond activation of the imidazolium salt precursor was achieved. These group 4 transition metal pincer NHC complexes were shown to catalyze hydroamination/cyclization of unactivated alkene-amines,\textsuperscript{25,26} and to undergo transmetallation to late metal centers.\textsuperscript{24-26,48} We report, herein, an extension of this methodology to the synthesis and characterization of Ti analogues and their catalytic activity in the hydroamination/cyclization of unactivated alkene-amines.
2.2 Results and Discussion

2.2.1 Synthesis and Characterization of $2\text{-}(1,3\text{-bis}(3\text{-butylimidazol}-1\text{-yl}-2\text{-idene})\text{phenylene})\text{bis(dimethylamido)(iodo)}$ titanium(IV), (7), and $2\text{-}(1,3\text{-bis}(3\text{-butylimidazol}-1\text{-yl}-2\text{-idene})\text{phenylene})\text{trichloro}$ titanium(IV), (8).

Similar to the previously reported procedures for the Zr analogue,\textsuperscript{24} bis(imidazolium) diiodide salt $\mathbf{1}$ was treated with an excess of Ti(NMe$_2$)$_4$ in toluene at 160 °C for 16 h yielding complex $\mathbf{7}$ (Scheme 2.2.1.1). The excess Ti(NMe$_2$)$_4$ was used to ensure that the initially produced (dimethylamido)diiodoTi complex was converted to the desired bis(dimethylamido)(iodo)Ti complex $\mathbf{7}$. The most obvious change from the $^1$H NMR spectrum of bis(imidazolium) diiodide salt $\mathbf{1}$ after treatment with Ti(NMe$_2$)$_4$ was the loss of the imidazolium proton signal at $\delta$ 11.27. Additionally, the signal corresponding to the butyl methylene group $\alpha$ to the nitrogen shifted from a triplet at $\delta$ 4.46 in salt $\mathbf{1}$ to a triplet at $\delta$ 3.93 in complex $\mathbf{7}$.\textsuperscript{24} As noted for the previously reported Zr analogue,\textsuperscript{24} the triplet was consistent with either a symmetric complex with trans amido groups or rapid interconversion within the cis amido coordination sphere. Rapid interconversion of a complex with cis amido coordination sphere would make the protons on the methylene group adjacent to the nitrogen magnetically equivalent, yielding the observed triplet. This data was consistent with data of the Zr complex, where the X-ray crystal structure contained cis amido groups, yet the NMR data showed a triplet. The carbene peak at $\delta$ 190.5 in the $^{13}$C NMR spectrum also indicated successful metallation of the salt. An aryl peak was also observed at $\delta$ 161.6 which was consistent with the formation of the Ti-C(aryl) bond. These data were consistent with triple C-H activation and formation of the desired CCC-NHC pincer bis(dimethylamido) complex. An extraneous peak at $\delta$ 2.2 was always observed in the final product. No aromatic toluene peaks observed in the $^1$H NMR, thus the peak
was attributed to dimethylamine. Complex 7 was washed more times with various solvents, and placed under reduced pressure at high temperatures, yet the excess dimethylamine could not be removed. Imidazolium salt I and the Ti(NMe$_2$)$_4$ were reacted under different conditions (THF at 100 °C and CH$_2$Cl$_2$ rt) to synthesize complex 7, but upon work up the dimethylamine could not be removed. Elemental analysis was performed on complex 7, but the data was not within acceptable range for the desired complex. This result was attributed to the extreme sensitivity of the complex to trace proton sources, in particular, humid air. Due to this result, elemental analyses of other similarly sensitive CCC-NHC pincer Ti complexes were not performed. Initial attempts at recrystallization of 7 employed CH$_2$Cl$_2$ and THF. After a prolonged period of time crystals formed. However, X-ray crystallography showed the crystals to be the (trichloro)Ti complex 8 (vide infra). This dimethylamido/halide ligand exchange had precedent, as the Zr analogue was known to undergo a dimethylamido/halide exchange affording the trihalide species when reacted with methyl iodide.$^{24}$ Bis(dimethylamido)(iodo)Ti complex 7 was later recrystallized from 1,2-dichlorobenzene and Et$_2$O, but the crystals crumbled when removed from the mother liquor. Addition of Paratone® to the mother liquor/crystal mixture also caused the crystals to crumble. Other solvent systems used to grow crystals such as; CH$_2$Cl$_2$/toluene or Et$_2$O, THF/toluene or ether did not yield crystalline product. Slow vapor diffusion of the same solvent systems at ambient or cold temperatures, also did not yield X-ray quality crystals.
2.2.2 Synthesis and Characterization of 2-(1,3-bis(3-butyrimidazol-1-yl-2-idene)phenylene)trichlorotitanium(IV), (8), and the geometric isomers 2-(1,3-bis(3-butyrimidazol-1-yl-2-idene)phenylene)dichloro(iodo) titanium(IV), (9a) and (9e)

After observing the stability of crystalline (trichloro)Ti complex 8, it was hypothesized that a direct synthesis of 8 was possible by reacting the bis(dimethylamido)(iodo)Ti complex 7 with TMSCl (Scheme 2.2.2.1). As expected, the dimethylamido/halide exchange occurred rapidly upon exposure of complex 7 to TMSCl. The signal corresponding to the dimethylamido ligands of complex 7 was not observed in the $^1$H NMR spectrum 1 h after TMSCl addition. New signals at $\delta$ 2.42 and $\delta$ 0.03 were observed, which corresponded to the expected side product, $N$-(trimethylsilyl)dimethylamine. The integral ratio of the signals at $\delta$ 2.42 and $\delta$ 0.03 was 6:9. This data provided evidence that the desired dimethylamido/halide reaction occurred. The
chemical shifts in the NMR spectra of the resulting complexes were similar to the chemical shifts of the (trichloro)Ti complex 8 crystals grown previously. However, the multiplicity of the signals in the $^1$H NMR spectrum was too high to be one product or isomer. In particular, the asymmetric splitting of the signals corresponding to the methyl group of the butyl chain ($\delta$ 1.05 - 0.98) was the result of overlapping protons of different complexes. Furthermore, three unique doublets ($\delta$ 7.53, $J = 1.8$ Hz), ($\delta$ 7.49, $J = 1.8$ Hz) and ($\delta$ 7.45, $J = 1.9$ Hz) along with three unique doublets of doublets ($\delta$ 7.40, $J_1 = 8.2$ Hz, $J_2 = 7.3$ Hz), ($\delta$ 7.35, $J_1 = 8.1$ Hz, $J_2 = 7.5$ Hz), ($\delta$ 7.29, $J_1 = 8.3$ Hz, $J_2 = 7.3$ Hz) were observed in the aromatic region. These unique signals corresponded to the aryl/heteroaryl protons of three different complexes. Three unique sets of signals were observed in the $^{13}$C NMR spectrum providing additional support for the assignment. Signals at $\delta$ 201.8, 197.1, and 194.5 were assignable as the carbene signals of three different complexes. One of the unique sets of aryl/heteroaryl signals previously described corresponded to the aryl/heteroaryl protons of complex 8. Also, all of the carbon signals of complex 8 were observed in the $^{13}$C NMR spectrum of the reaction. These observations were consistent with the formation of a small quantity of 8 upon reaction of 7 with TMSCl. The other sets of signals in the $^1$H and $^{13}$C NMR spectra were attributed to the axial and equatorial geometric isomers of the dichloro(iodo)Ti complex, 9a and 9e. The ratio of the geometric isomers was 3:1, though assignment of the major or minor isomer was not possible. The reaction depicted in Scheme 2.2.2.1 was carried out with excess TMSCl and prolonged reaction times in an effort to obtain only 8. After 104 h, no changes were observed in the $^1$H NMR spectrum of the reaction versus 1 h. Thus, the product isomer ratio of 8:9 major:9 minor∷3:6:2 appears to be the equilibrium ratio under these conditions.
Scheme 2.2.2.1 Synthesis of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro
titanium(IV), (8), and the geometric isomers 2-(1,3-bis(3-butylimidazol-1-yl-2-
idene)phenylene)dichloro(iodo) titanium(IV), (9a) and (9e).

2.2.3.1 Synthesis and Characterization of 2-(1,3-bis(3-butylimidazol-1-yl-2-
idene)phenylene)dichloro(dimethylamido) titanium(IV) (11) and 2-(1,3-bis(3-
butylimidazol-1-yl-2-idene)phenylene)(chloro)bis(dimethylamido) titanium(IV) (12)

Since the reaction of bis(dimethylamido)(iodo)Ti complex 7 with TMSI yielded a
mixture of (trichloro)Ti complex 8 and mixed-halide dichloro(iodo)Ti complexes 9a and 9e, it
became apparent that an efficient direct synthesis of the (trichloro)Ti complex 8 needed to avoid
starting materials with iodide. Accordingly, bis(imidazolium) dichloride salt 10 was treated
with 1.1 equivalents of freshly distilled Ti(NMe₂)₄ in toluene at 120 °C for 16 h (Scheme 2.2.3.1).
The imidazolium proton signal at (δ ~ 10-11) disappeared along with the methylene signal at
δ 4.42. A new signal was observed at δ 4.35 that was assigned to the methylene group α to the
nitrogen in the product. Additionally, the signal at $\delta$ 4.35 was a triplet of doublets, which was consistent with the Zr and Hf analogues.\textsuperscript{25,26} The molecular structure of complex 11 as determined by X-ray crystal structure analysis is represented in Figure 2.2.5.2. The carbene signal was observed at $\delta$ 196.4 in the $^{13}$C NMR spectrum. The signal corresponding to the Ti-C(aryl) bond was observed at $\delta$ 179.1. These data were consistent with the synthesis of dichloro(dimethylamido)Ti complex 11.

**Scheme 2.2.3.1** Synthesis of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(dimethylamido) titanium(IV), (11) and 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)(chloro)bis(dimethylamido) titanium(IV), (12).

In a range of solvents and temperatures (CH$_2$Cl$_2$, 25 $^\circ$C; THF, 100 $^\circ$C; and toluene, 120 $^\circ$C) chloro salt 10 was efficiently metallated with excess Ti(NMe$_2$)$_4$ to produce (chloro)bis(dimethylamido)Ti complex 12, at bulk and NMR tube reaction scales (Scheme 2.2.3.1). No imidazolium proton signal was observed after the salt was treated with Ti(NMe$_2$)$_4$, and the signal for the methylene protons $\alpha$ to the nitrogen shifted to a triplet at $\delta$ 3.93 in the
metallated species. The observed triplet in the metallated species was attributed to rapid Ti amido exchange, similar to complex 7 (vide supra) and the bis(dimethylamido)(iodo)Zr complex. A new dimethylamido peak was seen at δ 3.22 with an integration of 12H, which provided evidence for the synthesis of (chloro)bis(dimethylamido)Ti complex 12. The 13C NMR spectrum contained a signal at δ 189.9, which was assigned to the carbene carbon, and a signal at δ 161.2, which was attributed to the carbon of the Ti-C(aryl) bond. These data were consistent with assignment of the product as 12. Removal of the volatiles followed by spectroscopic characterization of the crude product revealed exclusively complex 12 and the excess Ti amido reagents. After washing the crude product to remove the excess Ti amido reagents, variable amounts of dichloro(dimethylamido)Ti complex 11 were observed along with 12, regardless of solvent used for washing (Et₂O, toluene). Additionally, observations of 12 in CD₂Cl₂ over time at room temperature revealed the formation of 11 (increase by 6% over 9 h). Furthermore, the 1H NMR spectral analysis of the isolated product of the reaction of salt 10 with excess Ti(NMe₂)₄ taken in nonhalogenated CD₃CN contained a similar ratio of 11:12 (15:85), as the analysis in CD₂Cl₂ (17:83) of the same batch of material.

