Inorganic Chemistry
Article
pubs.acs.org/IC

Piano-Stool Lutetium Amido and Imido Compounds Supported by a Constrained Bis(oxazoline)cyclopentadienyl Ligand

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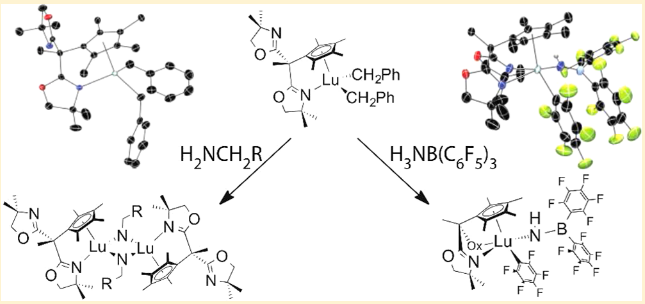
Ⓢ *Supporting Information*

ABSTRACT: $\{BoMCp^{tet}\}Lu(CH_2Ph)_2$ (**1**; $Bo^{M}Cp^{tet}$ = $MeC(Ox^{Me2})_2C_5Me_4$; Ox^{Me2} = 4,4-dimethyl-2-oxazoline) was prepared in 95% yield from the reaction of $Bo^{M}Cp^{tet}H$ and $Lu(CH_2Ph)_3THF_3$. Compound **1** reacts with 1 or 2 equiv of H_2NCH_2R (R = C_6H_5, 1-$C_{10}H_7$) to give the corresponding imido complexes $[\{Bo^{M}Cp^{tet}\}LuNCH_2R]_2$ (R = C_6H_5 (**2a**), 1-$C_{10}H_7$ (**2b**)) or amido complexes $\{Bo^{M}Cp^{tet}\}Lu(NHCH_2R)_2$ (R = C_6H_5 (**3a**), 1-$C_{10}H_7$ (**3b**)). Once isolated, the imido species are insoluble in nonprotic organic solvents. Crystallographic characterization reveals dimeric $[\{Bo^{M}Cp^{tet}\}LuNCH_2(1\text{-}C_{10}H_7)]_2$ in the solid state. The reaction of **1** and $NH_3B(C_6F_5)_3$ affords crystallographically characterized $\{Bo^{M}Cp^{tet}\}Lu\{NHB(C_6F_5)_2\}C_6F_5$. This species is proposed to form via a transient lutetium imido, which undergoes C_6F_5 migration to the lutetium center.



INTRODUCTION

The elusive nature of unsaturated lathananoid imido compounds and the chemistry of related, highly reactive, early transition-metal imido compounds provide impetus for developing environments for isolating [Ln]═NR moieties and controlling their reactivity.[1] The trends in stability and reactivity of group 4 imido compounds, which may provide guidance for synthesis of [Ln]═NR, reveal that monomeric species are more common with smaller titanium centers, whereas multimetallic products are often obtained with larger zirconium analogues.[2] Strategies involving choice of ancillary ligands, appropriate steric demands of the imido substituent, and transient generation of group 4 imido compounds have provided reactivity such as C−H bond activations,[3] imine metathesis,[4] and hydroamination.[3b,5] These tuning effects can give additional stabilization so that the [M]═NR moiety may even act as an ancillary ligand in catalytic polymerization reactions.[6] Thus, new ligand systems for larger lanthanide metal centers may stabilize the reactive [Ln]═NR group or allow access to new chemical transformations.

Recently, monomeric rare earth imido chemistry has advanced through Lewis base-promoted alkane elimination. This strategy was used elegantly by Chen and co-workers in the preparation of the first terminal scandium imido complex $\{\kappa^3\text{-}N,N,N\text{-}HC(MeCN^{Dipp})(MeCNCH_2CH_2NMe_2)\}Sc({=}NDipp)DMAP$ (Dipp = 2,6-diisopropylphenyl; DMAP = *N*,*N*-dimethylaminopyridine).[7] Later, the donor was incorporated into the diketiminate ancillary ligand,[8] which leads to a range of [2 + 2] cycloaddition and proton transfer chemistry. Likewise, the addition of pyridine or DMAP to a scandium anilide−methyl complex generates the transient complexes $\{PNP\}Sc({=}NDipp)NC_5H_5$ (PNP = bis(2-diisopropylphosphino-4-tolyl)amide)[9] or $\{HC(CtBuCNDipp)_2\}Sc({=}NDipp\}DMAP$.[10] This strategy provides isolable or reactive imido complexes of scandium, the smallest of the rare earth elements, and it was also recently extended to lutetium in an isolated imido complex supported by the bulky *tert*-butyl-substituted tris(pyrazolyl)borate ligand.[11]

Instead, the "NR" moieties typically bridge between multiple metal centers in lanthanoid chemistry. For example, the polymetallic benzylimido complexes $[(C_5Me_4SiMe_3)Ln(\mu_3\text{-}NCH_2Ph)]_4$ (Ln = Lu, Y) form from the reaction of tetranuclear polyhydrido complexes and benzonitrile.[12] In the presence of alkylaluminum compounds, heterobimetallic compounds of the type $[Ln]\{(\mu\text{-}R)(\mu\text{-}NR')AlR_2\}$ are obtained.[13] Bridging imido groups are also common in scandium chemistry. For example, insertion of benzonitrile into a Sc−C bond gives the μ^2-imido complex $[\{C_5H_4(CH_2)_2NMe_2\}Sc\{\mu^2\text{-}NC(Ph)C_6H_{10}\}]_2$, which is proposed to form through a mononuclear scandium imido intermediate.[14] Alternatively, mixed alkyl amido compounds are isolated with a *N*,*N*′,*N*-terpyridyl ligand[15] or mixed pentamethylcyclopentadienide−bipyridine ligands.[16]

New ligands for stabilizing or generating reactive rare earth imido compounds might be based on the presence of chelating labile donors constrained to a favorable geometry. Recently, we postulated that the high catalytic activity of a zirconium compound in hydroamination is related to the facile formation and stabilization of a zirconium-imido catalytic intermediate. The active zirconium site in that system is supported by a dianionic mixed cyclopentadienyl−bis(oxazolinyl)borate li-

Received: April 24, 2015
Published: June 25, 2015

DOI: 10.1021/acs.inorgchem.5b00927
Inorg. Chem. 2015, 54, 6938−6946

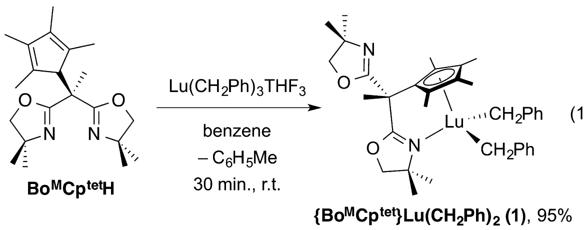
Table 1. Solid-State and Solution IR Stretching Frequencies

compound	ν_{CN} (KBr, cm^{-1})	IR ν_{CN} (C_6D_6, cm^{-1})
{Bo^{M}Cp^{tet}}Lu(CH_2Ph)$_2$ (**1**)	1664, 1591	1659, 1591
[{Bo^{M}Cp^{tet}}LuNCH$_2$Ph]$_2$ (**2a**)	1657, 1618	1655, 1618
[{Bo^{M}Cp^{tet}}LuNCH$_2$(1-$C_{10}H_7$)]$_2$ (**2b**)	1655, 1612	1657, 1612
{Bo^{M}Cp^{tet}}Lu($NHCH_2Ph$)$_2$ (**3a**)	1659, 1612	1658, 1613
{Bo^{M}Cp^{tet}}Lu{NHCH$_2$(1-$C_{10}H_7$)}$_2$ (**3b**)	1657, 1629	1657, 1626
{Bo^{M}Cp^{tet}}Lu{NHB(C_6F_5)$_2$}C_6F_5 (**4**)	1644	1644

gand.[5q,r] To transfer that [M]═NR stabilization to trivalent metal centers, a related monoanionic cyclopentadienyl–bis(2-oxazolinyl) ligand has been prepared. Herein, we report the reactivity of {Bo^{M}Cp^{tet}}Lu(CH_2Ph)$_2$ (Bo^{M}Cp^{tet} = tetramethylcyclopentadienyl–bis(4,4-dimethyl-2-oxazoline) with benzylic amines to give imido and amido compounds, as well as the interesting C_6F_5-migration chemistry observed in reactions of {Bo^{M}Cp^{tet}}Lu(CH_2Ph)$_2$ with $NH_3B(C_6F_5)_3$.[17]

■ RESULTS

The ligand 1,1-bis(4,4-dimethyl-2-oxazolinyl)-1-(tetramethylcyclopentadiene)ethane (**Bo^{M}Cp^{tet}H**) and Lu(CH_2Ph)$_3$THF$_3$ react in benzene at room temperature over 30 min to give {Bo^{M}Cp^{tet}}Lu(CH_2Ph)$_2$ (**1**) in 95% yield (eq 1). Remarkably, compound **1** persists for 2 days at 180 °C in toluene-d_8 in a Teflon-sealed NMR tube without a detectable decrease in signal intensity.



