Synthesis and reactivity of novel organo main group and rare earth metal complexes

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Synthesis and reactivity of novel organo main group and rare earth metal complexes

by

Jing Zhu

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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Program of Study Committee:
Aaron D. Sadow, Major Professor
Ning Fang
Javier Vela

Iowa State University
Ames, Iowa
2014

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Dedicated to my grandparents, my Mom, my Dad, and my family.
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**Abstract.**

An ambiphilic bis(oxazolinyl)borane proligand and zinc dialkyls react via alkyl group transfer or \(\beta\)-hydrogen abstraction. Both alkyl abstraction and \(\beta\)-hydrogen abstraction processes can be observed, and products vary with coordinating solvent or non-coordinating solvent. We interpret this by proposing that the latter process is favoured by formation of a bis(oxazolinyl)borane-zinc adduct that positions a \(\beta\)-hydrogen in the proximity of the Lewis acid center.

**Introduction.**

Reactions of hydrocarbyl metal compounds and Lewis acids such as tris(perfluorophenyl)borane typically proceed by anionic group abstraction to form cationic or zwitterionic metal complexes.\(^{1}\) These reactions have been studied primarily with \(\beta\)-hydrogen-free groups (H, Me, CH\(_2\)Ph), perhaps because transition-metal alkyls containing \(\beta\)-H often undergo elimination. In contrast, main group organometallics including Et\(_2\)Zn undergo \(\beta\)-elimination only under unusual photolytic or strongly
reducing conditions. Therefore, the interaction between a Lewis acid and a main group metal hydrocarbyl could provide insight into the nucleophilic sites of metal alkyls. These reactions could also clarify pathways concealed under catalytic conditions. For example, olefin polymerization systems contain Lewis acids, main group organometallics (e.g., \( \text{Et}_2\text{Zn} \)), and metal-alkyl chains containing \( \beta \)-hydrogen. While unsaturated polymer end groups are typically associated with \( \beta \)-elimination, \( \beta \)-abstraction also provides olefinic by-products.

In fact, \( \text{B}(\text{C}_6\text{F}_5)_3 \) or \([\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]\) react with main group organometallic compounds containing \( \beta \)-hydrogen through at least two pathways. \( \text{Et}_2\text{Zn} \) and \( \text{B}(\text{C}_6\text{F}_5)_3 \) react to give \( \text{EtZn}(\mu-\text{Et})\text{B}(\text{C}_6\text{F}_5)_3 \), but treatment with \([\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]\) gives \( \text{Ph}_3\text{CH} \), \( \text{C}_2\text{H}_4 \), and \([\text{EtZn}][\text{B}(\text{C}_6\text{F}_5)_3]\). Sterics may affect \( \beta \)-hydrogen vs. alkyl group abstraction; thus \((\kappa^2\text{-bzmp})\text{AlEt}_2\) (bzmp = bis(pyrazolyl)methane) and \( \text{B}(\text{C}_6\text{F}_5)_3 \) react by ethyl-group abstraction while the isobutyl aluminum compound gives isobutene and \( \kappa^2\text{-} (\text{bzmp})\text{Al}(\text{i-Bu})\text{HB}(\text{C}_6\text{F}_5)_3 \). The \( \beta \)-abstractions are not limited to alkyls, and a zinc amide and \( \text{B}(\text{C}_6\text{F}_5)_3 \) react via \( \beta \)-hydrogen abstraction. Furthermore, the proposed mechanisms of Meerwein-Pondorff-Verley reductions and Oppenhauer oxidations involve transfer of a \( \beta \)-hydrogen from a main group alkoxide to the electrophilic carbon of a coordinated carbonyl, and such reactions may be compared to a Lewis acid mediated \( \beta \)-hydrogen abstraction.

Interactions of borane-containing ligands with organometallics are interesting in this context, and recent studies of ambiphilic ligands in organometallic chemistry have described M-B bond formations as well as alkyl group abstractions. In the chemistry of
oxazolinylboranes, PhB(OxMe$_2$)$_2$ (OxMe$^2$ = bis(4,4-dimethyl-2-oxazolinyl)) and AlMe$_3$ react to form methide-abstracted {κ$^2$-PhMeB(OxMe$_2$)$_2$}AlMe$_2$, containing a bis(oxazolinyl)borate ligand. Here we report contrasting reactions of organozinc compounds and PhB(OxMe$_2$)$_2$ that involve alkyl group or β-hydrogen abstraction and strategies to control the relative rates of the two pathways.

Results and Discussion.

Synthesis and characterization of bis(oxazolinyl)phenylborane compounds

PhB(OxMe$_2$)$_2$ and ZnMe$_2$ react in benzene over 1 day via methide abstraction to give {κ$^2$-PhMeB(OxMe$_2$)$_2$}ZnMe [I; eqn. (1)]. The $^1$H NMR spectrum of I contained a singlet at -0.18 ppm for the zinc methyl and a broad signal at 0.94 ppm for the methyl bonded to boron. The latter resonance was unambiguously assigned by a crosspeak in the $^1$H-$^{11}$B HMBC experiment with a $^{11}$B NMR resonance at -16.7 ppm, which indicated that an anionic borate center had been formed. The $C_{2v}$-symmetric structural isomer Me$_2$B(OxMe$_2$)$_2$ZnPh is not observed nor is ZnMe/BMe exchange detected in an EXSY experiment, suggesting that B-Me bond formation is irreversible. The spectroscopic data is consistent with I as a monomeric species containing a three-coordinate zinc center because dimeric [{PhMeB(OxMe$_2$)$_2$}Zn(μ-Me)]$_2$ would likely be a mixture of diastereomers. In other words, compound I is $C_s$ symmetric, as indicated by equivalent oxazoline groups with diastereotopic CMe$_2$ and CH$_2$ groups.
This assignment is further supported by a DOSY experiment,\(^9\) where the diffusion coefficient of 1 is \(8.27 \times 10^{-10} \text{ m}^2/\text{s} \) (296 K) (Figure 1). For comparison, the diffusion coefficient of To\(^{\text{M}}\)ZnMe,\(^{10}\) which contains coordinatively saturated four-coordinate metal center and is monomeric species as shown by X-ray crystallography, is \(7.447 \times 10^{-10} \text{ m}^2/\text{s} \) (296 K). The similar diffusion coefficients supports the assertion that PhMeB(Ox\(^{\text{Me}2}\))\(_2\)ZnMe is monomeric in solution.
Figure 1. Plot of intensity versus gradient strength that was used to determine the diffusion coefficient for \( \kappa^2 \text{-PhMeB(Ox}^\text{Me}_2)_2 \) \( \text{ZnMe} \) (1).
Reactions of PhB(OxMe2)2 and ZnPh2 or ZnBn2 (Bn = CH2Ph) in benzene follow the same pathway as the reaction of ZnMe2, giving the phenyl- or benzyl-abstracted products \{κ2-Ph2Zn(OxMe2)2\}ZnPh (2) or \{κ2-Ph2Zn(OxMe2)2\}ZnBn (3) [eqn. (1)]. Notably, compound 2 is C2v symmetric, with equivalent oxazolines and magnetically equivalent CMe2 (and CH2 groups) within the oxazoline rings, because the two substituents bonded to boron are identical, whereas 1 and 3 are Cs symmetric.

Although 1 – 3 are monomeric, the organozinc substituents undergo intermolecular exchange. Thus, a solution of \{κ2-PhMeB(OxMe2)2\}ZnMe (1) and \{κ2-Ph(PhCH2)B(OxMe2)2\}ZnCH2Ph (3) in benzene-d6 gave a spectrum containing four species; resonances for 1 and 3 were observed, as well as one new zinc Me resonance at -0.36 ppm and one new ZnCH2Ph resonance at 2.18 ppm. Additional BMe (0.92 ppm) and BCH2Ph (2.98 ppm) resonances are observed. The two new species are assigned as \{κ2-PhMeB(OxMe2)2\}ZnCH2Ph and \{κ2-Ph(PhCH2)B(OxMe2)2\}ZnMe. The equilibrium mixture of \{κ2-PhMeB(OxMe2)2\}ZnMe (1), \{κ2-Ph(PhCH2)B(OxMe2)2\}ZnCH2Ph (3), \{κ2-PhMeB(OxMe2)2\}ZnCH2Ph, \{κ2-Ph(PhCH2)B(OxMe2)2\}ZnMe is obtained within 5 min of mixing 1 and 3, and the ratio of compounds remains the same for at least five days [eqn. (2)].
An EXSY experiment showed a crosspeak between the ZnMe resonances of \{\kappa^2-\text{PhMeB(OxMe}_2)\}_2\text{ZnMe} (1) and \{\kappa^2-\text{Ph(PhCH}_2)\text{B(OxMe}_2)\}_2\text{ZnMe} as well as a crosspeak between the CH\textsubscript{2}Ph resonances of \{\kappa^2-\text{Ph(PhCH}_2)\text{B(OxMe}_2)\}_2\text{ZnCH}_2\text{Ph} (3) and \{\kappa^2-\text{PhMeB(OxMe}_2)\}_2\text{ZnCH}_2\text{Ph}.

In contrast to the reactions of PhB(OxMe\textsubscript{2})\textsubscript{2} with ZnMe\textsubscript{2}, ZnPh\textsubscript{2}, and ZnBn\textsubscript{2} that each form a single product, reaction of PhB(OxMe\textsubscript{2})\textsubscript{2} and ZnEt\textsubscript{2} in benzene-$d_6$ gives a mixture of two oxazolinylborate-containing compounds (ethylborate and hydridoborate compounds) after 1 day [eqn. (2)]. The $^{11}$B NMR spectrum of an in situ reaction of PhB(OxMe\textsubscript{2})\textsubscript{2} and ZnEt\textsubscript{2} contained two signals; a singlet at -15.1 ppm was assigned to an ethylborate and a doublet resonance ($^1J_{\text{BH}} = 88$ Hz) at -19.1 ppm was assigned to a hydridoborate. In the $^1$H NMR spectrum, resonances from two zinc ethyl species were evident. Two virtual triplets (each composed of two overlapping diastereotopic doublets) indicated that two species are present each of which contain an inequivalently substituted borate center. Additionally, ethylene (d 5.25 in benzene-$d_6$) was detected in the $^1$H NMR spectrum. These data suggested ethyl-abstracted \{PhEtB(OxMe\textsubscript{2})\}_2\text{ZnEt} (4) and hydridoborate \{PhHB(OxMe\textsubscript{2})\}_2\text{ZnEt} (5) as the products. Based on the reactions of ZnMe\textsubscript{2}, ZnPh\textsubscript{2}, and Zn(CH\textsubscript{2}Ph)\textsubscript{2} described above and the NMR data, the former product
is suggested by the pathway described by equation 1, while the latter species is independently synthesized (see below) and apparently forms by transfer of a β-hydrogen from the ethyl ligand to boron. Mixtures of hydridoboratozinc and alkylborato organozinc compounds are also formed upon treatment of PhB(OxMe2)2 with n-Pr2Zn or i-Bu2Zn [eqn. (2)].

In contrast, these reactions are selective for hydridoborate formation in THF. For example, PhB(OxMe2)2 and Et2Zn give 5 in THF or THF-d8 as the only product detected over 1 day or isolated [eqn. (3)]. No evidence of ethyl group abstraction was obtained. The 1H NMR spectrum of {κ2-PhHB(OxMe2)2}ZnEt contains only one set of ethyl resonances (δ 0.62, 2 H, δ 1.51, 3 H). The product is Cs symmetric and monomeric, as indicated by one set of oxazoline resonances contain diastereotopic CH2 and CMe2 groups. The borohydride resonance at 3.53 ppm was supported by a 1H-11B HMQC experiment that contained a crosspeak to a 11B NMR signal at -19.1, which appeared as a doublet (J_{BH} = 88 Hz), and this is the same frequency as observed in the reaction mixtures obtained in benzene. These spectra confirm that 5 is one of the two species generated in benzene. Similar results are obtained upon treatment of PhB(OxMe2)2 with n-
Pr$_2$Zn or $i$-Bu$_2$Zn to form \( \{ \kappa^2\text{-PhHB(Ox} \text{Me}_2) \}_2 \text{Zn}(n\text{-Pr}) \) (7) and \( \{ \kappa^2\text{-PhHB(Ox} \text{Me}_2) \}_2 \text{Zn}(i\text{-Bu}) \) (9). Thus, zinc dialkyls containing $\beta$-CH groups react with PhB(Ox$^\text{Me}_2$)$_2$ in THF via $\beta$-hydrogen abstraction rather than alkyl group abstraction, whereas both alkyl group abstraction and $\beta$-hydrogen abstraction are observed in benzene.

**Comparison with Al system:** Given this surprising result and Milione’s $\beta$-hydride abstraction,$^{4b}$ the interactions of PhB(Ox$^\text{Me}_2$)$_2$ and aluminum alkyls was revisited. However, reaction of AlEt$_3$ and PhB(Ox$^\text{Me}_2$)$_2$ in benzene or THF results in formation of only the alkyl-abstracted product \( \{ k^2\text{-PhEtB(Ox} \text{Me}_2) \}_2 \text{AlEt}_2 \) (10) [eqn. (4)].

**Determination of reaction intermediate and reaction reversibility:** Given these observations, we suspected that the coordination number of the metal center, the accessibility of the boron center, and the nature of the interaction of PhB(Ox$^\text{Me}_2$)$_2$ and the metal center prior to the abstraction reaction influences the reaction pathway to favor alkyl group abstraction or $\beta$-hydrogen abstraction. First, we verified that alkyl or hydride group abstraction is irreversible. For example, dissolution of a solid mixture of \( \{ \kappa^2\text{-PhEtB(Ox} \text{Me}_2) \}_2 \text{ZnEt} \) (4) and \( \{ \kappa^2\text{-PhHB(Ox} \text{Me}_2) \}_2 \text{ZnEt} \) (5) (formed in benzene-$d_6$) in
THF-$d_8$ gives the same mixture in the same ratio as obtained in benzene. Heating this
THF-$d_8$ solution to 80 °C does not change the ratio of hydridoborate to ethylborate zinc.
Additionally, $\{\kappa^2$-PhHB(Ox$^{Me2}$)$_2\}ZnEt$ (5) is unchanged in benzene-$d_6$ at 80 °C for at
least 2 days. Although we do not know which product is thermodynamically favored, the
irreversibility of the reactions suggests that the products form under kinetic control.

**Concentration effect of the reaction:** In order to probe the mechanism further, we
investigated the effect of concentration on the ratio of $\beta$-hydride abstraction to alkyl
group abstraction in reactions of PhB(Ox$^{Me2}$)$_2$ and ZnEt$_2$. Table 1 shows that as the
concentration of the reaction mixture increases, the amount of alkyl group abstraction
increases from 2:1 to 4:1. The change in product ratio indicates that the rate of alkyl
group abstraction is increased as concentration increases, at the expense of $\beta$-hydrogen
abstraction. We suggest, then, that alkyl group abstraction may include a bi-molecular
interaction of PhB(Ox$^{Me2}$)$_2$ and ZnEt$_2$ whereas hydride abstraction occurs primarily
through an intramolecular rate-determining step and is less affected by changes in
concentration. Although quantitative kinetics were not measured, we qualitatively found
that the rate of reaction also increases as concentration increases.

Table 1. Reactant concentration and alkyl : hydridoborate product ratio. $^a$

<table>
<thead>
<tr>
<th></th>
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<th></th>
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<tbody>
<tr>
<td>10.1</td>
<td>4.23:1</td>
<td></td>
</tr>
<tr>
<td>5.3</td>
<td>3.34:1</td>
<td></td>
</tr>
<tr>
<td>2.7</td>
<td>2.85:1</td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>2.06:1</td>
<td></td>
</tr>
</tbody>
</table>
a Effect of concentration on the ratio of [Ph(Et)B(OxMe2)2ZnEt] (4) : [Ph(H)B(OxMe2)2ZnEt] (5) formed in the reaction of PhB(OxMe2)2 and Et2Zn in benzene-d6. The ratio was measured by integration of the 1H NMR spectrum of the reaction mixture.

In non-coordinating solvent, mixtures of β-H and alkyl group abstraction are observed: From this, we propose that β-hydrogen abstraction occurs in an intramolecular fashion from the coordination complex k2-PhB(OxMe2)2ZnEt2 (Figure 2). The oligomeric benzene solution-structure of PhB(OxMe2)2 is also a factor in this reaction, in that the oxazoline nitrogen are less available for coordination to zinc as they are occupied by coordination to the more Lewis acidic boron center.

![Figure 2. Proposed mechanism for β-hydrogen abstraction and alkyl group abstraction in non-coordinating solvent benzene.](image-url)
In coordinating solvent: Selective hydride abstraction in THF can be rationalized in the context of a competition between intramolecular and intermolecular reaction pathways that favors the former. Coordination of THF to PhB(OxMe\textsubscript{2})\textsubscript{2} to give (THF)BPh(OxMe\textsubscript{2})\textsubscript{2} inhibits alkyl group transfer during bi-molecular collisions by coordinating to the Lewis acid site.\textsuperscript{11} However, coordination of (THF)BPh(OxMe\textsubscript{2})\textsubscript{2} to Et\textsubscript{2}Zn is not blocked by formation of Et\textsubscript{2}Zn(THF)\textsubscript{2} but instead gives the intermediate (THF)BPh(OxMe\textsubscript{2})\textsubscript{2}ZnEt\textsubscript{2} [bis(oxazolines are better ligands for Zn(II) than THF]. Upon dissociation of THF to form BPh(OxMe\textsubscript{2})\textsubscript{2}ZnEt\textsubscript{2}, intramolecular β-hydrogen abstraction provides \{κ\textsuperscript{2}-PhHB(OxMe\textsubscript{2})\textsubscript{2}\}ZnEt (5) (Figure 3).