In an effort to minimize the formation of dichloro(dimethylamido)Ti complex 11 new strategies were employed. First the Ti(NMe₂)₄ was doubled to 10 molar excess to further favor complex 12 in the equilibrium. Additionally, the reaction was conducted in a mixture of CH₂Cl₂:toluene (5:1), and after 3 h it was flash cooled with liquid nitrogen in an attempt to freeze out the equilibrium and afford only bis(dimethylamido) product, 12. The slurry was thawed at -47 ºC and CH₂Cl₂ was removed under vacuum. The supernatant (toluene/excess Ti reagents) was decanted from the precipitated product. The precipitate was washed further at -78 ºC with precooled toluene. TiCl(NMe₂)₃ remained as a contaminant of the isolated product even
after numerous washes (8 × 5 mL) with toluene, at these low temperatures. Washing with THF (6 × 5 mL) also failed to remove the last traces of TiCl(NMe₂)₃ at these low temperatures. Employing this procedure yielded product that still contained a 11:12 mixture of ~15:85.

Consideration of all the experimental results led to the conclusion that 11 and 12 were in rapid equilibrium at room temperature even though 11 was not detectable by ¹H NMR spectroscopy in the crude material. Furthermore, 11 was much less soluble than 12 and was co-precipitating during isolation. Therefore, 11 precipitated preferentially from the crude material, even when it was not observable spectroscopically. As a result, the crude product was a mixture of 11, 12, and Ti amido reagents. When this crude product was dissolved in deuterated solvent for NMR spectroscopy, the equilibrium of 11 and 12 was in favor of 12 due to the excess Ti(NMe₂)₄. Thus, only 12 and Ti reagents were observed in the NMR spectrum of the crude product, while 11, 12, and Ti amido reagents were observed in the isolated product.

2.2.4 Direct Synthesis and Characterization of 2-(1,3-bis(3-butylimidazol-1-yl-2-idenepy)phenylene)trichloro titanium(IV) (12)

(Chloro)bis(dimethylamido)Ti complex 12 was reacted with TMSCl to achieve a direct synthesis of (trichloro)Ti complex 8 (Scheme 2.2.4.1). The most obvious change in the ¹H NMR spectrum was a shift of the signal corresponding to the methylene group α to the nitrogen from δ 3.93 in complex 12 to δ 4.47 in complex 8. The ¹³C NMR spectrum contained a carbene signal at δ 194.5, and an aryl signal at δ 180.9 corresponding to the carbon of a Ti-C(aryl) bond. Both the ¹H and ¹³C NMR spectra of the directly synthesized (trichloro)Ti complex 8 matched the spectra of the previously grown X-ray quality crystals obtained from 7 in CH₂Cl₂/THF. These data provided evidence for the efficient synthesis of (trichloro)Ti complex 8, via this direct route.
Scheme 2.2.4.1. Synthesis of 2-(1,3-bis(3-butylimidazol-1-yl-2-ylidene)phenylene)trichlorotitanium(IV) (8)

2.2.5 Molecular Structure Determination of Ti CCC-NHC Pincer Complexes

An ORTEP® plot of the molecular structure of (trichloro)Ti complex 8 is presented in Figure 2.2.5.1 along with selected metric data. X-ray quality crystals of complex 8 were obtained from the initial attempt at the recrystallization of the bis(dimethylamido)(iodo)Ti complex 2 in CH₂Cl₂ and THF. The X-ray crystallography data confirmed the tridentate bonding of the CCC-NHC pincer ligand to the Ti(IV) center. The structure of complex 8 was a distorted octahedral center due to the meridional-coordination and constraints of the CCC-NHC pincer ligand. The N-heterocyclic carbene ligands occupied coordination sites trans to each other and had a C(NHC)-Ti-C(NHC) bond angle of 143.01(4)°. This bond angle was about 3° greater than the only other reported Ti(IV) metal complex containing an aryl or heteroaryl bridged bis(NHC) pincer ligand. The Ti-C(NHC) bond lengths of complex 8 were 2.2192(10) Å and 2.2115(10) Å, which were less than 0.08 Å shorter than those in the CNC-NHC pincer Ti complex synthesized by Danopoulos. The larger angle C(NHC)-Ti-C(NHC) angle was due to the shorter Ti-C(Aryl) distance (2.2610(10) Å) in 8, versus the Ti-N(pyridyl) (2.332(5) Å) in the CNC pincer complex. The Ti-C(aryl) bond was 2.1610(10) Å, which was within ± 0.08 Å of other similar Ti-C(aryl) bonds, incorporated into a pincer ligand. Conversely, the Cl-Ti-Cl bond angle of (trichloro)Ti complex 3, 174.506(13)°, was significantly larger than the Danopoulos pincer analogue’s Cl-Ti-Cl bond angle of 161.42(7)°. The Ti-Cl bond lengths of
complex 8 (Ti-Cl(1) 2.3239(3) Å, Ti-Cl(2), 2.3119(3) Å, Ti-Cl(3), 2.3198(3) Å) were within ± 0.12 Å of known NHC pincer Ti metal complexes also containing a Ti-Cl bond. \(^{19,23,34}\)

**Figure 2.2.5.1** Molecular structure of 2-(1,3-bis(3-butylimidazol-1-yl-2- idene)phenylene)trichloro titanium(IV), (8), selected bond lengths (Å) and angles (°): Ti-C(2), 2.2192(10); Ti-C(7), 2.1610(10); Ti-C(13), 2.2115(10); Ti-Cl(1), 2.3237(3); Ti-Cl(2), 2.3119(3); Ti-Cl(3), 2.3198(3); C(7)-Ti-C(2) = 71.51(4); C(7)-Ti-C(13) = 71.52(4); Cl(1)-Ti-Cl(2) = 174.506(13).

An ORTEP\(^{\circledR}\) plot of the molecular structure of complex 11 is presented in Figure 2.2.5.2 along with selected metric data.\(^{49}\) Crystals of dichloro(dimethylamido)Ti complex 11 were grown from a solution of (chloro)bis(dimethylamido)Ti complex 12 in CH\(_2\)Cl\(_2\). Similar to (trichloro)Ti complex 8, the dichloro(dimethylamido)Ti complex 11 was found to have a distorted octahedral geometry with a C(NHC)-Ti-C(NHC) angle of 142.93(5)°, which was almost identical to 8. This C(NHC)-Ti-C(NHC) bond angle was slightly larger than the Zr (136.40(11)°) and Hf (137.6(11)°) complexes synthesized under similar conditions, but within 3°
of the CNC-NHC pincer angle by (140.5(2)) reported by Danopoulos.\textsuperscript{19,25,26} The larger angle C(NHC)-Ti-C(NHC) angle was again due to the shorter Ti-C(Aryl) distance (2.1593(14) Å) in 11, versus the Ti-N(pyridyl) (2.332(5) Å) in the CNC pincer complex.\textsuperscript{19} The Ti-C(aryl) bond of 2.1593(12) Å was within ± 0.08 Å of other similar Ti-C(aryl) bonds incorporated into a pincer ligand.\textsuperscript{50,51} The Ti-C(NHC) bond lengths were 2.2406(14) Å and 2.2172(14) Å. The halide ligands of complex 11 occupied cis coordination sites and had a Cl-Ti-Cl bond angle of 86.725(15)°. The Ti-Cl bond lengths of complex 11 were 2.4725(4) Å and 2.3686(4) Å. The Ti-(dimethylamido) bond length was 1.9032(12) Å. These metric data were similar to previously reported Ti NHC complexes.\textsuperscript{11,14,18-21,23,34}

\textbf{Figure 2.2.5.2.} Molecular structure of 2-(1,3-bis(3-butylimidazol-1-yl-2-\textsuperscript{idene})phenylene)dichloro(dimethylamido) titanium(IV), 11, selected bond lengths (Å) and angles (°): Ti-Cl(1), 2.4725(4); Ti-Cl(2), 2.3686(4); Ti-N(5), 1.9032(12); Ti-C(1), 2.1593(14); Ti-C(14), 2.2406(14); Ti-C(7), 2.2172(14); C(1)-Ti-C(7) = 71.44(5); C(1)-Ti-C(14) = 71.76(5); C(7)-Ti-C(14) = 142.93(5).
2.2.6. Catalytic Results

Catalytic hydroamination/cyclization is a highly atom-economical method to synthesize new C-N bonds. The subsequent nitrogen containing heterocycles produced by the reaction are prevalent in naturally occurring and/or biologically active molecules.\textsuperscript{52-55} Numerous metals have been employed for catalytic hydroamination/cyclization; however, group 4 complexes have been advantageous over late-transition metals due to their low cost and low toxicity.\textsuperscript{56-59} Group 4 hydroamination catalysts are also advantageous over organolanthanide catalysts due to their enhanced stability and functional group tolerance.\textsuperscript{58,60,61} It was previously reported that the CCC-NHC pincer Zr and Hf analogues were efficient catalysts for hydroamination/cyclization.\textsuperscript{25,26} Therefore, the catalytic activities of bis(dimethylamido)(iodo)Ti complex 7 and (chloro)bis(dimethylamido)Ti complex 12 in hydroamination/cyclization was evaluated under conditions similar to the previous reports to allow comparison.\textsuperscript{25,26} The best results for complexes 7 and 12 were achieved with substrates containing two phenyl substituents or a spirocyclohexane substituent (entries 1 and 2). Having a spirocyclopentane substituent on the substrate significantly decreased catalytic activity (entry 3). Complex 7 catalyzed the synthesis of piperidines in good yield, while complex 12 showed almost no activity (entry 4). However, 7-membered rings were not generated by either catalyst (entry 5). Complexes 7 and 12 were observed to have limited catalytic activity toward the cyclization of internally substituted alkenes (entry 6). In every case, complex 7 outperformed complex 12, yet both were not as fast as the Zr and Hf analogues.\textsuperscript{25,26} It is of note that the reaction temperature of 160 °C was need for the reaction. It was observed in experiments done at 150 °C that no reaction occurred.
Table 2.2.6.1 Substrate survey of hydroamination/cyclization catalytic activity of complexes 7 and 12.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
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<th>7[Ti-I]b</th>
<th>12[Ti-Cl]b</th>
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<tr>
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<td></td>
<td></td>
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<td>Conv (%)</td>
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</tr>
<tr>
<td>6</td>
<td>Ph</td>
<td>NH2</td>
<td>96 h</td>
<td>47%</td>
</tr>
</tbody>
</table>

a 5 mol% catalyst in toluene-d8 at 160 °C.
b Entries 1-4, catalyst used 86% 7 by 1H NMR spectroscopy.
Entries 5-6, catalyst used 34% 7 by 1H NMR spectroscopy.
c Conversions determined by 1H NMR spectroscopy.
d No reaction.

2.3 Conclusion

In conclusion, CCC-NHC pincer Ti complexes have been synthesized using the amine elimination pathway that exploits the basicity and electrophilicity of Ti(NMe2)4. The coordination spheres of these CCC-NHC pincer Ti complexes were manipulated by controlling the amount of Ti(NMe2)4 used. The reaction of an excess amount of Ti(NMe2)4 with the bis(imidazolium) diiodide salt 1 yielded bis(dimethylamido)(iodo)Ti complex 7, which reacted with CH2Cl2 to afford (trichloro)Ti complex 8. Complex 7 reacted with TMSCl to yield a mixture of (trichloro)Ti complex 8, and both geometric isomers of dichloro(iodo)Ti complexes.
9a and 9e. The reaction of the bis(imidazolium) dichloride salt 10 with a stoichiometric amount of Ti(NMe₂)₄ yielded dichloro(dimethylamido)Ti complex 11, while reacting bis(imidazolium) dichloride salt 10 with an excess amount of Ti(NMe₂)₄ yielded (chloro)bis(dimethylamido)Ti complex 12. An efficient synthesis of (trichloro)Ti complex 8 was accomplished by the reaction of (chloro)bis(dimethylamido)Ti complex 12 with TMSCl. Bis(dimethylamido)Ti complexes 7 and 12 were found to catalyze the hydroamination/cyclization of unactivated primary alkene-amines.