In the ^{1}H NMR spectrum of **1**, two singlets at 2.02 and 2.01 ppm (6 H each) revealed mirror-related methyls of the C_5Me_4. Diastereotopic doublets at 3.52 and 3.41 ppm (CH_2) and diastereotopic singlets at 0.89 and 0.97 ppm (Me) were assigned to the two equivalent oxazolines. The two equivalent benzylic CH_2 groups also appeared as diastereotopic doublets at 1.72 and 1.59 ppm in the ^{1}H NMR spectrum. The ^{1}H NMR spectra of **1** acquired from 298 to 183 K also exhibited this pattern of resonances, indicating that both the oxazoline groups and benzyl groups are either equivalent or undergoing rapid exchange even at low temperature. The oxazoline methyl resonances correlated to a single ^{15}N NMR resonance in a ^{1}H–^{15}N HMBC experiment. Only one CH_2Ph resonance at 59.2 ppm appeared in the ^{13}C{^{1}H} NMR spectrum, and together, these data further support pseudo-C_s symmetry for **1**. However, two bands in the IR spectrum of **1** at 1664 and 1591 cm^{-1}, assigned to oxazoline ν_{CN} (see Table 1), provide some evidence for coordinated and dissociated oxazolines that are undergoing rapid exchange on the NMR time scale. For comparison, the IR spectrum of Bo^{M}Cp^{tet}H, where both oxazolines are noncoordinated, contained two bands at 1661 and 1640 cm^{-1} separated by 21 cm^{-1}. The energy difference between the ν_{CN} bands in **1** is significantly greater (50 cm^{-1}). This change between Bo^{M}Cp^{tet}H and **1** suggests that the two bands in the protonated ligand result from symmetric and asymmetric stretching modes, whereas the two bands in the IR spectrum of **1** result from dissociated and coordinated oxazolines.

{Bo^{M}Cp^{tet}}Lu(CH_2Ph)$_2$ crystallizes with the tetramethylcyclopentadienyl, two benzyl, and one oxazoline donor bonded to lutetium in a three-legged piano-stool geometry (Figure 1).

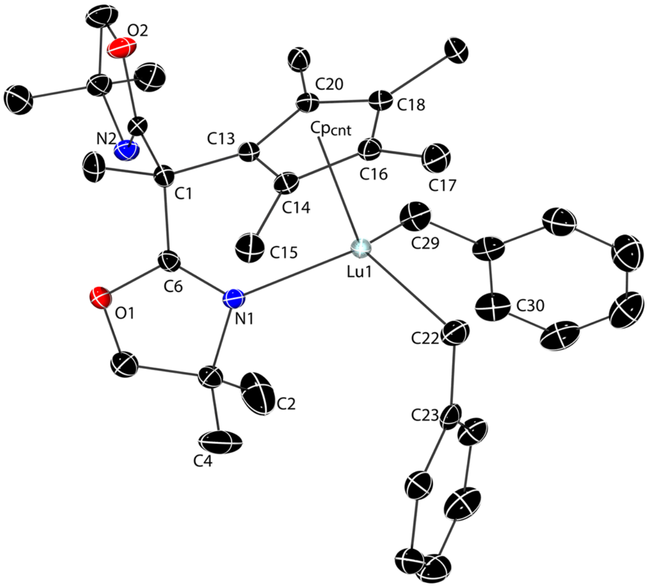


Figure 1. Rendered thermal ellipsoid plot of {Bo^{M}Cp^{tet}}Lu(CH_2Ph)$_2$ (**1**) depicted at 35% probability level. Selected interatomic distances (Å): Lu1–C22, 2.367(3); Lu1–C29, 2.379(3); Lu1–N1, 2.350(2); Lu1–C13, 2.552(2); Lu1–C14, 2.557(3); Lu1–C16, 2.601(3); Lu1–C18, 2.596(3); Lu1–C20, 2.566(3). Selected interatomic angles (deg): C22–Lu1–C29, 109.1(1); N1–Lu1–C29, 106.35(9); N1–Lu1–C22, 117.75(9).

The second oxazoline is dissociated from the lutetium center. The coordinated oxazoline and cyclopentadienyl ligands form a five-membered, unstrained chelate ring (Lu1, N1, C6, C1, C13). The lack of ring strain is apparent in the pentahapto–cyclopentadienyl–lutetium interaction and the Lu1–Cp$_{cnt}$–C1 angle of 87.1°, which is similar to the analogous acyclic angles of Lu1–Cp$_{cnt}$–CH$_3$ (e.g., Lu1–Cp$_{cnt}$–C15, 87.3°; Lu1–Cp$_{cnt}$–C17, 93.9°). The Lu1–N1 interatomic distance is 2.350(2) Å, which is longer than the Lu–N distances in the four-coordinate bis(oxazolinato) complex {MeC(Ox$^{4S\text{-}tBu}$)$_2$}Lu{CH(SiMe$_3$)$_2$}$_2$ of 2.259(3) and 2.255(3) Å, as might be expected based on the relative charges on the oxazoline donors in the two compounds.[18] Interestingly, the Lu1–N1 distance is shorter than the distances in the six-coordinate complex [Lu(*i*Pr-trisox)(CH$_2$SiMe$_2$Ph)$_3$] of 2.504(3), 2.510(3), and 2.522(3) Å.[19] The Lu1–C29 and Lu1–C22 distances of 2.379(3) and 2.367(3) Å, respectively, for the benzyl ligands are the same within 3σ. These distances are shorter than the Lu–C distances of 2.404(7), 2.408(4), and 2.413(5) Å in the Lu(η^1-

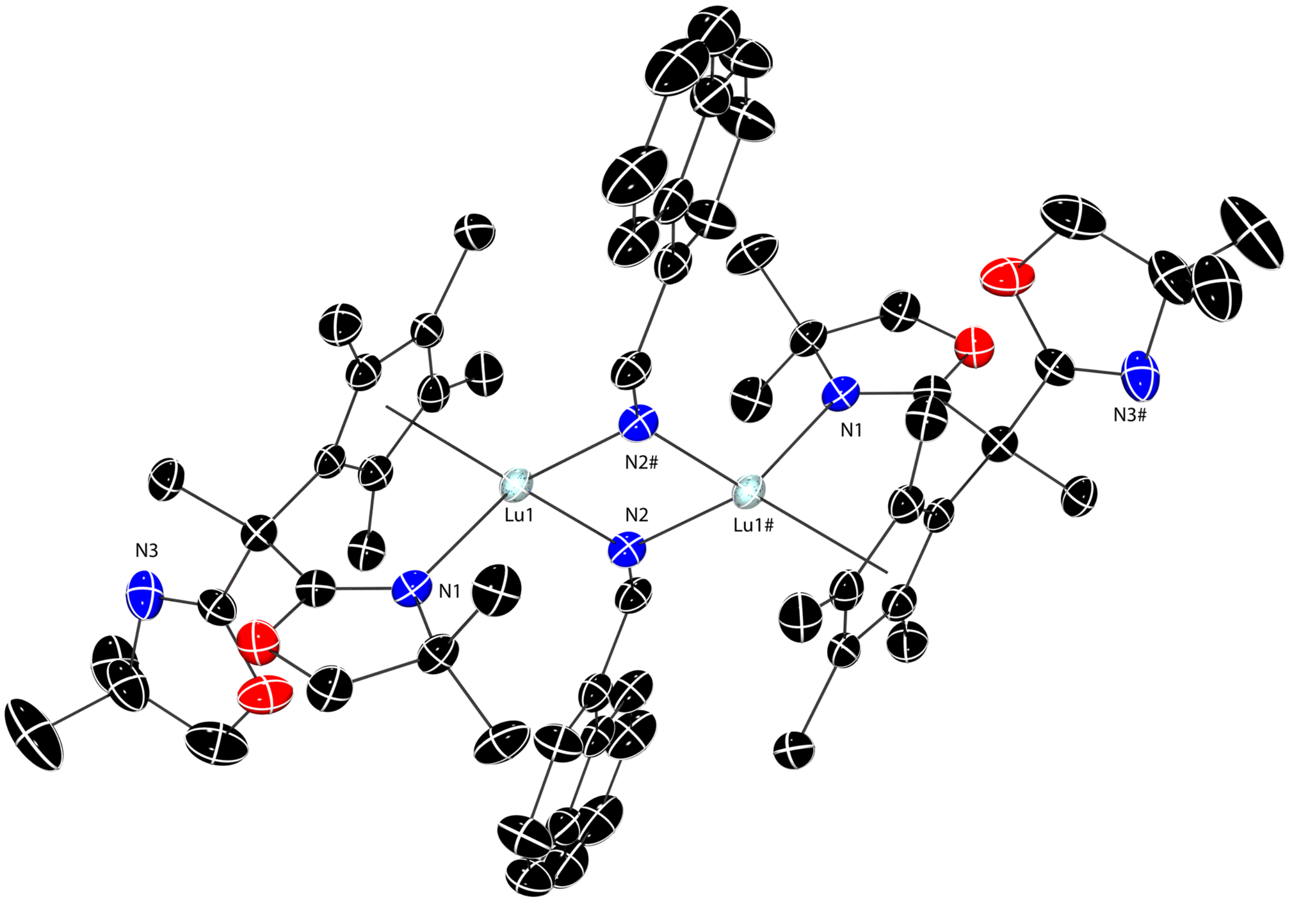
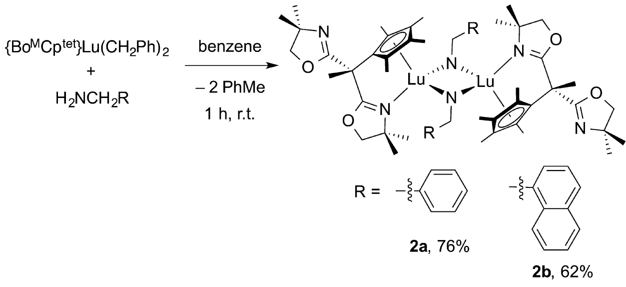


Figure 2. Rendered thermal ellipsoid plot of $[\{Bo^{M}Cp^{tet}\}LuNCH_2(1\text{-}C_{10}H_7)]_2$ (**2b**). Ellipsoids are plotted at 35% probability level; H atoms and a benzene molecule are not included in the illustration for clarity. Selected interatomic distances (Å): Lu1−N2, 2.116(4), 2.163(4); Lu1−N1, 2.426(4); Lu1−Lu1, 3.1739(4). Selected interatomic angles (deg): N2−Lu1−N2#, 84.2(2); N1−Lu1−N2, 119.3(2), 108.8(2).

