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Ligand strategies for green chemistry: Catalysts for amide reduction and hydroamination

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Ligand strategies for green chemistry: Catalysts for amide reduction and hydroamination

by

Megan Hovey

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Aaron D. Sadow, Major Professor
Wenyu Huang
Levi Stanley

Iowa State University

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To my husband, Brad

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ABSTRACT

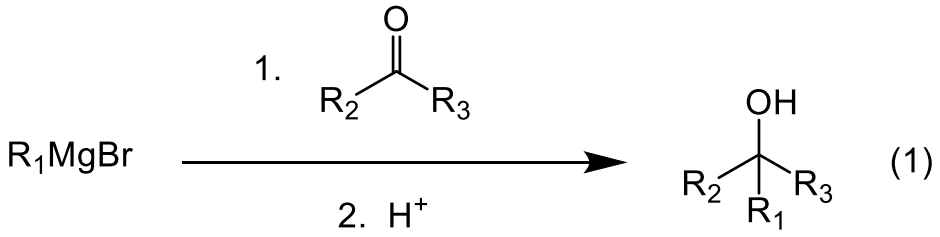
This thesis describes the synthesis of a new class of mixed monoanionic cyclopentadienyl-bis(oxazoline) ligands and synthesis of new metal complexes. Two achiral ligands were synthesized: $H_3CC(C_5H_5)(Ox^{Me2})_2$ ($H\{Bo^MCp\}$; Ox^{Me2} = 4,4-dimethyl-2-oxazoline) and $H_3CC(C_5HMe_4)(Ox^{Me2})_2$ ($H\{Bo^MCp^{tet}\}$). The chiral analogs were also prepared, $H_3CC(C_5H_5)(Ox^{iPr})_2$ ($H\{Bo^PCp\}$, Ox^{iPr} = 4*S*-isopropyl-2-oxazoline) and $H_3CC(C_5HMe_4)(Ox^{iPr})_2$ ($H\{Bo^PCp^{tet}\}$). These ligands support a wide variety of metals, including magnesium, zinc, titanium, and zirconium. $\{Bo^MCp\}MgCH_3$, $\{Bo^MCp^{tet}\}MgCH_3$, $\{Bo^PCp\}MgCH_3$, and $\{Bo^PCp^{tet}\}MgCH_3$ show excellent reactivity for catalyzing the hydroboration of ketones using pinacolborane. $\{Bo^MCp\}Zr(NMe_2)_3$, $\{Bo^MCp\}MgCH_3$, and $\{Bo^MCp^{tet}\}MgCH_3$ are also efficient catalysts for the hydroamination of aminoalkenes. This thesis also describes the catalytic reduction of amides to amines using pinacolborane as the reductant and catalytic amounts of [Mg]. To^MMgMe (To^M = tris(4,4-dimethyl-oxazolinyl)phenylborate is found to show excellent catalytic activity for the reduction of secondary and tertiary amides. Last, pyrene is functionalized with tertiary amine groups following a simple synthetic route from commercially available pyrene precursors. These pyrene compounds, including N-ethyl-N-(pyren-4-ylmethyl)ethanamine, N,N-diethyl-4-(pyren-4-yl)butanamine, and N,N-bis(pyren-4-ylmethyl)ethanamine were prepared to be adsorbed onto multi-walled carbon nanotubes as a catalyst.

CHAPTER 1

Introduction

General Introduction

Magnesium is a metal of interest because it is largely abundant and economical. It is the eighth most abundant element in the Earth's crust and the third most abundant element in Earth's oceans.[1] It is largely used as an alloying agent in industry, and also plays many important roles in the human body and in the function of many enzymes. Magnesium is well-known in chemistry for its rich Grignard history as a stoichiometric reagent for C-C bond formation (eq. 1).[1]



(1)

In addition to being used in stoichiometric transformations, magnesium has gained attention as a metal for use in catalytic applications as a green, low-cost, low-toxicity alternative to more commonly used transition metal catalysts such as rhodium, platinum, and palladium, which cost up to $450 per gram. Magnesium metal, on the other hand, can be purchased for $0.14 per gram.

Our group is exploring the chemistry of magnesium, as well as other main group and transition metals to develop new catalysts for green chemistry. Several new ligands have been developed, including a new oxazoline-based monoanionic scorpionate ligand, tris(4,4-

dimethyl-2-oxazolinyl)phenylborate [To^M], and the cyclopentadienyl-bis(oxazolinyl)borate ligand PhB(Ox)$_2$(C$_5$H$_5$) (Fig. 1).

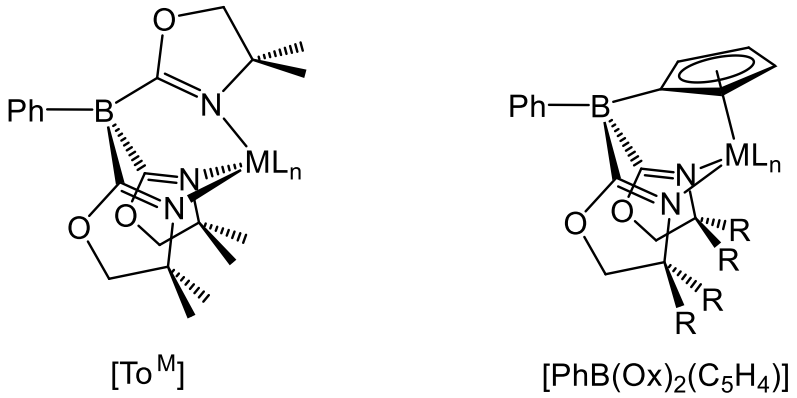
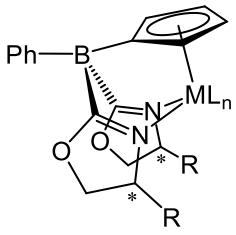


Figure 1: To^M and PhB(Ox)$_2$(C$_5$H$_4$)

To^M has supported a wide range of metals, including yttrium,[2] zirconium,[3] rhodium,[4] and magnesium.[5] To^{M}MgMe catalyzes the reduction of ketones, aldehydes, and esters with pinacolborane as the reductant, as well as the Tischenko coupling of aldehydes.[6] To^{M}ZnH catalyzes the hydroboration and hydrosilylation of aldehydes and ketones. Our group has found that cyclopentadienyl-bis(oxazolinyl)borate ligands support many metals, including titanium, zirconium, hafnium, and yttrium.[7] The oxazoline rings are easily varied to include stereogenic centers and a number of substituents, as shown in Figure 2. These compounds are excellent catalysts for the hydroamination of aminoalkenes, with enantioselectivities up to 99%.



M = Ti, Zr, Hf, Y
Ox^{Me2}, $Ox^{4S\text{-}iPr,\ Me2}$, $Ox^{4R\text{-}iPr,\ Me2}$, $Ox^{4S\text{-}tBu}$

Figure 2: Highly efficient and selective system for hydroamination

This thesis is about the development of a new class of ligands similar to the previously described cyclopentadienyl-bis(oxazolinyl)borate ligands, in which the boron center is replaced with carbon. The synthesis of complexes containing these new ligands is described, as well as further stoichiometric and catalytic reactivity of these compounds, including the hydroamination of aminoalkenes. This thesis also describes further catalytic reactivity of $To^{M}MgMe$ as a catalyst for amide reduction to amines using pinacolborane as the reductant.

Thesis Organization

This thesis contains five chapters. Chapter 1 is a general introduction to the chemistry described in the thesis. Chapters 2-4 describe research that has not been submitted for publication at this time. Chapter 5 is a general conclusion for the thesis.

Chapter 2 describes the synthesis of new mixed monoanionic cyclopentadienyl-bis(oxazoline) ligands. Mg, Zn, Ti, and Zr compounds are prepared, and catalytic activity for hydroboration of ketones and esters as well as hydroamination of aminoalkenes is observed.

Chapter 3 describes the catalytic hydroboration reduction of amides to amines using pinacolborane as the reductant and Mg complexes as the catalyst. To^{M}MgMe is found to be the best catalyst for the reduction of secondary and tertiary amides to amines.

Chapter 4 describes the preparation of functionalized pyrene compounds for the adsorption onto multi-walled carbon nanotubes. Various conditions for coronene functionalization are also screened.

Chapter 5 is a general conclusion for the thesis.

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CHAPTER 2

Synthesis of mixed monoanionic cyclopentadienyl bis(oxazoline) ligands and preparation of group 2 and 4 compounds

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Abstract

A new class of mixed monoanionic cyclopentadienyl bis(oxazoline) ligands has been prepared. Two achiral ligands were synthesized: $H_3CC(C_5H_5)(Ox^{Me2})_2$ ($H\{Bo^MCp\}$; Ox^{Me2} = 4,4-dimethyl-2-oxazoline) and $H_3CC(C_5HMe_4)(Ox^{Me2})_2$ ($H\{Bo^MCp^{tet}\}$). The chiral analogs were also prepared, $H_3CC(C_5H_5)(Ox^{iPr})_2$ ($H\{Bo^PCp\}$, Ox^{iPr} = 4*S*-isopropyl-2-oxazoline) and $H_3CC(C_5HMe_4)(Ox^{iPr})_2$ ($H\{Bo^PCp^{tet}\}$). These ligands support a wide variety of metal compounds. $H\{Bo^MCp\}$ reacts with $Zr(NMe_2)_4$ to give $\{Bo^MCp\}Zr(NMe_2)_3$ with the elimination of dimethylamine. $H\{Bo^MCp\}$ reacts with thallium ethoxide in diethyl ether to give the thallium salt, $Tl\{Bo^MCp\}$. $H\{Bo^MCp^{tet}\}$ reacts with thallium ethoxide in THF to form the thallium salt, $Tl\{Bo^MCp^{tet}\}$. $Tl\{Bo^MCp\}$ and $Tl\{Bo^MCp^{tet}\}$ react with $TiCl_3(THF)_3$ to give $\{Bo^MCp\}TiCl_2$ and $\{Bo^MCp^{tet}\}TiCl_2$. The four ligands also react with $Mg(CH_3)_2(dioxane)_2$ to give the magnesium methyl complexes $\{Bo^MCp\}MgCH_3$, $\{Bo^MCp^{tet}\}MgCH_3$, $\{Bo^PCp\}MgCH_3$, and $\{Bo^PCp^{tet}\}MgCH_3$. These magnesium compounds are excellent catalysts for the hydroboration of ketones and esters using pinacolborane. $\{Bo^MCp\}Zr(NMe_2)_3$, $\{Bo^MCp\}MgCH_3$, and $\{Bo^MCp^{tet}\}MgCH_3$ are also efficient catalysts for the hydroamination of aminoalkenes.

§ Other authors' contributions

Naresh Eedugurala: Characterization of {Bo^{M}Cp}Zr(NMe$_2$)$_3$ and its hydroamination reactions. Obtained X-ray quality crystals of {Bo^{M}Cp}Zr(NMe$_2$)$_3$. Collaborated on synthesis of H{Bo^{P}Cp}.
Barun Jana: Collaborated on synthesis and characterization of H{Bo^{M}Cp^{tet}}. First hydroamination reactions using Bo^{M}CpMgMe.
Hung-An Ho: First to make H{Bo^{M}Cp} and Bo^{M}CpZr(NMe$_2$)$_3$.

Introduction

Cyclopentadiene has been used as a very effective ligand with many metal complexes. Bent-metallocene "sandwich" complexes, with two cyclopentadiene rings bound to the metal center, have shown excellent catalytic abilities and application in synthesis. For example, zirconocene dichloride is an excellent Ziegler-Natta olefin polymerization catalyst, and Tebbe's reagent is used as a methylene transfer reagent (Fig. 1).

Ziegler-Natta catalyst
Olefin polymerization

Tebbe's reagent
Methylene transfer

Figure 1: Examples of bent-metallocene complexes

More recently, several mono-Cp-metal complexes have shown excellent catalytic activity. Mono-Cp scandium complexes are active polymerization catalysts for ethylene as well as the ring-opening polymerization of ε-caprolactone (Fig. 2). [1,2] Sundermeyer's mono-Cp rare earth metal catalysts are active for hydroamination.[3]

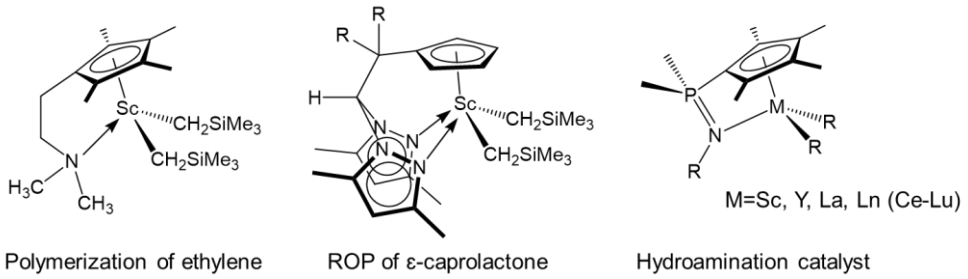
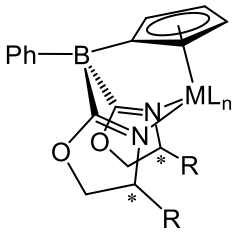


Figure 2: Catalysts containing cyclopentadiene

Recently, our group has reported several compounds that are highly active for hydroamination using cyclopentadienyl-bis(oxazolinyl)borate ligands (Fig. 3).[4] Stereogenic centers are easily introduced in the oxazoline rings, leading to catalysts with extremely high enantioselectivity (up to 99% ee) in hydroamination of aminoalkenes.



M = Ti, Zr, Hf, Y

Ox^{Me2}, $Ox^{4S\text{-}iPr,\ Me2}$, $Ox^{4R\text{-}iPr,\ Me2}$, $Ox^{4S\text{-}tBu}$

Figure 3: Highly efficient and selective system for hydroamination

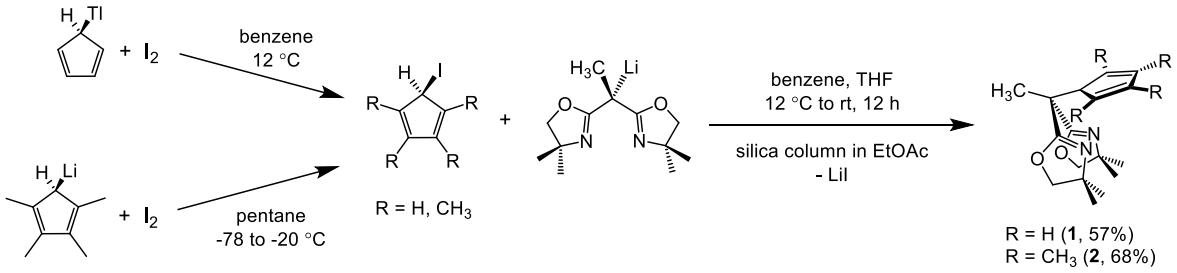
Small changes in the structure of these ligands had large effects on reactivity. For example, the Ox^{Me2}-based ligand gives a zirconium catalyst that is active at room temperature and can cycle the unsubstituted aminopentene. The $Ox^{iPr,Me2}$-based ligand is highly reactive and operates even at –30 °C, but cannot cyclize the parent aminoalkene. We wanted to study the effect of replacing the boron ligand center with carbon on the catalytic activity of these

compounds. Here we describe the synthesis and reactivity of mono-anionic cyclopentadienyl-bis(oxazoline) ligands with carbon centers instead of boron.

Results and Discussion

1. Synthesis and characterization of mixed monoanionic cyclopentadienyl bis(oxazoline) ligands

Cyclopentadienyliodide, C_5H_5I, is synthesized from thallium cyclopentadienide and iodine in benzene at low temperature. [5] Tetramethylcyclopentadienyliodide, C_5HMe_4I, is synthesized from lithium cyclopentadienide and iodine in pentane at low temperature. [6] These compounds are not isolated due to their instability at room temperature. Instead, they are prepared and used *in situ*. The compounds $H_3CC(C_5H_5)(Ox^{Me2})_2$ (**1**) ($H\{Bo^MCp\}$, Ox^{Me2} = 4,4-dimethyl-2-oxazoline) and $H_3CC(C_5HMe_4)(Ox^{Me2})_2$ (**2**) ($H\{Bo^MCp^{tet}\}$) are synthesized from $Li[H_3CC(Ox^{Me2})_2]$ and C_5HR_4I (R = H, Me) and are purified by silica gel chromatography (Scheme 1).



Scheme 1: Synthesis of $H\{Bo^MCp\}$ and $H\{Bo^MCp^{tet}\}$

$H\{Bo^MCp\}$ is obtained as a brown oil after chromatography and is a mixture of two isomers as indicated by ^1H and ^{13}C NMR spectroscopy. $H\{Bo^MCp\}$ has an infrared C=N

stretching frequency of 1656 cm^{-1}. H{Bo^{M}Cp^{tet}} is isolated as a white solid after chromatography and is isolated as only one isomer. H{Bo^{M}Cp^{tet}} has two infrared C=N stretching frequencies at 1661 and 1640 cm^{-1}, which is suprising. Only one oxazoline C=N stretching frequency is expected. X-ray-quality crystals of H{Bo^{M}Cp^{tet}} were obtained from a pentane solution of H{Bo^{M}Cp^{tet}} at –30 °C (Fig. 4).

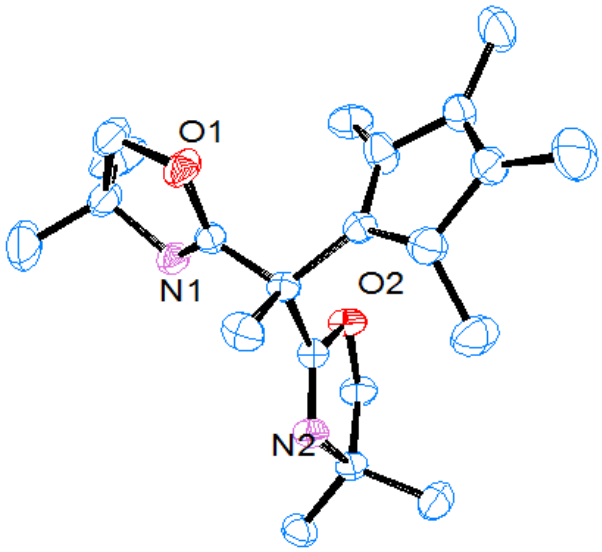
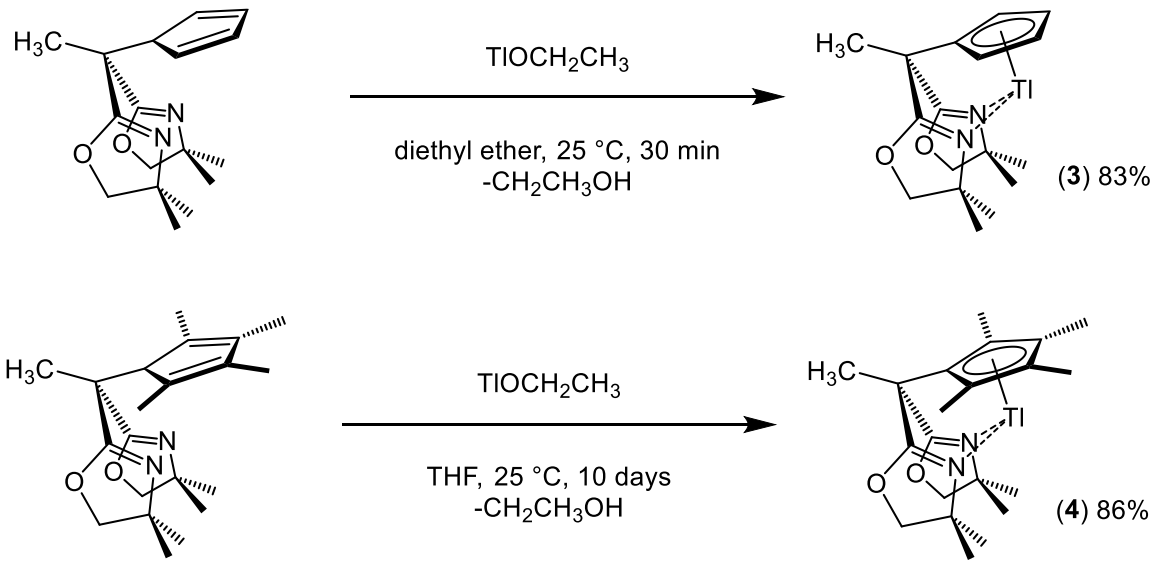


Figure 4: ORTEP diagram of H{Bo^{M}Cp^{tet}}

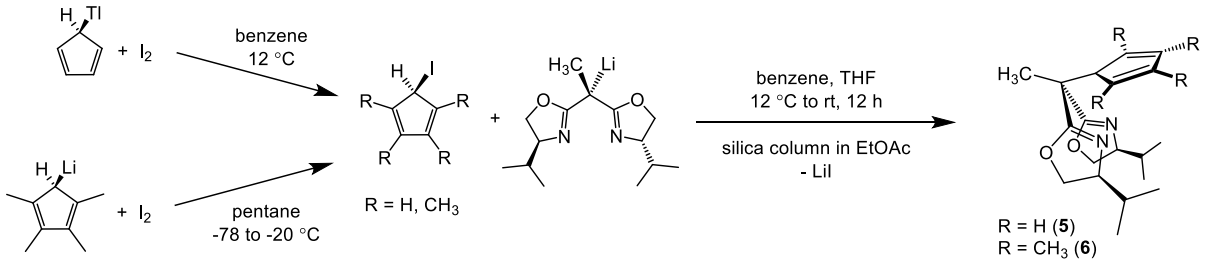
The thallium salts, Tl{Bo^{M}Cp} (**3**) and Tl{Bo^{M}Cp^{tet}} (**4**), are synthesized from thallium ethoxide and H{Bo^{M}Cp} or H{Bo^{M}Cp^{tet}} in solutions of diethyl ether or THF, respectively (Scheme 2).