2.3 Experimental Section

General Consideration. Standard inert atmosphere techniques were used unless stated otherwise. Et₂O, toluene, and CH₂Cl₂ were degassed with argon and passed through two columns of activated alumina. TMSCl was purified by distillation from triethylamine. Tetrakis(dimethylamido) titanium(IV) was purchased from Sigma Aldrich and purified by distillation under reduced pressure. CD₂Cl₂, and toluene-d₈ were purchased from Cambridge Isotopes and passed through a column of activated basic alumina. DMSO-d₆ was purchased from Cambridge Isotopes and used as received. ¹H and ¹³C NMR spectra were collected on a Bruker Avance 300 MHz or a Bruker Avance DRX 500 MHz NMR at ambient temperatures, unless otherwise stated. The ¹H NMR spectra were referenced internally from the residual protio-solvent signal: CD₂Cl₂ (δ 5.32), DMSO-d₆ (δ 2.50), and toluene-d₈ (δ 2.09). The ¹³C NMR spectra were referenced internally using the signal from the deuterated solvent: CD₂Cl₂ (δ 54.0), DMSO-d₆ (δ 39.51), and toluene-d₈ (δ 20.4).

Preparation of 2-(1,3-bis(3-butyrimidazol-1-yl-2-idene)phenylene)bis(dimethylamido)(iodo) titanium(IV) (7). 1,3-bis(3-butyrimidazol-1-yl)benzene diiodide 1 (0.300 g, 0.519 mmol),²⁶ Ti(NMe₂)₄ (593 µL, 2.60 mmol), and 100 mL of
toluene were added to a Schlenk flask. The mixture was heated to 160 °C for 16 h. The mother liquor was decanted, and the dark brown/black oily precipitate was washed with toluene (3 × 50 mL). Volatiles were removed under reduced pressure affording 7 (0.286 g, 94%). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.60 (d, J = 1.8 Hz, 2H), 7.40 (t, J = 7.8 Hz, 1H), 7.24 (s, 1H), 7.23 (s, 1H) 7.21 (s, 1H), 7.15 (s, 1H), 3.93 (t, J = 7.5 Hz, 4H), 3.23 (s, 12H), 1.72 (pseudo quintet, J = 7.6 Hz, 4H), 1.40 (sextet, J = 7.6 Hz, 4H), 0.99 (t, J = 7.3 Hz, 6H); ¹³C NMR (300 MHz, CD₂Cl₂): δ 190.5, 161.6, 147.9, 132.3, 122.6, 115.8, 110.8, 51.6, 40.8, 34.1, 20.5, 14.2. Anal. Calcd for C₂₄H₃₇IN₆Ti; C, 49.33; H, 6.38; N, 14.38. Found: C, 43.25; H, 5.38; N, 9.88. The discrepancy in calculated and found EA is attributed to decomposition as complex 7 is highly sensitive to trace proton sources, even humid air.

Preparation of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichlorotitanium(IV) (8). 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)(chloro)bis(dimethylamido) titanium(IV) 7 (0.300 g, 0.608 mmol), TMSCl (330. µL, 3.04 mmol), and CH₂Cl₂ (200 mL) were stirred at room temperature for 3 h. Volatiles were removed under reduced pressure to afford a crude brown/yellow solid. CH₂Cl₂ (24 mL) was added, and the mixture was passed through a 0.2 µm filter. Et₂O (10 mL) was added affording an orange crystalline precipitate. The crystalline precipitate was collected and washed with Et₂O (3 × 10 mL), and volatiles were removed under reduced pressure to afford 8 (0.054 g, 19%). X-ray quality crystals were grown from a saturated solution of 8 in CH₂Cl₂ layered with THF at room temperature. ¹H NMR (300 MHz, CD₂Cl₂): δ 7.45 (d, J = 1.9 Hz, 2H), 7.29 (dd, J₁ = 8.3 Hz, J₂ = 7.3, 1H), 7.09 (d, J = 7.4 Hz, 2H), 7.08 (d, J = 2.0 Hz, 2H), 4.47 (t, J = 7.5 Hz, 4H), 2.01 (m, 4H), 1.48 (sextet, J = 7.5 Hz, 4H), 1.0 (t, J = 7.4 Hz, 6H); ¹³C NMR (500 MHz, CD₂Cl₂): δ 194.5, 180.9, 144.1, 129.3, 120.8, 114.3, 110.5, 52.1, 34.1, 20.4, 14.1.
Preparation of 2-(1,3-bis(3-butylimidazol-1-yl-2-idenephene)trichlorotitanium(IV) (8) and (axial and equatorial) 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichlorotitaniu(mIV) (9a and 9e). NMR Scale Reaction: 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)bis(dimethylamido)(iodo) titanium(IV) 7 (0.012 g, 0.019 mmol), TMSCl (25 μL, 0.19 mmol), and CDCl₂ (0.5 mL) were combined in an NMR tube and maintained at room temperature for 104 h. Large scale experiment: 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)bis(dimethylamido)(iodo) titanium(IV) 7 (0.180 g, 0.308 mmol), TMSCl (197 μL, 1.55 mmol), and CH₂Cl₂ (50 mL) were stirred at room temperature for 3 h. Volatiles were removed under reduced pressure to afford a red solid mixture of 9a, 9e, and 8 (0.17 g, 97%). \(^1\)H NMR (300 MHz, CDCl₂): \(\delta \) 7.53 (d, \(J = 1.8 \) Hz, 0.33H, minor product), 7.49 (d, \(J = 1.8 \) Hz, 1H, major product), 7.45 (d, \(J = 1.9 \) Hz, 0.5H, 3), 7.40 (dd, \(J_1 = 8.2 \) Hz, \(J_2 = 7.3 \) Hz, 0.17H, minor product), 7.35 (dd, \(J_1 = 8.1 \) Hz, \(J_2 = 7.5 \) Hz, 0.5H, major product), 7.29 (dd, \(J_1 = 8.3 \) Hz, \(J_2 = 7.3 \) Hz, 0.25H, 8), 7.20-7.07 (m, 4H, overlapping of major, minor, and 8 products), 4.54-4.42 (m, 4H, overlapping of major, minor, and 8 products), 2.11-1.96 (m, 4H, overlapping of major, minor, and 8 products), 1.55-1.43 (m, 4H, overlapping of major, minor, and 8 products), 1.05-0.98 (m, 6H, overlapping of major, minor, and 8 products). \(^{13}\)C\(^{1}\)H NMR (300 MHz, CDCl₂): \(\delta \) 201.8, 197.1, 194.5, 183.5, 181.8, 180.8, 145.3, 144.5, 144.1, 129.3, 129.2, 129.1, 120.7, 120.6, 120.5, 115.0, 114.6, 114.3, 110.5, 111.0.4, 110.3, 52.1, 52.0, 34.0, 33.7, 33.3, 20.5, 20.4, 20.3, 14.1.

Preparation of 1,3-bis(3-butylimidazol-1-yl)benzene dichloride (10). 1,3-Bis-(imidazolyl)benzene (2.0 g, 9.5 mmol), \(^{26}\) 1-chlorobutane (20. mL, 190 mmol), and CH₃CN (100 mL) were added to a sealed flask. The mixture was heated to 160 °C for 24 h. The reaction was cooled to room temperature and a white solid precipitated. The mother liquor was decanted from
the solid. The solid was dissolved with CH$_2$Cl$_2$ and transferred to a Schlenk flask. All volatiles were removed under reduced pressure yielding 10 (3.2 g, 85%). $^1$H NMR (DMSO-$d_6$, 300 MHz): 10.66 (s, 2H), 8.77 (s, 3H), 8.15 (s, 2H), 8.10 (s, 1H), 8.07 (s, 1H), 7.94 (t, $J$ = 8.2 Hz, 1H), 4.30 (t, $J$ = 7.1 Hz, 4H), 1.93 (m, 4H), 1.34 (sextet, $J$ = 7.3 Hz, 4H) 0.94 (t, $J$ = 7.3 Hz, 6H); $^{13}$C{$^1$H} (DMSO-$d_6$, 300 MHz): δ 136.1, 135.8, 131.8, 123.5, 121.6, 120.9, 114.9, 49.2, 31.0, 18.8, 13.3. HRMS (MeOH, m/z): 359.2023 [M-Cl]$^+$

Preparation of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(dimethylamido) titanium(IV) (11). 1,3-bis(3-butylimidazol-1-yl)benzene dichloride 10 (0.300 g, 0.754 mmol), Ti(NMe$_2$)$_4$ (198 µL, 0.830 mmol), and toluene (150 mL) were heated at 120 °C for 16 h. The reaction was cooled to room temperature and a red solid precipitated. The mother liquor was decanted, and the red solid was washed with toluene (2 × 15 mL) and was dried under reduced pressure affording 11 (0.19 g, 48%). X-ray quality crystals of 11 were obtained from the attempted recrystallization of 12 in CH$_2$Cl$_2$. $^1$H NMR (CD$_2$Cl$_2$, 300 MHz): δ 7.41 (d, $J$ = 1.7 Hz, 2H), 7.16 (t, $J$ = 7.7 Hz, 1H), 7.05 (d, $J$ = 1.7 Hz, 2H), 7.00 (s, 1H), 6.97 (s, 1H), 4.35 (td, $J_1$ = 7.5 Hz, $J_2$ = 2.2 Hz, 4H) 3.40 (s, 6H) 3.40 (s, 6H) 1.89 (m, 4H), 1.45 (sextet, $J$ = 7.5 Hz, 4H) 0.99 (t, $J$ = 7.4 Hz, 6H); $^{13}$C{$^1$H} (300 MHz, CD$_2$Cl$_2$): δ 196.4, 179.1, 144.7, 128.0, 121.0, 114.6, 109.8, 51.5, 50.3, 35.0, 20.3, 14.1.

Preparation of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)(chloro)bis(dimethylamido) titanium(IV) (12). 1,3-bis(3-butylimidazol-1-yl)benzene dichloride 10 (0.260 g, 0.654 mmol), Ti(NMe$_2$)$_4$ (747 µL, 3.26 mmol), and toluene (200 mL) were heated at 120 °C for 16 h. The reaction was cooled to room temperature and a fine red solid precipitated. The mother liquor was decanted and the red solid was washed with toluene (2 × 20 mL). Volatiles were removed under reduced pressure affording 12 (0.170 g,
Second procedure: 1,3-Bis(1-butylimidazol-3-yl)benzene dichloride 10 (0.200 g, 0.502 mmol), Ti(NMe₂)₄ (599 μL, 2.51 mmol), and toluene (100 mL) were heated at 120 °C for 16 h. Volatiles were removed under reduced pressure. The red/brown product was washed with Et₂O (2 × 30 mL) and the volatiles were removed under reduced pressure, affording 12 (0.19 g, 70%).

Third Procedure: 1,3-bis(3-butylimidazol-1-yl)benzene dichloride 10 (0.10 g, 0.25 mmol), Ti(NMe₂)₄ (590 μL, 2.5 mmol), CH₂Cl₂ (5 mL), toluene (1 mL) were stirred at ambient temperatures for 4 h. The reaction was flash frozen in liquid nitrogen under positive Ar. The reaction was allowed to warm to -47 °C where the CH₂Cl₂ removed under reduced pressure, precipitating a red solid. The mother liquor was decanted at -47 °C and the red solid was cooled to -80 °C. The red solid was washed with toluene (8 × 5mL) precooled to -80 °C. The volatiles were removed under reduced pressure at ambient temperature affording 12 (0.05 g, 37%).

¹H NMR (300 MHz, CD₂Cl₂): δ 7.70 (d, J = 1.8 Hz, 1H), 7.41 (t, J = 7.8 Hz, 1H), 7.26 (s, 1H), 7.24 (s, 1H), 7.23 (s, 2H), 3.93 (t, J = 7.5 Hz, 4H), 3.22 (s, 12H), 1.72 (quintet, J = 7.5 Hz, 4H), 1.41 (quartet, J = 7.5 Hz, 4H), 0.99 (t, J = 7.3 Hz, 6H); ¹³C{¹H} (300 MHz, CD₂Cl₂): δ 189.9, 161.2, 147.4, 131.8, 122.0, 115.4, 110.4, 51.0, 40.3, 33.5, 20.0, 13.5.