$CH_2Ph)_3THF_3$ starting material.[20] The benzyl ligands in **1** are monohapto coordinated, and there is no evidence for π-coordination of the phenyl groups to the Lu center. Thus, the Lu1−C22−C23 and Lu1−C29−C30 angles of 111.4(2)° and 120.6(2)° result in long Lu1−C23 and Lu1−C30 distances of 3.211(3) and 3.383(3) Å from the lutetium to the *ipso*-carbon of the benzyl ligands. Any closer approach of the C23 carbon to the lutetium center is blocked by the C2 and C4 carbons of the coordinated 4,4-dimethyl-2-oxazoline.

The reactions of dibenzyl lutetium **1** and benzylamine or 1-naphthalenemethanamine ($H_2NCH_2(1\text{-}C_{10}H_7)$) in benzene yield the corresponding imido species $[\{Bo^{M}Cp^{tet}\}LuNCH_2Ph]_2$ (**2a**) or $[\{Bo^{M}Cp^{tet}\}LuNCH_2(1\text{-}C_{10}H_7)]_2$ (**2b**) after 1 h (eq 2). Two equivalents of toluene are formed in these reactions, as determined by integration of ^{1}H NMR spectra of micromolar scale reactions. Ligand substitution reactions in which alkyl groups are replaced with amido ligands are well-known, for example, as a catalyst initiation step in the organo-rare earth element catalyzed hydroamination of alkenes and alkynes.[21] This reaction, as well as the reaction of alkyls with nonacidic C−H bonds, is proposed to involve four-centered transition states through a proton transfer from the incoming ligand.[22]

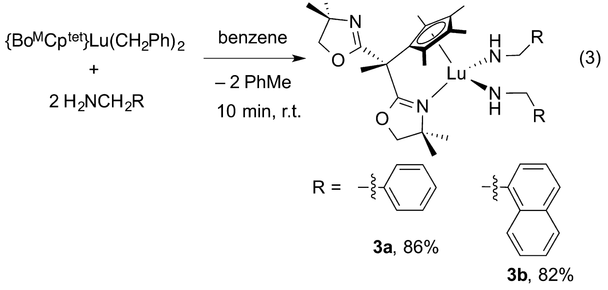


(2)

The compounds are assigned as dimers based on the similarity of oxazoline ν_{CN} bands in the solution-phase and solid-state IR spectra and a single-crystal diffraction study of **2b** that confirms the dimeric solid-state structure. The lutetium imido compounds **2a** and **2b**, when generated in situ, are soluble in benzene-d_6 or toluene-d_8, and these in situ samples were used for solution-phase spectroscopic characterization. The ^{1}H NMR spectra did not provide direct evidence for a dimeric structure, but the $Bo^{M}Cp^{tet}$ resonances, particularly one set of oxazoline peaks with diastereotopic methyl and methylene signals, followed the pattern established with $\{Bo^{M}Cp^{tet}\}Lu(CH_2Ph)_2$. Doublets at 5.41 and 4.87 ppm for **2a** and at 5.92 and 5.53 ppm for **2b** (1 H each) were assigned to methylene moieties of benzylic groups (NCH_2Aryl). This pattern provides indirect support for a dimeric structure because a monomeric $\{Bo^{M}Cp^{tet}\}Lu{=}NCH_2Aryl$, in a three-legged piano-stool geometry with both oxazolines coordinated to the lutetium center, would be expected to contain a mirror plane making the benzylic hydrogen equivalent. Over 12 h, **2a** and **2b** precipitate out of solution, and isolated **2a** does not dissolve even in polar solvents such as methylene chloride or THF while **2b** is minimally soluble in THF. While the insolubility of the dimeric precipitated material might suggest that the initially generated and soluble material is monomeric, no spectroscopic changes (other than intensity) were observed in the soluble portion of the samples as precipitation occurs, and the solution-phase and solid-state IR spectra contained similar bands for ν_{CN} (see Table 1). Moreover, the lower energy bands of 1618 and 1612 cm^{-1} for **2a** and **2b**, respectively, are ca. 20 cm^{-1} higher energy than the absorption in the dialkyl **1**, but similar in frequency to the lutetium bis(amido) complexes **3a** and **3b** (see below).

The dimeric structures of **2a** and **2b** are further supported by an X-ray crystallographic diffraction study of the latter compound. The crystal structure of **2b** reveals two bridging imido ligands that form Lu−N−Lu interactions (Figure 2). The two $\{Bo^{M}Cp^{tet}\}LuNCH_2C_{10}H_7$ monomeric units are related by a crystallographic inversion center located at the center of the planar Lu_2N_2 parallelogram (the compound crystallizes in a trigonal crystal system with $Z = 9$ in the space group $R\bar{3}$). The N2−N2# and Lu1−Lu1# distances are 2.870(7) and 3.1739(4) Å, respectively, while the Lu1−N2−Lu1# and N2−Lu1−N2# angles are 95.8(2)° and 84.2(2)°. The bridging N2 atoms are planar ($\sum$ = Lu1−N2−C22 + C22−N2−Lu1# + Lu1#−N2−Lu1 = 125.5(4) + 137.4(4) + 95.8(2) = 358.7°). The bridging Lu1−N2 and Lu1−N2# interatomic distances are 2.116(4) and 2.163(4) Å, and likely, these similar distances best describe equivalent interactions between Lu1−N2 and Lu1−N2#. These distances are slightly longer than the Lu−N distances in the monomeric lutetium ketimido complexes $[LuCl_2(NIm^{Dipp})\text{-}THF_3]$ and $[(\eta^8\text{-}C_8H_8)Lu(NIm^{Dipp})THF_2]$ (NIm^{Dipp} = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-imine).[23] The lutetium and $Bo^{M}Cp^{tet}$ ligand coordination is characterized by one bound and one noncoordinated oxazoline. Although this compound is dimeric, each lutetium center is coordinated in a three-legged piano-stool geometry that is comparable to the structure of **1**. The Lu1−N1 interatomic distance of 2.426(4) Å is longer than that in compound **1** (2.350(2) Å). Thus, **2b** has both a longer Lu−N distance and higher energy oxazoline ν_{CN} in comparison to **1**.

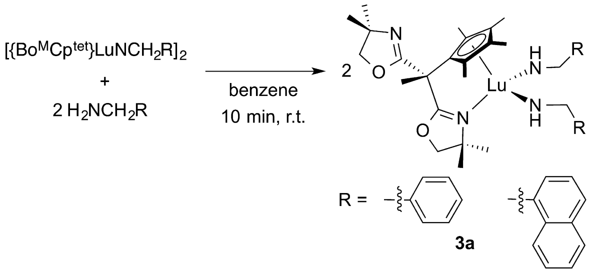
The related bis(amido)lutetium compounds were synthesized for comparison with **2a** and **2b**. Compound **1** and 2 equiv of benzyl amine or 1-naphthalenemethanamine react in benzene at room temperature to yield $\{Bo^{M}Cp^{tet}\}Lu(NHCH_2Ph)_2$ (**3a**) and $\{Bo^{M}Cp^{tet}\}Lu\{NHCH_2(1\text{-}C_{10}H_7)\}_2$ (**3b**) after 10 min. (eq 3).



(3)

A broad resonance at 1.24 ppm for **3a** and a triplet at 1.57 ppm for **3b** were assigned to the NH in the ^{1}H NMR spectra in benzene-d_6. The benzylic CH_2 groups were shifted upfield (**3a**: 4.08 ppm; **3b**: 4.77 ppm), and each appeared as a broad singlet compared to the diastereotopic signals in the imido compounds **2a** and **2b**. The signal pattern of the $Bo^{M}Cp^{tet}$ in ^{1}H NMR spectra acquired from 298 to 183 K again suggested equivalent oxazolines. However, based on the two IR stretching frequencies for ν_{CN} (see Table 1), we assign the structure of **3a** and **3b** as three-legged piano-stool compounds with one free oxazoline group and one coordinated oxazoline in solution and the solid state. Thus, the spectroscopic properties and structures of compounds **1**, **3a**, and **3b** are similar; moreover, **3a** and **3b** are persistent in toluene-d_8 at 200 °C for 2 days in sealed NMR tubes. Unlike isolated **2a** and **2b**, the bis(amido) compounds are soluble in benzene and toluene.