Scheme 2: Preparation of Tl{Bo^{M}Cp} and Tl{Bo^{M}Cp^{tet}}

Interestingly, H{Bo^{M}Cp} reacts readily with thallium ethoxide at room temperature within 30 minutes. H{Bo^{M}Cp^{tet}} reacts much more slowly. Tl{Bo^{M}Cp} has an infrared C=N stretching frequency at 1647 cm^{-1}. Similar to H{Bo^{M}Cp^{tet}}, Tl{Bo^{M}Cp^{tet}} has two C=N stretching frequencies at 1654 and 1637 cm^{-1}.

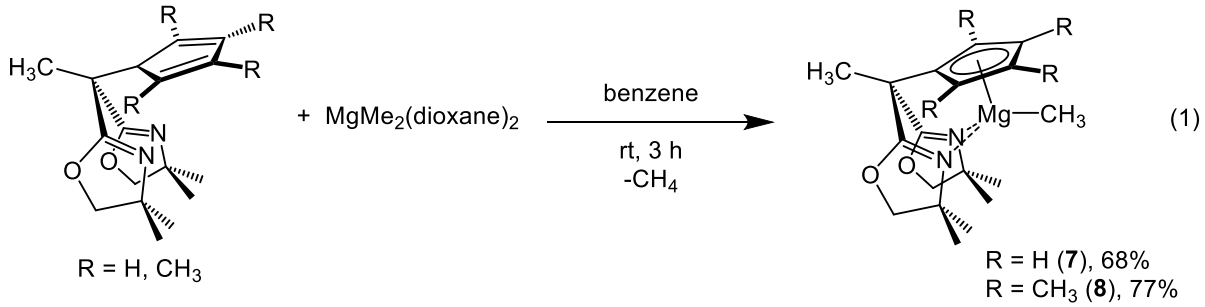
The optically-active compounds $H_3CC(C_5H_5)(Ox^{iPr})_2$ (**5**) (H{Bo^{P}Cp}, Ox^{iPr} = 4*S*-isopropyl-2-oxazoline) and $H_3CC(C_5HMe_4)(Ox^{iPr})_2$ (**6**) (H{Bo^{P}Cp^{tet}}) are synthesized in a similar manner as H{Bo^{M}Cp} and H{Bo^{M}Cp^{tet}} from Li[$H_3CC(Ox^{iPr})_2$] and C_5HR_4I (R = H, Me) and are purified by silica gel chromatography (Scheme 3).



Scheme 3: Synthesis of H{Bo^{P}Cp} and H{Bo^{P}Cp^{tet}}

2. Synthesis and characterization of cyclopentadienyl bis(oxazolinyl) metal complexes

H{Bo^{M}Cp} or H{Bo^{M}Cp^{tet}} reacts with $Mg(CH_3)_2(dioxane)_2$ to give the magnesium methyl complexes {Bo^{M}Cp}$MgCH_3$ (**7**) and {Bo^{M}Cp^{tet}}$MgCH_3$ (**8**) (eq. 1). The chiral analogs, {Bo^{P}Cp}$MgCH_3$ (**9**) and {Bo^{P}Cp^{tet}}$MgCH_3$ (**10**) were prepared in a similar manner. These compounds are isolated as off-white solids and are stored at –30 °C to avoid thermal decomposition.



(1)

The magnesium-methyl resonances are observed in the ^{1}H NMR spectra as broad singlets at –1 ppm. Only one infrared C=N stretch at 1658 cm^{-1} for {Bo^{M}Cp}$MgCH_3$ and 1658 cm^{-1} for {Bo^{M}Cp^{tet}}$MgCH_3$ was observed, which is similar to the stretching frequencies observed for the free ligand. A single-crystal X-ray diffraction study of {Bo^{M}Cp^{tet}}$MgCH_3$ show the compound crystallized as a dimer with only one oxazoline donor coordinating per magnesium center and bridging methyl groups between the two magnesium centers (Fig. 5).

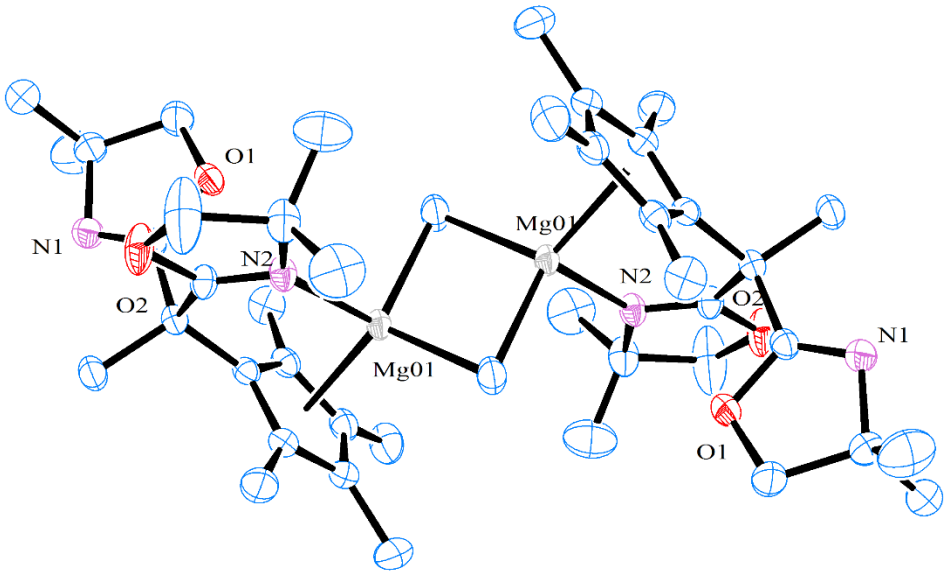
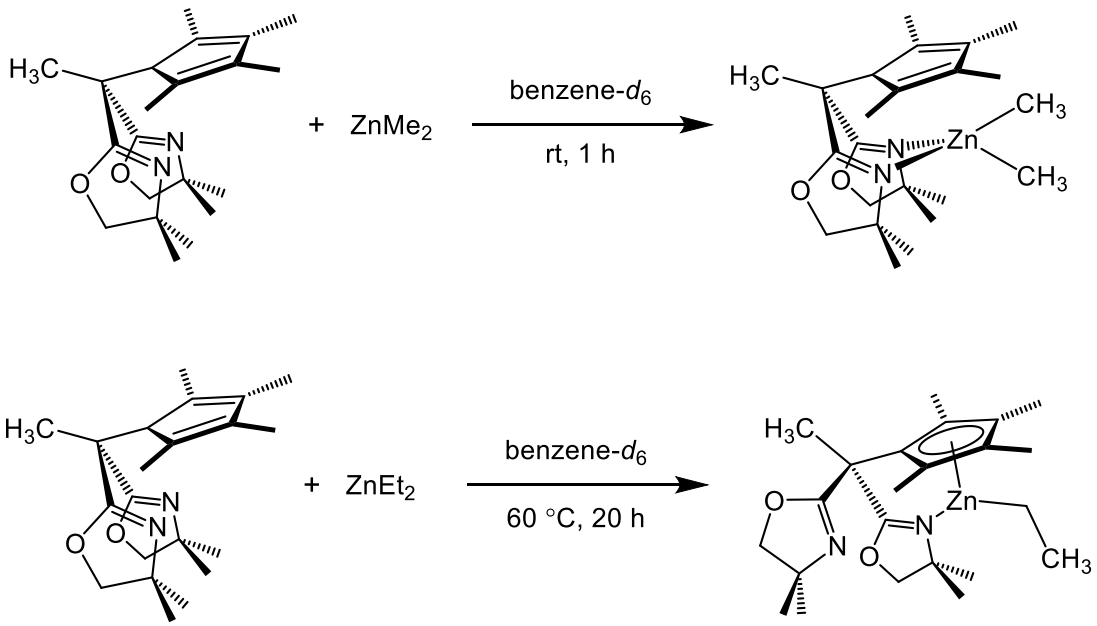


Figure 5: ORTEP diagram of $\{Bo^{M}Cp^{tet}\}MgCH_3$

$\{Bo^{M}Cp^{tet}\}MgCH_3$ reacts with Lewis acid $B(C_6F_5)_3$ in benzene in 10 minutes to form $\{Bo^{M}Cp^{tet}\}MgCH_3B(C_6F_5)_3$, which is insoluble in benzene but can be redissolved in CD_2Cl_2. The product has an ^{11}B NMR peak at –15 ppm, indicative of forming the borate $[H_3C–B(C_6F_5)_3]$. No further reaction occurs upon addition of phenyl silane. Interestingly, partial (C_6F_5) transfer from $B(C_6F_5)_3$ to Mg is observed when $\{Bo^{M}Cp^{tet}\}MgCH_3$ is reacted with $B(C_6F_5)_3$ in methylene chloride. A mixture of $\{Bo^{M}Cp^{tet}\}MgCH_3B(C_6F_5)_3$ and $\{Bo^{M}Cp^{tet}\}Mg(C_6F_5)$ is observed by ^{1}H NMR, along with the formation of BMe_3, which is observed in the ^{11}B NMR spectrum at +86 ppm.

$H\{Bo^{M}Cp^{tet}\}$ coordinates $ZnMe_2$ at room temperature in benzene-d_6 in 1 hour to form $H\{Bo^{M}Cp^{tet}\}ZnMe_2$. Upon heating at 60 °C for 1 day, $\{Bo^{M}Cp^{tet}\}ZnMe$ does not form. Contrastingly, $H\{Bo^{M}Cp^{tet}\}$ reacts with $ZnEt_2$ to form $\{Bo^{M}Cp^{tet}\}ZnEt$ after heating at 60 °C for 20 h in benzene-d_6 (Scheme 4).



Scheme 4: Reactions of H{Bo^{M}Cp^{tet}} with $ZnMe_2$ and $ZnEt_2$

X-ray-quality crystals of H{Bo^{M}Cp^{tet}}$ZnMe_2$ were obtained from a toluene solution at –30 °C, as shown in Figure 6. The structure shows two oxazoline rings coordinated to the zinc center, while the cyclopentadienyl ring does not coordinate to zinc.

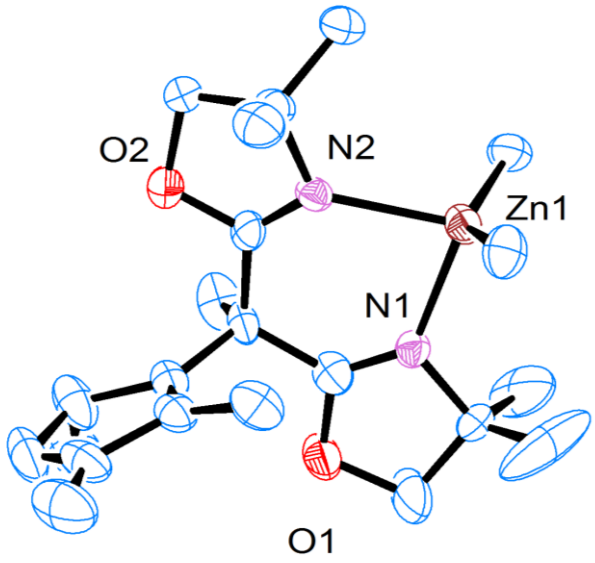


Figure 6: ORTEP diagram of H{Bo^{M}Cp^{tet}}$ZnMe_2$

X-ray-quality crystals of {Bo^{M}Cp^{tet}}ZnEt were obtained from a toluene solution at –30 °C, as shown in figure 7. The structure shows the cyclopentadienyl ring coordinated to zinc. One oxazoline coordinates to the zinc center, while the other oxazoline ring remains uncoordinated.

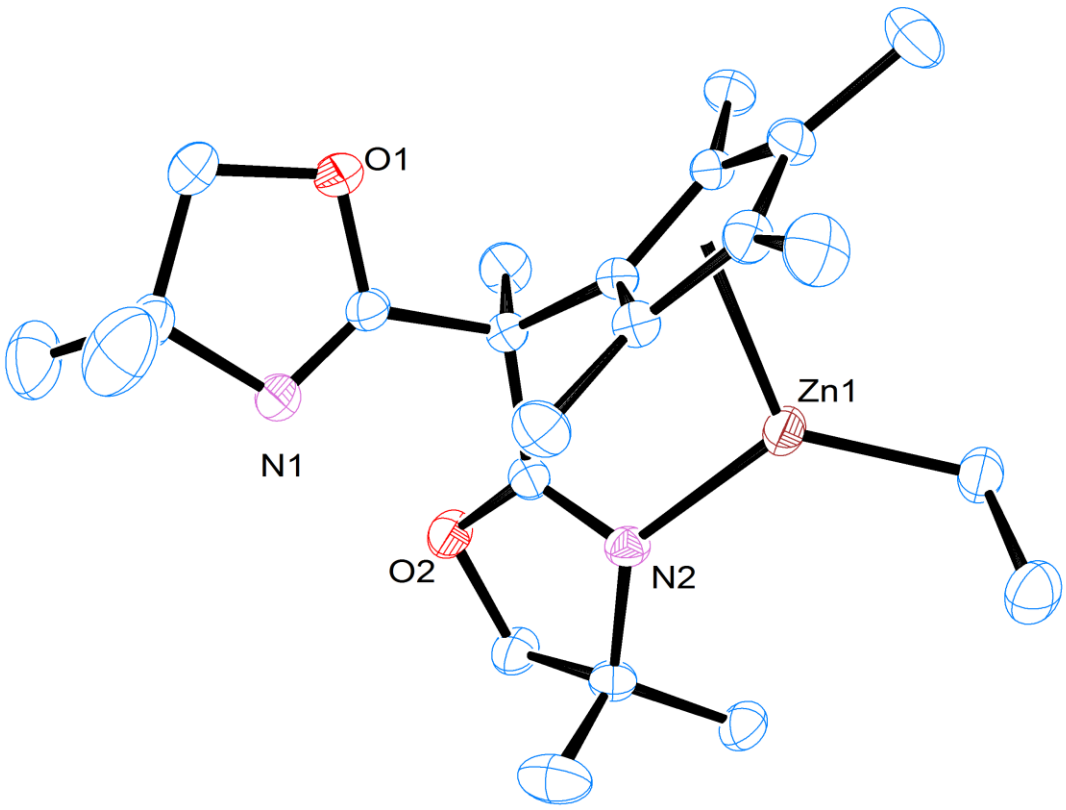
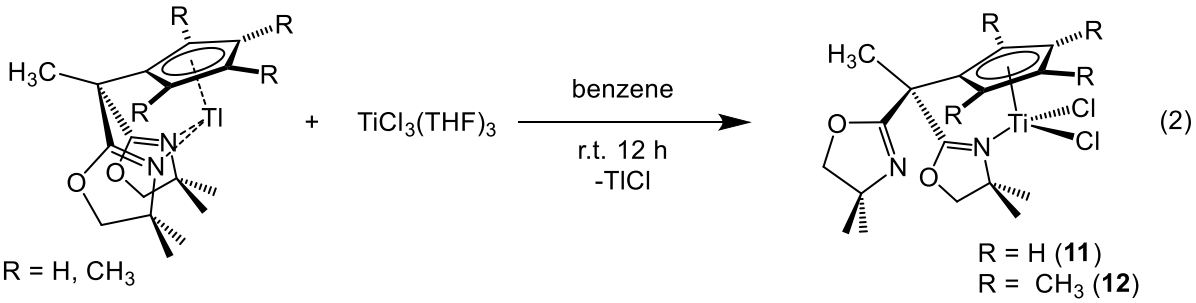


Figure 7: ORTEP diagram of Bo^{M}Cp^{tet}ZnEt

Group 4 titanium compounds are prepared from benzene solutions of Tl{Bo^{M}Cp} or Tl{Bo^{M}Cp^{tet}} and $TiCl_3(THF)_3$ to form {Bo^{M}Cp}$TiCl_2$ (**11**) and {Bo^{M}Cp^{tet}}$TiCl_2$ (**12**) as green solids (eq. 2). The ^{1}H NMR spectrum of each shows extremely broad, uninterpretable resonances because both compounds are Ti(III) and are paramagnetic.



(2)

X-ray-quality crystals of {Bo^{M}Cp}TiCl$_2$ were obtained from a toluene/pentane solution at –30 °C (Fig. 8). The X-ray crystal structure shows the compound crystallized as a dimer with two chlorine atoms bridging between two titanium centers. The crystal structure shows only one oxazoline ring coordinating per titanium center, which is also supported by the two infrared C=N stretching frequencies observed at 1635 and 1662 cm^{-1}.

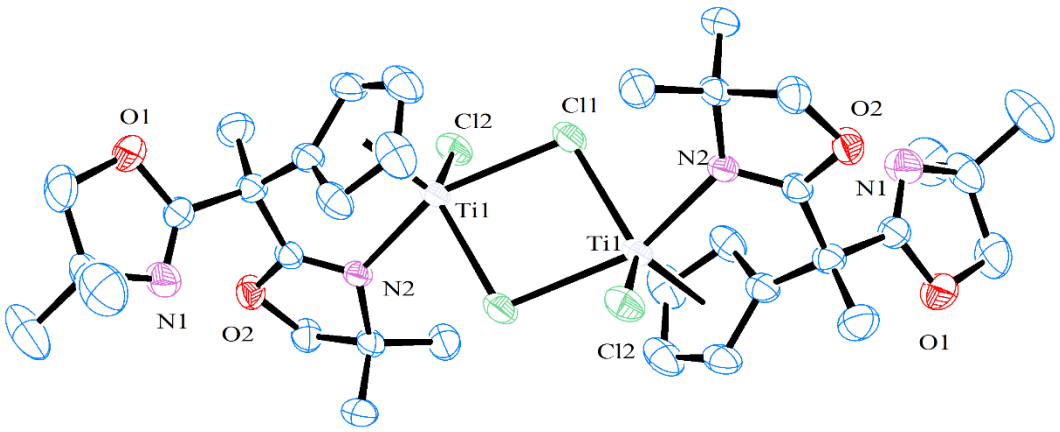


Figure 8: ORTEP diagram of {Bo^{M}Cp}TiCl$_2$

The infrared spectrum of {Bo^{M}Cp^{tet}}TiCl$_2$ shows C=N stretching frequencies at 1661 and 1641 cm^{-1} which suggests that only one oxazoline ring coordinates to titanium, as is seen in {Bo^{M}Cp}TiCl$_2$. One unpaired electron was observed for each compound using Evan's method, confirming the Ti(III) d^1 configuration.

We were interested in trying to reduce these titanium compounds in the presence of dinitrogen to see if we could nitrogen activation would occur. Reductions of $\{Bo^{M}Cp\}TiCl_2$ and $\{Bo^{M}Cp^{tet}\}TiCl_2$ were attempted using sodium mercury amalgam in toluene or THF, but in all cases the solutions went from green in color to black and the resulting product was not able to be characterized or crystallized. Addition of PMe_3 during the reduction produced the same result.