The experimental procedures for X-ray Crystallography were written and reproduced with permission from by Professor Edward J. Valente.

X-ray Crystallography

The structures of complexes 8 and 11 were solved by direct methods in SHELXS-97. All non-H atoms were found in the E-map. Refinements were done using SHELXL-97. All non-H atoms were refined with anisotropic librational factors. H-atoms were observable in difference electron density maps, and placed in idealize positions; all were refined as riding
atoms with relative isotropic displacement parameters of 120% of the U(eq) of the attached atom.

Crystals of complex 8 were immersed in fluorocarbon oil. The specimens were bright red-orange, and a specimen (about 0.3 x 0.3 x 0.3 mm) was removed quickly, determined to be birefringent and essentially a single crystal by microscopy, and snagged with a small nylon loop, and transferred to the goniostat already cooled to 150 K.\textsuperscript{65} The crystallographic properties and data were collected using Mo Kα radiation and the charge-coupled area detector (CCD) detector on an Oxford Diffraction Systems Gemini S diffractometer at 150 K.\textsuperscript{65} A preliminary set of cell constants was calculated from reflections observed on three sets of 5 frames which were oriented approximately in mutually orthogonal directions of reciprocal space. Data collection was carried out using Mo Kα radiation (graphite monochromator) with 8 runs consisting of 676 frames with a frame time of 8.7 s and a crystal-to-CCD distance of 50.000 mm. The runs were collected by omega scans of 0.8 degree width, and at detector position of 28.624, -30.343° in 2θ. The intensity data were corrected for absorption with an analytical correction.\textsuperscript{66} Final cell constants were calculated from 16033 stronger reflections from the actual data collection after integration.

The crystal of complex 8 was monoclinic. The space group was $\text{P2}_1/1$ as determined from the cell geometry, systematic absences, reflections statistics, and successful solution and refinement. There were no solvent molecules, and a molecular complex comprises the asymmetric unit. The final full-matrix least-squares refinement converged to $R_I = 0.0237$ (5491 reflections, $F^2$, I > 2σ(I)); $R_I = 0.0302$ and $wR_2 = 0.0593$ for all 6520 unique data, 253 parameters, 0 restraints, goodness-of-fit (S) = 1.003, and no extinction.
The asymmetric unit of complex 8 consisted of a six-coordinated titanium (IV) complex with the ligand engaged in three contacts with Ti, and one equatorial Cl and two axial Cl’s. Butyl side chains were ordered. All distances and angles were within normal ranges.

Crystals of complex 11 were a deep red-brown solid in a sealed NMR tube filled with fluorocarbon oil as protectant from air/water. This protectant was wise, since on exposure to the air even in fluorocarbon oil, the substance slowly becomes colorless from the exterior of the crystal to the interior. Small prisms were in the sample, and a suitable single crystal of 11 was selected (0.089 x 0.310 x 0.455 mm), which was adhered to a nylon loop with fluorocarbon oil; the loop was epoxied to a stout glass fiber mounted on a pin; the pin was placed on a goniometer head. The crystallographic properties and data were collected using Mo Kα radiation and the charge-coupled area detector (CCD) detector on an Oxford Diffraction Systems Gemini S diffractometer at 101.2 K. A preliminary set of cell constants was calculated from reflections observed on three sets of 5 frames which were oriented approximately in mutually orthogonal directions of reciprocal space. Data collection was carried out using Mo Kα radiation (graphite monochromator) with 4 runs consisting of 270 frames with a frame time of 30.00 s and a crystal-to-CCD distance of 50.000 mm, and a strategy to achieve a resolution of 0.7Å. The runs were collected by omega scans of 1.0° width, and at detector position of 28.468 and -30.187° in 2θ. The intensity data were corrected for absorption with an analytical correction. Final cell constants were calculated from 6347 stronger reflections from the actual data collection after integration.

The crystal of complex 11 was orthorhombic, space group P2₁(1)/n as determined from the cell geometry, reflections statistics, systematic absences, and successful solution and refinement. This cell would require that a molecule comprise the asymmetric unit, which was what was
found, and lacking any solvation. All atom positions were ordered. The final full-matrix least-squares refinement converged to $R_I = 0.0311$ (4879 reflections, $F^2$, $I > 2\sigma(I)$); $R_I = 0.0538$ and $wR_2 = 0.0658$ for all 7288 data, 271 parameters, 0 restraints, goodness-of-fit (S) 0.955, and no extinction. Data were included to $2\theta = 61^\circ$.

Molecules of complex 11 comprised the asymmetric unit, with four molecules in the cell. A central titanium was six coordinated, with bonds to two chlorides, one dimethylamido nitrogen and the three carbons of the CCC-NHC pincer ligand.
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CHAPTER 3

SYNTHESIS, CHARACTERIZATION, AND X-RAY MOLECULAR STRUCTURE OF TANTALUM CCC-N-HETEROCYCLIC CARBENE PINCER COMPLEXES WITH IMIDAZOLYL AND TRIAZOLYL BASED LIGANDS

3.1 Research Background

Since their discovery, stable carbenes have had widespread application in transition-metal chemistry. N-heterocyclic carbenes (NHCs) and their variants have become ubiquitous in late-transition-metal chemistry with applications in photoluminescence, olefin metathesis, C-C coupling, and hydrosilylation. Conversely, early-transition metal NHC complexes have yet to be explored to the same depth. Group 5 NHC metal complexes are particularly scarce. Fryzuk has reported the only four crystal structures of Ta complexes bearing an NHC ligand. No triazole-based-NHCs as ligands for groups 3, 4, or 5 metal centers have been, to our knowledge, reported previously. Reports of Ta NHC chemistry remain sparse despite significant reactivity with Ta which includes N2 activation, CO2 activation, chiral hydroaminoalkylation,
C-N bond activation.\textsuperscript{28,29} New ligand architectures often lead to improved properties or new reactivity; therefore, the development of methodologies to access novel systems remains significant.

The pincer ligand architecture is an important class of tridentate, meridional binding ligands that form robust metal complexes.\textsuperscript{30-32} Pincer ligands have application in a variety of reactivity;\textsuperscript{33-36} noteworthy examples include C-F bond activation,\textsuperscript{37,38} alkane dehydrogenation,\textsuperscript{32} and catalytic C-C bond formation.\textsuperscript{31} One of the reasons for the widespread use of pincer ligands is the ability to vary the lateral donor groups, providing an effective way to alter the properties of the metal center. Accordingly, incorporation of NHCs into pincer ligands has become of increasing interest.\textsuperscript{31,39-44} Although pincer complexes have been known since the 1970s,\textsuperscript{45-48} only a few examples of Ta pincer complexes have been reported.\textsuperscript{49-54} Herein, we report an efficient route to synthesize CCC-NHC pincer Ta complexes with imidazole and triazole-based-NHC ligands.

**Scheme 3.1.1** Metal Complexes Derived from Aryl-Bridged Bis(NHC)-Pincer Ligands.

Since the original report of Type B bis(NHC) pincer ligands (Scheme 3.1.1),\textsuperscript{55} several groups worldwide have continued developing this class of ligand.\textsuperscript{9,39,56-67} Use of early-transition-
metal amido starting materials to activate ligand precursors via amine elimination is an effective route to synthesize complexes bearing multidentate ligands.\textsuperscript{23,68-77} In particular, this methodology has yielded a facile route for the synthesis of group 4 CCC-NHC pincer complexes. The electrophilicity of the d\textsuperscript{0} metal center in conjunction with the basicity of the dimethylamido ligands were exploited to facilitate the necessary triple C-H bond activation of the imidazolium salt precursor. In the present work, this triple C-H bond activation methodology is successfully extended to Ta.

3.2 Results and Discussion

3.2.1 Synthesis and Characterization of (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (13)

In direct analogy with the previous work synthesizing group 4 CCC-NHC pincer complexes,\textsuperscript{55,60-62} Ta(NMe\textsubscript{2})\textsubscript{5} was first evaluated as a metalating reagent for imidazolium salt 1. No imidazolium signal (δ 11.27) was observed in the \textsuperscript{1}H NMR spectrum, indicating successful metalation after reacting Ta(NMe\textsubscript{2})\textsubscript{5} with imidazolium salt 1. However, an abundance of signals suggested multiple coordination spheres at Ta. These materials were never found to be tractable. It was reasoned that the requisite high coordination number prevented clean isolation with this ligand set. Therefore, a Ta reagent that would reduce the coordination number of the products was sought. (t-Butylimido)tris(dimethylamido)tantalum(V), which contains a dianionic ligand, proved to be a solution to the problem. Thus, bis(imidazolium) diiodide salt 1 was reacted with excess (t-butylimido)tris(dimethylamido)tantalum(V) in toluene at 160 °C for 16 h yielding complex 13 (Scheme 3.2.1.1). As before, no imidazolium signal at δ 11.27 was observed in the \textsuperscript{1}H NMR spectrum. Furthermore, the signal corresponding to the methylene group α to the nitrogen shifted from a triplet at δ 4.46 in salt 1 to a multiplet at δ 4.13. Unlike the previously
reported group 4 complexes, the dimethylamido signals of 13 were diasterotopic. Two unique singlets at δ 4.24 and δ 3.89 corresponding to the dimethylamido ligand were observed, which was the first time magnetically inequivalent methyl groups were observed in CCC-NHC pincer complexes. This phenomenon has been observed in other Ta complexes.\(^7\) The carbene peak at δ 199.2 in the \(^{13}\)C NMR spectrum also indicated successful metalation of the salt. An aryl peak was observed at δ 174.8, which was consistent with the formation of the Ta-C(aryl) bond. These data supported triple C-H activation and formation of the desired Ta CCC-NHC pincer complex.

VT-NMR experiments were performed in an attempt to find the temperature at which the signals for the dimethylamido ligand would coalesce. After heating 13 to 382 K (109 °C) in \(d_8\)-toluene two diasterotopic signals were still observed for the dimethylamido ligand. From spin saturation transfer experiments the free energy of activation for the rotation (\(\Delta G^\ddagger_{expt}\)) is estimated to be 23.5 kcal mol\(^{-1}\). This data is in reasonable agreement with results from PBEPBE DFT computations (\(\Delta G^\ddagger_{comp}\) 25.8 kcal mol\(^{-1}\)).

**Scheme 3.2.1.1** Synthesis of (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (\(\text{t-butylimido)(dimethylamido)}\) iodonium(tantalum(V) (13)).

\[ \text{Scheme 3.2.1.1 Synthesis of (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (t-butlimido)(dimethylamido)} \]
**Scheme 3.2.2.1** Attempted Catalytic Hydroamination/Cyclization Using (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (13).

![Chemical Structure](image)

X-ray quality crystals of Ta complex 13 were grown from a saturated benzene solution. An ORTEP® plot of the molecular structure of Ta complex 13 is presented in Figure 3.2.1 along with selected metric data. X-ray crystallographic data confirmed the tridentate bonding of the CCC-NHC pincer ligand to the Ta(V) center. Complex 13 has distorted octahedral coordination due to the constraints of the pincer ligand. The NHC ligands occupied coordination sites trans to each other and had a C\textsuperscript{NHC}-Ta-C\textsuperscript{NHC} bond angle of 139.1(2)°. The Ta-C\textsuperscript{NHC} bond lengths were 2.258(6) Å and 2.255(5) Å, comparable (±0.152 Å) to the Ta-C\textsuperscript{NHC} bond lengths of Fryzuk’s complexes.\textsuperscript{23} The Ta-C\textsuperscript{aryl} bond length was 2.248(5) Å, which was within 0.1 Å of other Ta pincer complexes with a similar aryl group flanked by neutral donors.\textsuperscript{51,79} With a bond length of 1.794(5) Å, the Ta-N\textsuperscript{imido} bond was 0.07 Å longer than another reported Ta complex containing a linear t-butylimido ligand trans to a halogen.\textsuperscript{80} The Ta-N\textsuperscript{amido} bond was 2.036(4) Å, which was within 0.07 Å of previously reported Ta pincer complexes.\textsuperscript{50} At 3.0669(4) Å, the Ta-I bond length of 13 was much longer than other reported Ta-I bond.\textsuperscript{81-89} The unusually long length of the Ta-I bond is attributed to the large trans-influence of the imido ligand.\textsuperscript{90}
**Figure 3.2.1.1** Molecular structure of complex 13 (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (t-butylimido) (dimethylamido)iodo tantalum(V). Hydrogens omitted for clarity.

Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°): Ta(1)-C(2), 2.258(6); Ta(1)-C(13), 2.255(5); Ta(1)-C(11), 2.248(5); Ta(1)-N(25), 1.794(5); Ta(1)-N(30), 2.036(4), Ta(1)-I(1), 3.0669(4); C(2)-Ta(1)-C(13), 139.1(2); C(11)-Ta(1)-C(2), 69.6(2); C(11)-Ta(1)-C(13), 69.6(2).

3.2.2 Synthesis and Characterization of (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (15)

Research into late-transition-metal triazole-based-NHC has been established, yet no early-transition-metal (group 3, 4, or 5) triazole-based-NHC complexes have been reported. Recently, the synthesis of a CCC-NHC triazolium pincer ligand precursor and its metalation to yield Ag NHC complexes was reported. Based on the successful metalation of the imidazolium based CCC-NHC ligand precursor with t-(butylimido)tris(dimethylamido)tantalum(V), the CCC-NHC triazolium pincer ligand precursor 14 was evaluated. Accordingly, upon reaction in toluene at 160 °C, a product with no triazolium signal in the $^1$H NMR spectrum was obtained (Scheme 3.2.2.1). In direct parallel to complex 13, the methylene group α to the nitrogen shifted
to $\delta$ 4.21 from $\delta$ 4.52 in triazolium salt 14. Diasterotopic singlets were observed for the methyl groups of the dimethylamido ligand at $\delta$ 4.31 and $\delta$ 4.00. The carbene signal was observed at $\delta$ 199.7 in the $^{13}$C NMR spectrum. All these data were consistent with the synthesis of Ta CCC-triazole-based NHC complex 15. It should also be noted complex 15 can be synthesized using THF as a solvent at 100 °C.

**Scheme 3.2.2.1** Synthesis of (1,3-bis(3-butytriazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (15).

As early-transition metal complexes are known to catalyze hydroamination/cyclization of unactivated alkene amines, complex 13 was also evaluated for the same reactivity. Treating the diphenyl substituted substrate with 13 at typical conditions for hydroamination/cyclization yielded no reaction even after prolonged periods of time (34h at 160 °C). The reaction temperature was increased to 170 °C for 2 d, yet still no reaction was observed. It was determined that complex 13 was not catalytically active for the hydroamination/cyclization of unactivated alkene amine under these conditions.

X-ray quality crystals of Ta complex 15 were grown by layering Et$_2$O onto a saturated toluene solution. An ORTEP® plot of one of the two molecules of Ta complex 15 found in the asymmetric unit is presented in Figure 3.2.2.1 along with selected metric data. The differences between the two molecules in the asymmetric unit were minor. No analogous bond lengths differed by more than 0.033 Å, nor did any analogous bond angles differ by more than 3.4°.
between the two molecules. Full X-ray crystallographic data on both molecules is found in the X-ray crystallography section of chapter 3. For simplicity only the bond lengths and angles of the molecule illustrated in Figure 3.2.2.1 will be discussed. Like complex 13, complex 15 was found to have a distorted octahedral geometry. The NHC ligands occupied coordination sites trans to each other with a bond angle of 138.69(11)°. With bond lengths of 2.286(3) Å and 2.283(3) Å, the Ta-C^{NHC} distances of complex 15 were comparable to 13 and Fryzk’s Ta NHC complexes. At 2.270(3) Å, the Ta-C^{aryl} bond length was consistent with other pincer Ta complexes (±0.12 Å) containing a similar aryl functionality flanked by neutral donors.\(^{51,79}\) The Ta-N^{imido} bond length was 1.780(3) Å, which is within 0.06 Å of the only reported Ta complex containing a linear t-butylimido trans to a halogen.\(^{80}\) With a bond length of 2.037(3) Å, the Ta-N^{amido} bond length was consistent with other Ta pincer complexes (±0.07 Å).\(^{50}\) Complex 15 also had an unusually long Ta-I bond length of 3.0480(4) Å, similar to that of complex 13.
**Figure 3.2.2.1** Molecular structure of complex 15 (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodo tantalum(V). Only one formula unit shown and the hydrogens have been omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°): Ta(1)-C(6), 2.283(3); Ta(1)-C(15), 2.286(3); Ta(1)-C(3), 2.270(3); Ta(1)-N(1), 2.037(3); Ta(1)-N(8), 1.780(3); Ta(1)-I(1), 3.0480(4), C(6)-Ta(1)-C(15) 138.69(11); C(3)-Ta(1)-C(6), 89.10(11); C(3)-Ta(1)-C(15), 69.82(11).

### 3.3 Conclusion

In conclusion, unprecedented CCC-NHC pincer complexes of Ta have been synthesized via an amine elimination pathway. Use of Ta(NMe₂)₅ as a metalating reagent for imidazolium salt 1 yielded intractable products. Use of (t-butylimido)tris(dimethylamido)-tantalum(V) as a metalating reagent for imidazolium salt 1 lowered the coordination number and yielded a single isolable CCC-NHC Ta pincer complex. Recently reported triazolium salt 14 was treated likewise and yielded triazole-based CCC-NHC complex 15. Complex 13 and 15 are only the fifth and sixth X-ray crystallographically determined molecular structures of Ta-NHC complexes. Furthermore, complex 15 is the first reported X-ray crystallographically determined molecular
structure of an early-transition-metal triazole-based-NHC complex. Further reactivity of complexes 13 and 15 will be reported in due course.

3.4 Experimental Section

**General Consideration.** Standard inert atmosphere techniques were used. Starting imidazolium and triazolium salts were prepared from previously reported literature references. Et₂O and toluene were degassed with argon and passed through two columns of activated alumina. Hexanes were purchased from Fisher Scientific, degassed with argon, and passed through a column of activated alumina prior to use. (t-Butylimido)tris(dimethylamido) tantalum(V) was purchased from Strem Chemicals and used as received. CD₂Cl₂, C₆D₆, d₈-toluene were purchased from Cambridge Isotopes and passed through a column of activated basic alumina prior to use. ¹H and ¹³C NMR spectra were collected on a Bruker Avance 300 MHz NMR or Bruker Avance DRX 500 MHz NMR at ambient temperatures. The ¹H NMR spectra were referenced internally from the residual protio-solvent signal: CD₂Cl₂ (δ 5.32) and d₈-toluene (δ 2.09). The ¹³C NMR spectra were referenced internally using the signal from the deuterated solvent: CD₂Cl₂ (δ 54.0).

**Preparation of (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (13).** 1,3-Bis(3-butylimidazol-1-yl)benzene diiodide (1; 1.00 g, 1.73 mmol), (t-butylimido)tris(dimethylamido)tantalum(V) (1.99 g, 5.19 mmol), and toluene (200 mL) were heated at 160 °C for 16 h. The reaction was cooled to room temperature, and a white crystalline solid precipitated. The mother liquor was decanted, and the white crystalline solid was washed with toluene (3 × 10 mL) precooled to -78 °C. Volatiles were removed under reduced pressure affording 13 (1.16 g, 90%). X-ray quality crystals were obtained from cooling an NMR tube scale reaction in C₆D₆. ¹H NMR (300 MHz, CD₂Cl₂): δ
7.54 (d, $J = 1.7$ Hz, 2H), 7.19 (dd, $J_1 = 8.6$ Hz, $J_2 = 6.6$ Hz, 1H), 7.10 (d, $J = 6.9$ Hz, 2H), 7.09 (d, $J = 1.7$ Hz, 2H), 4.24 (s, 3H), 4.13 (m, 4H), 3.89 (s, 3H), 1.99 (m, 4H), 1.48 (sextet, $J = 7.5$ Hz, 4H), 1.02 (t, $J = 7.3$ Hz, 6H), 0.70 (s, 9H)；

$^{13}$C$^1$H (300 MHz, CD$_2$Cl$_2$): $\delta$ 199.2, 174.8, 146.7, 126.4, 121.7, 116.0, 109.3, 63.7, 59.7, 52.2, 33.8, 33.3, 20.9, 14.2. Anal. Calcd for C$_{26}$H$_{40}$IN$_6$Ta; C, 41.95; H, 5.42; N, 11.29 Found: C, 42.02; H, 5.45; N; 10.95.

**Preparation of (1,3-bis(3-butyltriazol-1-yl-2-idenene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (15)**. 1,3-Bis(3-butyltriazol-1-yl)benzene diiodide (14, 0.200 g, 0.345 mmol), (t-butylimido)tris(dimethylamido)tantalum(V) (0.397 g, 0.103 mmol), and toluene (10 mL) were heated at 160 °C for 16 h. The reaction was cooled to room temperature. The volatiles were removed under reduced pressure affording a brown crude product. This crude product was washed with hexanes 3 × 5 mL. Volatiles were removed under reduced pressure. The product was dissolved with 3 mL toluene and layered with 10 mL hexanes. A light brown solid precipitated from solution after 16 h. The mother liquor was decanted from the light brown solid. The light brown solid was triturated with hexanes (3 × 3 mL) and the volatiles were removed under reduced pressure affording 15. (0.13 g, 51%). X-ray quality crystals were obtained by layering Et$_2$O onto a saturated solution in toluene. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 8.11 (s, 2H), 7.46 (d, $J = 7.7$ Hz, 2H), 7.27 (t, $J = 7.7$ Hz, 2H), 4.31 (s, 3H), 4.21 (t, $J = 7.4$ Hz, 4H), 4.00 (s, 3H), 2.04 (m, 4H), 1.49 (pseudoextet, $J = 7.5$ Hz, 4H), 1.04 (t, $J = 7.4$ Hz, 6H), 0.70 (s, 9H)；$^{13}$C$^1$H (300 MHz, CD$_2$Cl$_2$): $\delta$ 199.7, 171.0, 145.9, 142.7, 126.6, 111.6, 63.7, 60.4, 54.9, 50.0, 33.4, 33.1, 20.7, 14.0. Anal. Calcd for C$_{24}$H$_{38}$IN$_8$Ta; C, 38.62; H, 5.13; N, 15.01. Found: C, 37.25; H, 4.73; N, 13.91. Complex 15 is extremely sensitive to trace proton sources, even humid air. The calculated EA for the analogues complex of 15 where an (OH) replaces the (NMe$_2$) is C, 36.73; H, 4.62; N, 13.63. The calculated EA of
complex 15 where an (OH) replaces the (NMe₂) is in better agreement with the found EA. This data suggests partial hydrolysis of complex 15 during analysis.

The experimental procedures for X-ray Crystallography were written and reproduced with permission from by Mr. Henry Valle.

X-ray Crystallography

Experimental

Single crystals of C_{26}H_{40}N_{6}ITa (1,3-bis(3-butilimidazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (13) were crystallized via a saturated solution of complex 13 in benzene. A suitable crystal was selected and mounted on a 150um cryoloop and mounted on a Bruker Smart APEX II diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using CGLS minimisation.

Single crystals of C_{48}H_{80}N_{16}I_{2}Ta_{2} (1,3-bis(3-butiltriazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodo tantalum(V) (15) were crystallized via layering Et₂O to a saturated solution in toluene. A suitable crystal was selected and mounted on a 150 um mitogen mount on a Bruker Smart APEX II diffractometer. The crystal was kept at 100.13 K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the olex2.refine refinement package using Gauss-Newton minimisation.