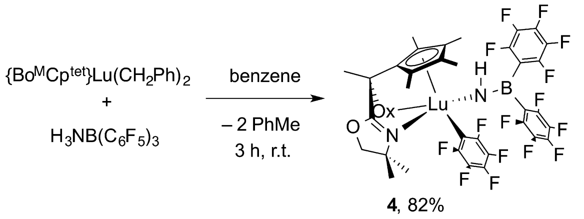
As expected, the dimeric imido compounds **2a** and **2b** react with benzylamine and naphthalenemethanamine to form **3a** and **3b**, respectively (eq 4).



(4)

In contrast, the reactions of **2a** or **2b** with pyridine or DMAP give complicated mixtures. An alternative strategy for stabilizing monomeric imido compounds involves coordination of main group Lewis acids to the nitrogen in **2a** and **2b** to displace the second lutetium center. However, reactions of **2a** or **2b** with $B(C_6F_5)_3$ or BPh_3 did not provide isolable products.

Instead, reactions of **1** and amine−Lewis acid adducts were investigated. Compound **1** reacts with $H_3NB(C_6F_5)_3$ in benzene at room temperature over 3 h to give 2 equiv of toluene and a single compound identified as $\{Bo^{M}Cp^{tet}\}Lu\text{-}\{NHB(C_6F_5)_2\}C_6F_5$ (**4**; eq 5).



(5)

4, 82%

The ^{1}H NMR spectrum of **4** revealed a broad singlet at 5.54 ppm that integrated to 1 H relative to the $Bo^{M}Cp^{tet}$ resonances and was assigned to an NH moiety. As in the above compounds, the pattern of the $Bo^{M}Cp^{tet}$ resonances suggested mirror symmetry, with two C_5Me_4 signals (6 H each), two oxazoline Me resonances (6 H each), and two diastereotopic oxazoline methylene peaks (2 H each). In contrast, the ^{19}F NMR spectrum was complicated and contained 11 resonances corresponding to inequivalent fluorine in **4**. These signals indicated that the $B(C_6F_5)_3$ group in $H_3NB(C_6F_5)_3$ lost all symmetry upon reaction with **1** (see below for comparison to other crystallographically characterized $[Ln]{-}C_6F_5$ compounds). The ^{11}B NMR chemical shift of **1** was 36 ppm, which is consistent with a three-coordinate boron center. The assignment of the NH was supported by a $^{1}H{-}^{15}N$ HMBC experiment, which revealed a correlation between a signal at −182 ppm in the ^{15}N NMR spectrum and the ^{1}H NMR signal at 5.54 ppm. This crosspeak appeared as a doublet, giving $^{1}J_{NH}$ = 60 Hz. A second $^{1}H{-}^{15}N$ crosspeak between a ^{15}N NMR

DOI: 10.1021/acs.inorgchem.5b00927
Inorg. Chem. 2015, 54, 6938−6946

signal at −149 ppm was assigned to the oxazoline nitrogen by its correlation to the methyl groups. In addition, only one oxazoline ν_{CN} band at 1644 cm^{-1} was observed in the IR spectrum, in contrast to the two ν_{CN} signals in **1**, **2a−b**, and **3a−b**.

A single-crystal X-ray diffraction study revealed a four-legged piano-stool compound in which both oxazolines are coordinated to the lutetium center and a C_6F_5 group has migrated from boron to lutetium (Figure 3). The nitrogen ligand is best described as an amidoboryl group. This structure is consistent with the ^{19}F NMR spectrum that suggested inequivalent C_6F_5 groups, assuming hindered rotation around N−C_6F_5, Lu−C_6F_5, and both Lu−N and N−B bonds. The complex is C_1 symmetric in the solid state and crystallizes in the chiral space group $Pna2_1$ as a single enantiomer, but comes from entirely achiral starting materials. Presumably, mixtures of enantiopure crystals are formed; we have not, however, surveyed the samples to separate crystals into enantiopure crystalline material because of the high reactivity of the lutetium compounds toward air and moisture. Moreover, the apparent C_s symmetry of the $Bo^{M}Cp^{tet}$ ligand in **4** suggests that the stereogenic lutetium center is racemized in solution.

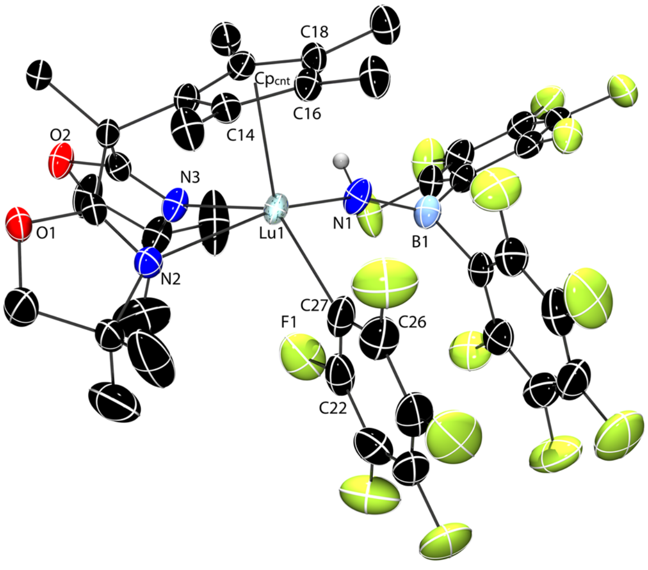


Figure 3. Rendered thermal ellipsoid plot of $\{Bo^{M}Cp^{tet}\}Lu\{NHB(C_6F_5)_2\}C_6F_5$ (**4**) plotted at 50% probability. Selected interatomic distances (Å): Lu1−N2, 2.558(4); Lu1−N3, 2.443(4); Lu1−N1, 2.251(4); Lu1−C27, 2.423(6); Lu1−F1, 2.820(4); N1−B1, 1.361(7). Selected interatomic angles (deg): N1−Lu1−N2, 153.7(2); N3−Lu1−C27, 132.9(2); N2−Lu1−N3, 70.9(1); N3−Lu1−N1, 88.8(2); N1−Lu1−C27, 98.3(12); N2−Lu1−C27, 84.7(2): Lu1−N1−B1, 141.6(4); Lu1−N1−H1n, 102(4); B1−N1−H1n, 112(4).

The single IR band for the ν_{CN} at 1644 cm^{-1} is consistent with a single strong mode of two coordinated oxazolines absorbing at lower energy than the band of a noncoordinated oxazoline but at higher energy than a single coordinated oxazoline (e.g., in **1**; see Table 1 for the comparison). This X-ray structure and the single ν_{CN} band, however, are incommensurate with the ^{1}H NMR pattern of the seemingly C_s-symmetric $Bo^{M}Cp^{tet}$ ligand. Likely, the $Bo^{M}Cp^{tet}$ signals are averaged by an oxazoline dissociation−coordination process that is fast on the NMR and even on the IR time scale, while the thermodynamically favored solid-state structure is the four-legged piano-stool. Alternatively, the exchange may be slow on the IR time scale to give symmetric and asymmetric ν_{CN}, but the intensity of one of the two modes is weak.

In this configuration, the oxazoline containing the N2 atom is pseudo-*trans* to the $NHB(C_6F_5)_2$ ligand (N1−Lu1−N2, 153.7(2)°) and the other oxazoline is pseudo-*trans* to the C_6F_5 (N3−Lu1−C27, 132.9(2)°). The Lu1−N1 interatomic distance of 2.251(4) Å is longer than the bridging Lu−N distances in **2b** ($[\{Bo^{M}Cp^{tet}\}LuN(1\text{-}C_{10}H_7)]_2$: 2.116(6) and 2.163(4) Å), as well as in the primary amido alkyllutetium compounds $Tp^{tBu,Me}LuMe(NHtBu)$ (2.126(2) Å), $[Tp^{tBu,Me}LuMe(NHAd)]$ (2.128(2) Å) ($Tp^{tBu,Me}$ = tris(3-*t*Bu-5-Me-pyrazolyl)borate, Ad = adamantyl),[12] and $(C_5Me_5)Lu(NHDipp)(CH_2SiMe_3)bpy$ (2.208(7) Å).[16a] In addition, the Lu−N distances in the $AlMe_3$-coordinated $Tp^{tBu,Me}Lu\{(\mu\text{-}Me)(\mu\text{-}NR)AlMe_2\}$ (R = *t*Bu, 2.081(3) Å, R = Ad, 2.083(2) Å) are significantly shorter than those in **4**.[13] The shorter distances in tris(pyrazolyl)borate-supported compounds may be a result of their lower coordination number vs **4**, a reduced steric demand of the bridging $AlMe_3$ moiety in the $[Lu]\{(\mu\text{-}Me)(\mu\text{-}NR)AlMe_2\}$ structure vs two ligands in the $[Lu]\{NHB(C_6F_5)_2\}C_6F_5$ structure, or from an electronic effect.

The amido N1 atom is nearly planar, as expected for a trivalent nitrogen bonded to two elements that can act as π-acceptors, with a Lu1−N1−B1 angle of 141.6(4)° and the sum of the angles around N of 355°. The N1−B1 distance of 1.361(7) Å is shorter than the N−B distances in $(Me_2N)_3Zr\{NH_2B(C_6F_5)_3\}(NHMe_2)$ (1.587(5) Å),[24] in the anion of $[Na(OEt_2)_4][H_2N\{B(C_6F_5)_3\}_2]$ (1.628(3), 1.636(3) Å),[25] and in the neutral compounds H_3NBH_3 (1.58(2) Å)[26] and $(NH_2BH_2)_3$ (1.576(2) Å).[27]

One of the *ortho*-fluorine of the Lu-bonded C_6F_5 group is located *trans* to the C_5Me_4 group with a long distance (Lu1−F1, 2.820(4) Å) and a nearly linear Cp_{cnt}−Lu1−F1 angle (179.3°). The C_6F_5 plane (defined by C22, C26, and C27) and the C_5Me_4 planes (defined by C14, C16, and C18) are nearly orthogonal (87.5°). A Lu1−F1 interaction may contribute to the hindered rotation that makes all fluorine in the Lu−C_6F_5 inequivalent in the ^{19}F NMR spectrum.