**Figure 3.** Proposed mechanism for selective hyridoborate formation.
An alternative pathway, in which a Et₂ZnL₂ species undergoes β-hydrogen elimination to give Et(H)ZnL₂ followed by zinc hydride abstraction, is unlikely for several reasons. First, diethylzinc itself does not readily β-H eliminate, and the higher coordinate, 18-electron Et₂Zn(THF)₂ and PhB(OxMe₂)₂ZnEt₂ species that lack open orbitals are even less likely to undergo β-elimination. Furthermore, the β-elimination intermediate, Et(H)ZnL₂, would likely transfer both hydride and ethyl groups to boron, whereas only hydrogen abstraction is observed in THF. Comparison of these mechanism also reveals that olefinic (or more generally, unsaturated) by-products do not provide sufficient evidence to distinguish β-hydrogen elimination from abstraction.

**Further support for proposed mechanism:** The proposed mechanism was further tested by treatment of PhB(OxMe₂)₂ with Et₂Zn(TMEDA) or Et₂Zn(DPE) (TMEDA = tetramethylethylenediamine; DPE = dipyrrolidine ethane), where the diamine zinc starting materials might inhibit formation of PhB(OxMe₂)₂ZnEt₂. In fact, increased alkyl group transfer relative to β-H abstraction occurs in the presence of TMEDA and DPE further supporting the notion that alkyl borate formation occurs through a bimolecular rate-determining step. Despite the effect by TMEDA and DPE on the reaction pathway, [Ph(R)B(OxMe₂)₂]⁻ (R = H, Et) are superior ligands for zinc, and the final zinc products are \( \kappa^2\text{-PhEtB(OxMe}_2)\text{)ZnEt (4) and } \kappa^2\text{-PhHB(OxMe}_2)\text{)ZnEt (5) (Figure 4).}
Here, the concentration of PhB(OxMe2)$_2$ZnEt$_2$ is lower due to competition with tmeda or dpe for coordination to zinc. Thus, the intramolecular pathway is inhibited and the amount of alkyl abstraction increases. (Table 2)

Table 2. Effect of diamine ligands on β-hydrogen vs. alkyl group abstraction.$^a$

<table>
<thead>
<tr>
<th>reactant</th>
<th>concentration (mM)</th>
<th>[4] : [5]$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et$_2$Zn</td>
<td>5.3</td>
<td>4.23:1</td>
</tr>
<tr>
<td>Et$_2$Zn(TMEDA)</td>
<td>5.1</td>
<td>3.34:1</td>
</tr>
<tr>
<td>Et$_2$Zn(DPE)</td>
<td>5.1</td>
<td>2.85:1</td>
</tr>
</tbody>
</table>

$^a$ Conditions: room temperature in benzene-$d_6$. $^b$ The ratio was measured by integration of the $^1$H NMR spectrum of the reaction mixture.

Upon addition of two equiv. of TMEDA or DPE (relative to Et$_2$Zn), reaction times exceed 2 days in both benzene and THF. Presumably, the diamines coordinate to PhB(OxMe2)$_2$ and Et$_2$Zn. However, the effect of TMEDA is sufficient to allow the observation of alkyl group abstraction in THF. Thus, reaction of L$_2$ZnEt and PhB(OxMe2)$_2$ in THF-$d_8$ provides PhHB(OxMe2)$_2$ZnEt with a trace amount alkyl abstraction product PhEtB(OxMe2)$_2$ZnEt after 1 day.
As in benzene, the presence of tmeda or dpe in THF decreases the concentration of (THF)PhB(OxMe2)2ZnEt2 and allows the intermolecular pathway to occur.

**Figure 4.** Proposed mechanism in THF in the presence of coordinating diamine ligand.

**Explanation of selective alkyl abstraction in the aluminum system:**

Finally, selective ethyl group transfer from AlEt3 by PhB(OxMe2)2 is consistent with alkyl abstraction following an intermolecular mechanism. Formation of the requisite {κ2-PhB(OxMe2)2}AlEt3 for β-H abstraction is unlikely based on the smaller ionic radius of four-coordiantae Al(III) (0.39 Å) vs. Zn(II) (0.6 Å) which gives apparent coordinative saturation at four ligands in these systems.
Controversy in literature: selective addition of diethylzinc to trifluoromethyl ketones.

Addition of dialkylzinc to ketones is a pathway to form secondary and tertiary alcohols. This method is limited to ZnMe$_2$ due to extensive $\beta$-hydride elimination process for higher alkyls (e.g., ZnEt$_2$) from literature proposed reason. Other zinc alkyls can be added through the addition of coordinating diamines (e.g., TMEDA) and bisoxazolines ligands. Without these ligands, trifluoromethyl ketones are reduced into secondary alcohols, while the desired tertiary alcohols are formed when the diamine TMEDA is present in the reaction mixture (Figure 5).

![Figure 5. Selective addition of trifluoromethyl ketone with / without TMEDA ligand.](image)

The anticipated mechanism reported for the formation of secondary alcohols was that ZnEt$_2$ undergoes $\beta$-hydride elimination to facility the hydride transfer. However, when adding TMEDA ligand, the activation of diethylzinc might be favored into carbon-carbon bond formation through alkyl transferring over $\beta$-hydride elimination to give tertiary alcohols (Figure 6).
However, we herein propose an alternative mechanism based on the observations in selective β-hydride versus alkyl group abstraction reaction system. That is, coordination of the substrate and positioning of a Lewis acid site in a transient alkylzinc complex favors β-hydrogen abstraction. In the synthetic system, the Zn center was pre-coordinated to ketones, and the hydrogen on the β position was transferred directly to the carbonyl via intramolecular pathway to give secondary alcohols, rather than ZnEt₂ itself β-eliminates first to give hydrogen source. While adding TMEDA ligand, ZnEt₂ was pre-coordinated with TMEDA to give TMEDA-ZnEt₂ intermediate. Thus, tertiary alcohols were formed via intermolecular pathway (Figure 7).
Conclusion.

Our results show that the β-hydrogen in zinc alkyls have significant nucleophilicity. These results contrast the lack of alkylzinc-based β-agostic structures and β-hydrogen elimination reactions that are typically associated with activated C-H's. Furthermore, we show that the selectivity between β-hydrogen and alkyl group abstraction is not only governed by steric, but also by the trajectory by which the electrophilic center encounters the alkyl ligand. Thus, β-hydrogen is readily transferred from an zinc alkyl group to electrophiles when the electrophile and alkyl ligand are appropriately positioned. These observations may provide strategies for controlling hydride and alkyl transfer processes in synthetic applications.
Experimental

**General Procedures.** All reactions were carried out under an inert atmosphere using standard Schlenk techniques or in a glovebox. All solvents were dried and degassed unless otherwise indicated. PhB(OxMe₂)₂, Ph₂Zn, n-Pr₂Zn, i-Bu₂Zn, Bn₂Zn, and DPE were prepared according to reported procedures. Me₂Zn (2 M in toluene), Et₂Zn, BnMgBr (1 M in Et₂O), PhMgBr (3 M in Et₂O), i-BuMgCl (2 M in Et₂O), and n-PrMgBr (2 M in Et₂O) were purchased from Aldrich and used as received. TMEDA was purchased from Aldrich and distilled from Na. All NMR spectra were obtained at room temperature using a Bruker DRX-400 spectrometer, Bruker Avance II-700 spectrometer, or Agilent MR400 spectrometer. ¹⁵N NMR chemical shifts were determined by ¹H-¹⁵N HMBC experiments recorded on an Avance II-700 spectrometer; the chemical shift values are reported relative to CH₃NO₂. ¹¹B NMR spectra chemical shifts are reported relative to BF₃·Et₂O. Elemental analyses were obtained at the Iowa State Chemical Instrumentation Facility using a Perkin-Elmer 2400 Series II CHN/S.

{κ²-PhMeB(OxMe₂)₂}ZnMe (1). PhB(OxMe₂)₂ (0.590 g, 2.09 mmol) was dissolved in 15 mL of benzene. A 2 M toluene solution of Me₂Zn (1.05 mL, 2.09 mmol) was added to the mixture via syringe to give a yellow solution. This solution was stirred for 24 h and then filtered to remove a white precipitate that slowly formed over time. The benzene filtrate was evaporated under reduced pressure to give a yellow solid. The crude solid was washed with 10 mL of pentane and dried under vacuum to give pale yellow, analytically pure {κ²-PhMeB(OxMe₂)₂}ZnMe (0.587 g, 1.55 mmol, 73.9%). ¹H NMR (benzene-$_d_6$, 400 MHz): δ 7.78 (d, $^3J_{HH} = 7.3$ Hz, 2 H, ortho-Ç₆H₅), 7.42 (t, $^3J_{HH} = 7.5$ Hz, 2 H, meta-Ç₆H₅), 7.23 (t, $^3J_{HH} = 7.3$ Hz, 1 H, para-Ç₆H₅), 3.32 (d, $^2J_{HH} = 8.6$ Hz, 2 H,
CNCMe$_2$CH$_2$O), 3.24 (d, $^2J_{HH} = 8.6$ Hz, 2 H, CNCMe$_2$CH$_2$O), 0.94 (s br, 3 H, BMe), 0.862 (s, 6 H, CNCMe$_2$CH$_2$O), 0.859 (s, 6 H, CNCMe$_2$CH$_2$O), -0.18 (s, 3 H, ZnMe).

$^{13}$C{${^1}$H} NMR (benzene-$d_6$, 125 MHz): d 198.81 (br, CNCMe$_2$CH$_2$O), 151.92 (ipso-C$_6$H$_5$), 132.87 (ortho-C$_6$H$_5$), 128.29 (meta-C$_6$H$_5$), 125.85 (para-C$_6$H$_5$), 78.67 (CNCMe$_2$CH$_2$O), 65.29 (CN-CMe$_2$CH$_2$O), 28.66 (CNCMe$_2$CH$_2$O), 28.47 (CNCMe$_2$CH$_2$O), 14.76 (br, BMe), 5.53 (br, ZnMe). $^{11}$B NMR (benzene-$d_6$, 128 MHz): $\delta$ -16.7. $^{15}$N NMR (benzene-$d_6$, 71 MHz): -174.3. IR (KBr, cm$^{-1}$): 3065 m, 3046 m, 2967 s, 2930 s, 2899 s, 1948 vw, 1887 vw, 1817 vw, 1569 vs (CN), 1462 s, 1431 s, 1367 s, 1272 s, 1196 s, 1158 s, 1081 s, 1011 s, 976 s, 891 m, 836 m, 774 w, 740 m, 713 s, 703 s.

Calcd. for C$_{18}$H$_{27}$BN$_2$O$_2$Zn: C, 56.95; H, 7.17; N, 7.38. Found: C, 57.30; H, 7.08; N, 7.01. mp 166-168 °C (dec.).

{[κ$_2$-Ph$_2$B(OxMe$_2$)$_2$]ZnPh (2).} PhB(OxMe$_2$)$_2$ (0.749 g, 2.65 mmol) was dissolved in 15 mL of benzene. A yellow solution formed upon addition of solid Ph$_2$Zn (0.582 g, 2.65 mmol), and this solution was stirred for 24 hours. A white precipitate slowly formed, and the reaction mixture was filtered removed this white solid. The benzene filtrate was evaporated under reduced pressure to give a yellow solid. The crude solid was washed with 10 mL of pentane and dried under reduced pressure giving the phenyl-abstracted product 2 (0.975 g, 1.94 mmol, 72.9%). $^1$H NMR (benzene-$d_6$, 400 MHz): $\delta$ 7.82 (d, $^3J_{HH} = 7.3$ Hz, 4 H, ortho-C$_6$H$_5$B), 7.61 (d, $^3J_{HH} = 7.2$ Hz, 2 H, ortho-C$_6$H$_5$Zn), 7.44 (t, $^3J_{HH} = 7.4$ Hz, 4 H, meta-C$_6$H$_5$B), 7.35 (t, $^3J_{HH} = 7.1$ Hz, 2 H, meta-C$_6$H$_5$Zn), 7.27 (t, $^3J_{HH} = 7.4$ Hz, 2 H, para-C$_6$H$_5$B), 7.22 (t, $^3J_{HH} = 7.4$ Hz, 1 H, para-C$_6$H$_5$Zn), 3.28 (s, 4 H, CNCMe$_2$CH$_2$O), 0.84 (s, 12 H, CNCMe$_2$CH$_2$O). $^{13}$C{${^1}$H} NMR (benzene-$d_6$, 125 MHz): $\delta$ 197.81 (br, CNCMe$_2$CH$_2$O), 150.93 (ipso-C$_6$H$_5$B), 150.40 (ipso-C$_6$H$_5$Zn), 138.96
(ortho-C₆H₅Zn), 134.96 (ortho-C₆H₅B), 128.92 (meta-C₆H₅Zn), 128.03 (meta-C₆H₅B), 127.77 (para-C₆H₅Zn), 126.14 (para-C₆H₅B), 78.89 (CNCMe₂CH₂O), 65.52 (CNCMe₂CH₂O), 28.63 (CNCMe₂CH₂O). ¹¹B NMR (benzene-d₆, 128 MHz): δ -12.4.

¹⁵N NMR d (benzene-d₆, 71 MHz): -172.7. IR (KBr, cm⁻¹): 3042 m, 2995 m, 2966 s, 2928 m, 2895 m, 2870 m, 1946 w, 1871 w, 1813 w, 1554 vs br (CN), 1462 m, 1424 m, 1369 s, 1354 s, 1278 s, 1248 s, 1239 s, 1159 s, 1076 m, 1032 m, 969 vs, 892 m, 743 s, 735 s, 724 s, 701 vs.

Calcd. for C₂₈H₃₁BN₂O₂Zn: C, 66.76; H, 6.20; N, 5.56. Found: C, 66.63; H, 6.17; N, 5.07. mp 126-130 °C.

{κ²-PhCH₂PhB(OxMe₂)₂}ZnCH₂Ph (3). PhB(OxMe₂)₂ (0.449 g, 1.59 mmol) was dissolved in 15 mL of benzene and Bn₂Zn (0.394 g, 1.59 mmol) was added. After 24 h, the mixture was filtered to remove a white precipitate. The benzene filtrate was evaporated under reduced pressure to give a yellow solid. The crude solid was washed with 10 mL of pentane and dried (0.658 g, 1.24 mmol, 77.9%). ¹H NMR (benzene-d₆, 400 MHz): δ 7.70 (d, ³JHH = 7.2 Hz, 2 H, ortho-C₆H₅), 7.41 (t, ³JHH = 7.2 Hz, 2 H, meta-C₆H₅), 7.24 (t, ³JHH = 7.6 Hz, 1 H, para-C₆H₅), 7.20-7.09 (m, 4 H, ortho-C₆H₅CH₂Zn and ortho-C₆H₅CH₂B) 7.07-6.97 (m, 4 H, meta-C₆H₅CH₂Zn and meta-C₆H₅CH₂B), 6.96-6.88 (m, 2 H, para-C₆H₅CH₂Zn and para-C₆H₅CH₂B), 3.38 (d, ³JHH = 8.8 Hz, 2 H, CNCMe₂CH₂O), 3.25 (d, ³JHH = 8.8 Hz, 2 H, CNCMe₂CH₂O), 2.92 (s br, 2 H, BCH₂Ph), 2.00 (s, 2 H, ZnCH₂Ph), 0.73 (s, 6 H, CNCMe₂CH₂O), 0.71 (s, 6 H, CNCMe₂CH₂O).

¹³C {¹H} NMR (benzene-d₆, 125 MHz): δ 196.98 (br, CNCMe₂CH₂O), 150.49 (br, ipso-C₆H₅B), 148.42 (ipso-C₆H₅CH₂B), 148.24 (ipso-C₆H₅CH₂Zn), 133.34 (ortho-C₆H₅B), 129.05 (meta-C₆H₅CH₂B), 128.65 (ortho-C₆H₅CH₂B), 128.33 (meta-C₆H₅CH₂Zn), 128.15 (meta-C₆H₅B), 127.72 (ortho-C₆H₅CH₂Zn), 126.10 (para-C₆H₅B), 123.91 (para-
C₆H₅CH₂Zn), 122.56 (para-C₆H₅CH₂B), 78.82 (CNCMe₂CH₂O), 65.30 (CNCMe₂CH₂O),
32.79 (BCH₂), 28.73 (CNCMe₂CH₂O), 28.23 (CNCMe₂CH₂O), 20.15 (ZnCH₂). ¹¹B NMR
(benzene-δ₆, 128 MHz): δ -14.9. ¹⁵N NMR (benzene-δ₆, 71 MHz): -170.5. IR (KBr, cm⁻¹):
3066 m, 3017 m, 2970 s, 2928 m, 2897 m, 1938 w, 1866 w, 1798 w, 1595 s (CN),
1572 vs (CN), 1488 vs, 1461 s, 1450 m, 1368 m, 1279 m, 1208 s, 1148 m, 1074 m,
1063 m, 970 m, 799 m, 753 s 770 vs. Calcd for C₃₀H₃₅BN₂O₂Zn: C, 67.75; H,
6.63; N, 5.27. Found: C, 67.94; H, 6.55; N, 4.88. mp 140–143 °C.