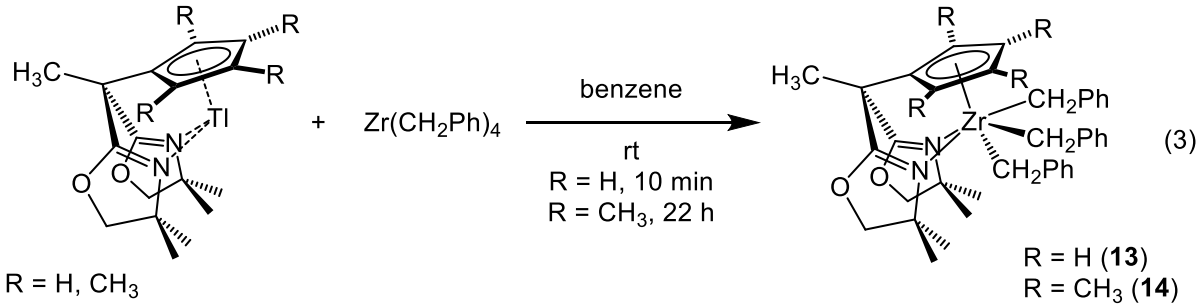
Alkylation attempts of $\{Bo^{M}Cp\}TiCl_2$ and $\{Bo^{M}Cp^{tet}\}TiCl_2$ were also challenging. Addition of two equivalents of methyl lithium or EtMgBr to cooled solutions of $\{Bo^{M}Cp\}TiCl_2$ and $\{Bo^{M}Cp^{tet}\}TiCl_2$ immediately resulted in a black solution and the product was not able to be characterized. However, addition of two equivalents of neopentyl lithium in diethyl ether at –30 °C resulted in dark red solutions that were presumably $\{Bo^{M}Cp\}Ti(CH_2{}^{t}Bu)_2$ and $\{Bo^{M}Cp^{tet}\}Ti(CH_2{}^{t}Bu)_2$, but rapidly decomposed over 10-15 minutes at –30 °C to a black solution. To avoid decomposition, silver triflate was added immediately upon formation of the red solutions, which immediately reacted to give yellow solutions that were isolated as yellow solids. The ^{1}H NMR showed these compounds were diamagnetic and were possibly the titanium alkylidenes, $\{Bo^{M}Cp\}Ti(=CH^{t}Bu)(OTf)$ and $\{Bo^{M}Cp^{tet}\}Ti(=CH^{t}Bu)(OTf)$. The ^{1}H NMR spectrum of the reaction with $\{Bo^{M}Cp\}TiCl_2$ shows a peak that could correspond to the [Ti](=C*H*^{t}Bu)(OTf) at 4.52 ppm, and the reaction with $\{Bo^{M}Cp^{tet}\}TiCl_2$ shows a peak at 4.81 that could correspond to [Ti](=C*H*^{t}Bu)(OTf). However, pure compounds were not isolated and crystals were not obtained to confirm the structure.

$\{Bo^{M}Cp^{tet}\}TiCl_2$ reacts with one equivalent of sodium azide at room temperature in THF over the course of four hours to give a red/orange product. The IR spectrum of the

product shows an azide stretching frequency at 2071 cm^{-1}, but crystals were not obtained to confirm the structure. Interestingly, {Bo^{M}Cp}$TiCl_2$ does not react with sodium azide; upon heating at 60 °C the starting material slowly decomposes to free ligand.

Reactions with $ZrCl_4$ and $HfCl_4$ were unsuccessful. H{Bo^{M}Cp} and H{Bo^{M}Cp^{tet}} do not react with $ZrCl_4$ or $HfCl_4$ in benzene or THF at temperatures up to 120 °C. Tl{Bo^{M}Cp} and Tl{Bo^{M}Cp^{tet}} react with $ZrCl_4$ and $HfCl_4$ in benzene-d_6, but multiple products are obtained and a pure compound was not able to be isolated. When Tl{Bo^{M}Cp} was refluxed with $ZrCl_4$ in benzene for 7 hours, the ^{1}H NMR spectrum showed many unidentifiable peaks, including a peak at 11.93 ppm that could not be identified. K{Bo^{M}Cp} and K{Bo^{M}Cp^{tet}} were generated *in situ* from H{Bo^{M}Cp} or H{Bo^{M}Cp^{tet}} and KBn in THF at room temperature in 12 hours, but when $ZrCl_4$ or $HfCl_4$ were added, a pure product was not formed.

Tl{Bo^{M}Cp} and Tl{Bo^{M}Cp^{tet}} react with $Zr(CH_2Ph)_4$ in benzene at room temperature over the course of 10 minutes or 22 hours, respectively, to give {Bo^{M}Cp}$Zr(CH_2Ph)_3$ (**13**) and {Bo^{M}Cp^{tet}}$Zr(CH_2Ph)_3$ (**14**) as orange solids. The byproduct, thallium benzyl, was not observed. Instead, the decomposition products bibenzyl and thallium metal are observed as byproducts of the reaction.

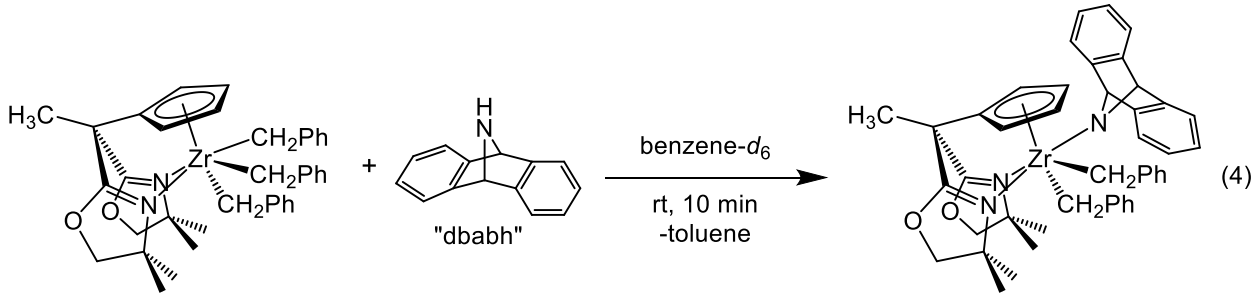


(3)

H{Bo^{M}Cp} and H{Bo^{M}Cp^{tet}} can also react with $Zr(CH_2Ph)_4$ to give {Bo^{M}Cp}$Zr(CH_2Ph)_3$ and {Bo^{M}Cp^{tet}}$Zr(CH_2Ph)_3$ with the loss of toluene, but the reactions

must be heated at 60 °C for several hours to complete. {Bo^{M}Cp}Zr(CH$_2$Ph)$_3$ and {Bo^{M}Cp^{tet}}Zr(CH$_2$Ph)$_3$ are extremely light sensitive, similar to Zr(CH$_2$Ph)$_4$, and are stored at –30 °C and are not exposed to light.

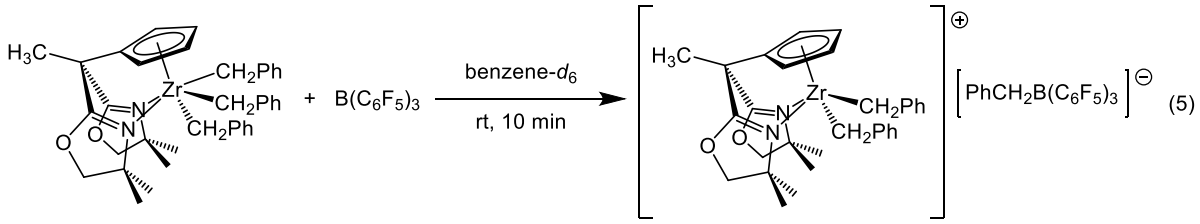
The benzyl groups on zirconium can be substituted by amines. {Bo^{M}Cp}Zr(CH$_2$Ph)$_3$ reacts with "dbabh" at room temperature in 10 minutes to substitute one of the CH$_2$Ph groups with the amine, and the loss of toluene is observed (eq. 4).



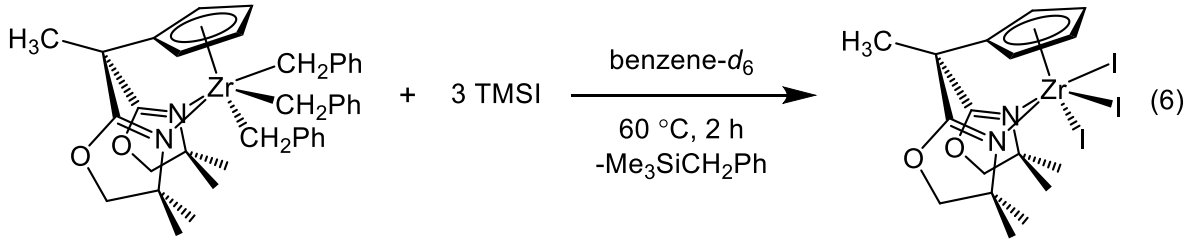
(4)

{Bo^{M}Cp}Zr(CH$_2$Ph)$_3$ reacts with 3 equivalents of benzyl amine in benzene-d_6 at room temperature in 10 minutes to form {Bo^{M}Cp}Zr(NHCH$_2$Ph)$_3$, but the solution must be pumped down immediately to isolate the product. {Bo^{M}Cp}Zr(CH$_2$Ph)$_3$ reacts with 1 or 3 equivalents of *t*-butyl amine in benzene-d_6 at room temperature in 10 minutes to give a mixture of products that were not able to be separated.

{Bo^{M}Cp}Zr(CH$_2$Ph)$_3$ reacts with the Lewis acid B(C$_6$F$_5$)$_3$ in benzene-d_6 at room temperature in 10 minutes to give the borane abstraction product [{Bo^{M}Cp}Zr(CH$_2$Ph)$_2$][PhCH$_2$B(C$_6$F$_5$)$_3$] (**15**) as a red oil that is insoluble in benzene but can be redissolved in bromobenzene (eq. 5).

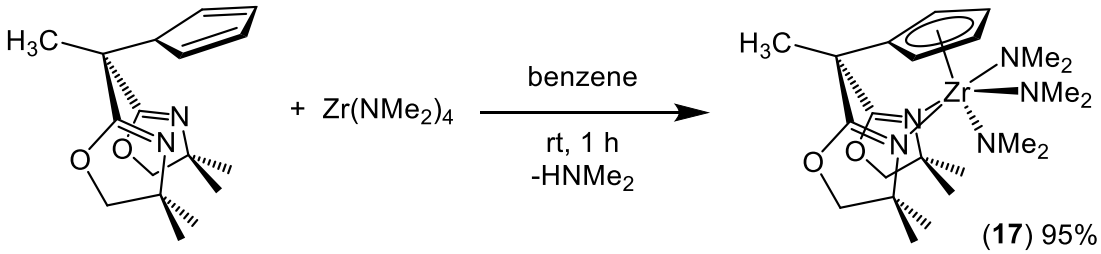


{Bo^{M}Cp}Zr(CH$_2$Ph)$_3$ reacts with 3 equivalents of trimethylsilyl iodide (TMSI) in benzene at 60 °C in 2 hours to form {Bo^{M}Cp}ZrI$_3$ (**16**) as a yellow solid (eq. 6).



When LiTMDS is added to {Bo^{M}Cp}ZrI$_3$ in benzene-d_6, no product formation is observed, only decomposition to unidentified products within 10 minutes at room temperature. When potassium graphite is added to attempt to reduce {Bo^{M}Cp}ZrI$_3$ in benzene-d_6, the {Bo^{M}Cp}ZrI$_3$ starts to decompose over 4 hours and no color change indicative of reduction is observed.

A zirconium amide compound was prepared from the reaction of Zr(NMe$_2$)$_4$ with H{Bo^{M}Cp} in benzene at room temperature to form Bo^{M}CpZr(NMe$_2$)$_3$ (**17**) with the loss of dimethylamine (eq. 7). Surprisingly, H{Bo^{M}Cp^{tet}} does not react with Zr(NMe$_2$)$_4$ in benzene or THF, even at temperatures up to 120 °C for two days in sealed flasks.



(7)

^{1}H NMR spectroscopy shows formation of Bo^{M}CpZr(NMe$_2$)$_3$ at room temperature within 10 minutes. ^{1}H NMR experiments at room temperature show equivalent oxazoline rings. However, in low temperature NMR experiments, the oxazoline rings become inequivalent, as shown by the ^{1}H splitting pattern. Solution IR experiments show two C=N stretching frequencies at 1659 and 1641 cm^{-1}, suggesting coordinating and non-coordinating oxazoline rings (Table 1). This data together suggests the oxazoline rings exchange.

Table 1: IR spectroscopy data for {Bo^{M}Cp}Zr(NMe$_2$)$_3$

IR experiment	**C=N stretch (cm^{-1})**
Solution (toluene)	1659, 1641
KBr (amorphous)	1646
KBr (from crystals)	1657, 1636

Interestingly, the IR spectrum of the amorphous solid in KBr has only one infrared C=N stretching frequency at 1646 cm^{-1}. X-ray-quality crystals were obtained from a solution of {Bo^{M}Cp}Zr(NMe$_2$)$_3$ in a mixture of toluene and pentane at –30 °C (Fig. 9). The crystal structure shows only one oxazoline ring coordinated to the zirconium center. This is confirmed by the two infrared C=N stretching frequencies from the isolated crystals at 1657 and 1636 cm^{-1}.

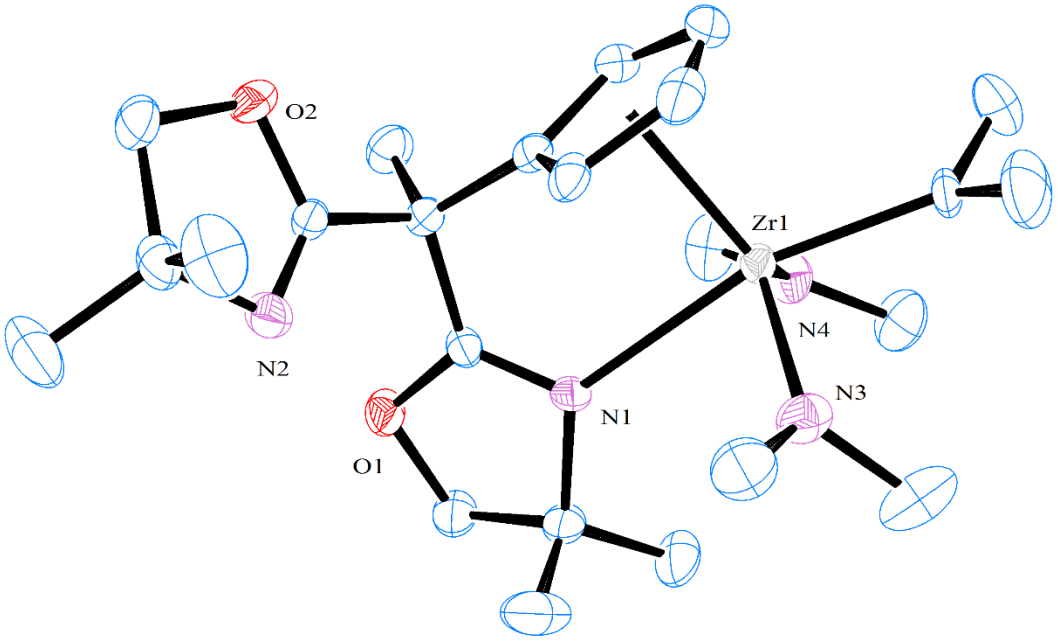
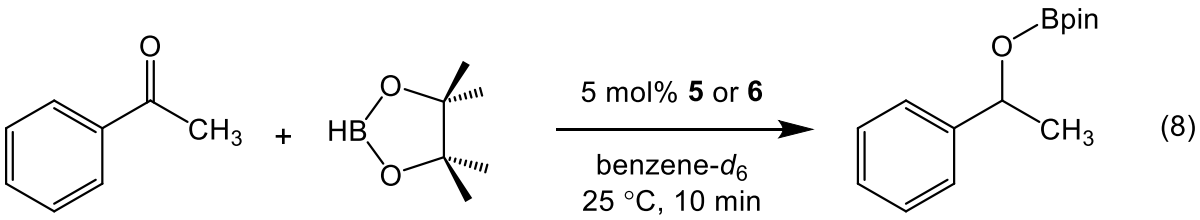


Figure 9: ORTEP diagram of $\{Bo^{M}Cp\}Zr(NMe_2)_3$

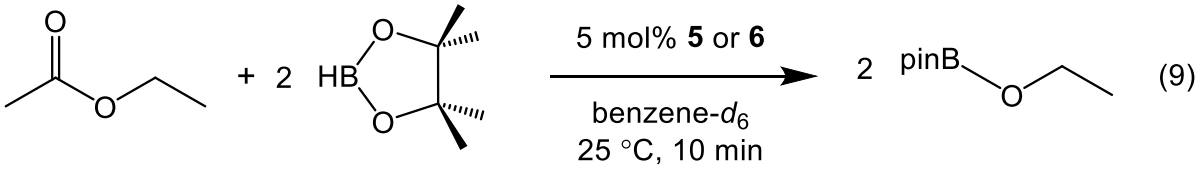
3. Catalytic hydroboration of ketones and esters using cyclopentadienyl bis(oxazolinyl) group 2 compounds

$\{Bo^{M}Cp\}MgCH_3$, $\{Bo^{M}Cp^{tet}\}MgCH_3$, $\{Bo^{P}Cp\}MgCH_3$, and $\{Bo^{P}Cp^{tet}\}MgCH_3$ catalyze the hydroboration of acetophenone and ethyl acetate using pinacol borane (HBpin) as the hydride source. Acetophenone reacts with one equivalent of HBpin in the presence of 5 mol% $\{Bo^{M}Cp\}MgCH_3$ or $\{Bo^{M}Cp^{tet}\}MgCH_3$ in benzene-d_6 at room temperature in 10 minutes (eq. 8).



(8)

Ethyl acetate reacts with two equivalents of HBpin in the presence of 5 mol% $\{Bo^{M}Cp\}MgCH_3$ or $\{Bo^{M}Cp^{tet}\}MgCH_3$ in benzene-d_6 at room temperature in 10 minutes to give the cleaved boryl ether product (eq. 9). Alkenes and alkynes do not react and are not reduced.



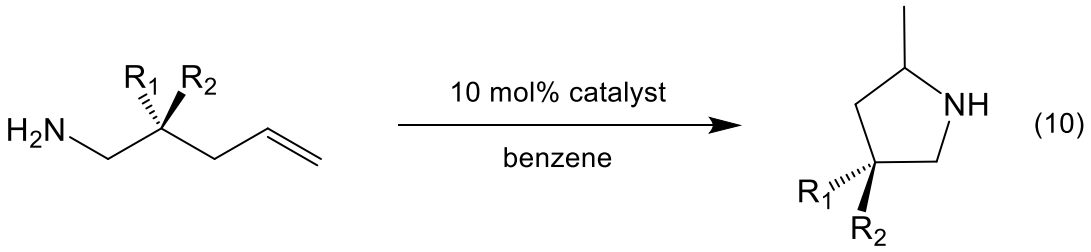
(9)

In comparison, $To^{M}MgMe$ was previously found to reduce acetophenone with pinacolborane in benzene, but the reaction had to be heated to 60 °C for 2 hours to complete when using 5 mol% catalyst. The catalysts studied here reduce acetophenone at room temperature within 10 minutes.

$\{Bo^{P}Cp\}MgCH_3$ and $\{Bo^{P}Cp^{tet}\}MgCH_3$ also catalyze the reduction of acetophenone and ethyl acetate. To determine if the reaction was enantioselective, the boryl ether products from reductions of acetophenone catalyzed by $\{Bo^{P}Cp\}MgCH_3$ and $\{Bo^{P}Cp^{tet}\}MgCH_3$ were converted to the corresponding alcohols through an aqueous workup using NaOH. GC and HPLC analysis of the alcohol products did not show any enantioselectivity, either due to the reaction not being enantioselective or the workup racemizing the products.

4. Catalytic hydroamination/cyclization of aminoalkenes using cyclopentadienyl bis(oxazolinyl) group 2 and 4 compounds

The hydroamination and cyclization of aminoalkenes is performed catalytically using $\{Bo^{M}Cp\}MgCH_3$, $\{Bo^{M}Cp^{tet}\}MgCH_3$, and $\{Bo^{M}Cp\}Zr(NMe_2)_3$ (Table 2). The use of $\{Bo^{M}Cp\}Zr(NMe_2)_3$ in these reactions requires heating at 60 °C, while reactions run with $\{Bo^{M}Cp\}MgCH_3$ or $\{Bo^{M}Cp^{tet}\}MgCH_3$ go to completion quickly (< 2 h) at room temperature. The only product obtained in these reactions is the cyclized aminoalkene, as shown in equation 10.