Few rare earth compounds containing [M]−C_6F_5 have been crystallographically characterized,[28] and no pentafluorophenyl lutetium compounds were found in a search of the Cambridge Structural Database. Regarding their syntheses, a few pentafluorophenyl lanthanide compounds are prepared from mercury reagents, including the trivalent $[Cp^*_2SmC_6F_5]_2$ (Cp^* = C_5Me_5),[28a] and the divalent $[Ln(C_6F_5)THF_5]^+$ (Ln = Eu, Yb),[28d] $Cp^*Yb(C_6F_5)THF_2$, and $Yb(C_6F_5)_2THF_4$.[28c] A pentafluorophenyl scandium was formed by addition of the C−I bond in C_6F_5I across a scandium N-heterocyclic carbene bond,[28h] whereas $(C_5{}^tBu_3H_2)_2CeH$ and C_6F_6 react to give $(C_5{}^tBu_3H_2)_2CeC_6F_5$ en route to $(C_5{}^tBu_3H_2)_2CeF$.[28e] In reactions that appear more closely related to the current transformation, $B(C_6F_5)_3$ reacts with diketiminate scandium or anilido-iminoyttrium dialkyl compounds to give perfluorophenyl rare earth compounds.[28b,f] The Lu1−C27 distance of 2.423(6) Å in **4** is slightly shorter than the Y−C distance of 2.460(3) Å in the anilido-iminoyttrium pentafluorophenyl compound[28b] and much shorter than the Sm−C distance of 2.60(1) Å in $[Cp^*_2SmC_6F_5]_2$.[28a] In the $(C_5{}^tBu_3H_2)_2CeC_6F_5$, yttrium, and $Cp^*Yb(C_6F_5)THF_2$ compounds, short contacts to *ortho*-fluorine are observed (Y−F, 2.786(2) Å; Ce−F, 2.682(2) Å; Yb−F, 3.16(4) Å). Both the ytterbium and the cerium compounds show spectroscopic features consistent with hindered Ln−C_6F_5 rotation. In the diamagnetic ytterbium compounds, *ortho*-fluorine signals appeared downfield at ca. −110 ppm and split into two signals at low temperature, whereas the ^{19}F NMR signal of the yttrium compound appeared at −130 ppm.[28b] In **4**, the signal at −118 ppm was assigned to one *ortho*-fluorine of the lutetium pentafluorophenyl group.

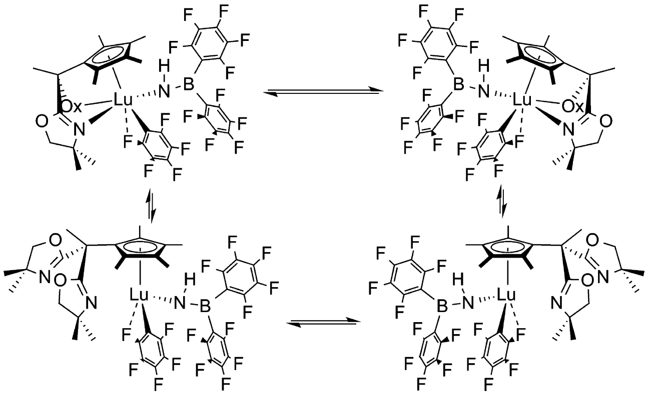
■ DISCUSSION

The formation of $\{\mathrm{Bo^{M}Cp^{tet}}\}\mathrm{Lu}\{\mathrm{NHB}(\mathrm{C_6F_5})_2\}\mathrm{C_6F_5}$ (**4**) likely involves the intermediate $\{\mathrm{Bo^{M}Cp^{tet}}\}\mathrm{LuNHB}(\mathrm{C_6F_5})_3$, which may be formulated as a $\mathrm{B(C_6F_5)_3}$ adduct of the parent imido $\{\mathrm{Bo^{M}Cp^{tet}}\}\mathrm{Lu{=}NH}$ or as a zwitterionic lutetium amidoborate. The former description is favored by the characterization of the $\mathrm{H_3NB(C_6F_5)_3}$ starting material as a Lewis acid−base adduct.[27] However, the substitution of two H^{+} in $\mathrm{H_3NB(C_6F_5)_3}$ for a $\{\mathrm{Bo^{M}Cp^{tet}}\}\mathrm{Lu^{2+}}$ in the putative intermediate $\{\mathrm{Bo^{M}Cp^{tet}}\}\mathrm{LuNHB(C_6F_5)_3}$ could modify the nature of the N−B interaction. That is, the latter formulation might be argued based on the trivalent boron center in the product **4**, where one valence is attributed to the N−B bond.

Irrespective of the formulation of a putative intermediate on the pathway to **4**, the migration of $\mathrm{C_6F_5}$ from boron to lutetium indicates that the lutetium center in such a species is a stronger electrophile than boron in the $\{\mathrm{Bo^{M}Cp^{tet}}\}\mathrm{LuHNB(C_6F_5)_3}$ system. Strategies to impede the $\mathrm{C_6F_5}$ migration could involve decreasing the electrophilicity of the Lu center through a more strongly donating ancillary ligand. Comparison of the dimeric three-legged piano-stool lutetium imido compounds **2a** and **2b** with monomeric four-legged piano-stool aryl amido **4** suggests that stabilization of a monomeric lutetium imido in a three-legged piano-stool geometry will not be solved simply by controlling the coordination number to impede dimerization. That is, a $\mathrm{CpL_2}$ ligand that binds via pentahapto−cyclopentadienyl−lutetium interaction and a bidentate $\mathrm{L_2}$−Lu coordination still could dimerize to give two four-legged piano-stool centers bridged by imido groups. Likely, both ancillary ligand and imido substituent are important as in group 4 and scandium imido chemistry.

In addition, the observation of similar ^{1}H NMR spectroscopic features of the Bo^{M}Cp^{tet} ligand in three-legged and four-legged piano-stool compounds suggests that the ligand's fluxionality involves both associative and dissociative mechanisms. For example, the equivalence of oxazoline groups in chiral **4** is not achieved by dissociation of only one oxazoline because the resulting three-legged piano-stool geometry still is a mixture of diastereomers and should give inequivalent oxazolines and four $\mathrm{C_5Me_4}$ signals in the ^{1}H NMR spectrum. Instead, apparent C_s symmetry is observed for the Bo^{M}Cp^{tet} ligand in **4**, while all the fluorine in three $\mathrm{C_6F_5}$ groups are persistently inequivalent. The latter observation indicates that fluxionality is not associated with processes of the $[\mathrm{Lu}]\{\mathrm{NHB(C_6F_5)_2}\}\mathrm{C_6F_5}$ groups, and even rotations that would reduce the five $\mathrm{C_6F_5}$ resonances to three signals are ruled out. The $\mathrm{NHB(C_6F_5)_2}$ and $\mathrm{C_6F_5}$ ligands need to exchange sites for epimerization to occur and the oxazolines to become equivalent, and this must occur without exchanging any fluorine. A reasonable pathway, then, for symmetrizing the Bo^{M}Cp^{tet} ligand in **4** involves dissociation of both oxazolines, rotation of the $\mathrm{C_5Me_4C(Ox^{Me2})_2}$, and inversion of the Lu center, followed by recoordination of the oxazolines (Scheme 1). Moreover, the isolation of the four-legged piano-stool geometry for **4** indicates that configuration is accessible with this new ligand class, and that exchange processes of coordinated and dissociated oxazolines in the three-legged piano-stool compounds **1**, **2a**−**2b**, and **3a**−**3b** may also occur through an associative mechanism.

Scheme 1. Possible Exchange Pathway That Gives a Pseudo C_s-Symmetric Bo^{M}Cp^{tet} Ligand without $\mathrm{C_6F_5}$ Exchange



■ EXPERIMENTAL SECTION

General Procedures. All reactions were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox, unless otherwise indicated. Benzene, toluene, pentane, diethyl ether, and tetrahydrofuran were dried and deoxygenated using an IT PureSolv system. Toluene-d_8 and benzene-d_6 were heated to reflux over Na/K alloy and vacuum-transferred. $\mathrm{Lu(CH_2Ph)_3THF_3}$[20] and $\mathrm{NH_3B(C_6F_5)_3}$[17] were synthesized according to literature procedures. Benzylamine and 1-naphthalenemethanamine were purchased from Sigma-Aldrich and purified by distillation under a dry argon atmosphere prior to use. ^{1}H, ^{13}C{^{1}H}, and ^{11}B NMR spectra were collected on Bruker AVII 700 or 600 spectrometers, a Bruker DRX-400 spectrometer, or a MR-400 spectrometer. ^{15}N chemical shifts were determined by ^{1}H−^{15}N HMBC experiments on a Bruker AVII 700 or 600 spectrometer; ^{15}N chemical shifts were originally referenced to an external liquid $\mathrm{NH_3}$ standard and recalculated to the $\mathrm{CH_3NO_2}$ chemical shift scale by adding −381.9 ppm. Elemental analyses were performed using a PerkinElmer 2400 Series II CHN/S in the Iowa State Chemical Instrumentation Facility. X-ray diffraction data were collected on a Bruker APEX II diffractometer.