{κ²-PhHB(OxMe₂)₂}ZnEt (5). PhB(OxMe₂)₂ (0.220 g, 0.781 mmol) was dissolved in 15
mL of THF. Et₂Zn (80.0 ml, 0.781 mmol) was added to the mixture via syringe to give a
yellow solution. This solution was stirred for 24 h, and then the volatile materials were
removed under reduced pressure. The residue was then extracted with benzene and the
benzene was evaporated. The solid residue was then washed with 10 mL of pentane and
dried (0.251 g, 0.662 mmol, 84.8%). ¹H NMR (benzene-δ₆, 400 MHz): δ 7.87 (d, ³JHH =
7.2 Hz, 2 H, ortho-C₆H₅), 7.42 (t, ³JHH = 7.2 Hz, 2 H, meta-C₆H₅), 7.23 (t, ³JHH = 7.2 Hz,
1 H, para-C₆H₅), 3.36 (d, ³JHH = 8.4 Hz, 2 H, CNCMe₂CH₂O), 3.53 (1 H, BH), 3.29 (d,
³JHH = 8.4 Hz, 2 H, CNCMe₂CH₂O), 1.51 (t, ³JHH = 8 Hz, 3 H, ZnCH₂CH₃), 0.87 (s, 6 H,
CNCMe₂CH₂O), 0.86 (s, 6 H, CNCMe₂CH₂O), 0.62 (q, ³JHH = 8.0 Hz, 2 H, ZnCH₂CH₃).

¹³C {¹H} NMR (benzene-δ₆, 125 MHz): δ 196.88 (br, CNCMe₂CH₂O), 149.46 (ipso-
C₆H₅), 135.39 (ortho-C₆H₅), 128.92 (meta-C₆H₅), 125.82 (para-C₆H₅), 78.72
(CNCMe₂CH₂O), 65.10 (CNCMe₂CH₂O), 28.78 (CNCMe₂CH₂O), 28.38
(CNCMe₂CH₂O), 13.35 (ZnCH₂CH₃), 1.63 (ZnCH₂CH₃). ¹¹B NMR (benzene-δ₆, 128
MHz): δ -19.1 (d, ¹JBH = 88 Hz). ¹⁵N NMR (benzene-δ₆, 71 MHz): -172.8. IR (KBr, cm⁻¹):
3066 w, 3044 w, 2965 s, 2931 s, 2896 s, 2871 s, 2342 w br (BH), 1945 vw, 1879 vw,
\( \kappa^2-\text{PhHB(OxMe}_2)\text{Zn(n-Pr)(7)} \). PhB(OxMe\text{2})_2 (0.269 g, 0.952 mmol) was dissolved in 15 mL of THF. A yellow solution was obtained upon addition of \( n\text{-Pr}_2\text{Zn} \) (0.145 g, 0.952 mmol), which was stirred for 24 h and then evaporated. The residue was then extracted with benzene. After evaporation of the benzene extracts, the resulting solid was washed with 10 mL of pentane and dried (0.273 g, 0.693 mmol, 72.8%). 

\( ^1\text{H NMR (benzene-}\text{d}_6, \ 400 \text{MHz): } \delta \ 7.82 \ (d, \ ^3J_{HH} = 7.2 \text{ Hz, 2 H, ortho-C}_6\text{H}_3), 7.41 \ (t, ^3J_{HH} = 7.2 \text{ Hz, 2 H, meta-C}_6\text{H}_3), 7.22 \ (t, ^3J_{HH} = 7.2 \text{ Hz, 1 H, para-C}_6\text{H}_3), 3.47 \ (1 \text{ H, BH}), 3.36 \ (d, ^3J_{HH} = 8.8 \text{ Hz, 2 H, CNCMe}_2\text{C}_2\text{O}), 3.28 \ (d, ^3J_{HH} = 8.6 \text{ Hz, 2 H, CNCMe}_2\text{C}_2\text{O}), 1.84 \ (m, 2 \text{ H, ZnCH}_2\text{C}_2\text{CH}_3), 1.21 \ (t, ^3J_{HH} = 7.2 \text{ Hz, 3 H, ZnCH}_2\text{C}_2\text{CH}_3), 0.88 \ (s, 6 \text{ H, CNCMe}_2\text{C}_2\text{O}), 0.87 \ (s, 6 \text{ H, CNCMe}_2\text{C}_2\text{O}), 0.70 \ (t, ^3J_{HH} = 8.0 \text{ Hz, 2 H, ZnCH}_2\text{C}_2\text{CH}_3). \)

\( ^{13}\text{C} \{^1\text{H}\} \text{ NMR (benzene-}\text{d}_6, \ 125 \text{ MHz): } \delta \ 196.75 \ (br, \ CNCMe}_2\text{C}_2\text{O}), 148.67 \ (ipso-C}_6\text{H}_3), 135.35 \ (ortho-C}_6\text{H}_3), 128.19 \ (meta-C}_6\text{H}_3), 125.86 \ (para-C}_6\text{H}_3), 78.75 \ (CNCMe}_2\text{C}_2\text{O}), 65.14 \ (CNCMe}_2\text{C}_2\text{O}), 28.78 \ (CNCMe}_2\text{C}_2\text{O}), 28.41 \ (CNCMe}_2\text{C}_2\text{O}), 22.75 \ (ZnCH}_2\text{C}_2\text{CH}_3), 22.43 \ (ZnCH}_2\text{C}_2\text{CH}_3), 14.03 \ (ZnCH}_2\text{C}_2\text{CH}_3). \)

\( ^{11}\text{B NMR (benzene-}\text{d}_6, \ 128 \text{ MHz): } \delta \ -19.5 \ (d, ^1J_{BH} = 89 \text{ Hz}). \)

\( ^{15}\text{N NMR (benzene-}\text{d}_6, \ 71 \text{ MHz): } -172.7. \) IR (KBr, cm\(^{-1}\): 3065 m, 3048 m, 2917 s, 2849 m, 2260 w (BH), 1563 s (CN), 1463m, 1432 m, 1386 m, 1368 m, 1279 m, 1262 m, 1199 m, 1029 s, 991 m, 956 m, 803 m, 718 m, 704 m. Calcd. for C\(_{19}\)H\(_{29}\)BN\(_2\)O\(_2\)Zn: C, 57.97; H, 7.43; N, 7.12. Found: C, 57.57; H, 7.30; N, 7.02. mp 122-128 °C.
\{κ²-PhHB(OxMe₂)₂\}Zn-i-Bu (9). PhB(OxMe₂)₂ (0.247 g, 0.875 mmol) was dissolved in 15 mL of THF and i-Bu₂Zn (0.157 g, 0.875 mmol) was added. This solution was stirred for 3 days, and then the volatile materials were removed in vacuo. The residue was then extracted with benzene. After evaporation of the benzene extracts, the resulting residue was washed with 10 mL of pentane and dried under reduced pressure (0.181 g, 0.445 mmol, 50.8%). ¹H NMR (benzene-\(d_6\), 400 MHz): \(δ\) 7.82 (d, \(³J_{HH} = 7.2\) Hz, 2 H, ortho-\(C₆H₅\)), 7.41 (t, \(³J_{HH} = 7.2\) Hz, 2 H, meta-\(C₆H₅\)), 7.22 (t, \(³J_{HH} = 7.3\) Hz, 1 H, para-\(C₆H₅\)), 3.35 (d, \(³J_{HH} = 8.8\) Hz, 2 H, CNCMe₂CH₂O), 3.27 (d, \(³J_{HH} = 8.4\) Hz, 2 H, CNCMe₂CH₂O), 2.17 (m, \(³J_{HH} = 6.8\) Hz, ZnCH₂CH₂Me₂), 1.19 (d, \(³J_{HH} = 6.8\) Hz, 2 H, ZnCH₂CH₂Me₂), 0.91 (s, 6 H, CNCMe₂CH₂O), 0.89 (s, 6 H, CNCMe₂CH₂O), 0.74 (d, \(³J_{HH} = 7.6\) Hz, 2 H, ZnCH₂CH₂Me₂). ¹³C\{¹H\} NMR (benzene-\(d_6\), 125 MHz): \(δ\) 197.16 (br, CNCMe₂CH₂O), 148.83 (br, ipso-\(C₆H₅\)), 135.30 (ortho-\(C₆H₅\), overlapped by C₆D₆, assigned by \(¹H-¹³C\) HMQC experiment), 125.90 (para-\(C₆H₅\), 78.80 (CNCMe₂CH₂O), 65.20 (CNCMe₂CH₂O), 30.10 (ZnCH₂CH₂Me₂), 29.20 (ZnCH₂CH₂Me₂) 28.80 (CNCMe₂CH₂O), 28.45 (CNCMe₂CH₂O), 24.00 (ZnCH₂CH₂Me₂). ¹¹B NMR (benzene-\(d_6\), 128 MHz): \(δ\) -20.0 (d, \(¹J_{BH} = 87\) Hz). ¹⁵N NMR (benzene-\(d_6\), 71 MHz): -172.8. IR (KBr, cm⁻¹): 3066 m, 3047 m, 2943 s, 2874 s, 2258 m br (BH), 2052 vw, 1948 vw, 1876 vw, 1818 vw, 1564 s (CN), 1461 s, 1432 s, 1386 s, 1361 s, 1282 s, 1197 s, 1159 s, 1028 s, 984 s, 956 s, 836 m, 741 w, 716 s, 704 s. Calcd. for C₂₀H₃₁BN₂O₂Zn: C, 58.92; H, 7.66; N, 6.87. Found: C, 59.13; H, 7.46; N, 6.51. mp 212-213 °C (dec.).

\{κ²-PhEtB(OxMe₂)₂\}AlEt₂ (10). PhB(OxMe₂)₂ (0.241 g, 0.856 mmol) was dissolved in 15 mL of benzene. AlEt₃ (117 ml, 0.856 mmol) was added to the mixture via syringe giving a yellow solution. This solution was stirred for 24 h and then filtered. The benzene filtrate
was evaporated under reduced pressure to give a yellow solid. The crude solid was washed with 10 mL of pentane and dried (0.210 g, 0.527 mmol, 61.6%). $^1$H NMR (benzene-$d_6$, 400 MHz): $\delta$ 7.71 (d, $^3J_{HH} = 7.2$ Hz, 2 H, ortho-$C_6H_5$), 7.39 (t, $^3J_{HH} = 7.2$ Hz, 2 H, meta-$C_6H_5$), 7.20 (t, $^3J_{HH} = 7.2$ Hz, 1 H, para-$C_6H_5$), 3.28 (d, $^3J_{HH} = 8.4$ Hz, 2 H, CNCMe$_2$CH$_2$O), 3.15 (d, $^3J_{HH} = 8.8$ Hz, 2 H, CNCMe$_2$CH$_2$O), 1.56 (s br, 2 H, AlCH$_2$C$_3$H$_3$), 1.34 (t, $^3J_{HH} = 8.0$ Hz, 3 H, AlCH$_2$C$_3$H$_3$). $^{13}$C NMR (benzene-$d_6$, 125 MHz): $\delta$ 200.98 (br, CNCMe$_2$CH$_2$O), 134.55 (ipso-$C_6H_5$), 133.26 (ortho-$C_6H_5$), 127.91 (meta-$C_6H_5$), 126.18 (para-$C_6H_5$), 79.58 (CNCMe$_2$CH$_2$O), 66.02 (CNCMe$_2$CH$_2$O), 27.42 (CNCMe$_2$CH$_2$O), 26.88 (CNCMe$_2$CH$_2$O), 13.18 (BCH$_2$CH$_3$), 10.12 (AlCH$_2$C$_3$H$_3$), 9.97 (AlCH$_2$C$_3$H$_3$), 9.86 (br, BCH$_2$CH$_3$, overlapped by AlCH$_2$C$_3$H$_3$). $^1$H-13C HMQC experiment) 3.30 (br, AlCH$_2$C$_3$H$_3$). $^{11}$B NMR (benzene-$d_6$, 128 MHz): $\delta$ -14.3. $^{15}$N NMR (benzene-$d_6$, 71 MHz): $\delta$ -186.5. IR (KBr, cm$^{-1}$): 3047 m, 3066 m, 2934 s, 2898 s, 2861 s, 2793 m, 2724 w, 1952 w, 1882 w, 1823 w, 1609 s (CN) 1464 s, 1432 m, 1411 m, 1372 w, 1297 s, 1201 s, 1162 s, 1042 s, 1026 s, 986 s, 965 s, 886 m, 845 m, 763 m, 712 s, 703 s. Calcd. for C$_{22}$H$_{36}$AlBN$_2$O$_2$: C, 66.34; H, 9.11; N, 7.03. Found: C, 66.06; H, 8.70; N, 6.55. mp 140-142 °C (dec.).

**Et$_2$Zn(DPE).** Et$_2$Zn (0.23 mL, 2.24 mmol) was added to a 12 mL benzene solution of dipyrroloidinylethane (0.335 g, 1.99 mmol), and the resulting solution was stirred for 1 h at room temperature. Evaporation of the volatile materials provided analytically pure Et$_2$Zn(DPE) (0.55 g, 1.88 mmol, 94.8 %). $^1$H NMR (benzene-$d_6$, 400 MHz): $\delta$ 2.29 (s, br, 8 H, NCH$_2$CH$_2$CH$_2$CH), 2.01 (s, 4 H, N(CH$_2$)$_2$N), 1.80 (t, $^3J_{HH} = 8$ Hz, 6 H, ZnCH$_2$CH$_3$),
1.60 (s, br, 8 H, NCH₂CH₂CH₂CH₂), 0.25 (q, \( \frac{3}{2} J_{HH} = 8 \text{ Hz} \), 4 H, ZnCH₂CH₃). \(^{13}\text{C}\{\text{¹H}\})\)

NMR (benzene-\(d_6\), 100 MHz): \( \delta \) 55.64 (NCH₂CH₂CH₂CH₂), 55.39 (N(CH₂)₂N), 23.81 (NCH₂CH₂CH₂CH₂), 15.30 (ZnCH₂CH₃), 1.50 (ZnCH₂CH₃). \(^{15}\text{N}\) NMR (benzene-\(d_6\), 41 MHz): \( \delta \) -127.9. IR (KBr, cm⁻¹): 2975 (m), 2927 (m), 2873 (s), 2846 (s), 2788 (m), 1458 (s, \( \nu_{\text{C-N}} \)), 1414 (w), 1345 (w), 1331 (m), 1299 (m), 1264 (m), 1226 (w), 1194 (w), 1123 (m), 1079 (w), 1035 (m), 980 (m), 947 (m), 903 (s), 866 (m), 607 (s), 605 (s), 569 (m), 488 (s), 439 (m). Anal. Calc. for C₁₄H₃₀N₂Zn: C, 57.62; H, 10.36; N, 9.60. Found: C, 57.54; H, 9.70; N, 9.59. mp 103-105 °C.

**Procedures for DOSY (Diffusion-Ordered Spectroscopy) experiment.** All the measurements were performed on a Bruker DRX400 spectrometer using a DOSY stimulated spin-echo pulse program with bipolar gradients.\(^{18}\) Accurately known concentrations of the species in question were used. The concentrations of \( \{\kappa^2\text{-PhMeB(OxMe}₂\}_2\text{ZnMe} \) (1) and \( \text{To}^\text{M}\text{ZnMe} \) were determined by integration of resonances corresponding to species of interest and integration of a tetrakis(trimethylsilyl)silane standard of accurately known concentration. The temperature in the NMR probe was preset to 296 K, and the probe was maintained at a constant temperature for each experiment. The delay time in between pulses was set to 5 s in order to ensure the spins are fully relaxed to their ground states. During the experiments, a series of 1D \(^1\text{H}\) NMR spectra were acquired at increasing gradient strength. The signal intensity decay was fit by non-linear least squares regression analysis to Equation 1 to obtain the diffusion coefficient D.\(^{18}\)

\[
\ln\left( \frac{I}{I_0} \right) = -\left( \gamma \delta \right)^2 G^2 \left( \Delta - \frac{\delta}{3} \right) D \quad (7)
\]
where $I$ is the observed intensity, $D$ is the diffusion coefficient, $\gamma$ is the gyromagnetic ratio of the nucleus, $\delta$ is the length of the gradient pulse, and $\Delta$ is the diffusion time.

References


(11) The $^{11}$B NMR spectrum of oligomeric PhB(OxMe$_2$)$_2$ in toluene is featureless at room temperature (see Ref. 7), but in THF a signal is observed at -8.77 ppm for a monomeric THF-borane adduct.


CHAPTER 2: RARE EARTH BORANE-PROTECTED IMIDO COMPLEXES FROM BIS-1,1-(2-OXAZOLINYL)-1-(TETRAMETHYLCYCLOPENTADIENYL)ETHANE RARE EARTH BENZYL COMPLEXES AND NH$_3$B(C$_6$F$_5$)$_3$

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Abstract.

Rare earth benzyl complexes $\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)_2\}_\text{Ln(CH}_2\text{Ph)}$ (Ln = Sc, Lu, Y) are prepared in high yield by reactions between $\text{Ln(CH}_2\text{Ph)}_3(\text{THF})_3$ and the $\text{H\{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)_2\}_\text{ligand}$. These compounds are precursors for the first examples of terminal lutetium and yttrium imidoborate complexes. $\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)_2\}_\text{Lu}=\text{NHB(C}_6\text{F}_5)_3$ and $\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)_2\}_\text{Y}=\text{NHB(C}_6\text{F}_5)_3$ are synthesized by the reaction of NH$_3$B(C$_6$F$_5$)$_3$ with $\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)_2\}_\text{Ln(CH}_2\text{Ph)}_2$ complexes (Ln = Lu, Y).

Introduction.

Organolanthanide alkyl complexes have been studied due to their high reactivity and relevance for olefin polymerization and related catalytic transformations such as olefin hydrogenation, hydrosilylation, and alkyne dimerization. Highly substituted cyclopentadienyl (Cp) ligands are favored to stabilize Ln(III) hydrocarbyl complexes. Reactions of lanthanide alkyl compounds and bulky acidic ligands can proceed by
protonolysis to form organo σ-bonded rare-earth metal (Ln) alkyls. Herein we report the use of H{MeC(C₅Me₄)(OxMe²)}₂ ligand to isolate organo-lanthanide benzyl complexes.