(10)

Table 2: Results of hydroamination of aminoalkenes

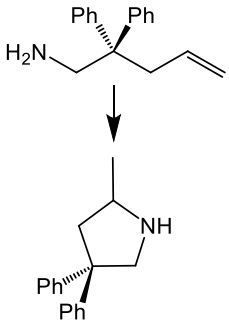
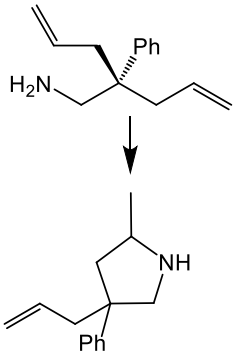
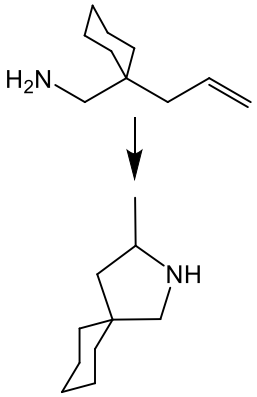
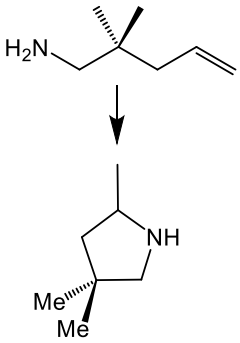
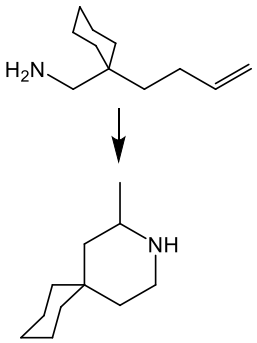
Substrate to Product	Precatalyst (10 mol%)	Temp (°C)	Time	Conversion (%)
	$\{Bo^{M}Cp\}MgCH_3$	25	45 min	>99
	$\{Bo^{M}Cp^{tet}\}MgCH_3$	25	1.5 h	>99
	$\{Bo^{M}Cp\}Zr(NMe_2)_3$	25	36 h	>99
	$\{Bo^{M}Cp\}MgCH_3$	25	2 h	>99
	$\{Bo^{M}Cp^{tet}\}MgCH_3$	25	2 h	>99
	$\{Bo^{M}Cp\}Zr(NMe_2)_3$	25	42 h	>99

Table 2 continued

	{Bo^{M}Cp}MgCH$_3$ {Bo^{M}Cp^{tet}}MgCH$_3$ {Bo^{M}Cp}Zr(NMe$_2$)$_3$	25 25 -	19 h 1.5 h -	21 >99
	{Bo^{M}Cp}MgCH$_3$ {Bo^{M}Cp^{tet}}MgCH$_3$ {Bo^{M}Cp}Zr(NMe$_2$)$_3$	25 80 60	- 1.5 h 12 h	- 50 50
	{Bo^{M}Cp}MgCH$_3$ {Bo^{M}Cp^{tet}}MgCH$_3$ {Bo^{M}Cp}Zr(NMe$_2$)$_3$	80 25 -	1.5 h 2 h -	25 >99 -

Conclusions

A new class of monoanionic cyclopentadienyl-bis(oxazoline) ligands has been prepared, including H{Bo^{M}Cp}, H{Bo^{M}Cp^{tet}}, H{Bo^{P}Cp}, and H{Bo^{P}Cp^{tet}}. These ligands support a wide variety of metal complexes, including Mg, Zn, Ti, and Zr compounds.

{Bo^{M}Cp}MgCH$_3$, {Bo^{M}Cp^{tet}}MgCH$_3$, {Bo^{P}Cp}MgCH$_3$, and {Bo^{P}Cp^{tet}}MgCH$_3$ show excellent reactivity for catalyzing the hydroboration of acetophenone and ethyl acetate using pinacolborane. {Bo^{M}Cp}Zr(NMe$_2$)$_3$, {Bo^{M}Cp}MgCH$_3$, and {Bo^{M}Cp^{tet}}MgCH$_3$ are also efficient catalysts for the hydroamination of aminoalkenes. Further work should be done to determine the enantioselectivity of {Bo^{P}Cp}MgCH$_3$ and {Bo^{P}Cp^{tet}}MgCH$_3$ in hydroboration reactions to make chiral alcohols. Also, new ligands can be readily made by varying the R-groups on the oxazoline rings or varying the backbone of the ligands.

Experimental Section

H{Bo^{M}Cp} (1) A slurry of cyclopentadienylthallium (1.44 g, 5.35 mmol) and benzene (10 mL) was prepared in a 100 mL Schlenk flask. The flask was fitted with an addition funnel, and the solution was cooled to 12 °C using a dioxane/dry ice bath. A solution of iodine (1.24 g, 4.86 mmol) in benzene (50 mL) was added to the slurry in a dropwise fashion over 1.5 h while maintaining the temperature at 12 °C to form a cloudy yellow solution. LiCMe(Ox^{Me2})$_2$ (1.12 g, 4.86 mmol) was dissolved in THF (20 mL) and was added to the cyclopentadienyliodide mixture via cannula. The solution was then warmed to room temperature and stirred overnight. The solution was filtered in air, and the solvent was evaporated on a rotovapor at 100 mTorr. The crude oily product was purified by silica gel chromatography in ethyl acetate to give a brown oil. The product was dried by dissolving in benzene and stirring with phosphorus pentoxide for 6 h. The solution was filtered and the solvent was removed under reduced pressure to provide brown, oily H{Bo^{M}Cp} as two isomers (0.789 g, 2.753 mmol, 56.6%). ^{1}H NMR (chloroform-*d*, 400 MHz, 25 °C): δ 6.57–6.29 (m, 4 H, HC$_5$*H*$_4$), 3.94 (m, 4 H, CNCMe$_2$C*H*$_2$O), 3.16 (s, 1 H, *H*C$_5$H$_4$), 1.78 (m, 3

H, backbone CH_3), 1.28 (m, 12 H, CNC$Me_2$$CH_2O$). $^{13}C\{^1H\}$ NMR (chloroform-*d*, chloroform-*d*, 101 MHz, 25 °C): (both isomers observed) δ 166.32 (*C*NCMe_2CH_2O), 165.98 (*C*NCMe_2CH_2O), 147.05 (H*C*$_5H_4$), 146.00 (H*C*$_5H_4$), 133.41 (H*C*$_5H_4$), 133.22 (H*C*$_5H_4$), 132.85 (H*C*$_5H_4$), 131.72 (H*C*$_5H_4$), 129.26 (H*C*$_5H_4$), 127.94 (H*C*$_5H_4$), 79.51 (CNCMe_2*C*H_2O), 67.29 (CN*C*Me_2CH_2O), 44.60 (backbone *C*CH_3), 43.93 (backbone *C*CH_3), 42.08 (sp^3 H*C*$_5H_4$), 41.25 (sp^3 H*C*$_5H_4$), 28.21 (CNC$Me_2$$CH_2O$), 24.58 (backbone C*C*$H_3$), 23.77 (backbone C*C*$H_3$). $^{15}N\{^1H\}$ NMR (chloroform-*d*, 41 MHz, 25 °C): δ –135.05 (C*N*CMe_2CH_2O). IR (KBr, cm^{-1}): 2968 s, 2930 m, 2890 m, 1656 s (C=N), 1462 m, 1364 m, 1286 m, 1249 w, 1193 m, 1084 m, 974 m, 933 w, 900 w, 732 w. Anal. Calcd for $C_{17}H_{24}N_2O_2$: C, 70.80; H, 8.39; N, 9.71. Found: C, 70.30; H, 8.78; N, 9.69.

H{Bo^{M}Cp^{tet}} (2) 500 mL Schlenk flask was charged with 2,3,4,5-tetramethylcyclopentadienyllithium (1.12 g, 8.74 mmol). Dry pentane (400 mL) was added and the mixture was cooled to –78 °C. Solid iodine (2.21 g, 8.73 mmol) was added to the flask. The mixture was stirred at –78 °C for 8 h and was then warmed to –20 °C and stirred for 12 h until all LiC_5Me_4 reacted. Over the course of the reaction, the solution turned dark yellow with a white precipitate. Li[$H_3CC(Ox^{Me2})_2$] (2.00 g, 8.73 mmol) was placed in a 100 mL Schlenk flask and dissolved in THF (30 mL). The THF solution was added via cannula to the pentane mixture at –20 °C. The solution was warmed to room temperature and was stirred 8 h. The reaction mixture was then filtered in air, and the solvent was removed using a rotovapor. The crude oily product was purified by silica gel chromatography in ethyl acetate to give the product as a white solid (2.04 g, 5.90 mmol, 68%). The solid was dried by dissolving in benzene and stirring with phosphorous pentoxide for 6 h. Crystallization from

pentane at –35 °C gave X-ray quality crystals. ^{1}H NMR (benzene-d_6, 700 MHz, 25 °C): δ 1.13 (s, 6 H, CNC*Me*$_2$CH$_2$O), 1.17 (s, 6 H, CNC*Me*$_2$CH$_2$O), 1.62 (s, 3 H, backbone C*H*$_3$), 1.70 (s, 6 H, C$_5$H*Me*$_4$), 1.95 (s, 6 H, C$_5$H*Me*$_4$), 3.65 (d, 2 H, $^{2}J_{HH}$ = 7.7 Hz, CNCMe$_2$C*H*$_2$O), 3.75 (d, 2 H, $^{2}J_{HH}$ = 7.7 Hz, CNCMe$_2$C*H*$_2$O), 4.17 (s, 1 H, C*H*Me$_4$). ^{13}C{^{1}H} NMR (benzene-d_6, 400 MHz, 25 °C): δ 11.68 (C$_5$H*Me*$_4$), 14.2 (C$_5$H*Me*$_4$), 16.4 (backbone *C*H$_3$), 28.1 (CNC*Me*$_2$CH$_2$O), 29.1 (CNC*Me*$_2$CH$_2$O), 44.34 (backbone *C*H$_3$), 59.79 (*C*$_5$HMe$_4$), 67.61 (CN*C*Me$_2$CH$_2$O), 79.43 (CNCMe$_2$*C*H$_2$O), 134.4 (*C*$_5$*H*Me$_4$), 138.21 (*C*$_5$*H*Me$_4$), 166.87 170.0 (*C*NCMe$_2$CH$_2$O); ^{15}N{^{1}H} NMR (benzene-d_6, 700 MHz, 25 °C): δ –131.1 (C*N*CMe$_2$CH$_2$O). IR (KBr, cm^{-1}): 615 w, 654 s, 733 w, 769 m, 852 m, 892 w, 926 m, 945 s, 975 s, 994 m, 1011 m, 1036 m, 1068 m, 1094 m, 1170 m, 1195 m, 1253 m, 1301 m, 1346 m, 1363 m, 1376 s, 1446 s, 1463 s, 1640 m (C=N), 1661 s (C=N), 2734 w, 2860 s, 2890 s, 2930 s, 2963 s, 3010 m, 3287 w. Anal. Calcd for C$_{21}$H$_{32}$N$_2$O$_2$: C, 73.22; H, 9.36; N, 8.13. Found: C, 73.16; H, 9.31; N, 8.12. mp 109–111 °C.

Tl{Bo^{M}Cp} (3). H{Bo^{M}Cp} (0.375 g, 1.31 mmol) was placed in a vial in the glovebox and dissolved in diethyl ether. Thallium ethoxide (102 μL, 1.44 mmol) was added, and brown precipitate immediately formed. The solution was stirred at room temperature for 2 h. To isolate the product, the vial was centrifuged, and the solvent was removed by pipet. The solid was washed with pentane (3×) and was then extracted with benzene, filtered, and dried under reduced pressure to give the product as a brown solid (0.537 g, 1.09 mmol, 83%). ^{1}H NMR (chloroform-*d*, 400 MHz, 25 °C): δ 1.01 (s, 6 H, CNC*Me*$_2$CH$_2$O), 1.03 (s, 6 H, CNC*Me*$_2$CH$_2$O), 2.13 (s, 3 H, C*H*$_3$), 3.60 (d, 2 H, ^{2}J = 4.4, CNCMe$_2$C*H*$_2$O), 3.65 (d, 2 H, ^{2}J = 4.8, CNCMe$_2$C*H*$_2$O), 6.29 (s, 2 H, C$_5$*H*$_4$), 6.56 (s, 2 H, C$_5$*H*$_4$). ^{13}C{^{1}H} NMR (chloroform-

d, 101 MHz, 25 °C): δ 170.92 (*C*NCMe$_2$CH$_2$O), 124.13 (*C*$_5$H$_4$), 107.90 (*C*$_5$H$_4$), 107.52 (*C*$_5$H$_4$), 80.13 (CNCMe$_2$*C*H$_2$O), 67.30 (CN*C*Me$_2$CH$_2$O), 44.20 (backbone *C*CH$_3$), 28.46 (CNC*Me*$_2$CH$_2$O), 28.38 (CNC*Me*$_2$CH$_2$O), 25.17 (backbone C*C*H$_3$). ^{15}N{^{1}H} NMR (chloroform-*d*, 41 MHz, 25 °C): δ –129.9 (C*N*CMe$_2$CH$_2$O). IR (KBr, cm^{-1}): 3075 m, 2966 s, 2930 m, 2887 s, 1647 s (C=N), 1463 m, 1383 w, 1365 m, 1349 w, 1276 m, 1248 m, 1200 m, 1080 s, 1042 vw, 1028 w, 975 m. Anal. Calcd for C$_{17}$H$_{23}$N$_2$O$_2$Tl: C, 41.52; H, 4.71; N, 5.70. Found: C, 41.14; H, 4.61; N, 5.67. mp 168–171 °C, dec.

Tl{Bo^{M}Cp^{tet}} (4) H{Bo^{M}Cp^{tet}} (0.377 g, 1.09 mmol) was placed in a vial in the glovebox and dissolved in THF (10 mL) to give a light yellow solution. Thallium ethoxide (84.9 μL, 1.20 mmol) was added, and the solution was stirred at room temperature for 10 days. The solvent was removed under reduced pressure, and the solid was washed with pentane (3×) and was then extracted with benzene, filtered, and dried under reduced pressure to give the product as a green solid (0.512 g, 0.933 mmol, 85.5%). ^{1}H NMR (benzene-*d*$_6$, 600 MHz, 25 °C): δ 3.64 (m, 4 H, CNCMe$_2$C*H*$_2$O), 2.37 (s, 6 H, C$_5$*Me*$_4$), 2.34 (s, 6 H, C$_5$*Me*$_4$), 2.21 (s, 3 H, backbone C*H*$_3$), 1.11 (s, 6 H, CNC*Me*$_2$CH$_2$O), 1.10 (s, 6 H, CNC*Me*$_2$CH$_2$O). ^{13}C{^{1}H} NMR (benzene-*d*$_6$, 700MHz): 11.14 (C$_5$*Me*$_4$), 12.63 (C$_5$*Me*$_4$), 26.31(backbone C*Me*), 27.29 (CNC*Me*$_2$CH$_2$O), 28.42 (CNC*Me*$_2$CH$_2$O), 46.20(backbone *C*Me), 67.28 (CN*C*Me$_2$CH$_2$O), 79.49 (CNCMe$_2$*C*H$_2$O), 114.38(*C*$_5$Me$_4$), 115.61(*C*$_5$Me$_4$), 170.0 (*C*NCMe$_2$CH$_2$O); ^{15}N{^{1}H} NMR (benzene-*d*$_6$, 700MHz): –128.1 (C*N*CMe$_2$CH$_2$O). IR (KBr, cm^{-1}): 2971 s, 2961 m, 2923 m, 2889 m, 2855 m, 1654 m (C=N), 1637 s (C=N), 1457 w, 1381 m, 1362 w, 1343 w, 1267 m, 1246 m, 1194 m, 1091 m, 1075 m, 1042 w, 993 m, 973 m, 936 w, 897 w. Anal.

Calcd for $C_{21}H_{31}N_2O_2Tl$: C, 46.04; H, 5.70; N, 5.11. Found: C, 46.21; H, 5.79; N, 5.06. mp 164 °C (dec).

H{Bo^{P}Cp} (5) A slurry of cyclopentadienylthallium (0.653 g, 2.42 mmol) and benzene (10 mL) was prepared in a 100 mL Schlenk flask. The flask was fitted with an addition funnel, and the solution was cooled to 12 °C using a dioxane/dry ice bath. A solution of iodine (0.560 g, 2.21 mmol) in benzene (30 mL) was added to the slurry in a dropwise fashion over 1 h while maintaining the temperature at 12 °C to form a cloudy yellow solution. Meanwhile, HCMe(Ox^{iPr})$_2$ (0.556 g, 2.20 mmol) was dissolved in THF (10 mL) in a 100 mL Schlenk flask and was cooled to –78 °C. *n*-BuLi (2.5 M solution in hexane, 0.882 mL, 2.20 mmol) was added dropwise via a 10 mL glass syringe to form LiCMe(Ox^{iPr})$_2$. The solution was warmed to room temperature while stirring and remained colorless and clear. The solution of LiCMe(Ox^{iPr})$_2$ in THF was added to the solution of cyclopentadienyliodide in benzene at 12 °C via cannula. The solution was then warmed to room temperature, sealed, and stirred at room temperature for 15 hours. The solution was then filtered, and the solvent was removed under reduced pressure using a rotovapor. The crude brown oil was purified using silica gel chromatography in ethyl acetate to give a brown oil. The product was dried by dissolving in benzene and stirring with phosphorus pentoxide for 6 h. The solution was filtered and the solvent was removed under reduced pressure to provide brown, oily H{Bo^{P}Cp} as three isomers (0.355 g, 1.12 mmol, 50.9%). ^{1}H NMR (benzene-d_6, 600 MHz, 25 °C): 3 isomers observed δ 6.59 – 6.33 (m, 4 H, HC$_5$*H*$_4$), 4.46 (s, 1 H, *H*C$_5$H$_4$), 3.87 (m, 2 H, CNC*H*(CH(CH$_3$)$_2$)CH$_2$O), 3.72 (m, 4 H, CNCH(CH(CH$_3$)$_2$)C*H*$_2$O), 2.14 (s, backbone

CC*H*$_3$), 2.08 (s, backbone CC*H*$_3$), 2.00 (s, backbone CC*H*$_3$), 1.56 (m, 2 H, CNCH(C*H*(CH$_3$)$_2$)CH$_2$O), 0.91 – 0.71 (m, 12 H, CNCH(CH(C*H*$_3$)$_2$)CH$_2$O).

H{Bo^{P}Cp^{tet}} (6) A 1 L Schlenk flask was charged with 2,3,4,5-tetramethylcyclopentadienyllithium (0.504 g, 3.90 mmol). Dry pentane (300 mL) was added and the mixture was cooled to –78 °C. Solid iodine (0.991 g, 3.90 mmol) was added to the flask. The mixture was stirred at –78 °C for 12 h and was then warmed to –20 °C and stirred for 12 h until all LiC$_5$Me$_4$ reacted. Over the course of the reaction, the solution turned dark yellow with a white precipitate. Meanwhile, HCMe(Ox^{iPr})$_2$ (0.985 g, 3.91 mmol) was dissolved in THF (10 mL) in a 100 mL Schlenk flask and was cooled to –78 °C. *n*-BuLi (2.5 M solution in hexane, 1.50 mL, 3.75 mmol) was added dropwise via a 10 mL glass syringe to form LiCMe(Ox^{iPr})$_2$. The solution was warmed to room temperature while stirring and remained colorless and clear. The solution of LiCMe(Ox^{iPr})$_2$ in THF was added via cannula to the pentane mixture at –20 °C. The solution was warmed to room temperature and was stirred 8 h. The reaction mixture was then filtered in air, and the solvent was removed using a rotovapor. The crude oily product was purified by silica gel chromatography in ethyl acetate to give the product as a yellow oil (0.568 g, 1.52 mmol, 39%). The solid was dried by dissolving in benzene and stirring with phosphorous pentoxide for 6 h. ^{1}H NMR (benzene-d_6, 600 MHz, 25 °C): 2 isomers observed? δ 4.22 (s, 1 H, *H*C$_5$Me$_4$), 3.98 (m, 2 H, CNCH(C*H*(CH$_3$)$_2$)CH$_2$O), 3.70 (m, 4 H, CNCH(CH(CH$_3$)$_2$)C*H*$_2$O), 1.94 (s, backbone CC*H*$_3$), 1.93 (s, backbone CC*H*$_3$), 1.72 (s, 6 H, HC$_5$*Me*$_4$), 1.62 (s, 6 H, HC$_5$*Me*$_4$), 1.03 – 0.71 (m, 12 H, CNCH(CH(C*H*$_3$)$_2$)CH$_2$O).