Bo^{M}Cp^{tet}H. A 500 mL Schlenk flask was charged with 2,3,4,5-tetramethylcyclopentadienyllithium (1.12 g, 8.74 mmol). Dry pentane (400 mL) was added, and the mixture was cooled to −78 °C. Solid iodine (2.21 g, 8.73 mmol) was added to the flask. The mixture was stirred at −78 °C for 8 h and was then warmed to −20 °C and stirred for 12 h until all $\mathrm{LiC_5Me_4}$ reacted. Over the course of the reaction, the solution turned dark yellow above a white precipitate. $\mathrm{Li[MeC(Ox^{Me2})_2]}$ (2.00 g, 8.73 mmol) was placed in a 100 mL Schlenk flask and dissolved in THF (30 mL). The THF solution was added via cannula to the pentane mixture at −20 °C. The solution was warmed to room temperature and was stirred for 8 h. The reaction mixture was then filtered in air, and the solvent was removed under reduced pressure. The crude oily product was purified by silica gel chromatography in ethyl acetate to give the product as a white solid (2.04 g, 5.90 mmol, 68%). The solid was dried by dissolving in benzene and stirring over phosphorus pentoxide for 6 h. ^{1}H NMR (benzene-d_6, 700 MHz, 25 °C): δ 4.17 (s, 1 H, $\mathrm{C}H\mathrm{Me_4}$), 3.75 (d, 2 H, $^{2}J_{\mathrm{HH}}$ = 7.7 Hz, $\mathrm{CNCMe_2C}H_2\mathrm{O}$), 3.65 (d, 2 H, $^{2}J_{\mathrm{HH}}$ = 7.7 Hz, $\mathrm{CNCMe_2C}H_2\mathrm{O}$), 1.95 (s, 6 H, $\mathrm{C_5H}Me_4$), 1.70 (s, 6 H, $\mathrm{C_5H}Me_4$), 1.62 (s, 3 H, $Me\mathrm{C(Ox^{Me2})_2}$), 1.17 (s, 6 H, $\mathrm{CNC}Me_2\mathrm{CH_2O}$), 1.13 (s, 6 H, $\mathrm{CNC}Me_2\mathrm{CH_2O}$). ^{13}C{^{1}H} NMR (benzene-d_6, 100 MHz, 25 °C): δ 170.0 ($\mathrm{CNCMe_2CH_2O}$), 166.87, 138.21 ($C_5\mathrm{HMe_4}$), 134.4 ($C_5\mathrm{HMe_4}$), 79.43 ($\mathrm{CNCMe_2CH_2O}$), 67.61 ($\mathrm{CNCMe_2CH_2O}$), 59.79 ($C_5\mathrm{HMe_4}$), 44.34 ($\mathrm{MeC(Ox^{Me2})_2}$), 29.1 ($\mathrm{CNC}Me_2\mathrm{CH_2O}$), 28.1 ($\mathrm{CNC}Me_2\mathrm{CH_2O}$), 16.4 ($Me\mathrm{C(Ox^{Me2})_2}$), 14.2 ($\mathrm{C_5H}Me_4$), 11.68 ($\mathrm{C_5H}Me_4$). ^{15}N{^{1}H} NMR (benzene-d_6, 70 MHz, 25 °C): δ −131.1

(CNCMe$_2$CH$_2$O). IR (KBr, cm^{-1}): IR (KBr, cm^{-1}): 3287 w, 3010 m, 2963 s, 2930 s, 2890 s, 2860 s, 2734 w, 1661 s (CN), 1640 m (CN), 1463 s, 1446 s, 1376 s, 1363 m, 1346 m, 1301 m, 1253 m, 1195 m, 1170 m, 1094 m, 1068 m, 1036 m,1011 m, 994 m, 975 s, 945 s, 926 m, 892 w, 852 m, 769 m, 733 w, 654 s, 615 w. Anal. Calcd for C$_{21}$H$_{32}$N$_2$O$_2$: C, 73.22; H, 9.36; N, 8.13. Found: C, 73.16; H, 9.31; N, 8.12. mp 109−111 °C.

{Bo^{M}Cp^{tet}}Lu(CH$_2$Ph)$_2$ (1). Bo^{M}Cp^{tet}H (0.106 g, 0.307 mmol) was dissolved in 5 mL of benzene. A light yellow colored solution formed upon addition of solid Lu(CH$_2$Ph)$_3$THF$_3$ (0.203 g, 0.307 mmol). This solution was stirred at r.t. for 30 min, and then the volatile materials were removed under reduced pressure. The residue was recrystallized from a toluene/pentane (1:1) mixture at −30 °C to give {Bo^{M}Cp^{tet}}Lu(CH$_2$Ph)$_2$ as a pale yellow solid (0.205 g, 0.293 mmol, 95.4%). ^{1}H NMR (benzene-*d$_6$*, 600 MHz): *δ* 7.19 (m, $^3J_{HH}$ = 7.2 Hz, 4 H, *meta*-C$_6$H$_5$), 6.96 (d, $^3J_{HH}$ = 7.2 Hz, 4 H, *ortho*-C$_6$H$_5$), 6.80 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, *para*-C$_6$H$_5$), 3.52 (d, $^2J_{HH}$ = 8.4 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 3.40 (d, $^2J_{HH}$ = 8.4 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 2.03 (s, 6 H, C$_5$Me$_4$), 2.01 (s, 6 H, C$_5$Me$_4$), 1.87 (s, 3 H, CMe), 1.72 (d, $^2J_{HH}$ = 9.5 Hz, 2 H, LuC*H*$_2$Ph), 1.59 (d, $^2J_{HH}$ = 9.5 Hz, 2 H, LuC*H*$_2$Ph), 0.89 (s, 6 H, CNC*Me*$_2$CH$_2$O), 0.87 (s, 6 H, CNC*Me*$_2$CH$_2$O). ^{13}C{^{1}H} NMR (benzene-*d$_6$*, 150 MHz): *δ* 175.07 (CNCMe$_2$CH$_2$O), 152.41 (*ipso*-C$_6$H$_5$), 129.69 (*meta*-C$_6$H$_5$), 125.06 (*ortho*-C$_6$H$_5$), 119.09 (C$_5$Me$_4$), 118.99 (*para*-C$_6$H$_5$), 117.90 (C$_5$Me$_4$), 114.12 (*ipso*-C$_5$Me$_4$), 80.56 (CNCMe$_2$CH$_2$O), 67.41 (CNCMe$_2$CH$_2$O), 59.23 (LuCH$_2$Ph), 46.41 (CMe), 27.59 (CNC*Me*$_2$CH$_2$O), 27.22 (CNC*Me*$_2$CH$_2$O), 24.01 (C*Me*), 13.73 (C$_5$*Me*$_4$), 11.52 (C$_5$*Me*$_4$). ^{15}N NMR (benzene-*d$_6$*, 61 MHz): *δ* −135.2. IR (KBr, cm^{-1}): *ν* 3064 m, 3053 m, 3012 m, 2967 s, 2904 s, 2868 s, 2767 w, 2737 w, 1664 s (CN), 1591 s (CN), 1480 s, 1462 s, 1448 s, 1396 m, 1365 m, 1279 m, 1252 m, 1211 s, 1191 s, 1176 s, 1109 m, 1087 s, 1026 m, 957 s, 934 s, 884 m, 867 m, 842 m, 794 s, 755 m, 739 m, 695 m, 679 s, 623 w, 585 w, 538 m, 526 m, 510 m, 477 m, 391 w. Calcd for C$_{35}$H$_{45}$LuN$_2$O$_2$: C, 59.99; H, 6.47; N, 4.00. Found: C, 60.10; H, 6.26; N, 4.02. mp 95−97 °C.