Metal imido complexes, which contain the M=N double bond, have caused much interest due to their unique structural properties and potential applications, such as C-H bond activation,⁴ imine metathesis,⁵ and alkyne hydroamination.⁶ For example, titanium imidos form readily and are often cited intermediates in hydroamination reactions (mainly alkyne). However, the other group 4 metal zirconium imidos are rare⁷ because of its larger metal center, which may cause poor pi bonding character.

Mountford’s group tried to use Lewis acid to stabilize terminal group 4 imidos by deprotonation of NH₃B(C₆F₅)₃.⁸ However, treatment of Zr(NMe₂)₄ with NH₃B(C₆F₅)₃ only resulted in the amido complex [Zr(NMe₂)₃{NH₂B(C₆F₅)₃}(HNMe₂)], as well as the titanium analog. (Fig. 1)

Figure 1. Synthesis of complexes [Zr(NMe₂)₃{NH₂B(C₆F₅)₃}(HNMe₂)] and [Ti(NMe₂)₅{NH₂B(C₆F₅)₃}(HNMe₂)]
The synthesis of imido complexes may be anticipated to become more difficult with larger metal centers. Thus, terminal imido complexes M=NR in group 3 metal and lanthanides are even rare. Only a few scandium terminal imido complexes were isolated and structurally characterized.\textsuperscript{9,10} For example, Chen’s group reported the first scandium terminal imido complex \( \text{CH}_3\text{C}(2,6-\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{CHC(CH}_3\text{HCH}_2\text{NMe}_2\text{)}\text{Sc(NAr)(DMAP)} \) via alkane elimination facilitated by the presence of a Lewis base.\textsuperscript{10} (Fig. 2) However, no terminal imido complexes of Yttrium and Lutetium have been isolated and structurally characterized yet.

\textbf{Figure 2.} Synthesis of complex \( \text{CH}_3\text{C}(2,6-\text{Pr}_2\text{C}_6\text{H}_3\text{N})\text{CHC(CH}_3\text{HCH}_2\text{NMe}_2\text{)}\text{Sc(NAr)(DMAP)} \), first terminal scandium imido complex from Chen’s group.

Recently, Issac in our group synthesized bis-1,1-(2-oxazoliny)-1-(tetramethylcyclopentadienyl)ethane ligand \( \text{H}\{\text{MeC(C}_5\text{H}_4\text{)(Ox}_2\text{Me})\}_{\text{2}}\} \) and Burun and Megan developed the tetramethyl analog \( \text{H}\{\text{MeC(C}_5\text{Me}_4\text{)(Ox}_2\text{Me})\}_{\text{2}}\}.\) (Fig. 3) Since cyclopentadienyl (Cp) ligands are favored to stabilize Ln(III) hydrocarbyl complexes, herein we applied this ligand to lanthanide metals.
Figure 3. Synthesis of bis-1,1-(2-oxazolinyl)-1-(cyclopentadienyl)ethane ligand $H\{\text{MeC(C}_5\text{H}_4)(\text{Ox}_2\text{Me})\}_2$ and $H\{\text{MeC(C}_5\text{Me}_4)(\text{Ox}_2\text{Me})\}_2$

Since cyclopentadienyl (Cp) ligands are favored to stabilize Ln(III) hydrocarbyl complexes, in this contribution, we applied this [$\text{MeC(C}_5\text{Me}_4)(\text{Ox}_2\text{Me})_2$] ligand to stabilize rare earth alkyl complexes. The synthesis and characterization of [$\text{MeC(C}_5\text{Me}_4)(\text{Ox}_2\text{Me})_2$]Ln(CH$_2$Ph)$_2$ are described, including the results of a single crystal X-ray diffraction study on [$\text{MeC(C}_5\text{Me}_4)(\text{Ox}_2\text{Me})_2$]Lu(CH$_2$Ph)$_2$. The compounds [$\text{MeC(C}_5\text{Me}_4)(\text{Ox}_2\text{Me})_2$]Ln(CH$_2$Ph)$_2$ react with NH$_3$B(C$_6$F$_5$)$_3$ to provide the first examples of Lewis acid-stabilized Yttrium and Lutetium terminal imido complexes. In addition, a series of zwitterionic lanthanide alkyls [[$\text{MeC(C}_5\text{Me}_4)(\text{Ox}_2\text{Me})_2$]LnCH$_2$Ph]$^+$ and lanthanido diiodides [$\text{MeC(C}_5\text{Me}_4)(\text{Ox}_2\text{Me})_2$]LnI$_2$ are described too.
Results and Discussion.

A. Synthesis and characterization of \{MeC(C_5Me_4)(Ox^{Me_2})_2\}Ln(CH_2Ph)_2 (Ln = Sc, Y, Lu) complexes.

The compounds H\{MeC(C_5Me_4)(Ox^{Me_2})_2\} and Sc(CH_2Ph)_3(THF)_3 react in benzene after 3 hours at 60 °C to give \{MeC(C_5Me_4)(Ox^{Me_2})_2\}Sc(CH_2Ph)_2 (1) as a THF-free material [eqn. (1)]. The $^1$H NMR spectrum of 1 contained two doublets at 1.9 ppm and 2.1 ppm for the Sc benzyl CH$_2$. Besides, toluene is observed during the reaction by $^1$H NMR spectroscopy on the crude reaction mixture. The product is suggested to be $C_5$ symmetric in benzene-$d_6$ solution, as indicated by one set of oxazoline resonances contain diastereotopic CH$_2$ and CMe$_2$ groups. However, solid state IR spectrum of 1 contained two different CN stretching at 1591 and 1664 cm$^{-1}$, indicating that two oxazoline groups were inequivalent.

\[
\begin{align*}
\text{H\{MeC(C_5Me_4)(Ox^{Me_2})_2\}} + \text{LnBn}_3\text{thf}_3 & \xrightarrow{\text{C}_6\text{H}_6, \text{rt}} \text{H\{MeC(C_5Me_4)(Ox^{Me_2})_2\}} \\
\text{Ln} & = \text{Sc (1), 81.3}\% \\
& \quad \text{Y (2), 74.7}\% \\
& \quad \text{Lu (3), 95.4}\%
\end{align*}
\]

Reactions of H\{MeC(C_5Me_4)(Ox^{Me_2})_2\} and Y(CH_2Ph)_3(THF)$_3$ or Lu(CH_2Ph)$_3$(THF)$_3$ in benzene follow the same pathway as the reaction of Y(CH_2Ph)_3(THF)$_3$, giving products \{MeC(C_5Me_4)(Ox^{Me_2})_2\}Y(CH_2Ph)$_2$ (2) or \{MeC(C_5Me_4)(Ox^{Me_2})_2\}Lu(CH_2Ph)$_2$ (3) [eqn. (1)]. Similar to complex
{MeC(C₅Me₄)(OxMe₂)₂}Sc(CH₂Ph)₂ (1), both 2 and 3 were C₅ symmetric in benzene-d₆ solution, as indicated by one set of oxazoline resonances contain diastereotopic CH₂ and CMe₂ groups from ¹H NMR spectroscopy. However, IR spectrum showed two different CN stretching which indicated that two oxazoline groups were not identical.

A cooled toluene solution of {MeC(C₅Me₄)(OxMe₂)₂}Lu(CH₂Ph)₂ (3) layered with pentane gave crystals suitable for X-ray structural analysis. The solution to the single-crystal X-ray diffraction study (Fig. 4) showed that only one oxazoline was coordinated to Sc center while the other one was dangling. This structure is consistent with the solid-state IR spectrum. However, variable temperature (VT) ¹H NMR spectroscopic experiments showed only equivalent oxaloline resonances from 298 K to 183 K. Either the solution structure of 3 is different from the solid state structure or two oxazoline groups were undergo exchange processes in solution. A solution-state IR should be taken to further explore the correct structure in solution.

Thermolysis experiments show that {MeC(C₅Me₄)(OxMe₂)₂}Ln(CH₂Ph)₂ complexes is persistent in toluene up to 180 °C for 2 days in a sealed J-young tube (Ln = Sc, Lu, Y).
B. Reactivity of \{\text{MeC(C}_5\text{Me}_4)(\text{Ox}_\text{Me}_2)\}_2\text{Lu(CH}_2\text{Ph})_2\} complexes.

B.1. Reaction between \{\text{MeC(C}_5\text{Me}_4)(\text{Ox}_\text{Me}_2)\}_2\text{Ln(CH}_2\text{Ph})_2\} complexes and \text{Me}_3\text{SiI}:

The reaction between \{\text{MeC(C}_5\text{Me}_4)(\text{Ox}_\text{Me}_2)\}_2\text{Lu(CH}_2\text{Ph})_2\} and two equivalent of \text{Me}_3\text{SiI} in benzene after a day at room temperature gives the product \{\text{MeC(C}_5\text{Me}_4)(\text{Ox}_\text{Me}_2)\}_2\text{LuI}_2\} \quad (4) \quad \text{[eqn. (2)]}. The by-product \text{Me}_3\text{SiCH}_2\text{Ph} was observed in the \text{^1H} NMR spectrum and can be removed by washing with pentane. Notably, after \{\text{MeC(C}_5\text{Me}_4)(\text{Ox}_\text{Me}_2)\}_2\text{LuI}_2\} complexes were isolated, the yellow color solid can not be re-dissolved back to benzene solution, due to dimerization as one possible reason.
B.2. Abstraction reaction of \{MeC(C_5Me_4)(OxMe_2)_2\}Ln(CH_2Ph)_2 with Lewis acid.

Reactions of hydrocarbyl metal compounds and Lewis acids such as tris(perfluorophenyl)borane typically proceed by anionic group abstraction to form cationic or zwitterionic metal complexes.\(^{13}\) Reaction of B(C_6F_5)_3 with \{MeC(C_5Me_4)(OxMe_2)_2\}Sc(CH_2Ph)_2 in benzene at room temperature produces \{MeC(C_5Me_4)(OxMe_2)_2\}Sc(CH_2Ph)_2^+ (5) cation via benzide abstraction [eqn. (3)]. The \(^1\)H NMR spectrum of 5 in bromobenzene contained a singlet at 1.99 ppm for the scandium benzyl CH\_2 and a broad signal at 3.33 ppm for the benzyl CH\_2 bonded to boron. The latter resonance was unambiguously assigned by a crosspeak in the \(^1\)H-\(^{11}\)B HMBC experiment with a \(^{11}\)B NMR resonance at –11.97 ppm, which indicated that an anionic borate center had been formed.
B.3. Other reactivity tests of \{MeC(C_5Me_4)(OxMe_2)\}_2Ln(CH_2Ph)_2 complexes:

Treatment of \{MeC(C_5Me_4)(OxMe_2)\}_2Ln(CH_2Ph)_2 [Ln = Sc (1), Y (2), Lu (3)] with H_2 does not result in isolable \{MeC(C_5Me_4)(OxMe_2)\}_2LnH_2 products. Toluene is formed during the reaction process but no intermediate is isolable.

Reactions of 1, 2, or 3 with PhSiH_3 also do not give isolable intermediates or the expected products \{MeC(C_5Me_4)(OxMe_2)\}_2LnH_2. However, two triplets at 4.44 ppm and 2.31 ppm in the \(^1\)H NMR spectrum indicated that the expected byproduct PhBnSiH_2 was formed during the reaction.

No reactions were detection when complexes 1, 2, or 3 reacted with isobutene, tert-butyl ethylene or diphenyl acetylene up to 180°C for 2 days, while reactions with CO and O_2 occurred rapidly to give toluene and not identified products. Besides, secondary amines and secondary phosphines do not react with complexes 1, 2, or 3, even at 180°C for 2 days.

C.1. Synthesis and characterization of lanthanide imidoborate \{MeC(C_5Me_4)(OxMe_2)\}_2Ln=NH\textsubscript{3}B(C_6F_5)\textsubscript{3} complexes (Ln=Lu, Y).

Treatment of \{MeC(C_5Me_4)(OxMe_2)\}_2Lu(CH_2Ph)_2 with NH_3B(C_6F_5)\textsubscript{3} in benzene solution at room temperature for 3 hours results in the formation of imidoborate complex \{MeC(C_5Me_4)(OxMe_2)\}_2Lu=NH\textsubscript{3}B(C_6F_5)\textsubscript{3} (6) [eqn. (4)]. This contrasts Mountford’s titanium and zirconium examples,\(^8\) which instead form bisimidoborate products. In the \(^1\)H NMR spectrum of 6, a singlet at 5.54 ppm (1 H) was observed for the Lutetium imido
NH proton. Besides, in the $^{11}$B NMR spectrum, a new signal at −9.8 ppm suggested a conversion from NH$_3$B(C$_6$F$_5$)$_3$ (δ −4.9) into an imidoborate NHB(C$_6$F$_5$)$_3$ ligand.

Additionally, the $^{15}$N NMR contained two signals; a singlet at −148.9 ppm was assigned to the N from the oxazoline groups, and a doublet resonance ($^3J_{NN} = 55.9$ Hz) at −181.1 ppm was assigned to the imido NH. (Fig. 5) The solution structure of 6 is $C_s$ symmetric, as indicated by one set of oxazoline resonances contain diastereotropic CH$_2$ and CMe$_2$ groups.
Figure 5. $^{15}$N NMR for imidoborate complex $\{\text{MeC(C}_5\text{Me}_4)(\text{Ox}_\text{Me}_2)_2\}\text{Lu}=\text{NHB(C}_6\text{F}_5)_3$ (6).

Even though an X-ray structure has not been successfully obtained, $\{\text{MeC(C}_5\text{Me}_4)(\text{Ox}_\text{Me}_2)_2\}\text{Lu}=\text{NHB(C}_6\text{F}_5)_3$ (6) is assigned as a terminal monomeric imidoborate complex. This structure is supported by a DOSY experiment,\textsuperscript{14} where the diffusion coefficient of 6 is $7.20 \times 10^{-10}$ m$^2$/s (296 K). For comparison, the diffusion coefficients of $\{\text{MeC(C}_5\text{Me}_4)(\text{Ox}_\text{Me}_2)_2\}\text{Lu}(\text{CH}_2\text{Ph})_2$ (3), which is monomeric species as shown by X-ray crystallography, is $7.38 \times 10^{-10}$ m$^2$/s (296 K). The similar diffusion coefficients between compound 6 and 3 further supports the assertion that $\{\text{MeC(C}_5\text{Me}_4)(\text{Ox}_\text{Me}_2)_2\}\text{Lu}=\text{NHB(C}_6\text{F}_5)_3$ is monomeric in solution.
The reaction between \( \text{MeC(C}_5\text{Me}_4\text{(OxMe}_2\text{)}_2\text{)}Y(\text{CH}_2\text{Ph})_2 \) and \( \text{NH}_3\text{B(C}_6\text{F}_5\text{)}_3 \) in benzene behaves similarly as the reaction of \( \text{MeC(C}_5\text{Me}_4\text{(OxMe}_2\text{)}_2\text{)}\text{Lu(Ch}_2\text{Ph})_2 \), giving the Yttrium imidoborate product \( \text{MeC(C}_5\text{Me}_4\text{(OxMe}_2\text{)}_2\text{)}Y=\text{NHB(C}_6\text{F}_5\text{)}_3 \) (7) after 30 minutes [eqn. (4)]. However, the scandium analog did not provide the isolable lighter congener. Even though \( \text{MeC(C}_5\text{Me}_4\text{(OxMe}_2\text{)}_2\text{)}\text{Sc=NHB(C}_6\text{F}_5\text{)}_3 \) species is observed during the reaction, the reaction does not go to completion and the imidoborate product was not isolated.

Other than \( \text{NH}_3\text{B(C}_6\text{F}_5\text{)}_3 \), similar amineborane compounds, such as \( \text{tBuNH}_2\text{B(C}_6\text{F}_5\text{)}_3 \), \( \text{NH}_2\text{NH}_2\text{B(C}_6\text{F}_5\text{)}_3 \), or \( \text{NH}_2\text{NH}_2\text{PhB(C}_6\text{F}_5\text{)}_2 \) were reacted with \( \text{MeC(C}_5\text{Me}_4\text{(OxMe}_2\text{)}_2\text{)}\text{Ln(Ch}_2\text{Ph})_2 \), but no isolable species were detected.

Furthermore, in order to synthesize \( \text{Ln oxoborate complex} \) \( \text{MeC(C}_5\text{Me}_4\text{(OxMe}_2\text{)}_2\text{)}\text{Lu=O} \) using the same method as the synthesis of \( \text{Ln imidoborate complexes} \), \( \text{MeC(C}_5\text{Me}_4\text{(OxMe}_2\text{)}_2\text{)}\text{Lu(Ch}_2\text{Ph})_2 \) was treated with \( \text{H}_2\text{O B(C}_6\text{F}_5\text{)}_3 \). However, boron signal was hardly observed from \( ^{11}\text{B NMR spectrum} \), indicating that products did not contain a borate ligand to stabilize terminal Lu oxo complex. Thus, the initial expected monomeric Lu oxo product might dimerize to form Lu-O-Lu bridging complex.

C.2. Reactivity tests of lanthanide imidoborate complexes

\( \text{MeC(C}_5\text{Me}_4\text{(OxMe}_2\text{)}_2\text{)}\text{Ln=NH}_{\text{B(C}_6\text{F}_5\text{)}_3} \) (\( \text{Ln=Lu, Y} \)).