{Bo^{M}Cp}MgCH$_3$ (7) H{Bo^{M}Cp} (0.066 g, 0.230 mmol) was placed in a vial in the glovebox and dissolved in benzene (3 mL). Mg(CH$_3$)$_2$(dioxane)$_2$ (0.049 g, 0.230 mmol) was added to the solution, and the solution was stirred at room temperature for 1.5 h. Gas formation was observed over the course of the reaction. The solution was then filtered and dried under reduced pressure to give a pink oil. The oil was washed with pentane (3×) and dried under reduced pressure to give a white solid that was stored at –30 °C (0.051 g, 0.157 mmol, 68.3%). ^{1}H NMR (benzene-d_6, 600 MHz, 25 °C): δ 6.45 (s, 2 H, C$_5$*H*$_4$), 6.32 (s, 2 H, C$_5$*H*$_4$), 3.66 (d, 2 H, $^2J_{HH}$ = 7.8 Hz, CNCMe$_2$C*H*$_2$O), 3.55 (d, 2 H, $^2J_{HH}$ = 8.4 Hz, CNCMe$_2$C*H*$_2$O), 2.05 (s, 3 H, backbone C*H*$_3$), 1.12 (br d, 12 H, CNC*Me*$_2$CH$_2$O), –0.89 (br s, 3 H, Mg-C*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 151 MHz, 25 °C): δ *C*NCMe$_2$CH$_2$O peaks under benzene-d_6, 118.09 (*C*$_5$H$_4$) , 108.12 (*C*$_5$H$_4$), 102.07 (*C*$_5$H$_4$), 58.29 (CN*C*Me$_2$CH$_2$O), 44.61 (backbone *C*CH$_3$), 27.95 (CNC*Me*$_2$CH$_2$O), 21.80 (backbone C*C*H$_3$), 1.43 (Mg-*C*H$_3$). C*N*CMe$_2$CH$_2$O not observed by ^{15}N{^{1}H} NMR. IR (KBr, cm^{-1}): 2968 s, 2931 m, 2897 m, 1658 s (C=N), 1547 w, 1463 m, 1366 m, 1309 w, 1292 w, 1255 w, 1202 w, 1192 m, 1084 s sh, 1041 s, 974 w, 960 w, 934 w, 874 m, 809 w, 750 m. Anal. Calcd for C$_{18}$H$_{26}$MgN$_2$O$_2$: C, 66.17; H, 8.02; N, 8.57. Found: C, 63.34; H, 7.61; N, 8.67. mp 145–147 °C, dec.

{Bo^{M}Cp^{tet}}MgCH$_3$ (8) H{Bo^{M}Cp^{tet}} (0.129 g, 0.373 mmol) was placed in a vial in the glovebox and dissolved in benzene (5 mL). Mg(CH$_3$)$_2$(dioxane)$_2$ (0.080 g, 0.373 mmol) was added to the solution, and the solution was stirred at room temperature for 4 h. Gas formation was observed over the course of the reaction. The solution was then filtered and dried under reduced pressure to give a yellow oil. The oil was washed with pentane (3×) and dried under reduced pressure to give a white solid that was stored at –30 °C (0.110 g, 0.286 mmol,

76.9%). ^{1}H NMR (600 MHz, benzene-d_6): 3.70 (d, 2 H, ^{2}J = 12.6 Hz, CNCMe$_2$CH_2O), 3.58 (d, 2 H, ^{2}J = 12.0 Hz, CNCMe$_2$CH_2O), 2.33 (s, 3 H, C$_5$(CH_3)$_4$), 2.24 (s, 3 H, C$_5$(CH_3)$_4$), 2.11 (s, 3 H, backbone CH_3), 1.08 (s, 3 H, CNCMe_2CH$_2$O), 1.05 (s, 3 H, CNCMe_2CH$_2$O), –0.91 (s, 3 H, Mg-CH_3). ^{13}C{^{1}H} NMR (600 MHz, benzene-d_6): δ *C*NCMe$_2$CH$_2$O peaks buried under benzene-d_6, 113.34 (*C*$_5$(CH$_3$)$_4$), 107.85 (*C*$_5$(CH$_3$)$_4$), 107.16 (*C*$_5$(CH$_3$)$_4$), 80.48 (CNCMe$_2$*C*H$_2$O), 66.17 (CN*C*Me$_2$CH$_2$O), 46.37 (backbone *C*CH$_3$), 28.28 (CNCMe_2CH$_2$O), 27.40 (CNCMe_2CH$_2$O), 23.79 (backbone C*C*H$_3$), 13.68 (C$_5$(*C*H$_3$)$_4$), 11.64 (C$_5$(*C*H$_3$)$_4$), –11.18 (Mg-*C*H$_3$). ^{15}N{^{1}H} NMR (benzene-d_6, 71 MHz): δ –145.7 (C*N*CMe$_2$CH$_2$O). IR (KBr, cm^{-1}): 2996 s, 2928 s, 2866 s, 2726 w sh, 1658 s (C=N), 1496 m, 1467 m, 1304 m, 1306 m, 1283 m, 1252 m, 1192 m, 1087 m, 1024 w, 991 w, 974 m, 962 m, 934 m, 893 w, 829 w. Anal. Calcd for C$_{22}$H$_{34}$MgN$_2$O$_2$: C, 69.02; H, 8.95; N, 6.95. Found: C, 67.48; H, 9.35; N, 6.95. mp 145–146 °C, dec.

{Bo^{P}Cp}MgCH$_3$ (9) H{Bo^{P}Cp} (0.0952 g, 0.301 mmol) was placed in a vial in the glovebox and dissolved in benzene (3 mL). Mg(CH$_3$)$_2$(dioxane)$_2$ (0.0403 g, 0.301 mmol) was added to the solution, and the solution was stirred at room temperature for 1 h. Gas formation was observed over the course of the reaction. The solution was then filtered and dried under reduced pressure to give a pink oil. The oil was washed with pentane (3×) and dried under reduced pressure to give {Bo^{P}Cp}MgCH$_3$ as a white solid that was stored at –30 °C (0.100 g, 0.282 mmol, 93.7%). ^{1}H NMR (benzene-d_6, 600 MHz, 25 °C): δ 6.38 (s, 2 H, C$_5$*H*$_4$), 6.33 (s, 2 H, C$_5$*H*$_4$), 3.90 – 3.70 (m, broad, 6 H, CNC*H*(CH(CH$_3$)$_2$)CH_2O), 2.08 (s, 3 H, backbone CCH_3), 0.89 – 0.66 (m, 12 H, CNCH(CH(CH_3)$_2$)CH$_2$O), – 1.03 (s, 3 H, Mg-CH_3).

{Bo^{P}Cp^{tet}}MgCH$_3$ (10) H{Bo^{P}Cp^{tet}} (0.0971 g, 0.261 mmol) was placed in a vial in the glovebox and dissolved in benzene (5 mL). Mg(CH$_3$)$_2$(dioxane)$_2$ (0.0349 g, 0.261 mmol) was added to the solution, and the solution was stirred at room temperature for 4 h. Gas formation was observed over the course of the reaction. The solution was then filtered and dried under reduced pressure to give a yellow oil. The oil was washed with pentane (3×) and dried under reduced pressure to give a white solid that was stored at –30 °C. ^{1}H NMR (benzene-d_6, 600 MHz, 25 °C): δ 3.99 – 3.57 (m, 6 H, CNC*H*(CH(CH$_3$)$_2$)C*H*$_2$O), 2.36 (s, 6 H, C$_5$*Me*$_4$), 2.28 (s, 3 H, C$_5$*Me*$_4$), 2.23 (s, 3 H, C$_5$*Me*$_4$), 2.15 (s, 3 H, backbone CC*H*$_3$), 0.86 (s, 6 H, CNCH(CH(C*H*$_3$)$_2$)CH$_2$O), 0.64 (s, 6 H, CNCH(CH(C*H*$_3$)$_2$)CH$_2$O), – 0.95 (s, 3 H, Mg-C*H*$_3$).

{Bo^{M}Cp}TiCl$_2$ (11) TiCl$_3$(THF)$_3$ (0.194 g, 0.523 mmol) was dissolved in benzene (10 mL) and added to a vial containing a solution of Tl{Bo^{M}Cp} (0.257 g, 0.523 mmol) dissolved in benzene (5 mL), resulting in a cloudy green solution. The reaction mixture was stirred for 8 h. The solution was filtered, and the filtrate was evaporated to dryness under reduced pressure to give a brown solid. The solid was recrystallized at –30 °C in a mixture of toluene/pentane to give green, paramagnetic X-ray quality crystals (0.113 g, 0.278 mmol, 53.1%). IR (KBr, cm^{-1}): 773 w, 808 s, 822 s, 874 w, 935 m, 960 s, 982 s, 1036 w, 1049 w, 1050 w, 1090 s, 1109 s, 1190 m, 1258 m, 1290 m, 1323 s, 1368 s, 1461 m, 1635 s (C=N), 1662 s (C=N), 2970 m, 3117 w. Anal. Calcd for C$_{17}$H$_{23}$Cl$_2$N$_2$O$_2$Ti: C, 50.27; H, 5.71; N, 6.90. Found: C, 49.92; H, 5.64; N, 6.84. mp 140–142 °C, dec.

Magnetic susceptibility was measured using Evan's method at room temperature using a Bruker 400 mHz NMR spectrometer. A sample of Bo^{M}CpTiCl$_2$ (5.7 mg, 0.014 mmol) was dissolved in benzene-d_6 (0.90 mL) to give a 15.6 mM solution. The solution (0.60

mL) was placed in an NMR tube. A capillary was charged with benzene-d_6 and placed in the NMR tube. The ^{1}H NMR spectrum shows a paramagnetic shift in the benzene-d_6 peak. Using Evan's method, the following values were obtained: $\Delta\delta$ = 0.070 ppm, χ_{mol} = 1.07 x 10^{-3} cm^3/mol, μ = 1.60 BM, n = 0.885 electrons. This is consistent with a d^1 Ti(III) complex.

{Bo^{M}Cp^{tet}}TiCl$_2$ (12) $TiCl_3(THF)_3$ (0.071 g, 0.192 mmol) was dissolved in benzene (5 mL) and added to a vial containing a solution of Tl{BoMCp^{tet}} (0.257 g, 0.523 mmol) dissolved in benzene (5 mL), resulting in a cloudy green solution. The reaction mixture was stirred for 18 h. The solution was filtered, and the filtrate was evaporated to dryness under reduced pressure. The solid was then extracted with benzene and dried under reduced pressure to give a green solid. IR (KBr, cm^{-1}): 2964 s, 2927 m, 2871 w, 1661 m sh (C=N), 1641 s (C=N), 1570 w, 1463 m, 1366 m, 1322 m, 1285 w, 1253 w, 1190 m, 1170 m, 1096 m, 1029 w, 973 m, 956 m, 935 w, 832 w. n=0.69 by Evan's method. Anal. Calcd for $C_{21}H_{31}Cl_2N_2O_2Ti$: C, 54.56; H, 6.76; N, 6.06. Found: C, 53.82; H, 6.75; N, 5.84. mp 141–143 °C, dec.

{Bo^{M}Cp}Zr(CH$_2$Ph)$_3$ (13) Tl{Bo^{M}Cp} (0.0870 g, 0.176 mmol) was dissolved in benzene (5 mL) and was added to a vial containing $Zr(CH_2Ph)_4$ (0.0811 g, 0.177 mmol). The vial was wrapped in foil to protect from light, and the solution was stirred at room temperature for 3 h. The solvent was then removed and the product was isolated as a red solid. ^{1}H NMR (benzene-d_6, 600 MHz, 25 °C): δ 7.23 – 6.86 (m, 15 H, $Zr(CH_2C_6H_5)_3$), 6.05 (d, 4 H, $^2J_{HH}$ = 4.2 Hz, C_5H_4), 3.48 (d, 2 H, $^2J_{HH}$ = 12.6 Hz, $CNCMe_2CH_2O$), 3.42 (d, 2 H, $^2J_{HH}$ = 12.6 Hz, $CNCMe_2CH_2O$), 2.51 (s, 6 H, $Zr(CH_2C_6H_5)_3$), 1.36 (s, 3 H, backbone CCH_3), 1.16 (s, 6 H, $CNCMe_2CH_2O$), 1.12 (s, 6 H, $CNCMe_2CH_2O$).

{Bo^{M}Cp^{tet}}Zr(CH$_2$Ph)$_3$ (14) Tl{Bo^{M}Cp^{tet}} (0.0606 g, 0.110 mmol) was dissolved in benzene (5 mL) and was added to a vial containing Zr(CH$_2$Ph)$_4$ (0.0507 g, 0.110 mmol). The vial was wrapped in foil to protect from light, and the solution was stirred at room temperature for 3 h. The solvent was then removed and the product was isolated as a red solid. ^{1}H NMR (benzene-d_6, 600 MHz, 25 °C): δ 7.25 – 6.91 (m, 15 H, Zr(CH$_2$C$_6$*H*$_5$)$_3$), 3.57 (d, 2 H, $^{2}J_{HH}$ = 12.6 Hz, CNCMe$_2$C*H*$_2$O), 3.45 (d, 2 H, $^{2}J_{HH}$ = 12.6 Hz, CNCMe$_2$C*H*$_2$O), 2.38 (s, 6 H, Zr(C*H*$_2$C$_6$H$_5$)$_3$), 1.94 (s, 6 H, C$_5$*Me*$_4$), 1.86 (s, 3 H, backbone CC*H*$_3$), 1.65 (s, 6 H, C$_5$*Me*$_4$), 0.96 (s, 6 H, CNC*Me*$_2$CH$_2$O), 0.93 (s, 6 H, CNC*Me*$_2$CH$_2$O).

[{Bo^{M}Cp}Zr(CH$_2$Ph)$_2$][PhCH$_2$B(C$_6$F$_5$)$_3$] (15) {Bo^{M}Cp}Zr(CH$_2$Ph)$_3$ (0.0112 g, 0.0172 mmol) was dissolved in benzene-d_6 and placed in an NMR tube. B(C$_6$F$_5$)$_3$ was added and the solution was shaken. A red oil crashed out of the benzene solution. The oil was dissolved in C$_6$D$_5$Br. ^{1}H NMR (bromobenzene-d_5, 400 MHz, 25 °C): δ 7.21 – 7.00 (m, 10 H, Zr(CH$_2$C$_6$*H*$_5$)$_2$), 6.03 (m, 2 H, C$_5$*H*$_4$), 5.49 (m, 2 H, C$_5$*H*$_4$), 3.74 (d, 2 H, $^{2}J_{HH}$ = 8.8 Hz, CNCMe$_2$C*H*$_2$O), 3.68 (d, 2 H, $^{2}J_{HH}$ = 8.4 Hz, CNCMe$_2$C*H*$_2$O), 1.98 (d, 2 H, $^{2}J_{HH}$ = 10 Hz, Zr(C*H*$_2$C$_6$H$_5$)$_2$), 1.58 (d, 2 H, $^{2}J_{HH}$ = 10 Hz, Zr(C*H*$_2$C$_6$H$_5$)$_2$), 1.58 (s, 3 H, backbone CC*H*$_3$), 0.89 (s, 12 H, CNC*Me*$_2$CH$_2$O). ^{11}B{^{1}H} NMR (bromobenzene-d_5, 128 MHz, 25 °C): δ – 12.1 ([PhCH$_2$*B*(C$_6$F$_5$)$_3$]).

{Bo^{M}Cp}ZrI$_3$ (16) {Bo^{M}Cp}Zr(CH$_2$Ph)$_3$ (0.114 g, 0.176 mol) was dissolved in benzene (10 mL) and placed in a 100 mL flask. (Me$_3$Si)I (75.4 μL, 0.530 mmol was added to the solution. The flask was wrapped in foil to protect from light, and the solution was stirred at 60 °C for 2

h. The solvent was removed to give the product as a yellow oil. The crude product was washed with pentane (5×) to give the product as a yellow solid. ^{1}H NMR (benzene-d_6, 400 MHz, 25 °C): δ 6.43 (s, 2 H, C_5H_4), 6.06 (s, 2 H, C_5H_4), 3.45 (d, 2 H, $^{2}J_{HH}$ = 8.4 Hz, $CNCMe_2CH_2O$), 3.39 (d, 2 H, $^{2}J_{HH}$ = 8.4 Hz, $CNCMe_2CH_2O$), 1.54 (s, 3 H, backbone CCH_3), 1.26 (s, 6 H, $CNCMe_2CH_2O$), 1.14 (s, 6 H, $CNCMe_2CH_2O$).

{Bo^{M}Cp}Zr(NMe$_2$)$_3$ (17) In the glovebox, H{Bo^{M}Cp} (0.100 g, 0.347 mmol) was dissolved in benzene (5 mL) and added to a solution of Zr(NMe$_2$)$_4$ (0.093 g, 0.347 mmol) in benzene (5 mL). The solution was stirred for 1 h at room temperature and then filtered. The filtrate was dried under reduced pressure providing a yellow gel. The gel was washed with pentane (3 × 5 mL) and further dried under vacuum yielding a yellow, analytically pure solid Bo^{M}CpZr(NMe$_2$)$_3$ (0.168 g, 0.329 mmol, 94.9%). X-ray-quality single crystals were obtained from a toluene/pentane solution of the product at –30 °C. ^{1}H NMR (600 MHz, benzene-d_6): 6.23 (t, 2 H, ^{3}J = 2.8 Hz, C_5H_5), 6.19 (t, 2 H, $^{3}J_{HH}$ = 2.8 Hz, C_5H_5), 3.62 (d, 2 H, $^{2}J_{HH}$ = 8.1 Hz, $CNCMe_2CH_2O$), 3.52 (d, 2 H, $^{2}J_{HH}$ = 8.1 Hz, $CNCMe_2CH_2O$), 1.90 (s, 3 H, backbone CH_3), 3.08 (s, 18 H, NMe_2), 1.01 (s, 6 H, $CNCMe_2CH_2O$), 0.96 (s, 6 H, $CNCMe_2CH_2O$). ^{13}C{^{1}H} NMR (600 MHz, benzene-d_6): δ 169.70 ($CNCMe_2CH_2O$), 125.58 (*ipso*-C_5H_4), 108.64 (C_5H_4), 108.25 (C_5H_4), 80.01 ($CNCMe_2CH_2O$), 67.09 ($CNCMe_2CH_2O$), 46.63 (NMe_2), 43.20 (CH_3CCNCN), 26.61 ($CNCMe_2CH_2O$), 26.31 ($CNCMe_2CH_2O$), 21.52 (backbone CH_3). ^{15}N{^{1}H} NMR (benzene-d_6, 71 MHz): δ –138.19 ($CNCMe_2CH_2O$), –138.45 ($CNCMe_2CH_2O$); Zr(NMe_2)$_3$ was not detected. IR (KBr, cm^{-1}, amorphous solid): 2965 s, 2930 m 2890 m, 2865 m, 2819 m, 2759 m, 2736 m, 1645 s (C=N), 1460 m, 1364 m, 1314 m, 1288 m, 1235 m, 1203 m, 1139 s, 1122 m, 1102 m, 1083 m, 1046 s, 975 s, 957 m, 938 m,

875 m, 786 s, 715 m, 712 s. Anal. Calcd. for $C_{23}H_{41}N_5O_2Zr$: C, 54.08; H, 8.09; N, 13.71.

Found: C, 53.63; H, 7.57; N, 13.30. mp 129–132 °C.

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CHAPTER 3

Magnesium-catalyzed reduction of tertiary and secondary amides to amines using pinacolborane

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In close collaboration with Nicole Lampland[§]

Abstract

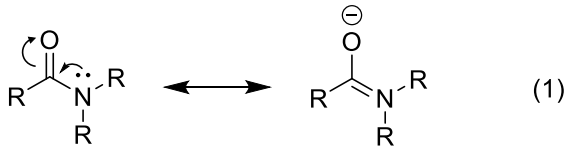
Several [Mg]-Me complexes are found to catalyze the deoxygenation of amides to amines using pinacolborane as the reductant. The best precatalyst observed for amide reduction is $To^{M}MgMe$ (To^{M} = tris(4,4-dimethyl-2-oxazolinyl)phenylborate). Secondary amides are reduced with good yields using four equivalents of pinacolborane and 10 mol% $To^{M}MgMe$, and tertiary amides are reduced with good yields in almost neat conditions (20 equivalents of pinacolborane) and 2 mol% $To^{M}MgMe$.

§ Other authors' contributions

Nicole Lampland: Close collaborator for screening of catalysts and conditions. Studied observed phenyl cleavage side product. Prepared $To^{M}MgMe$, $To^{P}MgMe$, $To^{M}MgHB(C_6F_5)_3$, $To^{MP}MgMe$, $PhB(Ox^{Me2})_2C_5H_5MgMe$, and $PhMeB(Ox^{Me2})_2MgMe$.
Debabrata Mukherjee: First to discover $To^{M}MgMe$ reduces N,N-dimethylformamide to triethylamine with pinacolborane.

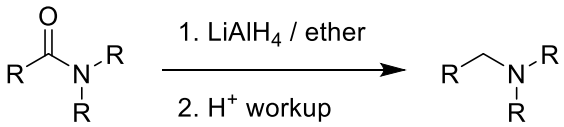
Introduction

Amides are important functional groups found in many biological compounds, such as proteins and many enzymes, as well as many pharmaceuticals and organic synthesis products. The amide functional group in much less reactive than other carbonyl functional groups because of its resonance stabilization (eq. 1), which makes the carbonyl carbon much less electrophilic and more difficult to reduce than other carbonyl functional groups.