Crystal Data for C_{26}H_{40}N_{6}ITa (M =744.49): monoclinic, space group P2₁/c (no. 14), a = 14.3134(5) Å, b = 14.0461(5) Å, c = 14.6772(5) Å, β = 95.1620(10)°, V = 2938.85(18) Å³, Z = 4, T = 100.15 K, μ(CuKα) = 15.326 mm⁻¹, Dealc = 1.683 g/mm³, 27074 reflections measured (6.2 ≤
$2\Theta \leq 139.862$), 5465 unique ($R_{\text{int}} = 0.0508$) which were used in all calculations. The final $R_1$ was 0.0491 ($I > 2\sigma(I)$) and $wR_2$ was 0.1370 (all data).

**Crystal Data** for $C_{48}H_{80}N_{16}I_{2}Ta_{2}$ ($M = 1492.95$): triclinic, space group $P-1$ (no. 2), $a = 10.6851(12)$ Å, $b = 10.9572(12)$ Å, $c = 24.299(3)$ Å, $\alpha = 89.884(1)^\circ$, $\beta = 84.039(1)^\circ$, $\gamma = 86.730(1)^\circ$, $V = 2824.9(5)$ Å$^3$, $Z = 2$, $T = 100.13$ K, $\mu(N/A) = 5.010$ mm$^{-1}$, $D_{\text{calc}} = 1.7550$ g/mm$^3$, 34679 reflections measured ($3.38 \leq 2\Theta \leq 58.12$), 13751 unique ($R_{\text{int}} = 0.0301$) which were used in all calculations. The final $R_1$ was 0.0241 ($I \geq 2\sigma(I)$) and $wR_2$ was 0.0617 (all data).

**Free Energy of Rotation Calculation Using Spin Saturation Transfer:** Using modifications of a procedure by Odom, the free energy of rotation of the dimethylamido ligand was calculated by NMR. A saturated solution of $2$ in $d_8$-toluene prepared at ambient temperature and was decanted from all solid for use in the spin saturation experiment. An 80% ethylene glycol/20% $d_6$-DMSO standard was used to measure the temperature of the NMR probe prior to the experiment. The sample was allowed to equilibrate to the desired temperature for 15 min. The $90^\circ$ pulse width was determined and set at the desired temperature. A quality $^1$H NMR spectrum was taken at the desired temperature. $T_1$ values of the dimethylamido ligand of $2$ were determined using the inversion recovery method. The delay was set to $5 \times T_1$. The saturation power was set to 59 dBW. An experiment was performed where the most upfield dimethylamido signal was saturated. A second experiment was performed where an equidistant offset point was saturation to ensure the decoupler sidebands did not overlap with the signal being studied for integration changes. The rate of exchange was then determined using the equation below. $M_0$ is the integration without saturation, $M_a$ is the integration with saturation, and $T_1$ is the relaxation time of the methyl signal most downfield.
Once the rate of exchange ($k_{obs}$) was determined the free energy of activation for the rotation was calculated using the Eyring equation below. $K$ is the transmission coefficient assumed to be 1, $k_b$ is the Boltzmann constant, $T$ is temperature in Kelvin, $h$ is Plank’s constant, and $R$ is the gas constant.\(^\text{102}\)

\[
k_{obs} = K \frac{k_B T}{h} e^{-\Delta G^+/RT}
\]
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CHAPTER 4

SYNTHESIS AND CHARACTERIZATION OF TANTALUM CCC-NHC BIS(IMIDO) COMPLEXES

4.1 Research Background.

The seminal work of Bertrand and Arduengo has shown that carbenes are not always the transient intermediates as chemists once believed,\textsuperscript{1-3} but can be persistent and bottleable carbon species. In particular, N-heterocyclic carbenes (NHCs) have become ever-present in late transition metal chemistry,\textsuperscript{4} yet the study of early-transition metal NHCs is still in its infancy.\textsuperscript{3} Group 5 NHC complexes are vastly understudied. Only 6 Ta NHC complexes have been reported to date.\textsuperscript{5,6} As the popularity of NHCs as ancillary ligands for new metal complexes increased, so has research into new NHC variants.\textsuperscript{7} One noteworthy NHC derivative is the imidazole-base-NHC bonded to the metal at the backbone C-4 or C-5 carbon, known as a mesionic carbene (MIC) or abnormal carbene. Crabtree reported the first MIC complex in...
2001, while the first free MIC was reported by Bertrand in 2009. Bonding via C-4 or C-5 carbon makes MICs even better σ-donors than the C-2 bound NHCs. The increased σ-donor ability is due to the presence of only one adjacent heteroatom, which decreases the inductive effect on the carbene. Robinson has further expanded alternative binding by imidazole-based NHCs with his recent report of imidazole ring containing simultaneous carbene centers at the C-2 and C-4 positions, known as the anionic N-heterocyclic dicarbene (NHDC). Currently no MIC or NHDC complexes for early-transition metals have been characterized by X-ray crystallography. Herein we report the synthesis of Ta CCC-NHC and CCC-NHC/NHDC bis(imido) complexes and their catalytic activity in oxidative amination.

4.2 Results and Discussion

4.2.1 Synthesis of (1,3-bis(3-butylietiazol-1-yl-2-idene)-2-phenylene) bis(t-butylietimo)tatantalum(V) (16).

Following a similar synthetic procedure to synthesize Ta bis(imido) complexes using lithium amides by Wigley, complex 13 was reacted with lithium t-butyliamide in C₆D₆ at ambient temperature, on an NMR tube scale (Scheme 4.2.1.1). The most obvious change in the ¹H NMR spectrum from complex 13 in C₆D₆ to bis(imido) complex 16 in C₆D₆, was the loss of the dimethylamido signals at δ 4.42 and 4.41. The signal corresponding to the methylene group adjacent to the imidazolyl nitrogen shifted from diastereotopic multiplets at δ 3.87 and 3.69 in 13 to a pseudotriplet at δ 4.42 in 16. The signal at δ 1.65 with an integration of 18H corresponds to the two t-butylietimo ligands, which is a great change from the t-butylietimo signal of 1 found at δ 0.86 and having an integration of only 9H. The ¹³C NMR spectrum contained a carbene peak at δ 201.8 and an aryl signal at δ 170.3. These data were consistent with the synthesis of a Ta CCC-NHC pincer bis(imido) complex.
**Scheme 4.2.1.1** Synthesis of (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(t-butylimido)tantalum(V) (16).

4.2.2 Synthesis of (1-(3-butylimidazol-1-yl-2-lithium-4-idene) 3-(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(t-butylimido)tantalum(V) (17).

Upon increasing the reaction to bulk scale, problems with converting the starting material to the desired bis(imido) complex were observed. In an effort to convert all the starting material to the bis(imido) complex, the reaction was heated to 80 °C (Scheme 4.2.2.1). After isolating the product, a set of signals corresponding to a second Ta CCC-NHC pincer complex was observed. Two signals at δ 1.5 and δ 1.0, with integrations of 9H each, corresponded to the t-butyl signals of the t-butylimido ligands of the second Ta CCC-NHC pincer complex. The magnetic inequivalent t-butylimido ligands provided evidence that the second Ta CCC-NHC pincer complex was not symmetrical. This material was not soluble enough in C₆D₆ and d₈-toluene for signals to be observed in the ¹³C NMR spectrum. The material reacted with other common deuterated solvents such as CD₃Cl, CD₂Cl₂, and CD₃CN. Consequently, no usable ¹³C NMR data has been obtained to date. However, the molecular structure of the second pincer complex was confirmed as a Ta CCC-NHC/NHDC by X-ray crystallography.
Scheme 4.2.2.1 Synthesis of (1-(3-butylimidazol-1-yl)-2-lithium-4-idene 3-(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(t-butylimido)tantalum(V) (17).

X-ray quality crystals of Ta complex 17 were grown from layering a saturated toluene solution of 16 and 17 with hexanes. An ORTEP® plot of the molecular structure of Ta complex 17 is presented in Figure 4.2.2.1 along with selected metric data. X-ray crystallographic data confirmed the tridentate bonding of the CCC-NHC pincer ligand to the Ta(V) center. Complex 17 has distorted trigonal bipyramidal coordination due to the constraints of the pincer ligand. The NHC and MIC ligands occupied coordination sites trans to each other and had a C\(^{\text{NHC}}\)-Ta-C\(^{\text{MIC}}\) bond angle of 139.10(13)°. The Ta-C\(^{\text{MIC}}\) bond length was 2.277(4) Å. This unprecedented bond was comparable (-0.01 Å) to the other Ta-C\(^{\text{NHC}}\) bond length in pincer ligand which was 2.286(4) Å. Both the Ta-C\(^{\text{MIC}}\) and Ta-C\(^{\text{NHC}}\) were in agreement (±0.13 Å) with other known Ta-C\(^{\text{NHC}}\) bond lengths.\(^5\)\(^6\) The Ta-C\(^{\text{aryl}}\) bond length was 2.282(5) Å, which was within 0.12 Å of other Ta pincer complexes with a similar aryl group flanked by neutral donors.\(^1\)\(^4\)\(^5\) With a bond lengths of 1.866(4) Å and 1.825(4), the Ta-N\(^{\text{imido}}\) bonds were similar (±0.081 Å) to other reported Ta bis(imido) complexes.\(^12\)\(^13\)\(^16\) At 117.67(19)°, the N\(^{\text{imido}}\)-Ta-N\(^{\text{imido}}\) angle was similar to other Ta bis(imido) angles.\(^13\)\(^16\) The C(7)-Li(7) bond length was 2.117 Å, analogous to the Li-C\(^{\text{NHC}}\) bond length (-0.058 Å) of the free NHDC by Robinson.\(^1\)^
**Figure 4.2.2.1** Molecular structure of complex 17 (1-(3-butylimidazol-1-yl-2-lithium-4-idene 3-(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(t-butylimido)tantalum(V). Only one formula unit shown and the hydrogens have been omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°): Ta(1)-C(1), 2.281(4); Ta(1)-C(8), 2.277(4); Ta(1)-C(14), 2.286(4), Ta(1)-N(5), 1.869(3); Ta(1)-N(6), 1.826(3); C(8)-Ta(1)-C(14), 139.10(13); C(1)-Ta(1)-C(14), 69.50(14); C(8)-Ta(1)-C(1), 69.69(13); N(6)-Ta(1)-N(5), 117.68.

### 4.2.2 Catalytic Oxidative Amination

The catalytic formation of cyclic imines from unactivated amino-alkenes (Oxidative Amination) is an extremely rare reaction. To date oxidative amination has only been seen with a Ru catalyst by Mitsudo and as a side product by Hartwig.\textsuperscript{17,18} Treating bis(imido) complex 16 with the diphenyl substituted substrate (entry 1 Table 4.2.3.1) yielded the cyclic imine and the reduced substrate in a 50:50 ratio, no starting material was observed. Isolation of the crude product of catalysis was attempted, however the cyclic imine and saturated substrate product were found to eleut in the same fraction. Determination of the products was still possible. The spectral data (\textsuperscript{1}H NMR, \textsuperscript{13}C NMR, and Mass Spectometry) matched the sum of the literature precedents for the products using the diphenyl substituted substrate. The oxidative amination catalysis was found to have catalytic activity with substrates containing a spirocyclopentane
(entry 2), spirocyclohexane (entry 3), and a phenyl and allyl substituent (entry 4) at the C-2 position. No signals for these substrates were observed after catalysis in the $^1$H NMR spectrum. A signal around $\delta$ 173 was observed in the $^{13}$C NMR spectra of the all these substrates (entries 2-4) after catalysis. This data suggests that the imine product is formed. The mass spectrum of the substrate with the phenyl and allyl substituent at the C-2 position of the substrate (entry 4) had signals at 200.1, 202.1, and 204.1 which suggest the products of catalysis were the protonated cyclic imine, protonated hydroamination, and protonated saturated substrate. Signals in the mass spectrum of the spirocyclohexyl substituted substrate (entry 2) had signals at 152.1 which corresponded to the cyclic imine product. The proposed products for entries 2-4 have no literature precedents. Separation and isolation of the products is currently underway. Once the products separated and isolated, accurate ratios of the amount of each product produced will can and will be reported. Furthermore, substrates with a terminal or internal substituted double bond were found to have no reactivity with the catalyst (entries 6 and 8). Also, no reactivity was observed in substrates that formed 6-membered rings, nor indole substrates (entries 7 and 9). Catalytic oxidative amination was also performed with bis(imido) samples that contained Ta HNDC complex 17, however no reaction was observed. 3,3-Dimethyl-1-butene was added as a hydrogen acceptor to produce only the cyclic imine product. Addition of this sacrificial olefin was found to impede all reactivity and only unreacted substrate was observed in the $^1$H NMR spectrum.
Scheme 4.2.3.1 Oxidative Amination of unactivated alkene amines using (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(t-butylimido)tantalum(V).
Table 4.2.3.1 Oxidative Amination of unactivated alkene amines.