Treatment of \( \text{MeC(C}_5\text{Me}_4\text{(OxMe}_2\text{)}_2\text{)}\text{Lu=NH}_{\text{B(C}_6\text{F}_5\text{)}_3} \) with another equivalent of \( \text{NH}_3\text{B(C}_6\text{F}_5\text{)}_3 \) does not give the expected bisimidoborate complexes \( \text{MeC(C}_5\text{Me}_4\text{(OxMe}_2\text{)}_2\text{)}\text{Lu}[\text{NH}_2\text{B(C}_6\text{F}_5\text{)}_3]_2 \). During the reaction, new species formed but
could not be identified and isolated before decomposition. Heating the reaction can only accelerate the decomposition rate.

Notably, Chen’s Scandium imido example showed that the addition of a Lewis base, such as DMAP, was necessary to facilitate the formation of terminal scandium imido complexes. However, in this imidoborate system, treatment of a Lewis base was not essential for the formation of the imidoborate products. Furthermore, the addition of a Lewis base such as pyridine or DMAP to the isolated \{MeC(C_5Me_4)(OxMe_2)_2\}Ln=NH\text{B}(C_6F_5)_3 (6 and 7) complexes causes immediate decomposition, rather than stabilizing the imidoborate complexes by coordinating to the lanthanide metal center.

Conclusion.

In conclusion, we demonstrated that reactive Lanthanids(III) alkyl complexes \{MeC(C_5Me_4)(OxMe_2)_2\}Ln(CH_2Ph)_2 (Ln = Sc, Y, Lu) can be prepared from protonolysis of Ln(CH_2Ph)_3(THF)_3 by the bulky H\{MeC(C_5Me_4)(OxMe_2)_2\} ligand and structurally characterized. Besides, the first Lutetium and Yttrium imidoborate complexes have been isolated from deprotonation of NH\text{3}B(C_6F_5)_3 with \{MeC(C_5Me_4)(OxMe_2)_2\}Ln(CH_2Ph)_2 complexes (Ln = Lu, Y), which demonstrates that the lanthanide terminal imido complexes is stabilized with a borate ligand present and attached to the terminal imido nitrogen as well as a sterically favored H\{MeC(C_5Me_4)(OxMe_2)_2\} ligand. The reactivities of these terminal imidoborate complexes are under investigation.
Experimental

General Procedures. All reactions were carried out under an inert atmosphere using standard Schlenk techniques or in a glovebox. All solvents were dried and degassed unless otherwise indicated. $\text{H}\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2$, $\text{Sc(CH}_2\text{Ph}_3(\text{THF})_3$, $\text{Y(CH}_2\text{Ph}_3(\text{THF})_3$, and $\text{Lu(CH}_2\text{Ph}_3(\text{THF})_3$ were prepared according to reported procedures. All NMR spectra were obtained at room temperature using a Bruker DRX-400 spectrometer, Bruker Avance II-700 spectrometer, or Agilent MR400 spectrometer. $^{15}\text{N}$ NMR chemical shifts were determined by $^1\text{H}$-$^{15}\text{N}$ HMBC experiments recorded on an Bruker DRX-600 spectrometer; the chemical shift values are reported relative to $\text{CH}_3\text{NO}_2$. $^{11}\text{B}$ NMR spectra chemical shifts are reported relative to $\text{BF}_3\cdot\text{Et}_2\text{O}$. Elemental analyses were obtained at the Iowa State Chemical Instrumentation Facility using a Perkin-Elmer 2400 Series II CHN/S. X-ray diffraction data was collected on a Bruker-AXS SMART or APEX II as described below.

$\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Sc(CH}_2\text{Ph}_2$ (1). $\text{H}[\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\] (0.204 g, 0.590 mmol) was dissolved in 15 mL of benzene. A light yellow solution formed upon addition of solid $\text{Sc(CH}_2\text{Ph}_3(\text{THF})_3$ (0.315 g, 0.590 mmol), and this solution was stirred at 60 °C for 3 hours. The volatile materials were removed under reduced pressure. The residue was then washed with pentane ($2 \times 2$ mL) and dried giving the product in good yield (0.274 g, 0.480 mmol, 81.3%). $^1\text{H}$ NMR (benzene-$d_6$, 600 MHz): $\delta$ 7.23 (t, $^3J_{\text{HH}} = 7.6$ Hz, 4 H, meta-$\text{C}_6\text{H}_5$), 7.09 (d, $^3J_{\text{HH}} = 7.5$ Hz, 4 H, ortho-$\text{C}_6\text{H}_5$), 6.88 (t, $^3J_{\text{HH}} = 7.1$ Hz, 2 H, para-$\text{C}_6\text{H}_5$), 3.54 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2 H, CNCMe$_2\text{CH}_2\text{O}$), 3.40 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2 H, CNCMe$_2\text{CH}_2\text{O}$), 2.09 (d, 2 H, ScCH$_2$Ph), 1.97 (s, 6 H, C$_5\text{Me}_4$), 1.96 (s, 6 H, C$_5\text{Me}_4$), 1.93 (d, 2 H, ScCH$_2$Ph), 1.83 (s, 3 H, backbone Me), 0.95 (s, 6 H, CNCMe$_2\text{CH}_2\text{O}$), 0.94 (s, 6
H, CNCMe₂CH₂O). ¹³C{¹H} NMR (benzene-<sub>d₆</sub>, 125 MHz): δ 174.72 (br, CNCMe₂CH₂O), 152.17 (ipso-C₆H₃CH₂Sc), 129.00 (meta-C₆H₅), 125.69 (ortho-C₆H₃CH₂Sc), 122.15 (C₅Me₄), 120.19 (C₅Me₄), 119.39 (para-C₆H₅), 115.58 (ipso-C₅Me₄), 80.58 (CNCMe₂CH₂O), 67.41 (CNMe₂CH₂O), 59.54 (br, ScCH₂C₆H₃), 46.47 (backbone CMe), 27.81 (CNCMe₂CH₂O), 27.13 (CNCMe₂CH₂O), 23.74 (backbone CMe), 13.97 (C₅Me₄), 11.61 (C₅Me₄).

¹⁵N NMR (benzene-<sub>d₆</sub>, 71 MHz): δ –138.5.

IR (KBr, cm⁻¹): 3064 m, 2695 s, 2924 m, 2868 m, 1664 m (CN), 1591 s (CN), 1485 m, 1461 m, 1396 w, 1365 m, 1316 w, 1280 m, 1211 s, 1192 m, 1176 m, 1109 m, 1088 s, 1026 m, 936 s, 888 w, 869 w, 797 m, 754 m, 740 m, 695 m, 678 m, 615 m. mp 97-101 °C.

{MeC(C₅Me₄)(OxMe₂)₂}Y(CH₂Ph)₂ (2). H[MeC(C₅Me₄)(OxMe₂)₂] (45.9 mg, 0.133 mmol) was dissolved in 5 mL of benzene. A light yellow solution formed upon addition of solid Y(CH₂Ph)₃(THF)₃ (76.9 mg, 0.133 mmol), and this solution was stirred at room temperature for 1 h. The volatile materials were removed under reduced pressure. The residue was then washed with pentane (2 × 2 mL) and dried to afford compound 2 (61.0 mg, 0.099 mmol, 74.7%). ¹H NMR (benzene-<sub>d₆</sub>, 600 MHz): δ 7.14 (t, ³JHH = 7.6 Hz, 4 H, meta-C₆H₅), 6.73 (d, ³JHH = 7.6 Hz, 4 H, ortho-C₆H₅), 6.71 (t, overlapping with ortho-C₆H₅, 2 H, para-C₆H₅), 3.52 (d, ³JHH = 8.3 Hz, 2 H, CNCMe₂CH₂O), 3.43 (d, ³JHH = 8.3 Hz, 2 H, CNCMe₂CH₂O), 2.07 (s, 6 H, C₅Me₄), 2.02 (s, 6 H, C₅Me₄), 1.91 (s, 3H, backbone Me), 1.83 (s br, 2 H, YCH₂Ph), 1.74 (s br, 2 H, YCH₂Ph), 0.88 (s, 6 H, CNCMe₂CH₂O), 0.87 (s, 6 H, CNCMe₂CH₂O). ¹³C{¹H} NMR (benzene-<sub>d₆</sub>, 125 MHz): δ 173.55 (CNCMe₂CH₂O), 152.18 (ipso-C₆H₃CH₂Y), 131.01 (meta-C₆H₃CH₂Y), 123.24 (ortho-C₆H₃CH₂Y), 119.31 (C₅Me₄), 118.24 (para-C₆H₃CH₂Y), 117.70 (C₅Me₄), 115.54 (ipso-C₅Me₄), 80.44 (CNCMe₂CH₂O), 67.66 (CNCMe₂CH₂O), 53.67 (d, ¹JYC = 30.1 Hz,
YCH2C6H5), 46.50 (backbone CMe), 27.64 (CNCMe2CH2O), 27.39 (CNCMe2CH2O),
24.01 (backbone CMe), 13.94 (C5Me4), 11.96 (C5Me4). 15N NMR (benzene-d6, 71 MHz):
δ –138.8. IR (KBr, cm⁻¹): 2964 s, 2926 s, 2884 m, 1654 s (CN), 1648 s (CN), 1460 m,
1364 m, 1303 w, 1261 m, 1213 w, 1192 w, 1093 s, 1025 m, 974 m, 868 m, 802 m, 730 w,
697 w, 622 w. mp 105–109 °C.

{MeC(C5Me4)(OxMe2)2}Lu(CH2Ph)2 (3). H[MeC(C5Me4)(OxMe2)2] (0.106 g, 0.307 mmol) was dissolved in 5 mL of benzene. A light yellow solution formed upon addition
of solid Lu(CH2Ph)3(THF)3 (0.203 g, 0.307 mmol), and this solution was stirred at 60 °C
for 30 minutes and then the volatile materials were removed under reduced pressure. The
residue was then washed with pentane (2 × 2 mL) and dried to give 3 in excellent yield
(0.205 g, 0.293 mmol, 95.4%). 1H NMR (benzene-d6, 600 MHz): δ 7.20 (t, 3JHH = 7.2 Hz,
4 H, meta-C6H5), 6.97 (d, 3JHH = 7.2 Hz, 4 H, ortho-C6H5), 6.81 (t, 3JHH = 7.2 Hz, 2 H,
para-C6H5), 3.52 (d, 3JHH = 8.4 Hz, 2 H, CNCMe2C2H2O), 3.39 (d, 3JHH = 8.4 Hz, 2 H,
CNCMe2C2H2O), 2.03 (s, 6 H, C5Me4), 2.02 (s, 6 H, C5Me4), 1.87 (s, 3H, backbone Me),
1.73 (d, 3JHH = 9.5 Hz, 2 H, LuCH2Ph), 1.60 (d, 3JHH = 9.5 Hz, 2 H, LuCH2Ph), 0.89 (s, 6
H, CNCMe2C2H2O), 0.86 (s, 6 H, CNCMe2C2H2O). 13C{1H} NMR (benzene-d6, 125
MHz): δ 175.06 (CNCMe2C2H2O), 152.40 (ipso-C6H5CH2Lu), 129.71 (meta-C6H5CH2Lu),
125.06 (ortho-C6H5CH2Lu), 119.10 (C5Me4), 119.01 (para-C6H5CH2Lu), 117.89 (C5Me4),
114.08 (ipso-C5Me4), 80.54 (CNCMe2C2H2O), 67.41 (CNCMe2C2H2O), 59.21
(LuCH2C6H5), 46.40 (backbone CMe), 27.58 (CNCMe2C2H2O), 27.20 (CNCMe2C2H2O),
24.02 (backbone CMe), 13.75 (C5Me4), 11.53 (C5Me4). 15N NMR (benzene-d6, 71 MHz):
δ –135.2. IR (KBr, cm⁻¹): 3059 m, 3001 s, 2975 m, 2894 m, 2866 m, 1655 s (CN), 1601 s
(CN), 1589 s (CN), 1485 s, 1395 s, 1314 s, 1282 w, 1211 s, 1176 m, 1095 s, 1176 m,
1027 w, 932 s, 865 m, 797 m, 739 m. Calcd for C$_{35}$H$_{45}$LuN$_2$O$_2$: C, 59.99; H, 6.47; N, 4.00. Found: C, 67.94; H, 6.55; N, 4.88. mp 95-97°C.

{MeC(C$_5$Me$_4$)(Ox$^{Me2}$)$_2$}LuI$_2$ (4). {MeC(C$_5$Me$_4$)(Ox$^{Me2}$)$_2$}Lu(CH$_2$Ph)$_2$ (0.305 g, 0.435 mmol) was dissolved in 10 mL of benzene. A light yellow solution formed upon addition of two equivalent of Me$_3$SiI (124 µL, 0.871 mmol), and this solution was stirred at room temperature for 3 h and then the volatile materials were removed under reduced pressure. The residue was then washed with pentane (2 x 5 mL) and dried (0.286 g, 0.371 mmol, 85.2%).$^1$H NMR (benzene-$d_6$, 600 MHz): δ 3.58 (d, $^3$J$_{HH}$ = 8.6 Hz, 2 H, CNCMe$^2$CH$_2$O), 3.54 (d, $^3$J$_{HH}$ = 8.6 Hz, 2 H, CNCMe$^2$CH$_2$O), 2.39 (s, 6 H, C$_5$Me$_4$), 2.12 (s, 3 H, backbone Me), 1.93 (s, 6 H, C$_5$Me$_4$), 1.41 (s, 6 H, CNCMe$^2$CH$_2$O), 1.17 (s, 6 H, CNCMe$^2$CH$_2$O).

$^{13}$C($^1$H) NMR (benzene-$d_6$, 125 MHz): δ 175.41 (CNCMe$^2$CH$_2$O), 123.44 (C$_5$Me$_4$), 122.16 (C$_5$Me$_4$), 115.81 (ipso-C$_5$Me$_4$), 82.71 (CNCMe$^2$CH$_2$O), 68.48 (CNCMe$^2$CH$_2$O), 46.89 (backbone CMe), 28.54 (CNCMe$^2$CH$_2$O), 27.97 (CNCMe$^2$CH$_2$O), 27.42 (backbone CMe), 16.18 (C$_5$Me$_4$), 14.26 (C$_5$Me$_4$). $^{15}$N NMR (benzene-$d_6$, 71 MHz): δ –139.8.

[[{MeC(C$_5$Me$_4$)(Ox$^{Me2}$)$_2$}ScCH$_2$Ph]|[(CH$_2$Ph)B(C$_6$F$_5$)$_3$]] (5). Benzene (10 ml) was added to a mixture of {MeC(C$_5$Me$_4$)(Ox$^{Me2}$)$_2$}Sc(CH$_2$Ph)$_2$ (0.156 g, 0.273 mmol) and B(C$_6$F$_5$)$_3$ (0.140 g, 0.273 mmol) at room temperature. The reaction mixture was stirred at room temperature for 10 minutes to form a yellow oil layer at the bottom of the vial. The clear top layer was removed by a pipette and the oil layer was washed with benzene (2 x 5 ml), followed by with pentane (2 ml). Volatile was removed under reduced pressure to yield light yellow solid of [[{MeC(C$_5$Me$_4$)(Ox$^{Me2}$)$_2$}ScCH$_2$Ph]|[(CH$_2$Ph)B(C$_6$F$_5$)$_3$]] (0.121 g, 0.152 mmol, 51.5%).$^1$H NMR (bromobenzene-$d_5$, 600 MHz, 25°C): δ 7.15 (d, $^3$J$_{HH}$ = 6.4 Hz, 2 H, BCH$_2$(ortho-C$_6$H$_5$)), 7.05 (t, $^3$J$_{HH}$ = 7.2 Hz, 2 H, ScCH$_2$(meta-C$_6$H$_5$)), 7.00 (t,
$J_{HH} = 7.6$ Hz, 2 H, BCH$_2$(meta-C$_6$H$_5$)), 6.84 (t, $J_{HH} = 7.6$ Hz, 1 H, BCH$_2$(para-C$_6$H$_5$)),
6.69 (t, $J_{HH} = 7.6$ Hz, 1 H, ScCH$_2$(para-C$_6$H$_5$)), 6.16 (d, $J_{HH} = 7.6$ Hz, 2 H, ScCH$_2$(ortho-C$_6$H$_5$)), 3.92 (d, $J_{HH} = 9.6$ Hz, 2 H, CNCMe$_2$CH$_2$O), 3.83 (d, $J_{HH} = 9.6$ Hz, 2 H, CNCMe$_2$CH$_2$O), 3.33 (s, 2 H, [(CH$_2$Ph)B(C$_6$F$_5$)$_3$]), 1.99 (s, 2 H, Sc(CH$_2$Ph)$^+$), 1.64 (s, 6 H, C$_5$Me$_4$), 1.44 (s, 3 H, backbone Me), 1.41 (s, 6 H, C$_5$Me$_4$), 0.82 (s, 6 H, CNCMe$_2$CH$_2$O), 0.74 (s, 6 H, CNCMe$_2$CH$_2$O).

$^{19}$F NMR (bromobenzene-$d_5$, 376 MHz, 25 ºC): δ -129.7 (d, $J_{FF} = 22.6$ Hz, 2 F, o-F), -163.2 (t, $J_{FF} = 20.7$ Hz, 1 F, p-F), -165.9 (t, $J_{FF} = 20.7$ Hz, 2 F, m-F).

$^{11}$B NMR (bromobenzene-$d_5$, 79.5 MHz, 25 ºC): -12.0 (br).

$^{15}$N NMR (benzene-$d_6$, 71 MHz): δ -139.8.