(1)

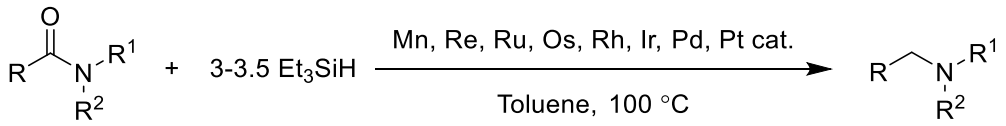
Forcing conditions are necessary to reduce amide functional groups. Lithium aluminum hydride in ether is commonly used to reduce amides (eq. 2).[1]



(2)

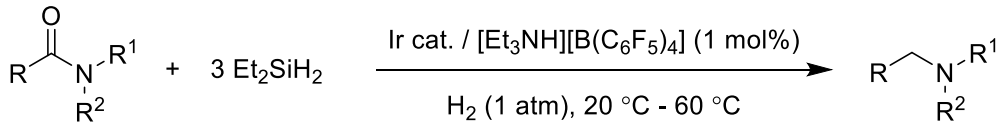
Using $LiAlH_4$ to reduce amides requires stoichiometric amounts of the metal hydride and is not tolerant of many other functional groups, including esters, aldehydes, ketones, epoxides, and lactones. There is a high demand for selective catalytic reduction of amides that are greener, more efficient, and more functional group-tolerant than $LiAlH_4$.

Reductions of amides using noble-metal catalysts and silanes have been reported. In 2001, Fuchikami described the reduction of tertiary amides using a variety of metal catalysts, including Mn, Ru, Re, Os, Rh, Ir, Pd, and Pt, with triethylsilane (eq. 3).[2]

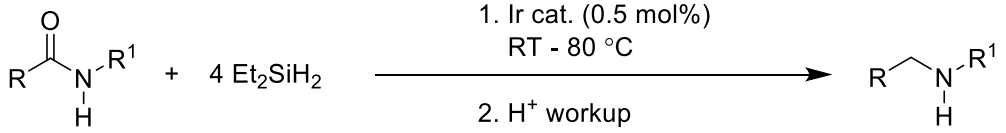


(3)

More recently, Brookhart has investigated Ir-catalyzed reduction of tertiary and secondary amides (eq. 4, 5).[3]



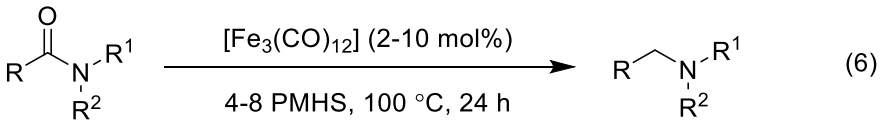
(4)



(5)

In 2013, Breit reported hydrogenation of tertiary and secondary amides to amines using H_2 and a Pd/Re/graphite catalyst.[4] Cleavage of the C–N bond has also been reported using Ru catalysts and H_2 as well as with bimetallic Mo complexes and diphenyl silane.[5,6]

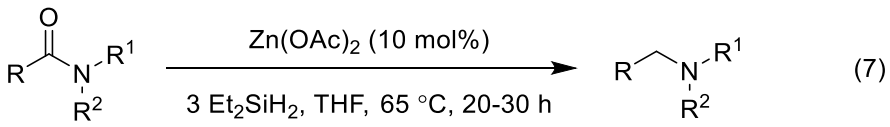
While these examples of catalytic amide reduction show progress toward finding better alternatives to $LiAlH_4$, expensive metal catalysts such as Ir limit the practical use. Examples using more earth-abundant and less expensive metals, such as Fe and Zn, have been recently reported.[7,8] Tertiary amides can be reduced using Fe catalysts and polymethylhydrosiloxane (PMHS) (eq. 6).[8]



(6)

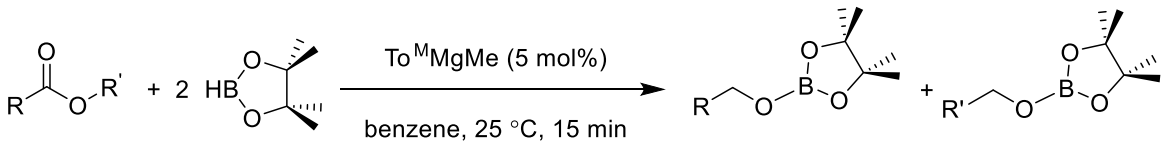
Primary amides were also reduced using a diiron system with methyldiethoxysilane and achieved yields from 49 to 70%.[9] Beller has reported zinc-catalyzed reduction of tertiary

and secondary amides.[10] Mild conditions are reported and wide functional group tolerance is achieved (eq. 7).



(7)

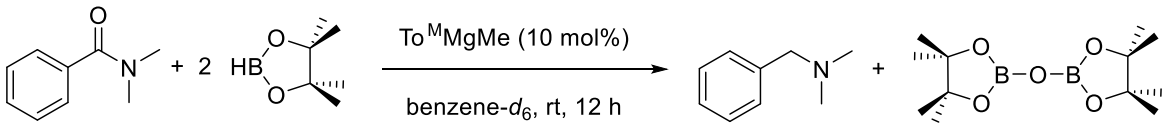
Our group has recently found that To^{M}MgMe (To^{M} = tris(4,4-dimethyl-2-oxazolinyl)phenylborate) catalytically reduces and cleaves esters with two equivalents of pinacolborane (HBpin) to give alkoxyboronic pinacol esters (ROBpin) (eq. 8) (Sadow, 2014).[11]



(8)

Results and Discussion

To^{M}MgMe is a precatalyst for the deoxygenation of amides to amines with pinacolborane as the reductant. This deoxgyenation pathway contrasts the previously observed HBpin-mediated ester cleavage and reduction with To^{M}MgMe as a catalyst. Thus, N,N-dimethylbenzamide reacts with two equivalents of pinacolborane in the presence of 10 mol% of To^{M}MgMe to give dimethylbenzylamine and pinBOBpin (eq. 9).



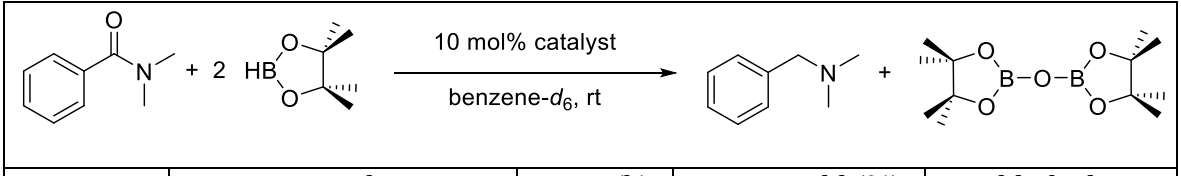
(9)

To^{M}MgMe decomposes in the presence of stoichiometric amounts of pinacolborane, so the order of addition in this reaction is important. A benzene solution of To^{M}MgMe is added to a mixture of amide and pinacolborane, or pinacolborane is injected into a benzene solution of To^{M}MgMe and amide to avoid decomposition. The background reaction of N,N-

dimethylbenzamide and two equivalents of pinacolborane gives only starting materials as observed by ^{1}H NMR after 24 hours at 120 °C. A stoichiometric reaction of To^{M}MgMe and N,N-dimethylbenzamide shows no reaction after two hours at room temperature and then decomposition of To^{M}MgMe over the next 24 hours. To^{M}MgMe reacts instantaneously with one equivalent of pinacolborane to presumably give To^{M}MgH, which rapidly decomposes to a black precipitate. With excess pinacolborane (20 equivalents), the decomposition of To^{M}MgMe in benzene is slower, and the complex To^{M}MgH$_2$Bpin can be isolated (Sadow, 2014).

Several [Mg]-Me complexes with different ligands were screened to optimize the reaction conditions of N,N-dimethylbenzamide to dimethylbenzylamine as shown in Table 1.

Table 1. Deoxygenation of N,N-dimethylbenzamide with 2 eq. pinacolborane and 10 mol% catalyst



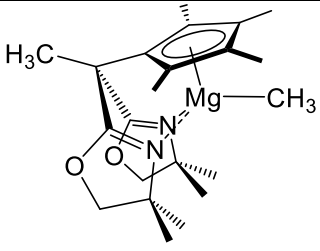
Entry	Precatalyst	Time (h)	NMR Yield (%)	Yield Ph cleav.
1	 Bo^{M}Cp^{tet}MgMe	12	25	23

Table 1 continued

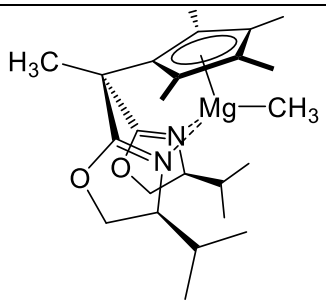
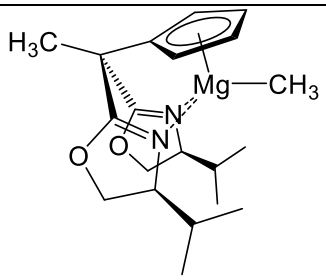
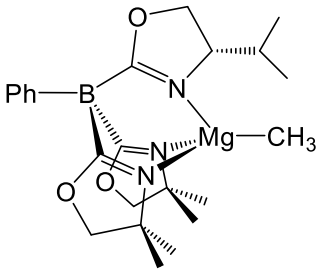
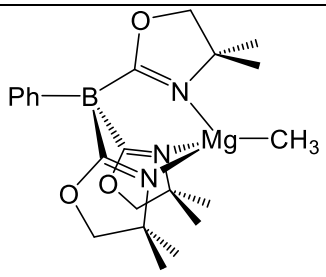
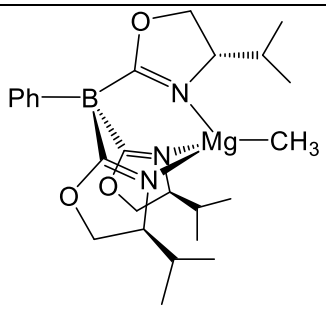
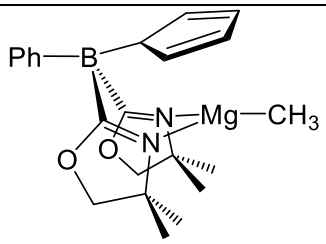
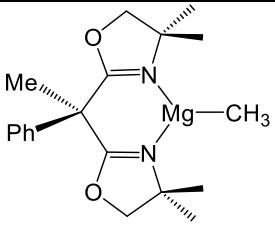
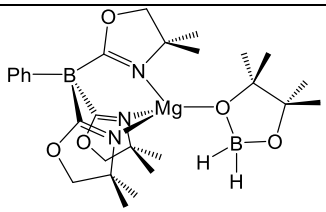
2	 Bo^{P}Cp^{tet}MgMe	26	24	-
3	 Bo^{P}CpMgMe	26	16	-
4	 To^{MP}MgMe	26	46	14
5	 To^{M}MgMe	12	54	24

Table 1 continued

6	 To^{P}MgMe	24	97	0
7	 PhB(Ox^{Me2})$_2$C$_5$H$_5$MgMe	12	10	10
8	 PhMeB(Ox^{Me2})$_2$MgMe	6	44	4
9	 To^{M}MgH$_2$Bpin	24	34	23

Surprisingly, To^{M}MgH$_2$Bpin performed relatively poorly, requiring a long reaction time and low yield, which provides convincing evidence that it is not the catalytic species.

Overall, To^{M}MgMe gives the cleanest conversion to N,N-dimethylbenzamide, even though it gave an intermediate reaction time and yield.

In all entries in Table 1, a side product was observed that appears to be the result of C–C cleavage. In the ^{1}H NMR spectrum, singlets at 2.4 and 4.5 ppm were observed in a 3:1 ratio, shifted downfield of the dimethylbenzylamine product peaks. This side product became the major product when the solvent was changed to methylene chloride (Table 2). This side product was proposed to be a partially deoxygenated amine with a cleaved aryl group (eq. 10).

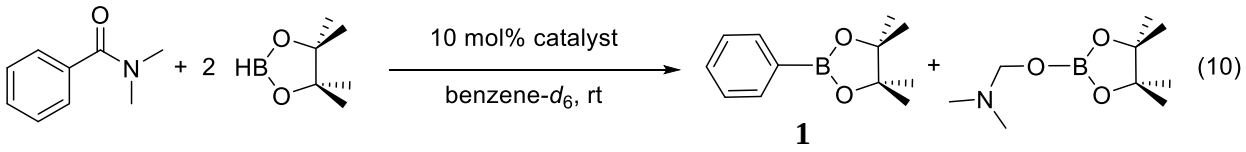
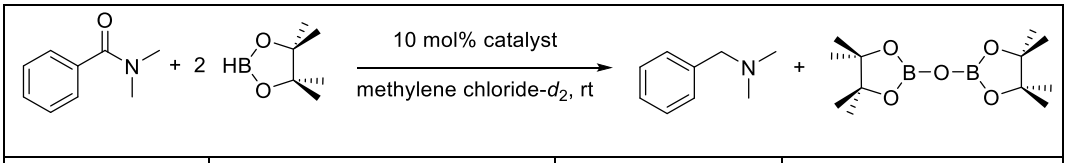


Table 2: Reduction of N,N-dimethylbenzamide in methylene chloride



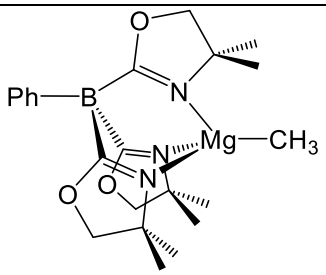
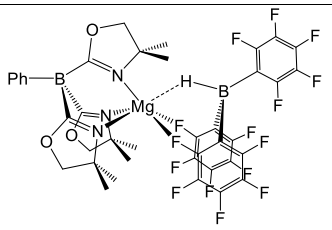
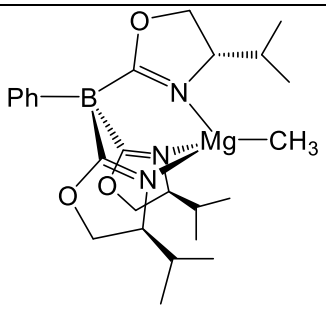
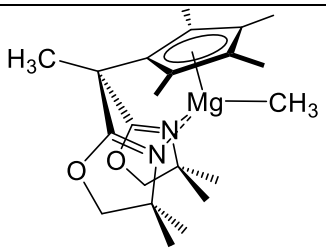
Entry	Precatalyst	NMR Yield (%)	Yield Ph cleav.
1	 To^{M}MgMe	12	23

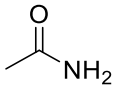
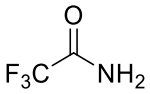
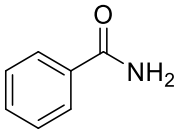
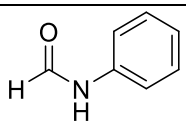
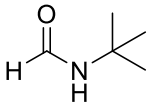
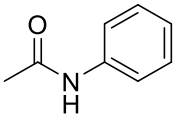
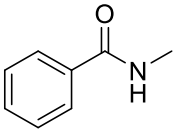
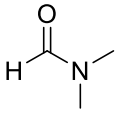
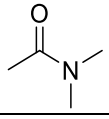
Table 2 continued

2	 $To^{M}MgHB(C_6F_5)_3$	8	2
3	 $To^{P}MgMe$	26	2
4	 $Bo^{M}Cp^{tet}MgMe$	4	-

Independently synthesized N,N-dimethylaminomethanol reacts with pinacolborane to show partial conversion to hydrogen and a species with the same ^{1}H and ^{11}B NMR resonances as **1**. Furthermore, the parent ion of **1** was identified by GC/MS in the reaction mixtures of N,N-dimethylbenzamide and two equivalents of pinacolborane with 10 mol% $To^{M}MgMe$ in CD_2Cl_2. This supports the formation of the proposed species.

Catalyst performance was found to be strongly substrate dependent. Therefore, the three highest yielding catalysts from Table 1 were used to extend the substrate scope (Table 3).

Table 3: Reduction of amides using various catalysts (10 mol%), 2 eq. HBpin, benzene-d_6

Entry	Substrate	$To^{M}MgMe$		$To^{P}MgMe$		$To^{M}MgHB(C_6F_5)_3$	
		Time (h)	NMR Yield	Time (h)	NMR Yield	Time (h)	NMR Yield
1*		24	0	4	0	24	0
2		24	0	24	0	24	0
3		24	0	24	0	24	0
4		2	66	2	36	1	3
5		24	12	24	0	24	15
6		24	12	24	0	4	11
7		12	6	24	0	30	29
8		0.17	74	1.5	53	6	62
9		12	40	24	38	30	39

Overall, $To^{M}MgMe$ performs better than $To^{P}MgMe$ or $To^{M}MgHB(C_6F_5)_3$ based on NMR yields of the amines. Tertiary amides give the highest yields compared to primary and secondary amides. Formamides are the fastest to react, followed by acetamides and

benzamides. Some product formation is observed with secondary amides. With primary amides, no amine products are observed in the ^{1}H NMR. However, hydrogen and methane are always observed.

The reactions proceed more slowly for substrates that are not very soluble in benzene. When methylene chloride is used as a solvent, the amides are completely soluble. However, the conversion of N,N-dimethylbenzamide with two equivalents pinacolborane to dimethylbenzylamine decreases, even though the [Mg]-Me compounds are stable in methylene chloride. Additionally, conversion to side product **1** increased. Therefore, we reverted to benzene-d_6 and tried varying the equivalents of pinacolborane. For secondary amides, four equivalents of pinacolborane resulted in the highest yields (Table 4). Increasing above four equivalents caused yields to decrease again. However, for tertiary amides, 20 equivalents of pinacolborane resulted in the highest yields and allowed us to decrease catalyst loading to 2 mol% To^{M}MgMe (Table 5).

Table 4. Secondary amides with 10 mol% To^{M}MgMe, 4 eq. HBpin, C_6D_6, rt

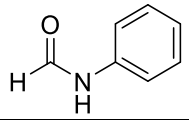
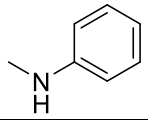
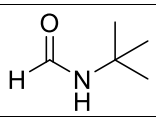
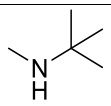
Entry	Substrate	Product	Time (h)	NMR Yield
1			48	99
2			24	72

Table 4 continued

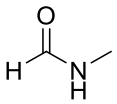
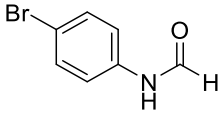
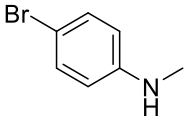
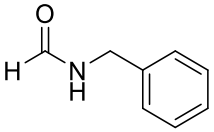
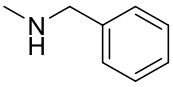
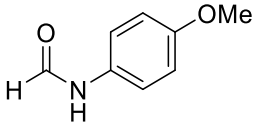
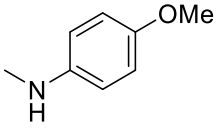
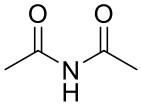
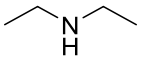
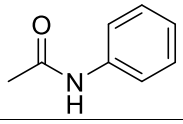
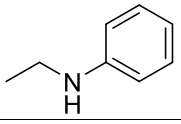
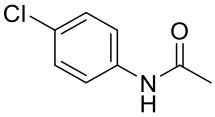
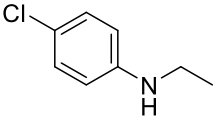
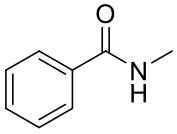
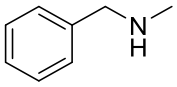
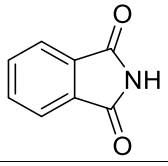
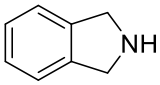
3			< 10 min	97
4			48	71
5			48	86
6			12	99
7			48	44
8			2	12
9			48	11
10			24	49
11			24	9

Table 5. Tertiary amides with 2 mol% To^{M}MgMe, 20 eq. HBpin, drop C_6D_6

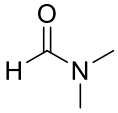
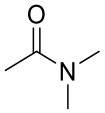
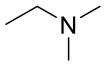
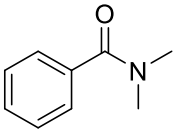
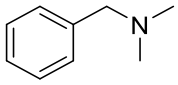
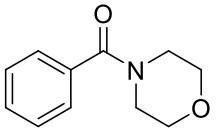
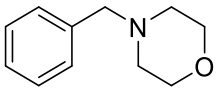
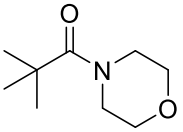
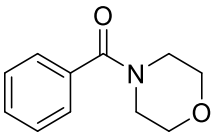
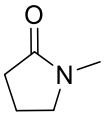
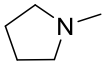
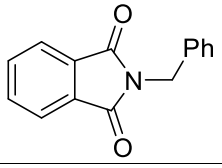
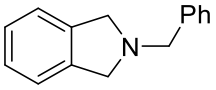
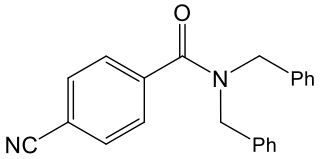
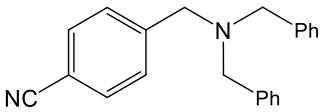
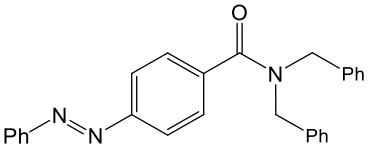
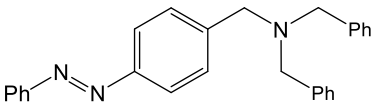
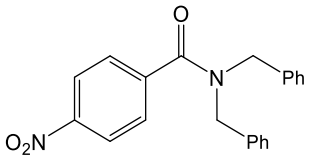
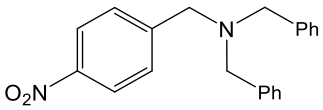
Entry	Substrate	Product	Time (h)	NMR Yield
1			0.17	77

Table 5 continued

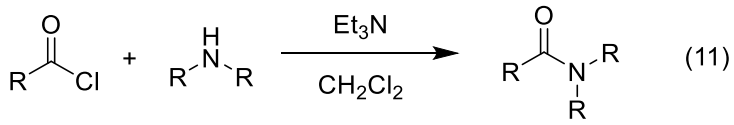
2			6 h	99
3			3 h	99
4			6 h	99
5			6	99
6			10	74
7			8	99
8[a]			15	60
9[a]			15	63
10[a]			15	83

[a]More dilute conditions because of lower solubility of amide (0.5 mL benzene)

With excess pinacolborane, the deoxygenation runs under mild conditions and tolerates a variety of functional groups that common stoichiometric reductants such as LAH

do not. An exception is N,N-dimethyl acrylamide, which rapidly polymerizes in the presence of To^{M}MgMe. For entries 10–13 in Table 4, the starting amide had a very low solubility in neat pinacolborane; therefore, these reactions were run at more dilute conditions by adding benzene.