[{Bo^{M}Cp^{tet}}LuNCH$_2$Ph]$_2$ (2a). A yellow solution was obtained from addition of H$_2$NCH$_2$Ph (0.035 mL, 0.323 mmol) to {Bo^{M}Cp^{tet}}Lu(CH$_2$Ph)$_2$ (0.226 g, 0.323 mmol) dissolved in 5 mL of benzene. This solution was stirred at room temperature for 1 h, and then the volatile materials were evaporated under reduced pressure to give [{Bo^{M}Cp^{tet}}LuNCH$_2$Ph]$_2$ as a white solid (0.153 g, 0.246 mmol, 76.2%). Solution-phase characterization is performed on *in situ* generated samples because the precipitated product does not redissolve in benzene or toluene and decomposes in halogenated solvents. ^{1}H NMR (benzene-*d$_6$*, 400 MHz): *δ* 7.52 (d, $^3J_{HH}$ = 7.1 Hz, 2 H, *ortho*-NCH$_2$C$_6$H$_5$), 7.41 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, *meta*-NCH$_2$C$_6$H$_5$), 7.22 (t, $^3J_{HH}$ = 7.1 Hz, 1 H, *para*-C$_6$H$_5$), 5.41 (d, $^2J_{HH}$ = 15.3 Hz, 1 H, LuNC*H*$_2$Ph), 4.87 (d, $^2J_{HH}$ = 15.3 Hz, 1 H, LuNC*H*$_2$Ph), 3.74 (d, $^2J_{HH}$ = 8.3 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 3.64 (d, $^2J_{HH}$ = 8.3 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 2.12 (s, 6 H, C$_5$*Me*$_4$), 2.05 (s, 3 H, CMe), 2.02 (s, 6 H, C$_5$*Me*$_4$), 1.37 (s, 6 H, CNC*Me*$_2$CH$_2$O), 1.32 (s, 6 H, CNC*Me*$_2$CH$_2$O). ^{13}C{^{1}H} NMR (benzene-*d$_6$*, 150 MHz): *δ* 175.42 (CNCMe$_2$CH$_2$O), 152.37 (*ipso*-NCH$_2$C$_6$H$_5$), 128.01 (*meta*-NCH$_2$C$_6$H$_5$), 127.94 (*ortho*-NCH$_2$C$_6$H$_5$), 125.13 (*para*-NCH$_2$C$_6$H$_5$), 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), 67.66 (CNCMe$_2$CH$_2$O), 58.01 (LuCH$_2$C$_6$H$_5$), 46.43 (CMe), 29.17 (CNC*Me*$_2$CH$_2$O), 28.49 (CNC*Me*$_2$CH$_2$O), 24.67 (C*Me*), 13.45 (C$_5$*Me*$_4$), 11.75 (C$_5$*Me*$_4$). ^{15}N NMR (benzene-*d$_6$*, 61 MHz): *δ* −137.5 (s, C*N*CMe$_2$CH$_2$O). IR (KBr, cm^{-1}): *ν* 3090 w, 3073 w, 3021 s, 2968 s, 2906 s, 2867 s, 2743 m, 1657 s (CN), 1618 s (CN), 1463 m, 1363 m, 1308 m, 1284 m, 1250 w, 1190 m, 1172 m, 1087 s, 1069 s, 1023 m, 973 m, 955 m, 936 w, 832 w, 806 w, 746 m, 704 w, 677 w, 612 w, 568 w, 531 w, 483 m. Calcd for C$_{28}$H$_{38}$LuN$_3$O$_2$: C, 53.93; H, 6.14; N, 6.74. Found: C, 53.99; H, 6.23; N, 6.71. mp 150−152 °C (dec).

[{Bo^{M}Cp^{tet}}LuNCH$_2$(1-C$_{10}$H$_7$)]$_2$ (2b). H$_2$NCH$_2$(1-C$_{10}$H$_7$) (0.041 mL, 0.283 mmol) was added to a benzene solution of {Bo^{M}Cp^{tet}}Lu(CH$_2$Ph)$_2$ (0.198 g, 0.283 mmol) to give a yellow solution. This solution was stirred at room temperature for 1 h, and then the volatile materials were removed under reduced pressure to give [{Bo^{M}Cp^{tet}}LuNCH$_2$(1-C$_{10}$H$_7$)]$_2$ as a white solid (0.118 g, 0.176 mmol, 62.1%). ^{1}H NMR (benzene-*d$_6$*, 600 MHz): *δ* 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, 8-C$_{10}$H$_7$), 7.86 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, 4-C$_{10}$H$_7$), 7.75 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, 5-C$_{10}$H$_7$), 7.69 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, 3-C$_{10}$H$_7$), 7.51 (vt, $^3J_{HH}$ = 7.7 Hz, 1 H, 7-C$_{10}$H$_7$), 7.38 (vt, $^3J_{HH}$ = 7.4 Hz, 1 H, 6-C$_{10}$H$_7$), 5.92 (d, $^2J_{HH}$ = 17.5 Hz, 1 H, LuNC*H*$_2$(1-C$_{10}$H$_7$)), 5.53 (d, $^2J_{HH}$ = 17.5 Hz, 1 H, LuNC*H*$_2$(1-C$_{10}$H$_7$)), 3.69 (d, $^2J_{HH}$ = 8.6 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 3.60 (d, $^2J_{HH}$ = 8.6 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 2.07 (s, 6 H, C$_5$*Me*$_4$), 1.99 (s, 3 H, CMe), 1.84 (s, 6 H, C$_5$*Me*$_4$), 1.43 (s, 6 H, CNC*Me*$_2$CH$_2$O), 1.33 (s, 6 H, CNC*Me*$_2$CH$_2$O). ^{13}C{^{1}H} NMR (benzene-*d$_6$*, 150 MHz): *δ* 175.03 (CNCMe$_2$CH$_2$O), 147.04 (*ipso*-C$_{10}$H$_7$CH$_2$NLu), 134.35 (C$_{10}$H$_7$), 132.55 (C$_{10}$H$_7$), 129.51 (C$_{10}$H$_7$), 128.92 (C$_{10}$H$_7$), 126.43 (C$_{10}$H$_7$), 126.04 (C$_{10}$H$_7$), 125.68 (C$_{10}$H$_7$), 125.58 (C$_{10}$H$_7$), 125.36 (C$_{10}$H$_7$), 124.89 (C$_{10}$H$_7$), 115.76 (*C*$_5$Me$_4$), 114.43 (*C*$_5$Me$_4$), 114.15 (*ipso*-C$_5$Me$_4$), 80.38 (CNCMe$_2$CH$_2$O), 67.73 (CNCMe$_2$CH$_2$O), 53.91 (LuNCH$_2$C$_{10}$H$_7$), 46.44 (CMe), 29.15 (CNC*Me*$_2$CH$_2$O), 28.57 (CNC*Me*$_2$CH$_2$O), 24.63 (C*Me*), 13.40 (C$_5$*Me*$_4$), 11.79 (C$_5$*Me*$_4$). ^{15}N NMR (benzene-*d$_6$*, 61 MHz): *δ* −137.4 (s, C*N*CMe$_2$CH$_2$O). IR (KBr, cm^{-1}): *ν* 3060 w, 3036 w, 2965 s, 2926 s, 2899 s, 2866 m, 2724 w, 1655 s (CN), 1612 s (CN), 1509 w, 1460 m, 1365 m, 1307 m, 1281 m, 1192 m, 1175 m, 1107 s, 1026 w, 974 m, 955 m, 935 w, 849 w, 792 s, 773 m, 733 w, 679 s, 639 m, 533 m. Calcd for C$_{32}$H$_{40}$LuN$_3$O$_2$: C, 57.05; H, 5.99; N, 6.24. Found: C, 57.37; H, 5.88; N, 5.96. mp 160−162 °C (dec).

{Bo^{M}Cp^{tet}}Lu(NHCH$_2$Ph)$_2$ (3a). H$_2$NCH$_2$Ph (0.128 mL, 1.18 mmol) was added to a benzene solution of {Bo^{M}Cp^{tet}}Lu(CH$_2$Ph)$_2$ (0.412 g, 0.588 mmol) to give a yellow solution. This solution was stirred at room temperature for 10 min, and then the volatile materials were evaporated to give {Bo^{M}Cp^{tet}}Lu(NHCH$_2$Ph)$_2$ as a pale yellow solid (0.371 g, 0.507 mmol, 86.3%). ^{1}H NMR (benzene-*d$_6$*, 600 MHz): *δ* 7.26 (s, br, 4 H, *ortho*-NHCH$_2$C$_6$H$_5$), 7.21 (t, $^3J_{HH}$ = 7.1 Hz, 4 H, *meta*-NHCH$_2$C$_6$H$_5$), 7.10 (t, $^3J_{HH}$ = 7.1 Hz, 2 H, *para*-NHCH$_2$C$_6$H$_5$), 4.08 (s, br, 4 H, NHC*H*$_2$Ph), 3.70 (d, $^2J_{HH}$ = 8.3 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 3.60 (d, $^2J_{HH}$ = 8.3 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 2.19 (s, 6 H, C$_5$*Me*$_4$), 2.08 (s, 6 H, C$_5$*Me*$_4$), 2.07 (s, 3 H, CMe), 1.24 (s, br, 2 H, N*H*CH$_2$Ph), 1.20 (s, 6 H, CNC*Me*$_2$CH$_2$O), 1.17 (s, 6 H, CNC*Me*$_2$CH$_2$O). ^{13}C{^{1}H} NMR (benzene-*d$_6$*, 150 MHz): *δ* 173.31 (CNCMe$_2$CH$_2$O), 146.96 (*ipso*-NHCH$_2$C$_6$H$_5$), 128.86 (*meta*-NHCH$_2$C$_6$H$_5$), 127.53 (*ortho*-NHCH$_2$C$_6$H$_5$), 126.71 (*para*-NHCH$_2$C$_6$H$_5$), 115.81 (C$_5$Me$_4$), 114.40 (C$_5$Me$_4$), 114.38 (*ipso*-C$_5$Me$_4$), 80.61 (CNCMe$_2$CH$_2$O), 67.54 (CNCMe$_2$CH$_2$O), 50.26 (LuNHCH$_2$C$_6$H$_5$), 46.37 (CMe), 28.32 (CNC*Me*$_2$CH$_2$O), 27.69 (CNC*Me*$_2$CH$_2$O), 24.35 (C*Me*), 13.72 (C$_5$*Me*$_4$), 11.77 (C$_5$*Me*$_4$). ^{15}N NMR (benzene-*d$_6$*, 61 MHz): *δ* −137.4 (s, C*N*CMe$_2$CH$_2$O). IR (KBr, cm^{-1}): *ν* 3273 w, 3059 w, 3023 w, 2964 s, 2925 s, 2867 s, 2772 w, 2728 w, 1659 s (CN), 1612 s (CN), 1493 w, 1451 s, 1366 s, 1308 s, 1278 m, 1250 w, 1190 m, 1082 s, 1026 m, 976 m, 828 w, 732 m, 700 s, 640 m, 611 w, 587 w. Calcd for C$_{35}$H$_{47}$LuN$_4$O$_2$: C, 57.53; H, 6.48; N, 7.67. Found: C, 57.67; H, 6.44; N, 7.58. mp 123−125 °C.