IR (KBr, cm$^{-1}$): 3057 w, 2976 m, 2925 m, 2874 w, 1640 m (CN), 1623 m (CN), 1511 s, 1456 s, 1372 m, 1314 m, 1270 m, 1214 w, 1168 w, 1082 s, 981 s, 819 m, 798 m, 767 w, 703 m, 681 m, 651 w, 621 w.

{MeC(C$_5$Me$_4$)(Ox$^{Me2}$)$_2$}YNHB(C$_6$F$_5$)$_3$ (6). Benzene (5 mL) was added to a mixture of {MeC(C$_5$Me$_4$)(Ox$^{Me2}$)$_2$}Y(CH$_2$Ph)$_2$ (0.094 g, 0.152 mmol) and NH$_3$B(C$_6$F$_5$)$_3$ (0.080 g, 0.152 mmol) at room temperature. This solution was stirred at room temperature for 30 minutes, and then the volatile materials were removed under reduced pressure. The residue was then washed with (3 x 3 mL) of pentane and dried (0.125 g, 0.129 mmol, 85.4%).

$^{1}$H NMR (benzene-$d_6$, 600 MHz): δ 5.84 (s, 1 H, YNH), 3.36 (d, $J_{HH} = 8.8$ Hz, 2 H, CNCMe$_2$CH$_2$O), 3.34 (d, $J_{HH} = 8.8$ Hz, 2 H, CNCMe$_2$CH$_2$O), 2.20 (s, 6 H, C$_5$Me$_4$), 1.75 (s, 6 H, C$_5$Me$_4$), 1.55 (s, 3 H, backbone Me), 0.81 (s, 6 H, CNCMe$_2$CH$_2$O), 0.79 (s, 6 H, CNCMe$_2$CH$_2$O).

$^{13}$C ($^1$H) NMR (benzene-$d_6$, 125 MHz): δ 177.13 (CNCMe$_2$CH$_2$O), 150.11 (br C$_6$F$_5$), 148.23 (br C$_6$F$_5$), 146.77 (br C$_6$F$_5$), 138.71 (br C$_6$F$_5$), 137.13 (br C$_6$F$_5$), 121.70 (C$_5$Me$_4$), 121.29 (C$_5$Me$_4$), 118.31 (ipso-C$_5$Me$_4$), 82.30 (CNCMe$_2$CH$_2$O), 68.26 (CNCMe$_2$CH$_2$O), 46.70 (backbone CMe), 28.17 (CNCMe$_2$CH$_2$O), 26.38
(CNCMe₂CH₂O), 20.26 (backbone CMe), 15.15 (C₅Me₄), 11.26 (C₅Me₄). ¹⁵N NMR (benzene-d₆, 71 MHz): δ −150.4 (s, CNCMe₂CH₂O), −182.7 (d, ³JNN = 55.3 Hz, Lu-NH).

¹¹B NMR (benzene-d₆, 128 MHz): δ −10.0. IR (KBr, cm⁻¹): 2971 m, 2931 m, 2873 s, 1644 s, 1516 s, 1472 s, 1388 m, 1368 m, 1305 m, 1182 m, 1096 s, 1030 m, 973 s, 845 w, 824 w, 737 w, 621 m, 576 w. Calcd for C₃₉H₃₀B₂F₁₅YN₄O₃: C, 48.82; H, 3.36; N, 4.38. Found: C, 67.94; H, 6.55; N, 4.88. mp 118-122 °C

{MeC(C₅Me₄)(OxMe₂)}₂LuNHB(C₆F₅)₃ (7). Benzene (5mL) was added to a mixture of {MeC(C₅Me₄)(OxMe₂)}₂Lu(CH₂Ph)₂ (0.107 g, 0.153 mmol) and NH₃B(C₆F₅)₃ (0.081 g, 0.153 mmol) at room temperature. This solution was stirred at room temperature for 3 hours and then the volatile materials were removed under reduced pressure. The residue was then washed with (3 × 3 mL) of pentane and dried (0.135 g, 0.125 mmol, 81.7%). ¹H NMR (benzene-d₆, 600 MHz): δ 5.54 (s, 1 H, LuN₁H), 3.33 (d, ³JHH = 8.6 Hz, 2 H, CNCMe₂CH₂O), 3.29 (d, ³JHH = 8.5 Hz, 2 H, CNCMe₂CH₂O), 2.23 (s, 6 H, C₅Me₄), 1.78 (s, 6 H, C₅Me₄), 1.55 (s, 3 H, backbone Me), 0.75 (s, 6 H, CNCMe₂CH₂O), 0.70 (s br, 6 H, CNCMe₂CH₂O). ¹³C{¹H} NMR (benzene-d₆, 125 MHz): δ 177.55 (CNCMe₂CH₂O), 149.74 (br C₆F₅), 148.35 (br C₆F₅), 146.74 (br C₆F₅), 138.76 (br C₆F₅), 137.17 (br C₆F₅), 121.09 (C₅Me₄), 120.57 (C₅Me₄), 116.69 (ipso-C₅Me₄), 82.39 (CNCMe₂CH₂O), 68.31 (CNCMe₂CH₂O), 46.55 (backbone CMe), 28.15 (CNCMe₂CH₂O), 26.16 (CNCMe₂CH₂O), 20.41 (backbone CMe), 14.70 (C₅Me₄), 11.27 (C₅Me₄). ¹⁵N NMR (benzene-d₆, 71 MHz): δ −148.9 (s, CNCMe₂CH₂O), −181.8 (d, ³JNN = 55.9 Hz, Lu-NH).

¹¹B NMR (benzene-d₆, 128 MHz): δ −9.8. IR (KBr, cm⁻¹): 2969 m, 2927 s, 1645 s br (CN), 1516 s, 1475 s, 1402 m, 1300 m, 1192 m, 1099 s, 1033 w, 974 s, 847 w, 809 w,
737 w, 679 m. Calcd for C$_{39}$H$_{30}$B$_2$F$_{15}$LuN$_4$O$_3$: C, 43.20; H, 2.79; N, 5.17. Found: C, 67.94; H, 6.55; N, 4.88. mp 112-115 °C.

**Procedures for DOSY (Diffusion-Ordered Spectroscopy) experiment.** All the measurements were performed on a Bruker DRX400 spectrometer using a DOSY stimulated spin-echo pulse program with bipolar gradients. Accurately known concentrations of the species in question were used. The concentrations of \{MeC(C$_5$Me$_4$)(OxMe$_2$)$_2$\}_$_2$LuNHB(C$_6$F$_5$)$_3$ (7) and To$^M$ZnMe were determined by integration of resonances corresponding to species of interest and integration of a tetrakis(trimethylsilyl)silane standard of accurately known concentration. The temperature in the NMR probe was preset to 296 K, and the probe was maintained at a constant temperature for each experiment. The delay time in between pulses was set to 5 s in order to ensure the spins are fully relaxed to their ground states. During the experiments, a series of 1D $^1$H NMR spectra were acquired at increasing gradient strength. The signal intensity decay was fit by non-linear least squares regression analysis to Equation 1 to obtain the diffusion coefficient D.$^{14}$

$$\ln \left( \frac{I}{I_0} \right) = -\left( \frac{\gamma \delta}{3} \right)^2 G^2 \left( \Delta - \frac{\delta}{3} \right) D$$

where I is the observed intensity, D is the diffusion coefficient, $\gamma$ is the gyromagnetic ratio of the nucleus, $\delta$ is the length of the gradient pulse, and $\Delta$ is the diffusion time.
References


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CHAPTER 3: β-CH AGOSTIC INTERACTION STABILIZED NEW RARE EARTH (LU, Y) TERMINAL IMIDO COMPLEXES

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Abstract.

The bis-1,1-(2-oxazolinyl)-1-(tetramethylcyclopentadienyl)ethane ligand [MeC(C₅Me₄)(OxMe₂)₂]⁻ is sterically favored to stabilize high reactive rare earth metal alkyl complexes {MeC(C₅Me₄)(OxMe₂)₂}Ln(CH₂Ph)₂ (Ln = Sc, Lu, Y). These compounds are precursors for the first examples of terminal lutetium and yttrium imido complexes containing β-CH. Reactions between one equivalent of benzylic amines NH₂CH₂(Aryl) and {MeC(C₅Me₄)(OxMe₂)₂}Ln(CH₂Ph)₂ give imido complexes {MeC(C₅Me₄)(OxMe₂)₂}Lu=NCH₂Ar and {MeC(C₅Me₄)(OxMe₂)₂}Y=NCH₂Ar. β-CH agostic interactions are observed to stabilize these imido complexes. Bisamide complexes {MeC(C₅Me₄)(OxMe₂)₂}Ln(NHCH₂Ar)₂ are formed by the reaction of two equivalent of NH₂CH₂Ar amine and {MeC(C₅Me₄)(OxMe₂)₂}Ln(CH₂Ph)₂ complexes.
**Introduction.**

Terminal imido complexes containing a Ln=N double bond are highly reactive (Ln = lanthanide or group 3 metal center). For example, they are proposed intermediates in many catalytic reactions, such as imine metathesis\(^1\) and hydroamination catalyzed by early-transition-metals.\(^2\) Besides, Bergman\(^3\) and Wolczanski\(^4\) demonstrated that terminal early-metal imides can activate the C−H bonds of hydrocarbons, including methane.\(^5\)

However, terminal imido complexes in group 3 metal and lanthanides are rare. Only Piers\(^6\) and Chen\(^7\) reported isolated and structurally characterized scandium terminal imido complexes examples, formed via alkane elimination, facilitated by the presence of a Lewis base. Monometallic imido compounds based on larger rare earth metal centers were previously unknown. The challenge may relate to poor pi bonding of the rare earths, and this is anticipated to become more difficult with larger metal centers. An additional challenge to form terminal monomeric lanthanide imido complexes is that dimerization, to form bridging Ln-NR-Ln structures can be facile due to strong Ln-N bonds.\(^8\)

Recently, we observed that the [MeC(C\(_5\)Me\(_4\))(Ox\(_{Me2}\))\(_2\)]\(^-\) ligand is sterically favored to stabilize rare earth alkyl complexes (see Chapter 2). Furthermore, we successfully isolated the first examples of Lewis acid-stabilized yttrium and lutetium terminal imidoborate complexes \{MeC(C\(_5\)Me\(_4\))(Ox\(_{Me2}\))\(_2\})\text{Lu=NHB(C}_6\text{F}_5)_3\} and \{MeC(C\(_5\)Me\(_4\))(Ox\(_{Me2}\))\(_2\})\text{Y=NHB(C}_6\text{F}_5)_3\}.

In this contribution, we report the isolation and characterization of the first examples of terminal lutetium and yttrium imido complexes. These compounds are prepared without Lewis acid coordination. In particularly, the compounds \{MeC(C\(_5\)Me\(_4\))(Ox\(_{Me2}\))\(_2\})\text{Ln(CH}_2\text{Ph)}_2\} react with one equivalent of a benzylic amine
NH₂CH₂Ar to provide the highly sought yttrium and lutetium terminal imido complexes \{MeC(C₅Me₄)(OxMe₂)₂\} Y=NCH₂Ar and \{MeC(C₅Me₄)(OxMe₂)₂\} Lu=NCH₂Ar. β-CH agostic interactions are observed to stabilize these imido complexes. Evidence can be found from \(^1\)H NMR spectrum and IR spectrum for the agostic β-CH signal.

In addition, bisamide complexes \{MeC(C₅Me₄)(OxMe₂)₂\} Ln(NHCH₂Ar)₂ formed by the reaction of two equivalent of NH₂CH₂Ar amine and \{MeC(C₅Me₄)(OxMe₂)₂\} Ln(CH₂Ph)₂ are also described.

Results and Discussion.

Synthesis and characterization of \{MeC(C₅Me₄)(OxMe₂)₂\} Ln(NHCH₂Ar)₂ bisamide complexes.

Reactions between \{MeC(C₅Me₄)(OxMe₂)₂\} Ln(CH₂Ph)₂ (Ln = Sc, Lu) and two equivalents of primary amine NH₂CH₂(Aryl) gives lanthanide bisamide products \{MeC(C₅Me₄)(OxMe₂)₂\} Ln(NHCH₂Ar)₂ [eqn. (1)].

\[
\text{Ln} = \text{Sc, Lu}
\]

For example, \{MeC(C₅Me₄)(OxMe₂)₂\} Lu(CH₂Ph)₂ reacts with two equivalent of NH₂CH₂Ph in benzene at room temperature to provide the bisamide \{MeC(C₅Me₄)(OxMe₂)₂\} Lu(NHCH₂Ph)₂ (2) within 15 minutes [eqn. (2)]. The \(^1\)H NMR
spectrum of 2 contained a broad signal, integrated as four protons, at 4.08 ppm, representing CH$_2$ group in the lutetium bisamide, as well as a singlet at 1.24 ppm, integrated as 2 protons for NH group. Besides, two equivalents of toluene were detected during the reaction by $^1$H NMR spectroscopy on the crude reaction mixture. In the $^{15}$N NMR spectrum, only one singlet at -137.4 ppm was detected and assigned to the CN from oxazolines, while the imido N signal was not observed, even at lower temperature. Additionally, the product is suggested to be C$_5$ symmetric in benzene-$d_6$ solution, as indicated by one set of oxazoline resonances (CH$_2$ and CMe$_2$ groups are diastereotopic). However, a solid state IR spectrum of 2 contained two different CN stretching at 1629 and 1647 cm$^{-1}$, indicating two oxazoline groups were inequivalent. For comparison, the IR spectrum of MeC(Ox$^{Me_2}$)$_2$(C$_5$Me$_4$H) contains a band at 1661 cm$^{-1}$ associated with a non-coordinated oxazoline. However, variable temperature (VT) $^1$H NMR spectroscopic experiments showed only equivalent oxazoline resonances from 298 K to 183 K. Either the solution structure of 2 is different from the solid state structure or two oxazoline groups were undergo exchange processes in solution. A solution-state IR should be taken to further explore the correct structure in solution.

\[\text{Ln} = \text{Sc(1), 89.8%} \]
\[\text{Lu(2), 86.3%} \]
Reactions of $\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Sc(CH}_2\text{Ph)}_2$ and two equivalent of NH$_2$CH$_2$Ph in benzene follow the same pathway to provide scandium bisamide product
$\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Sc(NHCH}_2\text{Ph)}_2$ $[1, \text{eqn. (2)}]$.

Thermolysis experiments show that both complexes
$\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Sc(NHCH}_2\text{Ph)}_2$ and $\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Lu(NHCH}_2\text{Ph)}_2$ are persistent in toluene up to 200 °C for 2 days in a sealed J-Young tube.

Additionally, several other benzyl type primary amines also react to give bis(amide) rare earth compounds. Treatment of $\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Ln(CH}_2\text{Ph)}_2$ ($\text{Ln} = \text{Sc, Lu}$) with two equivalent of NH$_2$CH$_2$(1-C$_{10}$H$_7$) in benzene at room temperature results in a related lutetium bisamide product $\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Ln[NHCH}_2(1-C_{10}H_7)]_2$ after 10 minutes [$\text{Ln} = \text{Sc (3), Lu (4), eqn. (3)}$]. The $^1$H NMR spectrum of 3 contained four doublets, integrated as four protons, at 5.17 ppm, 5.14 ppm, 5.06 ppm, and 5.03 ppm, representing two CH$_2$ group in lutetium bisamide complex, as well as a triplet at 3.99 ppm, integrated as 2 protons for the NH group. Two equivalent of toluene byproduct were observed during the reaction by $^1$H NMR spectroscopy on the crude reaction mixture.

In the $^1$H NMR spectrum of the lutetium analog
$\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Lu[NHCH}_2(1-C_{10}H_7)]_2$, a broad signal at 4.71 ppm, integrated as four protons, was assigned to be the two CH$_2$ group, while a singlet at 1.49 ppm, integrated as 2 protons was assigned to be the NH group.
Similar to complex \{\text{MeC}(C_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Sc}(\text{CH}_2\text{Ph})_2\ (1), all 2, 3 or 4 are $C_s$ symmetric in benzene-$d_6$ solution, as indicated by one set of oxazoline resonances contain diastereotopic CH$_2$ and CMe$_2$ groups, while the IR spectra showed two different CN stretching bands, indicating two oxazoline groups are not equivalent. Besides, thermolysis experiments show that complexes 3 or 4 are also persistent in toluene up to 200 °C for 2 days in a sealed J-young tube.

Variable temperature (VT) $^1$H NMR spectroscopic experiments for complexes 1, 2, 3 or 4 showed only equivalent oxazoline resonances from 298 K to 183 K. Either the solution structure of them is different from the solid state structure or two oxazoline groups were undergo exchange processes in solution. A solution-state IR should be taken to further explore the correct structure in solution.