Many of the amides were not commercially available and were synthesized using a procedure similar to that used by Beller, where an acid chloride was reacted with a secondary amine to give the tertiary amide (eq. 11).[10a]



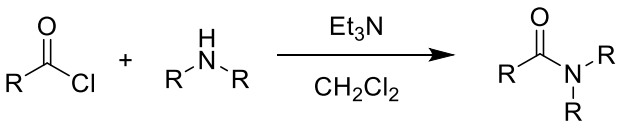
(11)

Conclusions

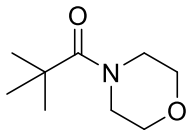
Overall, we have the first example of magnesium-catalyzed reduction of amides, as well as the first example of amide reduction using pinacolborane, not silanes. This system is attractive because all reactions run at room temperature. Tertiary amides can be reduced in neat pinacolborane without the presence of solvent. Further work should be done to study the mechanism of this reaction because little work has been done to study the mechanism of other amide deoxygenation systems, and understanding the mechanism would help us understand how to optimize reaction conditions and prevent side product formation. We also find it interesting that magnesium is able to perform catalytically in this system and does not stop at a Mg–O species.

Experimental Section

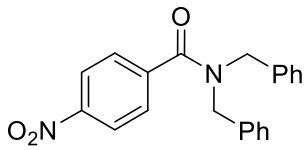
General procedure for preparation of amides[10a]



The acid chloride (0.010 mol) was added in one portion to the amine (0.0110 mol) and triethylamine (0.0125 mol) in methylene chloride (20 mL) at room temperature, resulting in a rapidly boiling solution. The mixture was stirred at room temperature for one hour and was then diluted with methylene chloride (30 mL). The solution was transferred to a separatory funnel and was washed with 1 M HCl (50 mL). The organic layer was filtered on a short silica gel column and then the solution was dried over sodium sulfate. The solution was filtered and the solvent was removed. Some products were oils that solidified after standing overnight.

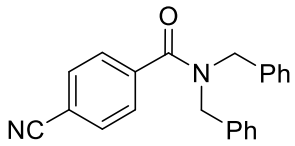


2,2-dimethyl-1-morpholinopropanone: **:** ^{1}H NMR (benzene-d_6, 600 MHz, 25 °C): 3.27 (s, 8 H, N(CH_2CH_2)$_2$O), 1.10 (s, 9 H, C(CH_3)$_3$). ^{15}N{^{1}H} NMR (benzene-d_6, 60 MHz, 25 °C): –273.4 (*N*(CH$_2$CH$_2$)$_2$O). ^{13}C{^{1}H} NMR (benzene-d_6, 151 MHz, 25 °C): 175.37, 66.89, 45.91, 38.50, 28.39 (-C(*C*H$_3$)$_3$).

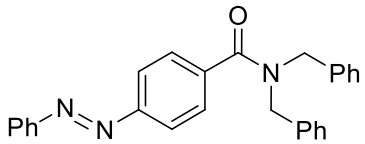


N,N-dibenzyl-4-nitrobenzamide: ^{1}H NMR (benzene-d_6, 600 MHz, 25 °C): 7.59 (d, 2 H, $^{2}J_{HH}$ = 7.8 Hz, *meta*-C*H*), 7.20 (br s, 4 H, -N(CH$_2$C$_6$*H*$_5$)$_2$ (*ortho*-C*H*)), 7.11 (br s, 4 H, -

N($CH_2C_6H_5$)$_2$ (*meta*-C*H*)), 7.04 (d, 2 H, $^2J_{HH}$ = 8.4 Hz, *ortho*-C*H*), 6.81 (br s, 2 H, -N($CH_2C_6H_5$)$_2$ (*para*-C*H*)), 4.64 (s, 2 H, -N(C$H_2C_6H_5$)$_2$), 3.91 (s, 2 H, -N(C$H_2C_6H_5$)$_2$). ^{15}N{^{1}H} NMR (benzene-d_6, 60 MHz, 25 °C): -12.3 (-$C_6H_4NO_2$). ^{13}C{^{1}H} NMR (benzene-d_6, 151 MHz, 25 °C): (many peaks overlap with benzene-d_6 resonances) 169.69, 148.37, 142.33, 137.38, 136.48, 130.82, 129.21, 129.03, 128.99, 128.35, 128.02, 127.63, 126.95, 51.18 (-N(*C*$H_2C_6H_5$)$_2$), 47.34 (-N(*C*$H_2C_6H_5$)$_2$).



N,N-dibenzyl-4-cyanobenzamide: ^{1}H NMR (chloroform-*d*, 600 MHz, 25 °C): 7.58–7.01 (m, 14 H, aromatic C-*H*), 4.63 (s, 2 H, (-N(C$H_2C_6H_5$)$_2$), 4.25 (s, 2 H, (-N(C$H_2C_6H_5$)$_2$). ^{15}N resonances not detected by ^{15}N{^{1}H} HMBC experiments. ^{13}C{^{1}H} NMR (chloroform-*d*, 151 MHz, 25 °C): 170.45, 167.56, 140.49, 136.39, 133.93, 132.55, 132.29, 130.55, 130.41, , 128.94, 128.57, 128.09, 127.93, 127.48, 126.86, 118.10, 116.68, 113.61, 51.53, 48.94, 47.42.



N,N-dibenzyl-4-(phenyldiazenyl)benzamide: ^{1}H NMR (benzene-d_6, 600 MHz, 25 °C): 7.97 (d, 2 H, $^2J_{HH}$ = 7.2 Hz), 7.83 (d, 2 H, $^2J_{HH}$ = 8.4 Hz), 7.51 (d, 2 H, $^2J_{HH}$ = 8.4 Hz), 7.19 – 7.09 (br m, 13 H), 4.73 (br s, 2 H, -C$H_2C_6H_5$), 4.16 (br s, 2 H, -C$H_2C_6H_5$). ^{15}N{^{1}H} NMR (benzene-d_6, 60 MHz, 25 °C): -272.35 (-*N*=*N*C_6H_5). ^{13}C{^{1}H} NMR (benzene-d_6, 151 MHz, 25 °C): (peaks overlap with benzene-d_6 resonances) 171.00, 170.72, 155.00, 153.99, 153.36, 153.14, 139.29, 137.85, 137.17, 135.27, 131.50, 129.37, 129.02, 128.84, 128.35, 128.14,

127.98, 127.75, 127.45, 127.16, 123.43, 123.33, 120.80, 120.45, 51.38 (-N($CH_2C_6H_5$)$_2$), 47.32 (-N($CH_2C_6H_5$)$_2$).

General procedure for NMR-scale catalytic amide reductions To^{M}MgMe (0.05 eq, 0.0039 mmol) was dissolved in 0.5 mL benzene-d_6 and added to the amide (1 eq, 0.078 mmol), pinacolborane (4 eq, 0.31 mmol) and tetrakis(trimethylsilyl)silane standard (0.05 eq, 0.0039 mmol). Reactions were monitored by ^{1}H and ^{11}B NMR.

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CHAPTER 4

Derivatization of pyrene for carbon nanotube functionalization

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Abstract

Pyrene, a polycyclic aromatic hydrocarbon, is functionalized with tertiary amine groups following a simple synthetic route from commercially available pyrene precursors. These pyrene compounds, including N-ethyl-N-(pyren-4-ylmethyl)ethanamine, N,N-diethyl-4-(pyren-4-yl)butanamine, and N,N-bis(pyren-4-ylmethyl)ethanamine were prepared to be adsorbed onto multi-walled carbon nanotubes as a catalyst. Various conditions for coronene functionalization were also screened.

§ Other authors' contributions

Chi Liu: Collaborated on coronene functionalization screening and pyrene functionalization. Adsorption studies of pyrene on MWCNTs.

Introduction

Heterogeneous catalysts are often favored by industry over homogeneous catalysts because of simple catalyst recovery and increased catalyst stability. Important industrial

processes that utilize heterogeneous catalysts include the Haber-Bosch process, Ziegler-Natta olefin polymerization, and the Fischer-Tropsch reaction of syngas to hydrocarbons.[1] Drawbacks of heterogeneous catalysts compared to homogeneous catalysts include lack of selectivity and activity. Heterogeneous catalysts are difficult to study and characterize by standard spectroscopic methods, which makes studying the active sites and mechanism difficult. On the other hand, homogeneous catalysts can be characterized by spectroscopic techniques, such as NMR, IR, UV-Vis, and X-ray crystallography and often exhibit high activity and selectivity. Our strategy is to synthesize and characterize small-molecule catalysts that can then be adsorbed onto a solid support, such as multi-walled carbon nanotubes (MWCNTs).

Multi-walled carbon nanotubes have been covalently functionalized in the past by exploiting defects on the nanotube surface, but the products are difficult to characterize and functionalization is limited. Commonly, MWCNTs are oxidized with nitric acid to form carboxylic acid groups on the surface which can then be further functionalized. However, these harsh conditions are not selective and often shorten the chain length of the nanotubes. In 2009, Schögl reported an alternative route where MWCNTs are reacted with excess *n*-BuLi to deprotonate C–H bonds near defects in the nanotubes.[2] 2-bromotriethylamine is added to form MWCNTs functionalized with a tertiary amine group. Catalytic activity is tested for transesterifaction of glyceryl tributyrate with methanol and achieved a 77% yield after eight hours. Characterization of the functionalized nanotubes was difficult so methods such as electron microscopy and acid-base titrations were used to gain information about the structure.

Noncovalent functionalization of nanotubes allows the characterization and study of the catalytic species before adsorption onto the carbon surface. In 2001, Dai reported anchoring protein groups to single-walled carbon nanotubes (SWCNTs).[3] Pyrene is functionalized with a succinimidyl ester group, and is then irreversibly adorbed on the sidewall of the SWCNTs via π-stacking. Amine groups on the proteins then react with anchored succinimidyl ester groups to form amide bonds for protein immobilization. Gray recently reported noncovalent immobilization of pyrene-based electrocatalysts on carbon electrodes (Fig. 1).[4]

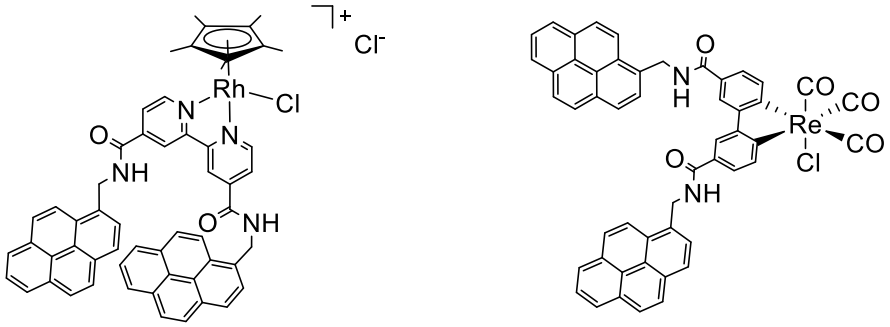
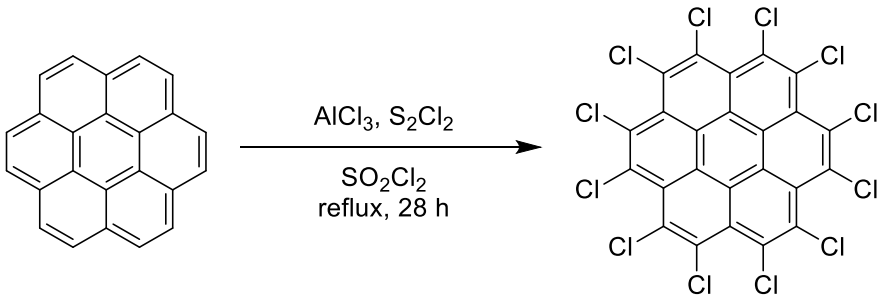


Fig. 1: Rh and Re pyrene-based electrocatalysts

Pyrene groups were attached to bipyridine, which then reacted to form complexes with their Rh or Re catalysts. The functionalized pyrene groups were easily adsorbed onto carbon electrodes by soaking the electrodes in a solution of the functionalized pyrene in methylene chloride, followed by washing with acetonitrile.

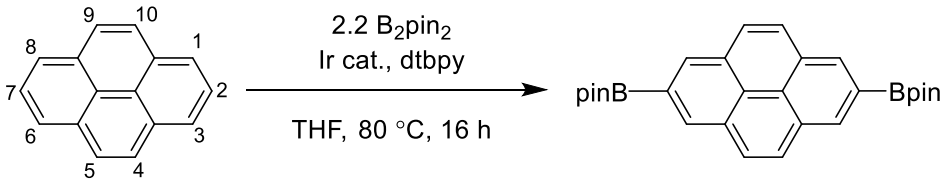
Functionalization of polyaromatic compounds such as coronene and pyrene can be challenging because of the lack of functional groups. Coronene is desirable to use because of the strong π-interaction with the carbon support, but it is difficult to functionalize, and coronene derivatives are not commercially available. Michie reports the chlorination of coronene to perchloronene.[5] Coronene was refluxed with $AlCl_3$ and S_2Cl_2 in SO_2Cl_2 to get the perchlorinated product (eq. 1).



(1)

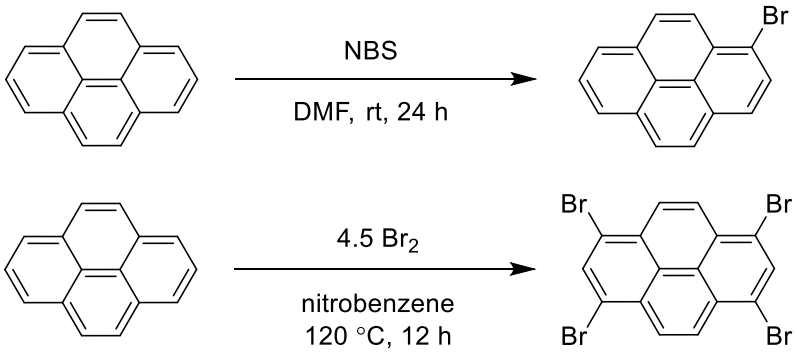
Unfortunately, the reaction cannot be stopped before all positions are substituted.

Pyrene derivatives are commercially available and functionalization of pyrene is less challenging. Selective borylation of pyrene is reported on the 2,7 positions using pinacolato diboron and an iridium catalyst, which is useful for making symmetrically functionalized pyrene derivatives (eq. 2).[6]



(2)

Pyrene is brominated using NBS[7] or Br_2[8] to give mono- or tetra-brominated pyrene as shown in Scheme 1.



Scheme 1: Bromination of pyrene

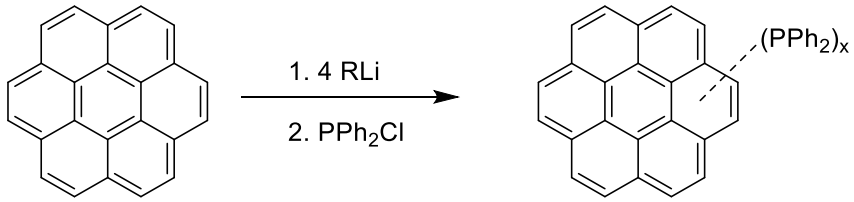
Large aromatic systems such as coronene and pyrene are ideal to serve as the "linker" to adsorb to the carbon surface because of their strong pi-pi interactions with the carbon surface.

Results and Discussion

Our focus was to synthesize tertiary amine-substituted polyaromatic compounds that would adsorb on carbon nanotubes so that simple isomerization reactions catalyzed by tertiary amines could be studied.

The first attempts focused on the functionalization of coronene because of its strong π-stacking interactions. Based on Schögl's report on using *n*-BuLi to deprotonate sites on multi-walled carbon nanotubes, we tried extending that strategy to coronene. We were encouraged to find that coronene appeared to be deprotonated by benzyl potassium. The formation of toluene was observed when benzyl potassium was added to a solution of coronene in benzene-d_6. Different deprotonation conditions were then screened and are summarized in Table 1. Different alkyllithium reagents were added to a solution of coronene at low temperature, and then the solution was warmed to room temperature and stirred for one hour before adding chlorodiphenylphosphine, which was used as a ^{31}P NMR handle to evaluate if substitution had occurred. All deprotonation conditions tested gave mixtures of products that were difficult to characterize.

Table 1: Attempts at deprotonation and substitution of coronene



Deprotonation Reagents	Solvent	Temp (˚C)	Color change with addition of RLi	^{31}P NMR results with PPh_2Cl
LDA	Et_2O	–78 to rt	No color change	Doublets at 34 and –23 ppm Singlet at 23 ppm
nBuLi	THF	–78 to rt	At -78, turned blue, then purple	Doublets at 34 and –23 ppm
nBuLi/TMEDA	THF	–78	purple	Doublets at 36 and –21 ppm Singlets at –16 and 111
nBuLi/TMEDA	Et_2O	–78 to rt	Yellow at -78, turned green/grey at rt	Doublets at 36 and –21 ppm Singlets at –16 (large) and 110
tBuLi	Et_2O	–78 to rt	No color change, stayed yellow	Two doublets at 36 and –21 ppm Singlet at 81

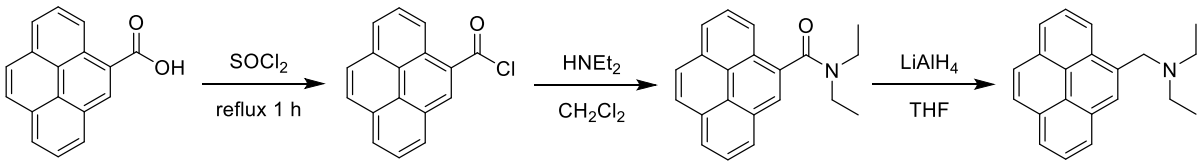
Table 1 continued

tBuLi/TMEDA	Et_2O	–78 to rt	No color change, stayed yellow	Two doublets at 36 and –21 ppm Singlet at 81
nBuLi/KOtBu	Et_2O	–78 to rt	At -78, turned bright blue immediately. At rt, color changed to pink, then yellow/green, then yellow after 1h	Two doublets 36 and –21 ppm Singlet 110 ppm
tBuLi/KOtBu	Et_2O	–78 to rt	At -78, turned pink immediately. At rt, color changed to purple, then green/black, then purple, then yellow after 2h	Sample decomp in $CDCl_3$ Mult. peaks at 110, 85, 44, 31, –14

Because of the challenges encountered trying to functionalize coronene, functionalized pyrene molecules were synthesized from commercially available pyrene precursors. Tertiary amine-substituted pyrene compounds were prepared to then adsorb onto MWCNTs and test for catalytic activity. The amine groups were attached to pyrene via different chain lengths to study the effect of flexibility of the molecule or distance of the amine group from pyrene on catalytic activity.