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<th>Proposed Reduced Product</th>
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<tr>
<td>9</td>
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</tr>
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</table>

*Sum if singals in isolated $^1$H and $^{13}$C NMR match literature precedent for imine and reduced products*
Scheme 4.2.3.1 Attempted Oxidative Amination of unactivated alkene amines using

4.3 Conclusion

In conclusion, unprecedented Ta CCC-NHC and CCC-NHC/NHDC bis(imido) complexes have been synthesized. Reacting Ta starting material 13 with lithium t-butylamide at ambient temperatures yielded the Ta CCC-NHC bis(imido) complex 16. Upon increasing the reaction to bulk scale, problems converting all of staring material 13 to the desired bis(imido) complex were observed. In an effort to remedy this issue, excess lithium t-butylamide was added and the temperature of the reaction was increased to 80 °C. The resulting product of these changes in reaction condition was a mixture of Ta CCC-NHC complex 16 and Ta CCC-NHC/NHDC complex 17. Novel NHDC complex 17 is the first X-ray crystallographically determined molecular structure of an early-transition-metal NHDC complex. Complex 16 was found to be catalytically active in converting unactivated amino-alkenes to a mixture of cyclic imines and the reduced substrate.

4.4 Experimental Section

General Consideration. Standard inert atmosphere techniques were used. Ta starting material 13 and lithium t-butylamide were synthesized according to previous reported literature references.\(^6,19\) Solvents were degassed with argon, and passed through a column of activated alumina prior to use.\(^20\) \(^1\)H and \(^13\)C NMR spectra were collected on a Bruker Avance 300 MHz
NMR or Bruker Avance DRX 500 MHz NMR at ambient temperatures. The $^1$H NMR spectra were referenced internally from the residual protio-solvent signal: $d_8$-toluene ($\delta$ 2.09) $C_6D_6$ ($\delta$ 7.16). The $^{13}$C NMR spectra were referenced internally using the signal from the deuterated solvent: $C_6D_6$ and ($\delta$ 128.39).

**Preparation of Synthesis of (1,3-bis(3-butytriazol-1-yl-2-idene)-2-phenylene) bis(t-butylimido)tantalum(V) (16).** NMR Scale Reaction: (1,3-bis(3-butytrimidazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (0.025g, 0.0034 mmol), lithium t-butyamide (0.0058g, 0.074mmol), and $C_6D_6$ (0.5mL) were added to an NMR tube and maintained at ambient temperature for 3 days. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 7.04 (t, $J$ = 7.7 Hz, 1H), 6.69 (d, $J$ = 7.4 Hz, 2H), 6.68 (d, $J$ = 1.8 Hz, 2H), 6.26 (d, $J$ = 1.7 Hz, 2H), 4.42 (pseudotriplet, 4H), 1.77 (m, 4H), 1.65 (s, 18H), 1.37 (m, 4H), 0.95 (triplet, $J$ = 7.4 Hz, 6H); $^{13}$C($^1$H) (300 MHz, $C_6D_6$): $\delta$ 201.8, 170.3, 149.6, 128.7-128.8 (signal overlaps with $C_6D_6$), 120.4, 115.6, 108.9, 64.3, 52.7, 51.8, 48.7, 38.8, 38.2, 37.4, 33.1, 32.5, 20.8, 14.4.

**Preparation of Synthesis of (1,3-bis(3-butytriazol-1-yl-2-idene)-2-phenylene) bis(t-butylimido)tantalum(V) (16) and (1-(3-butytrimidazol-1-yl-2-lithium-4-idene 3-(3-butytrimidazol-1-yl-2-idene)-2-phenylene) bis(t-butylimido)tantalum(V) (17).** (1,3-bis(3-butytrimidazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (0.204g, 0.270 mmol), lithium t-butyamide (0.0470g, 0.60mmol), and toluene (10mL) were stirred at ambient temperature for 16 h. Additional lithium t-butyamide (0.030, 0.379 mmol) was added and the reaction was heated at 80 °C for 16 h. The volatiles were removed under reduced pressure. Toluene (10 mL) was added to the crude material in an attempt to dissolve the product. Pentane (8 mL) was layered on to the mixture to precipitate any product in solution. The mother liquor was removed and the product was washed with pentane (3×3 mL). Volatiles
were removed under reduced pressure to afford a mixture of 16 and 17 (0.06g, 34%). X-ray quality crystals of 17 were grown from layering pentane onto a saturated solution of 16 and 17.

$^1$H NMR (300 MHz, d$_8$-toluene, sample not homogenous): $\delta$ 7.86 (broad s, 1H, 17) 6.85 (broad s, 2H, 17), 6.80 (broad s, 1H, 17), 6.78 (broad s, 1H, 17), 6.66 (broad s, 1H, 16), 6.63 (broad s, 1H, 16), 6.61(broad s, 1H, 16) 6.27 (broad s, 2H, 16), 6.25 (broad s, 1H, 17), 4.40 (pseudotriplet, 5H, overlapping 16 and 17), 4.04 (quartet, 3H, 17), 1.76 (m, 11H, overlapping 16 and 17), 1.60 (s, 9H, 17), 1.56 (s, 18H, 16), 1.44 (m, 6H, overlapping 16 and 17) 1.32 (m, 6H, overlapping 16 and 17) 0.86 (s, 9H, 17).

The experimental procedures for X-ray Crystallography were written and reproduced with permission from Mr. Henry Valle.

X-ray Crystallography

Experimental

Single crystals of C$_{28}$H$_{43}$N$_6$OTaF$_{0.25}$Cl$_{0.25}$Si$_{0.25}$Br$_{0.25}$Li$_{0.25}$ 1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(t-butylimido)tantalum(V) (17) were crystallized via layering pentane onto a saturated toluene solution of 16 and 17. A suitable crystal was selected and placed on a 150 um cryoloop. X-ray crystallographic analysis was performed on a Bruker Smart APEX II diffractometer. The crystal was kept at 100.08 K during data collection. Using Olex2,$^{21}$ the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXS refinement package using Least Squares minimisation.$^{22}$

Crystal Data for C$_{28}$H$_{43}$N$_6$OTaF$_{0.25}$Cl$_{0.25}$Si$_{0.25}$Br$_{0.25}$Li$_{0.25}$ ($M$ =702.98): monoclinic, space group P2$_1$/n (no. 14), $a = 11.095(3)$ Å, $b = 15.178(3)$ Å, $c = 17.651(4)$ Å, $\beta = 93.664(2)^\circ$, $V = 2966.4(11)$ Å$^3$, $Z = 4$, $T = 100.08$ K, $\mu$(MoK$\alpha$) = 4.107 mm$^{-1}$, $D_{calc} = 1.574$ g/mm$^3$, 34837
reflections measured ($3.542 \leq 2\Theta \leq 57.988$), 7427 unique ($R_{int} = 0.0503$) which were used in all calculations. The final $R_1$ was 0.0316 ($I > 2\sigma(I)$) and $wR_2$ was 0.0799 (all data).
LIST OF REFERENCES
References

(22) SHELX, Sheldrick, G. M. *Acta Cryst.* **2008**, *112*. 

75
APPENDIX
X-ray Crystallography
Figure A1. 2-(1,3-bis(3-butylimidazol-1-yl)-2-idene)phenylene)trichloro titanium(IV) (3).

Relevant Equations used in this report:

\[ R_{\text{int}} = \frac{\Sigma |F_o|^2 - <F_o|^2 >}{\Sigma |F_o|^2} \]
\[ R_1 = \frac{\Sigma||F_o||-|F_c||}{\Sigma|F_o|} \]
\[ wR2 = \sqrt{\frac{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}} \]

where \( w = q / [\sigma^2 (F_o^2) + (a^*P)^2 + b^*P + d + e^*\sin(\theta)] \)

\[ \text{Goof} = S = \sqrt{\frac{\Sigma[w(F_o^2 - F_c^2)^2]}{(n-p)}} \]
Table A1-1. Crystal data and structure refinement for 2-(1,3-bis(3-butylimidazol-1-y1-2-idene)phenylene)trichlorotitanium(IV) (8).

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| Unit cell dimensions                          | a = 12.3079(3) Å, $\alpha$ = 90°,  
b = 11.1195(2) Å, $\beta$ = 105.153(2)°,  
c = 16.0997(4) Å, $\gamma$ = 90°. |
| Volume                                        | 2126.76(8) Å$^3$              |
| Z, Calculated density                         | 4, 1.486 Mg/m$^3$             |
| Absorption coefficient                        | 0.793 mm$^{-1}$               |
| F(000)                                        | 984                           |
| Crystal size                                  | 0.3 x 0.3 x 0.3 mm            |
| $\theta$ range for data collection           | 3.29° to 30.63°               |
| Limiting indices                              | -17$\leq$h$\leq$17, -15$\leq$k$\leq$15, -23$\leq$l$\leq$22 |
| Reflections collected / unique                | 25102 / 6520 [R(int) = 0.0197] |
| Completeness to $\theta = 30.63$              | 99.5 %                        |
| Absorption correction                         | Semi-empirical from equivalents |
| Max. and min. transmission                    | 1 and 0.97044                 |
| Refinement method                             | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters                | 6520 / 0 / 253                |
| Goodness-of-fit on F$^2$                      | 1.003                         |
Final R indices [I > 2σ(I)]  
\[ R_1 = 0.0237, \ wR_2 = 0.0581 \]

R indices (all data)  
\[ R_1 = 0.0302, \ wR_2 = 0.0593 \]

Largest diff. peak and hole  
0.396 and -0.289 e. Å\(^{-3}\)

**Table A1-2.** Atomic coordinates (x 10\(^4\)) and equivalent isotropic displacement parameters (Å\(^2\) x 10\(^3\)) for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichlorotitanium(IV) (8). U(eq) is defined as one third of the trace of the orthogonalized U\(_{ij}\) tensor.

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Table A1.3. Bond lengths [Å] and angles [°] for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichlorotitanium(IV) (8).

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Table A1-4. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV) (8). The anisotropic displacement factor exponent takes the form: $-2 \pi^2 \left( h^2 a^* a^* U_{11} + \ldots + 2 h k a^* b^* U_{12} \right)$.

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Table A1-5. Hydrogen coordinates \((x \times 10^4)\) and isotropic displacement parameters \((\AA^2 \times 10^3)\) for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichlorotitanium(IV) titan(IV) (8).

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<tr>
<td>N(3)-C(2)-Ti-Cl(3)</td>
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Figure A2. 2-(1,3-bis(3-butylimidazol-1-yl-2-idenephylene)dichloro(dimethylamido) (11).
Table A2-1. Crystal data and structure refinement for 2-(1,3-bis(3-butylimidazol-1-yl-2- idene)phenylene)dichloro(dimethylamido) titanium(IV) (11).