**Synthesis and characterization of \{\text{MeC}(C_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Ln=NH}_2\text{Ar imido}**

**complexes. (Ln = Y, Lu)**

In contrast to the reactions of \{\text{MeC}(C_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Ln}(\text{CH}_2\text{Ph})_2 with two equivalent of primary amine NH$_2$CH$_2$Ar that form product, reaction of
{MeC(C₅Me₄)(OxMe₂)₂}Ln(CH₂Ph)₂ and only one equivalent of primary amine in benzene gave lanthanide imido products \{MeC(C₅Me₄)(OxMe₂)₂}Ln=NH₂CH₂Ar [eqn. (4)].

\[
\text{MeC(C₅Me₄)(OxMe₂)₂} + \text{NH₂CH₂Ar} \rightarrow \text{MeC(C₅Me₄)(OxMe₂)₂}Ln=NH₂CH₂Ar
\]

\( \text{Ln} = \text{Y, Lu} \)

\{MeC(C₅Me₄)(OxMe₂)₂\}Lu(CH₂Ph)₂ and one equivalent of NH₂CH₂Ph reacted in benzene at room temperature within 10 minutes to provide imido products \{MeC(C₅Me₄)(OxMe₂)₂\}LuNCH₂Ph [(5), eqn. (5)]. In the \(^1\)H NMR spectrum of complex 5, two doublets, each integrated as one proton, at 4.87 ppm and 5.41 ppm, were assigned to two \(\beta\)-CH protons in LuNCH₂Ph. One equivalent of toluene was detected during the reaction by \(^1\)H NMR spectroscopy on the crude reaction mixture. In the \(^{15}\)N NMR spectrum, only one singlet at -137.6 ppm was detected and assigned to the CN from oxazolines, while the imido N signal was not observed, even at lower temperature. Besides, the product is suggested to be \(C₅\) symmetric in benzene-\(d₆\) solution, as indicated by one set of diastereotopic oxazoline resonances. However, solid state IR spectrum of 5 contained two different CN stretching at 1618 and 1655 cm\(^{-1}\), indicating two oxazoline groups were not identical. However, variable temperature (VT) \(^1\)H NMR spectroscopic experiments showed only equivalent oxazoline resonances from 298 K to 183 K. Either the solution structure of 5 is different from the solid state structure or two oxazoline groups were undergo exchange processes in solution. A solution-state IR should be taken to further explore the correct structure in solution.
Even though an X-ray structure has not yet been successfully obtained, \( \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)_2\}_\text{Lu}=\text{NCH}_2\text{Ph} \) (5) was assigned to be a terminal monomeric imido complex, supported by a DOSY experiment,\(^{10}\) where the diffusion coefficient of 4 is \( 7.32 \times 10^{-10} \) m\(^2\)/s (296 K). For comparison, the diffusion coefficients of \( \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)_2\}_\text{Lu}(\text{CH}_2\text{Ph})_2 \), which is monomeric species as shown by X-ray crystallography, is \( 7.38 \times 10^{-10} \) m\(^2\)/s (296 K). The similar diffusion coefficients between compound 5 and \( \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)_2\}_\text{Lu}(\text{CH}_2\text{Ph})_2 \) further supports the assertion that \( \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)_2\}_\text{Lu}=\text{NCH}_2\text{Ph} \) is monomeric in solution.

Notably, imido complexes \( \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)_2\}_\text{Lu}=\text{NCH}_2\text{Ar} \) are suggested to contain one agostic \( \beta \)-CH. One of the evidence can be from the IR experiment. In the contrast of the non-agostic CH, the agostic CH stretching signal is more up-field. For example, in the lower temperature IR spectrum of the agostic complex \( \text{CpTi(iPr}_2\text{N})\text{Cl}_2 \), a more up-filed signal representing the agostic CH was observed.\(^9\) For imido complex \( \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)_2\}_\text{Lu}=\text{NCH}_2\text{Ph} \) (5), a weak signal at 2727 cm\(^{-1}\) was assigned to be the agostic \( \beta \)-CH, while the IR of relative bisamide complex \( \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)_2\}_\text{Lu}(\text{NHCH}_2\text{Ph})_2 \) (2) did not contain any similar agostic CH signal.

This deduction can be further supported by the \( \beta \)-CH chemical shift in \(^1\)H NMR spectrum. According to literature example,\(^9\) the \( \beta \)-CH signal in agostic d\(^0\) amides are typically shifted downfield in the \(^1\)H NMR spectrum compared to the non-agostic CH. In the \(^1\)H NMR spectrum for the imido complex \( \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)_2\}_\text{Lu}=\text{NCH}_2\text{Ph} \) (5), \( \beta \)-CH signals are shifted downfield to 4.87 ppm and 5.41 ppm, compared to 4.08 for the bisamide complex \( \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)_2\}_\text{Lu}(\text{NHCH}_2\text{Ph})_2 \) (2).
This imido formation reaction pattern is not limited to benzyl amine. Treatment of \{\text{MeC(C}_{5}\text{Me}_{4})(\text{Ox}_{\text{Me}_2})_{2}\}\text{Lu(CH}_{2}\text{Ph})_{2}\} with one equivalent of \text{NH}_2\text{CH}_{2}(1-C_{10}\text{H}_{7}) in benzene at room temperature results in relative lutetium imido product \{\text{MeC(C}_{5}\text{Me}_{4})(\text{Ox}_{\text{Me}_2})_{2}\}\text{Ln=NCH}_{2}(1-C_{10}\text{H}_{7}) (6) after 3 hours [eqn. (6)]. Only one equivalent of toluene byproduct was observed during the reaction by $^1\text{H}$ NMR spectroscopy on the crude reaction mixture. 6 also contained an agostic $\beta$-CH, which is observed at 5.92 ppm or 5.53 ppm from $^1\text{H}$ NMR spectrum.

Notably, only benzyl type primary amines \text{NH}_2\text{CH}_2\text{Ar} can follow this reaction pathway to provide relative imido products. In the reactions between \{\text{MeC(C}_{5}\text{Me}_{4})(\text{Ox}_{\text{Me}_2})_{2}\}\text{Ln(CH}_{2}\text{Ph})_{2}\} and one equivalent of isopropyl amine, phenyl amine or 2,6 diisopropyl aniline, half equivalent lanthanide bisamide complexes were the only
products observed while no relative imido products were detected, from room temperature to 180 °C for 2 days in a sealed J-young tube in toluene.

Additionally, among benzyl type primary amines, only those amines which contain two β-CH give imido products. of \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Ln(CH}_2\text{Ph)}_2 with \text{NH}_2\text{CHCH}_3\text{Ph or NH}_2\text{CHPh}_2 only resulted in bisamide products from room temperature to 180 °C in toluene for 2 days in a sealed J-young tube.

Reactivity of \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Ln}=\text{NCH}_2\text{Ar imido complexes and BO}^\text{M}\text{Cp}^\text{tet}\text{Ln(NHCH}_2\text{Ar)}_2 \text{bisamide complexes. (Ln = Y, Lu)}

Diphenyl acetylene does not react with \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{LnNCH}_2\text{Ar} up to 120 °C in toluene-\text{d}_8 for 24 h. This contrasts Bergman’s \text{Cp}_2\text{Zr}=\text{NR imido examples, which instead react with acetylene to give cycloaddition products.}^{11}

Only starting materials were detected when imido complexes \text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{LnNCH}_2\text{Ar (5 and 6)} were mixed with large or bulky olefin, such as tert-butyl ethylene, 1-octane, or phenyl methyl ethylene in benzene-\text{d}_6 up to 120 °C for 2 days in toluene-\text{d}_8, while reactions with ethylene, isopropene, and butadiene occurred rapidly to give complicated \text{^1H NMR spectra in which well-defined products could not be identified. Besides, MeOTf, MeI and H}_2\text{NNMe}_2 \text{were also tested to react with complex } \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{LnNCH}_2\text{Ar while no reactions were detected even at 120 °C in in benzene-\text{d}_6 for 1 day.}
The imido compounds \{MeC(C_5Me_4)(OxMe^2)_2\}_LNCHAr are inert to H\(_2\) or PhMeSiH\(_2\) up to 120 °C for 24 h in benzene-\(d_6\), while treatments of CO\(_2\), PhCN, or acetone result in instant decomposition.

From Chen’s scandium imido example, the addition of a Lewis base, such as DMAP, was necessary to facilitate the formation of terminal scandium imido complexes. However, in our system, treatment of Lewis base was not essential for the formation of the \{MeC(C_5Me_4)(OxMe^2)_2\}_LNCHAr imido complexes. Furthermore, adding a Lewis base such as pyridine or DMAP to \{MeC(C_5Me_4)(OxMe^2)_2\}_LNCHAr (5 and 6) causes instant decomposition, rather than stabilizing the imidoborate complexes by coordinating to the lanthanide metal center.

![Chemical structure](https://example.com/structure.png)

The lanthanide imido complex can be protonated into relative bisamide complex by another equivalent of primary amine. Treating \{MeC(C_5Me_4)(OxMe^2)_2\}_LuNCH\(_2\)Ph (5) with one equivalent of NH\(_2\)CH\(_2\)Ph in benzene at room temperature results in \{MeC(C_5Me_4)(OxMe^2)_2\}_Lu(NHCH\(_2\)Ph)_2 product within 10 minutes [eqn. (7)]. The product is matching with complex 2 which was independently synthesized from the
reaction between \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Lu(CH}_2\text{Ph)}_2\text{ and two equivalent of NH}_2\text{CH}_2\text{Ph} [\text{eqn. (2)}].

This protonation can also apply to a different primary amine to give a mixed bisamide complex. Reaction of \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{LuNCH}_2\text{Ph} (5) with 2-methyl benzyl amine in benzene gives mixed \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Lu(NCH}_2\text{Ph}[\text{NCH}_2(2\text{-methyl phenyl})] (7) bisamide product instantly at room temperature [\text{eqn. (8)}]. On a NMR scale reaction, disappearance of both starting materials is observed by $^1\text{H}$ NMR spectroscopy. Besides, two singlet at 4.26 and 4.16 ppm, integrated as four protons, representing two new CH$_2$ group, as well as a broad singlet at 1.38 ppm, integrated as 2 protons for NH groups, was detected during the reaction.

Conclusion.

In summary, our results showed that lanthanids(III) bisamide complexes \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Ln(NHCH}_2\text{Ar)}_2\ (\text{Ln} = \text{Sc, Y, Lu}) can be prepared from protonation of \{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Ln(CH}_2\text{Ph)}_2\ complexes by two equivalent of NH$_2$CH$_2$Ar. In contrast, treatment of one equivalent of NH$_2$CH$_2$Ar with
{MeC(C₅Me₄)(OₓMe²)₂}Ln(CH₂Ph)₂ resulted in the first lutetium and yttrium terminal imido complexes {MeC(C₅Me₄)(OₓMe²)₂}Ln=NCH₂Ar (Ln = Y, Lu) containing β-CH. In these imido complexes, β-CH gostic interactions are observed, which demonstrates that the lanthanide terminal imido complexes can be achieved and stabilized with a sterically favored H{MeC(C₅Me₄)(OₓMe²)₂} ligand as well as β-CH agostic interaction. The reactivities of these terminal imido complexes are under investigation.

Experimental

General Procedures. All reactions were carried out under an inert atmosphere using standard Schlenk techniques or in a glovebox. All solvents were dried and degassed unless otherwise indicated. H{MeC(C₅Me₄H)(OₓMe²)₂}, {MeC(C₅Me₄)(OₓMe²)₂}Sc(CH₂Ph)₂, {MeC(C₅Me₄)(OₓMe²)₂}Sc(NHCH₂Ph)₂, {MeC(C₅Me₄)(OₓMe²)₂}Sc(CH₂Ph)₂ (0.375 g, 0.657 mmol) was dissolved in 5 mL of benzene. H₂NCH₂Ph (0.144 mL, 1.314 mmol) was added to the mixture via syringe to give a yellow solution. This solution was stirred
at room temperature for 10 minutes, and then the volatile materials were removed under reduced pressure to give pale yellow complex \(\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Sc(NHCH}_2\text{Ph)}_2\) (0.354 g, 0.590 mmol, 89.8%). \(^1\)H NMR (benzene-\(d_6\), 600 MHz): \(\delta 7.51 (d, \; \frac{3}{4}J_{HH} = 6.8\) Hz, 4 H, \(\text{ortho-C}_6\text{H}_5\)), \(7.31 (t, \; \frac{3}{4}J_{HH} = 6.8\) Hz, 4 H, \(\text{meta-C}_6\text{H}_5\)), \(7.15 (t, \; \frac{3}{4}J_{HH} = 6.8\) Hz, 2 H, \(\text{para-C}_6\text{H}_5\)), \(4.69 (t, \; \frac{3}{4}J_{HH} = 11.9\) Hz, 2 H, \(\text{Sc(NHCH}_2\text{Ph)}_2\)), \(4.59 (t, \; \frac{3}{4}J_{HH} = 11.9\) Hz, 2 H, \(\text{Sc(NHCH}_2\text{Ph)}_2\)), \(3.65 (d, \; \frac{3}{4}J_{HH} = 8.5\) Hz, 2 H, \(\text{CNCMe}_2\text{O})\)), \(3.54 (d, \; \frac{3}{4}J_{HH} = 8.5\) Hz, 2 H, \(\text{CNCMe}_2\text{O})\)), \(2.93 (t, \; \frac{3}{4}J_{HH} = 8.1\) Hz, 2 H, \(\text{Sc(NHCH}_2\text{Ph)}_2\)), \(2.21 (s, 6\) H, \(\text{C}_5\text{Me}_4\)), \(2.08 (s, 6\) H, \(\text{C}_5\text{Me}_4\)), \(1.97 (s, 3\) H, backbone Me), \(1.11 (s, 6\) H, \(\text{CNCMe}_2\text{O})\)), \(1.10 (s, 6\) H, \(\text{CNCMe}_2\text{O})\)), \(1.08 (s, 6\) H, \(\text{CNCMe}_2\text{O})\)). \(^13\)C \(^1\)H NMR (benzene-\(d_6\), 125 MHz): \(\delta 173.67 (\text{CNCMe}_2\text{O}), 149.46 (\text{ipso-C}_6\text{H}_5\text{CH}_2), 128.92 (\text{meta-C}_6\text{H}_5\text{CH}_2), 127.48 (\text{ortho-C}_6\text{H}_5\text{CH}_2), 126.13 (\text{para-C}_6\text{H}_5\text{CH}_2), 118.50 (\text{C}_5\text{Me}_4), 115.97 (\text{C}_5\text{Me}_4), 114.81 (\text{ipso-C}_5\text{Me}_4), 80.54 (\text{CNCMe}_2\text{O}), 67.12 (\text{CNCMe}_2\text{O}), 53.44 (\text{LuCH}_2\text{C}_6\text{H}_5), 46.48 (\text{backbone CMe}), 28.34 (\text{CNCMe}_2\text{O}), 27.64 (\text{CNCMe}_2\text{O}), 23.90 (\text{backbone CMe}), 13.62 (\text{C}_5\text{Me}_4), 11.89 (\text{C}_5\text{Me}_4)\). \(^{15}\)N NMR (benzene-\(d_6\), 71 MHz): \(\delta –141.2 (\text{CNCMe}_2\text{O})\). IR (KBr, cm\(^{-1}\)): 2966 s, 2926 s, 2868 s, 1659 s (CN), 1623 s (CN), 1491 w, 1452 s, 1364 s, 1283 m, 1252 m, 1191 m, 1087 m, 1026 w, 972 m, 958 m, 906 w, 807 w, 780 m, 729 m, 699 w.

\(\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Lu(NHCH}_2\text{Ph)}_2\) \(\text{(2)}\). \(\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Lu(CH}_2\text{Ph)}_2\) (0.412 g, 0.588 mmol) was dissolved in 5 mL of benzene. NH\(_2\)CH\(_2\)Ph (0.128 mL, 1.176 mmol) was added to the mixture via syringe to give a yellow solution. This solution was stirred at room temperature for 10 minutes and then the volatile materials were removed under reduced pressure to give pale yellow \(\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Lu(NHCH}_2\text{Ph)}_2\) (0.371 g, 0.507 mmol, 86.3%). \(^1\)H NMR (benzene-\(d_6\), 600 MHz): \(\delta 7.26 (s, \text{br}, 4\) H,
ortho-C₆H₅), 7.21 (t, 3J_HH = 7.1 Hz, 4 H, meta-C₆H₅), 7.10 (t, 3J_HH = 7.1 Hz, 2 H, para-C₆H₅), 4.08 (s, br, 4H, Lu(NHCH₂Ph₂)), 3.70 (d, 3J_HH = 8.3 Hz, 2 H, CNCMe₂CH₂O), 3.60 (d, 3J_HH = 8.3 Hz, 2 H, CNCMe₂CH₂O), 2.19 (s, 6H, C₅Me₄), 2.08 (s, 6H, C₅Me₄), 2.07 (s, 3H, backbone Me), 1.24 (s, br, 2H, Lu(NHCH₂Ph₂)), 1.20 (s, 6 H, CNCMe₂CH₂O), 1.17 (s, 6 H, CNCMe₂CH₂O). ¹³C{¹H} NMR (benzene-d₆, 125 MHz): δ 173.30 (CNCMe₂CH₂O), 146.95 (ipso-C₆H₅CH₂), 128.85 (meta-C₆H₅CH₂), 127.52 (ortho-C₆H₅CH₂), 126.69 (para-C₆H₅CH₂), 115.80 (C₅Me₄), 114.39 (C₅Me₄), 114.37 (ipso-C₅Me₄), 80.60 (CNCMe₂CH₂O), 67.53 (CNCMe₂CH₂O), 50.28 (LuCH₂C₆H₅), 46.36 (backbone CMe), 28.30 (CNCMe₂CH₂O), 27.68 (CNCMe₂CH₂O), 24.34 (backbone CMe), 13.71 (C₅Me₄), 11.76 (C₅Me₄). ¹⁵N NMR (benzene-d₆, 71 MHz): δ -137.4 (s, CNCMe₂CH₂O). IR (KBr, cm⁻¹): 2963 s, 2922 s, 2854 s, 1647 s (CN), 1629 s (CN), 1495 w, 1454 s, 1382 m, 1365 s, 1307 m, 1284 m, 1193 m, 1094 m, 1025 w, 977 m, 907 w, 884 w, 825 w, 813 w, 732 w.