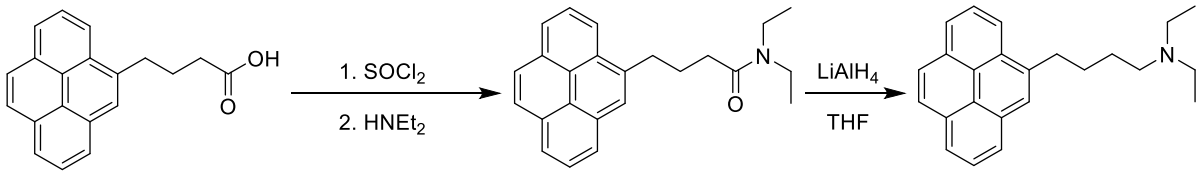
N-ethyl-N-(pyren-4-ylmethyl)ethanamine was synthesized from pyrene carboxylic acid. The acid chloride was formed by refluxing with thionyl chloride, followed by the addition of diethylamine to form the amide, which was then reduced with lithium aluminum hydride to form the tertiary amine (Scheme 2). The product was isolated as a yellow oil in

good yield (66%) after aqueous workup and was characterized by ^{1}H NMR, ^{13}C NMR, ^{15}N NMR, and IR spectroscopy.



Scheme 2: Synthesis of N-ethyl-N-(pyren-4-ylmethyl)ethanamine

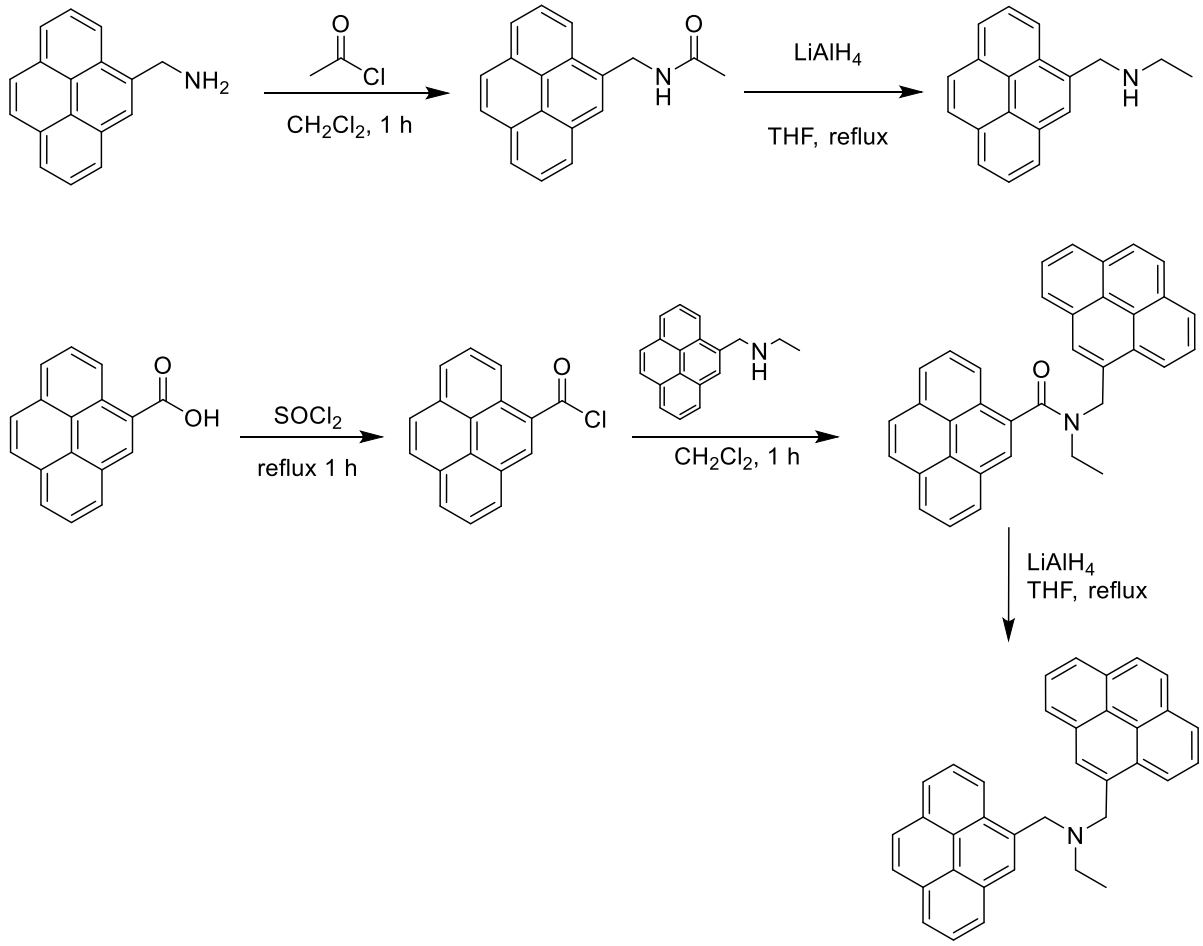
N,N-diethyl-4-(pyren-4-yl)butan-1-amine was prepared from pyrene butyric acid in a similar method to that described for N-ethyl-N-(pyren-4-ylmethyl)ethanamine (Scheme 3). The product was isolated as a brown oil after aqueous workup, but several small impurities remained and could not be separated.



Scheme 3: Synthesis of N,N-diethyl-4-(pyren-4-yl)butan-1-amine

In addition, a tertiary amine containing two pyrene groups was also synthesized because the presence of two pyrene groups could increase the ability to π-stack on the MWCNTs. First, the secondary amine N-(pyren-4-ylmethyl)ethanamine was synthesized from commercially available aminomethylpyrene (Scheme 4). Acetyl chloride was added to form the secondary amide, followed by reduction of the amide to the secondary amine with lithium aluminum hydride. Pyrene carboxylic acid was then converted to the acid chloride

using thionyl chloride, and N-(pyren-4-ylmethyl)ethanamine was added to form the tertiary amide containing two pyrene groups. The tertiary amide has low solubility, so the aqueous workup should be done quickly or the product will crash out of solution. The amide is then reduced with $LiAlH_4$ to the tertiary amine product, N,N-bis(pyren-4-ylmethyl)ethanamine, and isolated as a yellow solid.

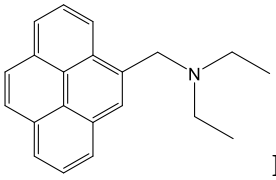


Scheme 4: Synthesis of N,N-bis(pyren-4-ylmethyl)ethanamine

Conclusions

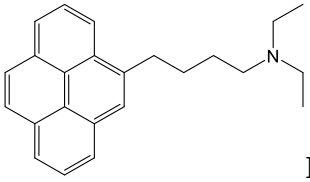
Tertiary-amine substituted pyrene compounds were prepared and characterized following simple organic chemistry techniques. Future experiments will explore the adsorption of these pyrene compounds onto MWCNTs and will test their catalytic activity.

Experimental Section

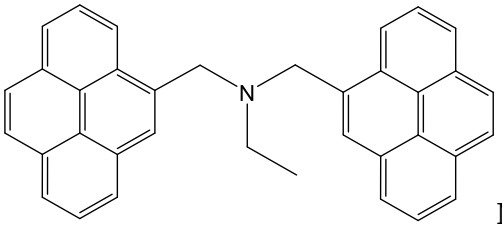


N-ethyl-N-(pyren-4-ylmethyl)ethanamine Pyrene carboxylic acid (1.00 g, 0.00406 mol) was placed in a 500 mL three-necked round bottom flask under argon and fitted with a condenser. Thionyl chloride (5.0 mL, 0.069 mol) was added and the slurry was heated to reflux at 80 °C for two hours. The excess thionyl chloride was removed by distillation. The flask was cooled to room temperature, and then dry methylene chloride (50 mL) was added to dissolve the yellow solid. Diethylamine (0.84 mL, 0.00810 mol) was dissolved in methylene chloride (10 mL) and added dropwise. The solution was quenched with 50 mL 10% NaOH (aq) and was transferred to a separatory funnel and washed with additional 10% NaOH (aq) (3 × 100 mL) and then NaCl (aq) (100 mL). The organic layer was dried over sodium sulfate and was then filtered and the solvent removed to give the amide as a brown oil that solidified into a tan solid after standing overnight. Lithium aluminum hydride (1.20 g, 0.0316 mol) was added to a 500 mL three-necked round bottom flask under argon and fitted with a condenser. The flask was cooled to 0 °C and THF (150 mL) was added via cannula. The amide product was dissolved in THF (100 mL) and added slowly to the LAH slurry at 0 °C. The solution was warmed to room temperature and then heated to reflux for 24 hours. While refluxing, the solution changed from dark purple to dark

black/green. The solution was then cooled to 0 °C and quenched by the dropwise addition of 1 mL water, 1 mL 10% NaOH (aq), and 3 mL water. After quenching, the solution was cloudy yellow. $MgSO_4$ was added to dry the solution, and the mixture was then filtered to give a clear yellow solution. The solvent was removed to yield a brown oil. To purify further, the oil was dissolved in diethyl ether (250 mL) and 1 M HCl (150 mL) was added. The ammonium salt immediately partitioned into the aqueous layer. The mixture was transferred to a separatory funnel and the yellow aqueous layer was washed with diethyl ether (3 × 100 mL). 10 % NaOH (aq) was then added to the aqueous layer to neutralize remaining acid and form the amine. The solution turned cloudy white once neutralized (about 300 mL NaOH). The solution was then extracted with diethyl ether (4 × 200 mL). The organic layer was dried with sodium sulfate and the solvent was removed to give a yellow oil. Yield: 0.8198 g (66%). ^{1}H NMR (chloroform-*d*, 600 MHz, 25 °C): 8.47 – 7.85 (m, 9 H, aromatic pyrene C–H), 4.12 (s, 2 H, -C*H*$_2$N(CH$_2$CH$_3$)$_2$), 2.53 (q, 4 H, $^4J_{HH}$ = 7.2 Hz, -CH$_2$N(C*H*$_2$CH$_3$)$_2$), 1.01 (t, $^3J_{HH}$ = 6.6 Hz, -CH$_2$N(CH$_2$C*H*$_3$)$_2$). ^{15}N NMR (chloroform-*d*, 60 MHz, 25 °C): -330.5 (-CH$_2$*N*(CH$_2$CH$_3$)$_2$). ^{13}C NMR (chloroform-*d*, 151 MHz, 25 °C): 133.89, 131.45, 131.06, 130.61, 129.89, 128.46, 128.08, 127.58, 127.13, 127.00, 125.86, 125.11, 124.99, 124.99, 124.95, 124.52, 124.21 (16 C, pyrene C), 56.19 (-*C*H$_2$N(CH$_2$CH$_3$)$_2$), 47.12 (-CH$_2$N(*C*H$_2$CH$_3$)$_2$), 11.82 (-CH$_2$N(CH$_2$*C*H$_3$)$_2$). IR (oil between two NaCl plates, cm^{-1}): 3039 m, 2967 s, 2932 m sh, 2871 m, 2800 m, 2720 w, 1919 w, 1791 w, 1679 w, 1603 w, 1588 w, 1508 w, 1454 m, 1417 w, 1382 m, 1311 w, 1289 w, 1259 w, 1199 m, 1182 m, 1166 m, 1119 w, 1064 m, 1037 w sh, 90 w, 956 w, 845 s, 819 w, 768 w, 754 m, 723 w, 709 s, 678 m.



N,N-diethyl-4-(pyren-4-yl)butan-1-amine Pyrene butyric acid (0.989 g, 0.00343 mol) was placed in a three-necked round bottom flask fitted with a condenser and addition funnel. Thionyl chloride (2.0 mL, 0.0274 mol) was added and the slurry was heated to reflux. The slurry turned dark red after heating at 60 °C for two hours. Excess thionyl chloride was removed by distillation. The solid was then dissolved in 25 mL dry methylene chloride, and diethylamine (1.06 mL, 0.0103 mol) dissolved in 50 mL methylene chloride was added dropwise slowly via the addition funnel. The solution was then quenched with 10% NaOH (aq) (50 mL) and then transferred to a separatory funnel. The organic layer was diluted with methylene chloride to 500 mL, and then the solution was washed with 10% NaOH (aq) (3 × 150 mL), then 1 M HCl (3 × 100 mL), and then NaCl (aq) (3 × 150 mL). The organic layer was then dried over sodium sulfate, then filtered and the solvent removed to give the amide as a red solid. Lithium aluminum hydride (1.04 g, 0.0274 mol) was added to a three-necked 500 mL flask fitted with a condenser and addition funnel. The flask was cooled to 0 °C and dry THF (100 mL) was added. The amide product was dissolved in dry THF (100 ML) and added slowly to the LAH slurry via the addition funnel while maintaining the temperature at 0 °C. The solution was then warmed to room temperature and then heated to reflux for 14 hours. The solution was then cooled to 0 °C and then quenched by the slow dropwise addition of 1.0 mL water, 1.0 mL 10% NaOH (aq), and 3.0 mL water. Magnesium sulfate was added to dry the solution, and then the dark red solution was filtered and the solvent was removed.



N,N-bis(pyren-4-ylmethyl)ethanamine Pyrene methylamine•HCl (1.33 g, 0.00497 mol) was added to a 500 mL flask. Methylene chloride (250 mL) was added to partially dissolve the ammonium salt. Triethylamine (1.52 mL, 0.0109 mol) was added and the solution was stirred for 1 hour, until the pyrene methylamine completely dissolved. Acetyl chloride (0.337 mL, 0.00472 mol) was added and the solution was stirred at room temperature for 1 hour. The orange solution was washed with 1 M HCl (3 × 150 mL) and then NaCl (aq) (2 × 300 mL). The organic layer was dried over sodium sulfate overnight. The solvent was removed to give the amide as a yellow/white powder. Lithium aluminum hydride (1.47 g, 0.388 mol) was added to a three-necked 1 L round bottom flask fitted with a condenser and addition funnel and cooled to 0 °C. Dry THF (200 mL) was added. The amide was dissolved in THF (100 mL) and was added slowly to the LAH slurry via addition funnel. The solution was heated to reflux for 16 hours. The dark black/green solution was cooled to 0 °C and was quenched with 1.5 mL water, 1.5 mL 10% NaOH (aq), and 4.5 mL water. Magnesium sulfate was added and the solution was filtered and the solvent was removed to give the amine as a yellow oil. The amine was then dissolved in methylene chloride (250 mL) and transferred to a separatory funnel and washed with 10% NaOH (3 × 100 mL) and NaCl (aq) (2 × 100 mL). The yellow organic layer was dried over sodium sulfate and the solvent was removed to give a yellow oil. Pyrene carboxylic acid (0.600 g, 0.00244 mol) was added to a three-necked 500 mL round bottom flask fitted with a condenser and addition funnel and attached to an oil bubbler. Thionyl chloride (6.0 mL, 0.0826 mol) was added and the slurry was heated to reflux for 1 hour. The excess thionyl

chloride was removed by distillation. The yellow solid was then dissolved in dry methylene chloride (100 mL). The pyrenemethylethanamine was dissolved in methylene chloride (50 mL) and was added dropwise to the solution via the addition funnel. The solution was stirred for 1 hour and then quenched with 10% NaOH (aq) (50 mL). The solution was washed with 1 M HCl (2 × 100 mL) and NaCl (aq) (2 × 100 mL). The yellow organic layer was dried with sodium sulfate, and then immediately filtered and the solvent was removed (the amide product begins to crash out of methylene chloride over time, so the workup should be done quickly). The product is completely soluble in DMF and DMSO. Lithium aluminum hydride (0.470 g, 0.0124 mol) was added to a three-necked 1 L round bottom flask fitted with a condenser. The flask was cooled to 0 °C and THF (250 mL) was added. The N-ethyl-N-(pyren-4-ylmethyl)pyrene-4-carboxamide (0.755 g, 0.00155 mol) was slowly added to the LAH slurry as a solid in four portions while maintaining the temperature at 0 °C. The solution was warmed to room temperature. The orange solution was refluxed for 24 hours and then cooled to 0 °C and quenched with 0.5 mL water, 0.5 mL 10% NaOH (aq), and 1.5 mL water. Magnesium sulfate was added to dry the solution, and then the solution was filtered and the solvent was removed.

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CHAPTER 5

Conclusions

A new class of mixed monoanionic cyclopentadienyl-bis(oxazoline) ligands were prepared, including H{Bo^{M}Cp}, H{Bo^{M}Cp^{tet}}, H{Bo^{P}Cp}, and H{Bo^{P}Cp^{tet}}. These ligands were found to support many metal complexes with Mg, Zn, Ti, and Zr. {Bo^{M}Cp}MgCH$_3$, {Bo^{M}Cp^{tet}}MgCH$_3$, {Bo^{P}Cp}MgCH$_3$, and {Bo^{P}Cp^{tet}}MgCH$_3$ catalyze the hydroboration of ketones and esters using pinacolborane. {Bo^{M}Cp}Zr(NMe$_2$)$_3$, {Bo^{M}Cp}MgCH$_3$, and {Bo^{M}Cp^{tet}}MgCH$_3$ are also efficient catalysts for the hydroamination of aminoalkenes, but these compounds are not as reactive for hydroamination as compounds made with the borate ligands of the type [PhB(Ox)$_2$(C$_5$H$_4$)]. Further work should be done to determine the enantioselectivity of {Bo^{P}Cp}MgCH$_3$ and {Bo^{P}Cp^{tet}}MgCH$_3$ in hydroboration reactions to make chiral alcohols and hydroamination reactions to make enantiopure cyclized aminoalkenes. More ligands of this type can easily be developed; varying the R groups on the oxazoline rings or the backbone of the ligand could impart very different reactivity.

The observed reduction of secondary and tertiary amides with pinacolborane and [Mg] catalysts is promising. Mechanistic studies, including kinetics, should be done to provide valuable insight into the mechanism of this reaction. Further work should be done to understand the phenyl-cleavage byproduct observed in the reduction of N,N-dimethylbenzamide.

Several functionalized pyrene compounds were synthesized with tertiary amine groups. Future plans include adsorption of these compounds onto multi-walled carbon

nanotubes and testing their ability as heterogeneous catalysts once adsorbed. Other functional groups could be easily incorporated onto pyrene. For example, pyrene could become part of the backbone of H{Bo^{M}Cp} or H{Bo^{M}Cp^{tet}} (Fig. 1). This would provide a way to make heterogeneous catalysts that include H{Bo^{M}Cp} or H{Bo^{M}Cp^{tet}} moieties, which would be interesting to study.

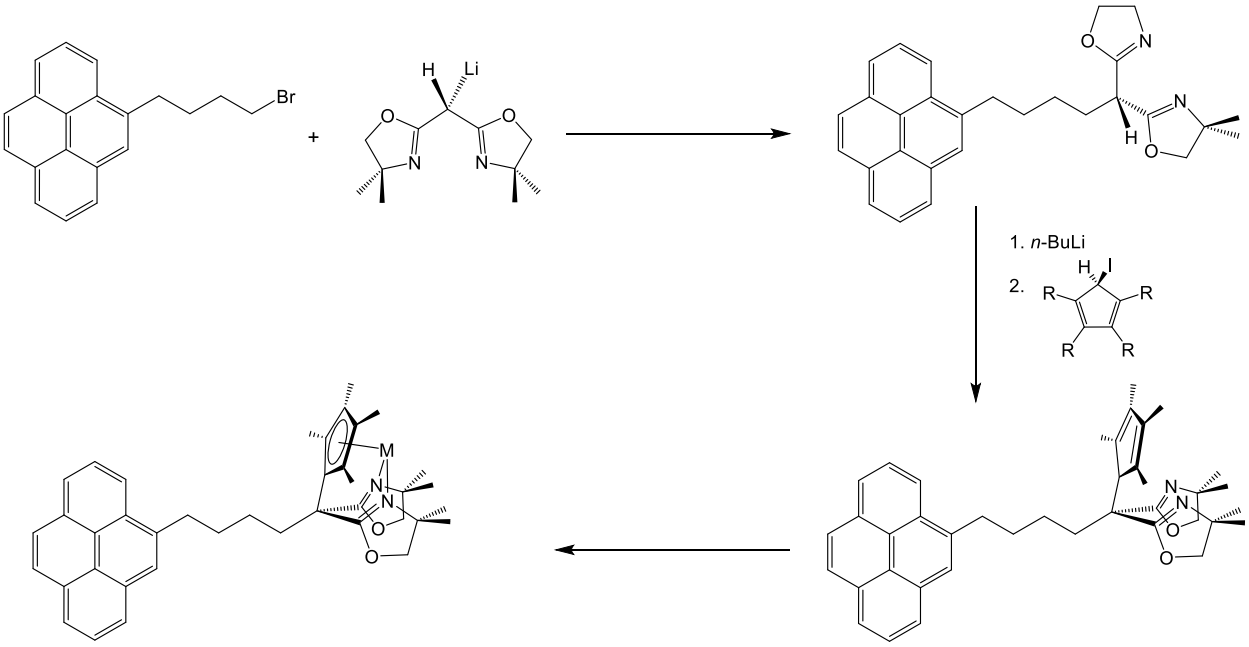

Figure 1: Proposed synthetic route to {Bo^{M}Cp^{tet}} on pyrene