{Bo^{M}Cp^{tet}}Lu{NHCH$_2$(1-C$_{10}$H$_7$)}$_2$ (3b). NH$_2$CH$_2$(1-C$_{10}$H$_7$) (0.088 mL, 0.602 mmol) was added to a benzene solution of {Bo^{M}Cp^{tet}}Lu(CH$_2$Ph)$_2$ (0.211 g, 0.301 mmol) to give a yellow solution. This solution was stirred at room temperature for 10 min, and then the volatile materials were removed under reduced pressure to give {Bo^{M}Cp^{tet}}Lu(NHCH$_2$(1-C$_{10}$H$_7$)$_2$ as a pale yellow solid (0.205 g, 0.247 mmol, 82.1%). ^{1}H NMR (benzene-*d$_6$*, 600 MHz): *δ* 8.14 (br, 2 H, 2-C$_{10}$H$_7$), 7.69 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, 8-C$_{10}$H$_7$), 7.61 (br, 2 H, 4-C$_{10}$H$_7$), 7.56 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, 5-C$_{10}$H$_7$), 7.34 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, 3-C$_{10}$H$_7$), 7.30 (t, $^3J_{HH}$ = 6.6 Hz, 2 H, 7-C$_{10}$H$_7$), 7.28 (t, $^3J_{HH}$ = 6.6 Hz, 2 H, 6-C$_{10}$H$_7$), 4.77 (br, 4 H, NHC*H*$_2$(1-C$_{10}$H$_7$)), 3.68 (d, $^2J_{HH}$ = 8.4 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 3.57 (d, $^2J_{HH}$ = 8.4 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 2.18 (s, 6 H, C$_5$*Me*$_4$), 2.11 (s, 6 H, C$_5$*Me*$_4$), 2.05 (s, 3 H, Me), 1.57 (t, $^3J_{HH}$ = 8.4 Hz, 2 H, N*H*CH$_2$(1-C$_{10}$H$_7$)), 1.17 (s, 6 H, CNC*Me*$_2$CH$_2$O), 1.13 (s, 6 H, CNC*Me*$_2$CH$_2$O). ^{13}C{^{1}H} NMR (benzene-*d$_6$*, 150 MHz): *δ* 173.69 (CNCMe$_2$CH$_2$O), 143.77 (*ipso*-CH$_2$C$_{10}$H$_7$), 134.67 (C$_{10}$H$_7$), 132.37 (C$_{10}$H$_7$), 129.37 (C$_{10}$H$_7$), 128.68 (C$_{10}$H$_7$), 127.16 (C$_{10}$H$_7$), 126.30 (C$_{10}$H$_7$), 126.18 (C$_{10}$H$_7$), 125.89 (C$_{10}$H$_7$), 124.24 (C$_{10}$H$_7$), 124.07 (C$_{10}$H$_7$), 116.24 (*C*$_5$Me$_4$), 114.71 (*C*$_5$Me$_4$), 114.30 (*ipso*-C$_5$Me$_4$), 80.58 (CNCMe$_2$CH$_2$O), 67.47 (CNCMe$_2$CH$_2$O), 48.85 (LuNHCH$_2$C$_{10}$H$_7$), 46.43 (CMe), 28.30

DOI: 10.1021/acs.inorgchem.5b00927
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$(CNC\mathit{Me}_2CH_2O)$, 27.70 $(CNC\mathit{Me}_2CH_2O)$, 24.34 $(C\mathit{Me})$, 13.67 $(C_5\mathit{Me}_4)$, 11.73 $(C_5\mathit{Me}_4)$. ^{15}N NMR (benzene-d_6, 61 MHz): δ −135.6 (s, $CNCMe_2CH_2O$). IR (KBr, cm^{-1}): ν 3342 w, 3272 w, 3052 m, 2963 s, 2926 s, 2866 s, 2762 w, 2729 w, 1657 s (CN), 1629 s (CN), 1597 m, 1510 m, 1365 s, 1307 m, 1282 m, 1262 m, 1193 m, 1166 m, 1090 s, 1025 m, 973 m, 850 w, 792 s, 772 s, 733 w, 657 w, 532 m. Calcd for $C_{43}H_{51}LuN_4O_2$: C, 62.16; H, 6.19; N, 6.74. Found: C, 62.18; H, 6.20; N, 6.24. mp 86−87 °C.

$\{Bo^MCp^{tet}\}Lu\{NHB(C_6F_5)_2\}C_6F_5$ (4). Toluene (1 mL) was added to a mixture of $\{Bo^MCp^{tet}\}Lu(CH_2Ph)_2$ (0.107 g, 0.153 mmol) and $H_3NB(C_6F_5)_3$ (0.081 g, 0.153 mmol) at room temperature. This solution was stirred at room temperature for 3 h, and then the reaction mixture was cooled to −30 °C. After several days, a yellow solution was decanted from colorless crystals. The crystals were washed with pentane (3 × 5 mL), and the solvent was evaporated under reduced pressure to afford a white solid (0.135 g, 0.125 mmol, 81.7%). ^{1}H NMR (benzene-d_6, 400 MHz): δ 5.54 (s br, 1 H, LuNH), 3.29 (q, $^2J_{HH}$ = 8.0 Hz, 4 H, $CNCMe_2\mathit{CH}_2O$), 2.23 (s, 6 H, $C_5\mathit{Me}_4$), 1.77 (s, 6 H, $C_5\mathit{Me}_4$), 1.55 (s, 3 H, CMe), 0.74 (s, 6 H, $CNC\mathit{Me}_2CH_2O$), 0.69 (s br, 6 H, $CNC\mathit{Me}_2CH_2O$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 150 MHz): δ 177.15 $(CNCMe_2CH_2O)$, 149.85 (br C_6F_5), 148.47 (br C_6F_5), 147.03 (br C_6F_5), 138.72 (br C_6F_5), 137.12 (br C_6F_5), 121.72 (C_5Me_4), 121.30 (C_5Me_4), 118.32 (*ipso*-C_5Me_4), 82.31 $(CNCMe_2CH_2O)$, 68.27 $(CNCMe_2CH_2O)$, 46.71 (CMe), 28.18 $(CNC\mathit{Me}_2CH_2O)$, 26.38 $(CNC\mathit{Me}_2CH_2O)$, 20.26 $(C\mathit{Me})$, 15.15 $(C_5\mathit{Me}_4)$, 11.26 $(C_5\mathit{Me}_4)$. ^{15}N NMR (benzene-d_6, 61 MHz): δ −148.9 (s, $CNCMe_2CH_2O$), −181.8 (s, Lu-NH). ^{11}B NMR (benzene-d_6, 192 MHz): δ 35.5 (s br). ^{19}F (benzene-d_6, 545 MHz): δ −118.24 (br, 2 F), −133.94 (d br, 3JFF = 25 Hz, 3 F), −133.32 (d br, 3JFF = 25 Hz, 3 F), −139.11 (q, 3JFF = 21.8 Hz, 1 F), −154.07 (t, 3JFF = 19.6 Hz, 1 F), −155.09 (t, 3JFF = 19.6 Hz, 1 F), −155.69 (t, 3JFF = 19.6 Hz, 1 F), −156.15 (t, 3JFF = 19.6 Hz, 1 F), −159.45 (m, 3JFF = 19.6 Hz, 2 F), −162.34 (td, 3JFF = 21.3, 7.6 Hz, 1 F), −162.76 (qd, 3JFF = 21.3, 7.6 Hz, 4 F).. IR (KBr, cm^{-1}): ν 3435 w br, 2925 s, 2856 m, 1644 m (CN), 1515 m, 1477 s, 1429 m, 1416 m, 1366 m, 1310 m, 1298 m, 1252 w, 1215 w, 1180 m, 1095 s, 1035 m, 976 s, 944 m, 922 m, 847 w, 678 w, 620 w, 577 w. Calcd for $C_{39}H_{32}BF_{15}LuN_3O_2$: C, 44.81; H, 3.09; N, 4.02. Found: C, 45.14; H, 3.02; N, 4.21. mp 112−115 °C.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic information files for compounds $\{Bo^MCp^{tet}\}$-$Lu(CH_2Ph)_2$ (**1**), $[\{Bo^MCp^{tet}\}LuNCH_2(1\text{-}C_{10}H_7)]_2$ (**2b**), and $\{Bo^MCp^{tet}\}Lu\{NHB(C_6F_5)_2\}C_6F_5$ (**4**) and spectra of new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00927.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully thank the National Science Foundation (CHE-0955635) for financial support. $Bo^MCp^{tet}H$ was first prepared by M.H. and B.J.; M.H. was supported by the Office of Workforce Development for Teachers and Scientists through the Summer Undergraduate Laboratory Internship Program through the Ames Laboratory. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358. B.J. was supported by a grant from the Iowa Energy Center.

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