{MeC(C₅Me₄)(OₓMe²)₂}Sc[NHCH₂(1-C₁₀H₇)]₂ (3). {MeC(C₅Me₄)(OₓMe²)₂}Sc(CH₂Ph₂) (0.298 g, 0.522 mmol) was dissolved in 5 mL of benzene. NH₂CH₂(1-C₁₀H₇) (0.153 mL, 1.044 mmol) was added to the mixture via syringe to give a yellow solution. This solution was stirred at room temperature for 10 minutes and then the volatile materials were removed under reduced pressure to give pale yellow {MeC(C₅Me₄)(OₓMe²)₂}Sc[NHCH₂(1-C₁₀H₇)]₂ (0.308 g, 0.440 mmol, 84.2%). ¹H NMR (benzene-d₆, 600 MHz): δ 8.35 (d, 3J_HH = 8.4 Hz, 1 H, 2-C₁₀H₇), 7.81 (d, 3J_HH = 6.6 Hz, 1 H, 9-C₁₀H₇), 7.76 (d, 3J_HH = 7.8 Hz, 1 H, 4-C₁₀H₇), 7.64 (d, 3J_HH = 8.4 Hz, 1 H, 6-C₁₀H₇), 7.47 (t, 3J_HH = 7.2 Hz, 1 H, 3-C₁₀H₇), 7.39 (t, 3J_HH = 7.2 Hz, 1 H, 8-C₁₀H₇), 7.33 (t, 3J_HH = 7.2 Hz, 1 H, 7-C₁₀H₇), 5.16 (d, 3J_HH = 8.4 Hz, 1 H, NHCH₂(1-C₁₀H₇)), 5.14 (d, 3J_HH = 8.4
Hz, 1 H, NHCH$_2$(1-C$_{10}$H$_7$)), 5.06 (d, $^3J_{HH} = 8.4$ Hz, 1 H, NHCH$_2$(1-C$_{10}$H$_7$)), 5.03 (d, $^3J_{HH} = 8.4$ Hz, 1 H, NHCH$_2$(1-C$_{10}$H$_7$)), 3.65 (d, $^3J_{HH} = 8.4$ Hz, 2 H, CNCMe$_2$CH$_2$O), 3.53 (d, $^3J_{HH} = 8.4$ Hz, 2 H, CNCMe$_2$CH$_2$O), 2.99 (t, $^3J_{HH} = 8.4$ Hz, 2 H, NHCH$_2$(1-C$_{10}$H$_7$)), 2.16 (s, 6H, C$_5$Me$_4$), 2.08 (s, 6H, C$_5$Me$_4$), 1.97 (s, 3H, backbone Me), 1.09 (s, 6 H, CNCMe$_2$CH$_2$O), 1.08 (s, 6 H, CNCMe$_2$CH$_2$O).

{MeC(C$_5$Me$_4$)(OxMe$_2$)$_2$}Lu[NHCH$_2$(1-C$_{10}$H$_7$)]$_2$ (4). {MeC(C$_5$Me$_4$)(OxMe$_2$)$_2$}Lu(CH$_2$Ph)$_2$ (0.211 g, 0.301 mmol) was dissolved in 5 mL of benzene. H$_2$NCH$_2$(1-C$_{10}$H$_7$) (0.088 mL, 0.602 mmol) was added to the mixture via syringe to give a yellow solution. This solution was stirred at room temperature for 10 minutes and then the volatile materials were removed under reduced pressure to give pale yellow {MeC(C$_5$Me$_4$)(OxMe$_2$)$_2$}Lu[NHCH$_2$(1-C$_{10}$H$_7$)]$_2$ (0.205 g, 0.247 mmol, 82.1%).

$^1$H NMR (benzene-$d_6$, 500 MHz): δ 8.13 br, 1 H, 2-C$_{10}$H$_7$), 7.69 (d, $^3J_{HH} = 7.8$ Hz, 1 H, 9-C$_{10}$H$_7$), 7.62 (br, 1 H, 4-C$_{10}$H$_7$), 7.56 (d, $^3J_{HH} = 7.8$ Hz, 1 H, 6-C$_{10}$H$_7$), 7.34 (t, $^3J_{HH} = 7.2$ Hz, 1 H, 3-C$_{10}$H$_7$), 7.31 (t, $^3J_{HH} = 6.6$ Hz, 1 H, 8-C$_{10}$H$_7$), 7.28 (t, $^3J_{HH} = 6.6$ Hz, 1 H, 7-C$_{10}$H$_7$), 4.71 (br, 4 H, NHCH$_2$(1-C$_{10}$H$_7$)), 3.68 (d, $^3J_{HH} = 8.4$ Hz, 2 H, CNCMe$_2$CH$_2$O), 3.57 (d, $^3J_{HH} = 8.4$ Hz, 2 H, CNCMe$_2$CH$_2$O), 2.18 (s, 6H, C$_5$Me$_4$), 2.11 (s, 6H, C$_5$Me$_4$), 2.05 (s, 3H, backbone Me), 1.49 (t, $^3J_{HH} = 8.4$ Hz, 2 H, NHCH$_2$(1-C$_{10}$H$_7$)), 1.17 (s, 6 H, CNCMe$_2$CH$_2$O), 1.13 (s, 6 H, CNCMe$_2$CH$_2$O).

{MeC(C$_5$Me$_4$)(OxMe$_2$)$_2$}LuNCH$_2$Ph (5). {MeC(C$_5$Me$_4$)(OxMe$_2$)$_2$}Lu(CH$_2$Ph)$_2$ (0.226 g, 0.323 mmol) was dissolved in 5 mL of benzene. NH$_2$CH$_2$Ph (0.035 mL, 0.323 mmol) was added to the mixture via syringe to give a yellow solution. This solution was stirred at room temperature for 10 mins and then the volatile materials were removed under reduced pressure to give pale yellow {MeC(C$_5$Me$_4$)(OxMe$_2$)$_2$}LuNCH$_2$Ph (0.153 g, 0.246
mmol, 76.2%). $^1$H NMR (benzene-$d_6$, 600 MHz): $\delta$ 7.52 (d, $^3J_{HH} = 7.1$ Hz, 2 H, ortho-$C_6H_5$), 7.41 (t, $^3J_{HH} = 7.4$ Hz, 2 H, meta-$C_6H_5$), 7.22 (t, $^3J_{HH} = 7.1$ Hz, 1 H, pera-$C_6H_5$), 5.41 (d, $^3J_{HH} = 15.3$ Hz, 1 H, LuNCH$_2$Ph), 4.87 (d, $^3J_{HH} = 15.3$ Hz, 1 H, LuNCH$_2$Ph), 3.74 (d, $^3J_{HH} = 8.3$ Hz, 2 H, CNCMe$_2$CH$_2$O), 3.64 (d, $^3J_{HH} = 8.3$ Hz, 2 H, CNCMe$_2$CH$_2$O), 2.12 (s, 6H, C$_5$Me$_4$), 2.05 (s, 3H, backbone Me), 2.02 (s, 6H, C$_5$Me$_4$), 1.37 (s, 6 H, CNCMe$_2$CH$_2$O), 1.32 (s, 6 H, CNCMe$_2$CH$_2$O).

$^{13}$C {$^1$H} NMR (benzene-$d_6$, 125 MHz): $\delta$ 175.42 (CNCMe$_2$CH$_2$O), 152.37 (ipso-$C_6H_5CH_2$Lu), 128.01 (meta-$C_6H_5CH_2$Lu), 127.94 (ortho-$C_6H_5CH_2$Lu), 125.12 (para-$C_6H_5CH_2$Lu), 115.76 (C$_5$Me$_4$), 114.21 (C$_5$Me$_4$), 114.12 (ipso-C$_5$Me$_4$), 80.41 (CNCMe$_2$CH$_2$O), 67.65 (CNCMe$_2$CH$_2$O), 58.00 (LuCH$_2$C$_6$H$_5$), 46.42 (backbone CMe), 29.16 (CNCMe$_2$CH$_2$O), 28.48 (CNCMe$_2$CH$_2$O), 24.66 (backbone CMe), 13.44 (C$_5$Me$_4$), 11.74 (C$_5$Me$_4$). $^{15}$N NMR (benzene-$d_6$, 71 MHz): $\delta$ -137.6 (s, CNCMe$_2$CH$_2$O). IR (KBr, cm$^{-1}$): 2985 s, 2926 s, 2895 s, 2866 m, 2727 w (agostic CH), 1655 s (CN), 1618 s (CN), 1462 s, 1364 m, 1307 m, 1283 m, 1250 w, 1192 m, 1174 m, 1087 s, 1025 w, 976 m, 956 m, 936 w, 889 w, 732 w.

$\{\text{MeC}(C_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{LuNCH}_2(1\text{-C}_{10}\text{H}_7)$ (6). $\{\text{MeC}(C_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Lu(CH}_2\text{Ph)}_2$ (0.198 g, 0.283 mmol) was dissolved in 5 mL of benzene. NH$_2$CH$_2$(1-C$_{10}$H$_7$) (0.041 mL, 0.283 mmol) was added to the mixture via syringe to give a yellow solution. This solution was stirred at room temperature for 3 hours and then the volatile materials were removed under reduced pressure to give pale yellow, analytically pure $\{\text{MeC}(C_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{LuNCH}_2(1\text{-C}_{10}\text{H}_7)$ (0.118 g, 0.176 mmol, 62.1%). $^1$H NMR (benzene-$d_6$, 600 MHz): $\delta$ 8.49 (d, $^3J_{HH} = 8.3$ Hz, 1 H, 2-C$_{10}$H$_7$), 8.03 (d, $^3J_{HH} = 7.7$ Hz, 1 H, 9-C$_{10}$H$_7$), 7.86 (d, $^3J_{HH} = 7.7$ Hz, 1 H, 4-C$_{10}$H$_7$), 7.74 (d, $^3J_{HH} = 7.7$ Hz, 1 H, 6-C$_{10}$H$_7$),
7.69 (t, $^3J_{HH} = 7.5$ Hz, 1 H, 3-C$_{10}$H$_7$), 7.51 (t, $^3J_{HH} = 7.7$ Hz, 1 H, 8-C$_{10}$H$_7$), 7.38 (t, $^3J_{HH} = 7.4$ Hz, 1 H, 7-C$_{10}$H$_7$), 5.92 (d, $^3J_{HH} = 17.5$ Hz, 1 H, LuNCH$_2$(1-C$_{10}$H$_7$)), 5.53 (d, $^3J_{HH} = 17.5$ Hz, 1 H, LuNCH$_2$(1-C$_{10}$H$_7$)), 3.69 (d, $^3J_{HH} = 8.6$ Hz, 2 H, CNCMe$_2$CH$_2$O), 3.60 (d, $^3J_{HH} = 8.6$ Hz, 2 H, CNCMe$_2$CH$_2$O), 2.07 (s, 6H, C$_5$Me$_4$), 1.99 (s, 3H, backbone Me), 1.84 (s, 6H, C$_5$Me$_4$), 1.43 (s, 6 H, CNCMe$_2$CH$_2$O), 1.33 (s, 6 H, CNCMe$_2$CH$_2$O).

$^{15}$N NMR (benzene-$d_6$, 71 MHz): $\delta$ -138.1 (s, CNCMe$_2$CH$_2$O). IR (KBr, cm$^{-1}$): 2964 s, 2926 s, 2896 s, 2866 m, 1653 w, 1631 s (CN), 1510 w, 1495 w, 1462 s, 1365 m, 1306 m, 1282 m, 1193 m, 1176 m, 1088 s, 1026 w, 991 m, 974 m, 956 m, 936 w, 886 w, 850 w.

$\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Lu(NHCH}_2\text{Ph)[NHCH}_2\text{(2-MePh)}})$ (7).

$\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Lu}=\text{NHCH}_2\text{Ph}$ (11.5 mg, 0.018 mmol) was dissolved in 0.7 mL of benzene-$d_6$. NH$_2$CH$_2$(2-MePh)] (2.3 $\mu$L, 0.018 mmol) was added to the mixture via a micro syringe to give a yellow solution for 10 minutes, and then the volatile materials were removed under reduced pressure to give pale yellow $\{\text{MeC(C}_5\text{Me}_4)(\text{OxMe}_2)\}_2\text{Lu(NHCH}_2\text{Ph)[NHCH}_2\text{(2-MePh)}})$ (0.126 mg, 0.017 mmol, 92.1%). $^1$H NMR (benzene-$d_6$, 600 MHz): $\delta$ 7.65 (s br, 1 H, C$_6$H$_5$), 7.49 (s br, 2 H, C$_6$H$_5$), 7.33 (s br, 2 H, C$_6$H$_5$), 7.24 (m, 4 H, C$_6$H$_5$), 4.26 (s br, 2 H, Lu(NHCH$_2$Ph)[NHCH$_2$(2-MePh)]), 4.16 (s, br, 2 H, Lu(NHCH$_2$Ph)[NHCH$_2$(2-MePh)]), 3.68 (d, $^3J_{HH} = 8.2$ Hz, 2 H, CNCMe$_2$CH$_2$O), 3.58 (d, $^3J_{HH} = 8.2$ Hz, 2 H, CNCMe$_2$CH$_2$O), 2.18 (s, 6H, C$_5$Me$_4$), 2.16 (s, 3H, backbone Me), 2.13 (s, 6H, C$_5$Me$_4$), 2.05 (s, 3H, NHCH$_2$(2-MePh)), 1.38 (s, br, 2H, Lu(NHCH$_2$Ph)[NHCH$_2$(2-MePh)]), 1.18 (s, 6 H, CNCMe$_2$CH$_2$O), 1.15 (s, 6 H, CNCMe$_2$CH$_2$O).

**Procedures for DOSY (Diffusion-Ordered Spectroscopy) experiment.** All the measurements were performed on a Bruker DRX400 spectrometer using a DOSY
stimulated spin-echo pulse program with bipolar gradients.\textsuperscript{18} Accurately known concentrations of the species in question were used. The concentrations of \{MeC(C\textsubscript{5}Me\textsubscript{4})(OxMe\textsubscript{2})\textsubscript{2}\}LuN\textsubscript{2}CH\textsubscript{2}Ph (5) and \{MeC(C\textsubscript{5}Me\textsubscript{4})(OxMe\textsubscript{2})\textsubscript{2}\}Lu(CH\textsubscript{2}Ph)\textsubscript{2} were determined by integration of resonances corresponding to species of interest and integration of a tetrakis(trimethylsilyl)silane standard of accurately known concentration. The temperature in the NMR probe was preset to 296 K, and the probe was maintained at a constant temperature for each experiment. The delay time in between pulses was set to 5 s in order to ensure the spins are fully relaxed to their ground states. During the experiments, a series of 1D \textsuperscript{1}H NMR spectra were acquired at increasing gradient strength. The signal intensity decay was fit by non-linear least squares regression analysis to Equation 1 to obtain the diffusion coefficient D.\textsuperscript{10}

\[
\ln\left(\frac{I}{I_0}\right) = - (\gamma \delta)^2 G^2 \left(\Delta - \frac{\delta}{3}\right) D \quad (9)
\]

where \(I\) is the observed intensity, \(D\) is the diffusion coefficient, \(\gamma\) is the gyromagnetic ratio of the nucleus, \(\delta\) is the length of the gradient pulse, and \(\Delta\) is the diffusion time.

References


CHAPTER 4: CONCLUSION

First of all, our results show that the β-hydrogen in zinc alkyls have significant nucleophilicity. These results contrast the lack of alkylzinc-based β-agostic structures and β-hydrogen elimination reactions that are typically associated with activated C-H's. Furthermore, we show that the selectivity between β-hydrogen and alkyl group abstraction is not only governed by steric, but also by the trajectory by which the electrophilic center encounters the alkyl ligand. Thus, β-hydrogen is readily transferred from an zinc alkyl group to electrophiles when the electrophile and alkyl ligand are appropriately positioned. These observations may provide strategies for controlling hydride and alkyl transfer processes in synthetic applications.

Secondly, we demonstrated that reactive Lanthanids(III) alkyl complexes \{MeC(C_5Me_4)(OxMe_2)_2\}Ln(CH_2Ph)_2 (Ln = Sc, Y, Lu) can be prepared from protonolysis of Ln(CH_2Ph)_3(THF)_3 by the bulky H{MeC(C_5Me_4)(OxMe_2)_2} ligand and structurally characterized. Besides, the first Lutetium and Yttrium imidoborate complexes have been isolated from deprotonation of NH_3B(C_6F_5)_3 with \{MeC(C_5Me_4)(OxMe_2)_2\}Ln(CH_2Ph)_2 complexes (Ln = Lu, Y), which demonstrates that the lanthanide terminal imido complexes is stabilized with a borate ligand present and attached to the terminal imido nitrogen as well as a sterically favored H{MeC(C_5Me_4)(OxMe_2)_2} ligand. The reactivities of these terminal imidoborate complexes are under investigation.

In addition, our results showed that lanthanids(III) bisamide complexes \{MeC(C_5Me_4)(OxMe_2)_2\}Ln(NHCH_2Ar)_2 (Ln = Sc, Y, Lu) can be prepared from protonation of \{MeC(C_5Me_4)(OxMe_2)_2\}Ln(CH_2Ph)_2 complexes by two equivalent of NH_2CH_2Ar. In contrast, treatment of one equivalent of NH_2CH_2Ar with
{MeC(C₅Me₅)(OxMe²)₂}Ln(CH₂Ph)₂ resulted in the first lutetium and yttrium terminal imido complexes {MeC(C₅Me₅)(OxMe²)₂}Ln=NCH₂Ar (Ln = Y, Lu) containing β-CH. In these imido complexes, β-CH gnostic interactions are observed, which demonstrates that the lanthanide terminal imido complexes can be achieved and stabilized with a sterically favored H{MeC(C₅Me₅)(OxMe²)₂} ligand as well as β-CH agostic interaction. The reactivities of these terminal imido complexes are under investigation.