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<tr>
<td>Wavelength</td>
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<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P2(1)/n</td>
</tr>
<tr>
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<tr>
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<td>Z, Calculated density</td>
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</tr>
<tr>
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<td>Completeness to θ = 30.57°</td>
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<td>Refinement method</td>
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R indices (all data) \( R_1 = 0.0548, \ wR_2 = 0.0658 \)

Largest diff. peak and hole 0.401 and -0.351 e.Å\(^{-3}\)
Table A2-2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 2-(1,3-bis(3-butylimidazol-1-yl-2-ylidene)phenylene)dichloro(dimethylamido) (11).

$U(\text{eq})$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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Table A2-3. Bond lengths [Å] and angles [°] for 2-(1,3-bis(3-butylimidazo-1-yl-2-idene)phenylene)dichloro(dimethylamido) (11).

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Table A2-4. Anisotropic displacement parameters (Å\(^2\) x 10\(^3\)) for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(dimethylamido) (11). The anisotropic displacement factor exponent takes the form: -2 π\(^2\) [ h\(^2\) a*\(^2\) U11 + ... + 2 h k a* b* U12 ].

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Table A2-5. Hydrogen coordinates ($x \times 10^4$) and isotropic displacement parameters ($\AA^2 \times 10^3$) for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(dimethylamido) (11).

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Table A2-6. Torsion angles [°] for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(dimethylamido) (11).

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Figure A3. (1,3-bis(3-butylimidazol-1-yl-2-ideine)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (13).
Table A3-1. Crystal data and structure refinement (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (13).

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Table A3-2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\AA^2 \times 10^3$) for (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) ($t$-butylimido)(dimethylamido)iodotantalum(V) (13). $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{ij}$ tensor.

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Table A3.3. Anisotropic Displacement Parameters (Å²×10³) for (1,3-bis(3-butyimidazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (13). The Anisotropic displacement factor exponent takes the form: -2π²[h²a*²U₁₁+...+2hka×b×U₁₂].

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Table A3-4. Bond Lengths for (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (13).

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Table A3-5. Bond Angles for (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (13).

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**Table A3-6.** Torsion Angles for (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodo tantalum(V) (13).
N1  C6  C7  C8  -178.5(5)  C11  Ta1  N25  C26  -2.8(19)
N1  C6  C11  Ta1  6.0(6)  C11  C6  C7  C8  -0.8(9)
N1  C6  C11  C10  178.5(5)  C11  C10  N12  C13  1.9(7)
C2  Ta1  N25  C26  66.9(19)  C11  C10  N12  C16  179.2(5)
C2  N1  C5  C4  -1.1(7)  N12  C10  C11  C6  -179.7(5)
C2  N1  C6  C7  174.8(5)  N12  C13  N14  C15  -0.7(6)
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N3  C17  C18  C19  -175.9(6)  C13  N14  C15  C16  0.3(6)
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**Table A3-7.** Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (13).
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Experimental

Single crystals of C_{26}H_{40}N_{6}ITa (1,3-bis(3-butylimidazol-1-yl-2-ide-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (13) were crystallized via a saturated solution of complex 2 in benzene. A suitable crystal was selected and mounted on a 150um cryoloop and mounted on a Bruker Smart APEX II diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using CGLS minimisation.

Crystal Data for C_{26}H_{40}N_{6}ITa (M = 744.49): monoclinic, space group P2_1/c (no. 14), a = 14.3134(5) Å, b = 14.0461(5) Å, c = 14.6772(5) Å, β = 95.1620(10)°, V = 2938.85(18) Å³, Z = 4, T = 100.15 K, μ(CuKα) = 15.326 mm⁻¹, \(D_{\text{calc}} = 1.683 \text{ g/mm}^3\), 27074 reflections measured (6.2 ≤ 2θ ≤ 139.862), 5465 unique (\(R_{\text{int}} = 0.0508\)) which were used in all calculations. The final \(R_1\) was 0.0491 (I > 2σ(I)) and \(wR_2\) was 0.1370 (all data).
Figure A4. (1,3-bis(3-butyltriazol-1-yl-2-ylene)-2-phenylene) (t-butylimido)(dimethylamido)iodo tantalum(V) (15).
Table A4-1. Crystal data and structure refinement for (1,3-bis(3-butytriazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (15).

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Table A4-2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (15). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

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Experimental

Single crystals of C_{48}H_{80}N_{16}I_{2}Ta_{2} (1,3-bis(3-butyltriazol-1-yl-2-iden)-2-phenylene) (t-butylimido)(dimethylamido)iodo tantalum(V) were crystallized via layering Et_{2}O to a saturated solution in toluene. A suitable crystal was selected and mounted on a 150um mitogen mount on a Bruker Smart APEX II diffractometer. The crystal was kept at 100.13 K during data collection. Using Olex2,^{4} the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the olex2.refine refinement package using Gauss-Newton minimisation.\(^{5,7}\)

Crystal Data for C_{48}H_{80}N_{16}I_{2}Ta_{2} (M=1492.95): triclinic, space group P-1 (no. 2), a = 10.6851(12) Å, b = 10.9572(12) Å, c = 24.299(3) Å, α = 89.884(1)°, β = 84.039(1)°, γ = 86.730(1)°, V = 2824.9(5) Å\(^3\), Z = 2, T = 100.13 K, μ(N/A) = 5.010 mm\(^{-1}\), Decalc = 1.7550 g/mm\(^3\), 34679 reflections measured (3.38 ≤ 2Θ ≤ 58.12), 13751 unique (R\(_{\text{int}}\) = 0.0301) which were used in all calculations. The final R\(_{1}\) was 0.0241 (I>2u(I)) and wR\(_{2}\) was 0.0617 (all data).
Figure A5. 1,3-bis(3-butylimidazol-1-yl-2-ide)ne)-2-phenylene) bis(t-butylimido)tantalum(V) (17)
Table A5-1. Crystal data and structure refinement for 1,3-bis(3-butylimidazol-1-yl-2-iden)-2-phenylene) bis(t-butylimido)tantalum(V) (17).

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Table A5-2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement
Parameters (Å$^2\times 10^3$) for 1,3-bis(3-butylimidazol-1-yl-2-ene)-2-phenylene) bis($t$-butylimido)tantalum(V) (17). $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{ij}$
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Table A5-3. Anisotropic Displacement Parameters (Å²×10³) for 1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(3-butylimido)tantalum(V) (17). The Anisotropic displacement factor exponent takes the form: -2π²[h²a²U₁₁+...+2hka×b×U₁₂].

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Table A5-4. Bond Lengths for 1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(t-butylimido)tantalum(V) (17).
Table A5-5. Bond Angles for 1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene)-bis(t-butylimido)tantalum(V) (17).

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C21 & N5 & Ta1 & & C21 & C23 & Li7^1 & 82.0(3) \\
C21 & N5 & Li7^1 & & 104.0(3) & N6 & C25 & C26 & 109.1(4) \\
C25 & N6 & Ta1 & & 172.7(3) & N6 & C25 & C27 & 109.2(4) \\
C2 & C1 & Ta1 & & 122.3(3) & N6 & C25 & C28 & 110.5(4) \\
C2 & C1 & C6 & & 116.5(3) & C27 & C25 & C26 & 110.1(4) \\
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C1 & C2 & N1 & & 112.6(3) & C28 & C25 & C26 & 107.6(4) \\
C1 & C2 & C3 & & 122.6(3) & N5^1 & Li7 & Ta1^1 & 40.76(16) \\
C3 & C2 & N1 & & 124.8(3) & N5^1 & Li7 & C7 & 153.1(4) \\
C4 & C3 & C2 & & 118.3(3) & N5^1 & Li7 & C8 & 87.3(3) \\
C3 & C4 & C5 & & 121.5(4) & N5^1 & Li7 & C21^1 & 30.59(17) \\
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N1 & C7 & Li7 & & 126.3(3) & C8^1 & Li7 & Ta1^1 & 50.02(16) \\
N2 & C7 & Li7 & & 123.3(3) & C8^1 & Li7 & C21^1 & 112.0(3) \\
Ta1 & C8 & Li7^1 & & 73.9(2) & C8^1 & Li7 & C23^1 & 128.2(4) \\
N1 & C8 & Ta1 & & 118.7(2) & C21^1 & Li7 & Ta1^1 & 70.58(19) \\
N1 & C8 & Li7^1 & & 100.8(3) & C23^1 & Li7 & Ta1^1 & 100.9(3) \\
C9 & C8 & Ta1 & & 139.7(3) & C23^1 & Li7 & C21^1 & 32.88(18) \\
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\]

**Table A5-6.** Torsion Angles for 1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(tert-butylimido)tantalum(V) (17).

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N1 C8 C9 N2 -0.8(4) C9 N2 C10 C11A 163.1(6)
N2 C10 C11 C12 -179.1(7) C10 N2 C7 N1 179.8(3)
N2 C10 C11A C12A -179.4(7) C10 N2 C7 Li7 -30.6(6)
N3 C15 C16 N4 0.0(7) C10 N2 C9 C8 -179.9(3)
N4 C17 C18 C19 -169.9(5) C10 C11 C12 C13 -62.4(12)
N5 C21 C23 Li7 1 9.8(5) C10 C11A C12A C13A -175.8(9)
N6 Ta1 N5 C21 -9.0(8) C11 C10 C11A C12A -97.9(12)
C1 Ta1 N5 C21 172.3(7) C14 Ta1 N5 C21 99.2(8)
C1 Ta1 N5 Li7 1 -48.7(3) C14 Ta1 N5 Li7 1 -121.8(3)
C1 C2 C3 C4 0.8(6) C14 N3 C6 C1 4.5(6)
C2 N1 C7 N2 -176.4(3) C14 N3 C6 C5 -174.6(4)
C2 N1 C7 Li7 1 35.3(6) C14 N3 C15 C16 -0.2(7)
C2 N1 C8 Ta1 -1.4(4) C14 N4 C16 C15 0.3(6)
C2 N1 C8 C9 177.7(3) C14 N4 C17 C18 105.8(5)
C2 N1 C8 Li7 1 -78.8(3) C15 N3 C6 C1 -174.7(5)
C2 C1 C6 N3 178.8(3) C15 N3 C6 C5 6.2(8)
C2 C1 C6 C5 -2.1(6) C15 N3 C14 Ta1 177.8(4)
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C3 C4 C5 C6 0.5(6) C16 N4 C14 Ta1 -177.2(4)
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C6 N3 C14 N4 -179.0(4) C17 N4 C14 N3 -174.2(4)
C6 N3 C15 C16 179.0(5) C17 N4 C16 C15 174.1(5)
C6 C1 C2 N1 179.9(3) C17 C18 C19 C20 158.2(12)
C6 C1 C2 C3 0.9(6) C17 C18 C19 C20A -170.7(6)
C7 N1 C2 C1 176.0(3) C22 C21 C23 Li7 1 131.9(4)
C7 N1 C2 C3 -5.1(6) C24 C21 C23 Li7 1 -109.7(4)
C7 N1 C8 Ta1 -179.5(2) Li7 1 Ta1 N5 C21 -139.0(9)
C7 N1 C8 C9 -0.4(4) Li7 1 N5 C21 C22 -134.7(4)
C7 N1 C8 Li7 1 103.1(3) Li7 1 N5 C21 C23 -12.6(7)
C7 N2 C9 C8 1.8(4) Li7 1 N5 C21 C24 106.3(5)
C7 N2 C10 C11 -52.7(6) Li7 1 C8 C9 N2 -104.3(3)

12-X,2-Y,2-Z
Table A5-7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å²×10^3) for 1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(t-butylimido)tantalum(V) (17).

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</table>
NMR SPECTRA
$^1$H NMR, 600 MHz, d$_6$-Toluene

43 h, 120 °C
\[ \text{13C NMR, 600 MHz, d$_8$-Toluene} \]

$43 \text{ hr, } 120^\circ \text{C}$

\[
\begin{align*}
\text{HNH}_2 + \text{N} & \xrightarrow{43 \text{ hr, } 120^\circ \text{C}} \text{HNH}_2 \\
\text{HNH}_2 + \text{N} & \xrightarrow{120^\circ \text{C}} \text{HNH}_2
\end{align*}
\]
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