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Synthesis, Structural Characterization, and Reactivity of Mono(amidinate) Rare-Earth-Metal Bis(aminobenzyl) Complexes

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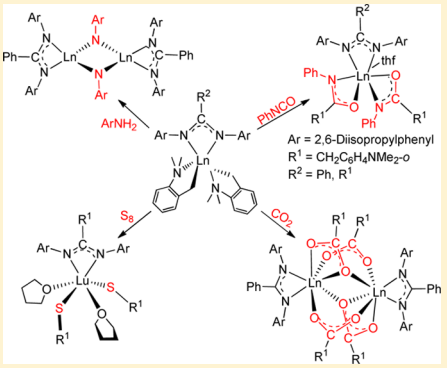
Supporting Information

ABSTRACT: Three kinds of solvated lithium amidinates with different coordination models were obtained via recrystallization of [PhC(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]Li(THF) (**1a**) in different solvents. Treatment of *o*-Me$_2$NC$_6$H$_4$CH$_2$Li with LLnCl$_2$(THF)$_n$ (**2**; L = [PhC(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]$^-$ (NCN^{dipp}), [*o*-Me$_2$NC$_6$H$_4$CH$_2$C(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]$^-$ (NCN$^{dipp'}$)) formed in situ from reaction of LnCl$_3$(THF)$_x$ with LLi(THF) gave the rare-earth-metal bis(aminobenzyl) complexes LLn(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$ (L = NCN^{dipp}, Ln = Sc (**3a**), Y (**3b**), Lu (**3c**); L = NCN$^{dipp'}$, Ln = Sc (**3d**), Lu (**3e**)) in high yields. Reactions of complexes **3** with CO$_2$, PhNCO, 2,6-diisopropylaniline, and S have been explored. CO$_2$ inserted into each Ln−C bond of complexes **3a**−**c** to form the dual-core complexes [(NCN^{dipp})Sc(μ-η^1:η^1-O$_2$CCH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$]$_2$ (**4a**) and [(NCN^{dipp})Ln(μ-η^1:η^2-O$_2$CCH$_2$C$_6$H$_4$NMe$_2$-*o*)(μ-η^1:η^1-O$_2$CCH$_2$C$_6$H$_4$NMe$_2$-*o*)]$_2$ (Ln = Y (**4b**), Lu (**4c**)). The reaction of **3b**,**c**,**e** with PhNCO produced LLu[OC(CH$_2$C$_6$H$_4$NMe$_2$-*o*)NPh]$_2$(thf) (L = NCN^{dipp}, Ln = Y (**5b**), Lu (**5c**); L = NCN$^{dipp'}$, Ln = Lu (**5e**)). Protonolysis of **3a**,**b** by 2,6-diisopropylaniline formed straightforwardly the μ_2-imido complexes [(NCN^{dipp})Ln(μ-NC$_6$H$_4$^{i}Pr$_2$-2,6)]$_2$ (Ln = Sc (**6a**), Lu (**6c**)). Reaction of **3e** with S$_8$ afforded the sulfur insertion products (NCN$^{dipp'}$)Lu(CH$_2$C$_6$H$_4$NMe$_2$-*o*)(SCH$_2$C$_6$H$_4$NMe$_2$-*o*)(thf) (**7e**) and (NCN$^{dipp'}$)Lu(SCH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$(thf)$_2$ (**7f**) in high yields, respectively, depending on the stoichiometric ratio. All of these complexes were fully characterized by elemental analysis, NMR spectroscopy, and X-ray structural determinations.



INTRODUCTION

Rare-earth-metal dialkyl complexes have attracted considerable attention, due to their great potential as catalysts in olefin transformations such as hydrosilylation,[1] hydroamination,[2] and polymerization.[3] In general, rare-earth-metal dialkyl complexes have been synthesized by the reaction of the corresponding tris(alkyl) complexes with neutral ligands. The use of classic salt metathesis protocols for the synthesis of such complexes remains a significant challenge due to the intrinsic tendency toward the formation of ate complexes and facile ligand redistribution.[4] One way to avoid these difficulties is the introduction of a chelating substituent on the alkyl or a bulky coligand capable of stabilizing these complexes by the steric saturation of the coordination sphere around the metal ions. So far, rare-earth-metal alkyl species have been overwhelmingly stabilized by the cyclopentadienyl group and its derivatives as the ancillary ligands.[3a,5] Thus, significant efforts have focused on development of coligands as alternatives to cyclopentadienyl ligands and new functionalized alkyls. Among them, the non-Cp ligands with N, O, and P heteroatoms such as amidinate ligands have received particular attention because of their strong metal−ligand bonds and exceptional and tunable steric and electronic features, and a broad new chemistry is developing with these ligands.[4,6,7] Recent pioneering works reported by Hessen and Hou showed that neutral mono(amidinate) rare-earth-metal bis(alkyl)/bis(aminobenzyl) complexes are excellent precatalysts for the polymerization of olefins.[8] However, the reaction chemistry of rare-earth-metal dibenzyl complexes possessing these ligands toward some small molecules is still relatively undeveloped.[7e,9]

On the other hand, *o*-aminobenzyl is among the most important alkyl ligands and is widely used to improve stability and/or create new reactions of transition-metal complexes.[10,11] Recently, rare-earth-metal complexes bearing *o*-aminobenzyl ligands have proven to be attractive precursors for the preparation of other organolanthanide derivatives.[7e,12] In order to better understand the nature of the structures and reactivities of this class of complexes and expand their synthetic utility in organolanthanide chemistry, the direct synthesis of *o*-aminobenzyl rare-earth-metal complexes from rare-earth-metal trichloride, with the possibility of varying the ancillary ligands, should be very helpful.

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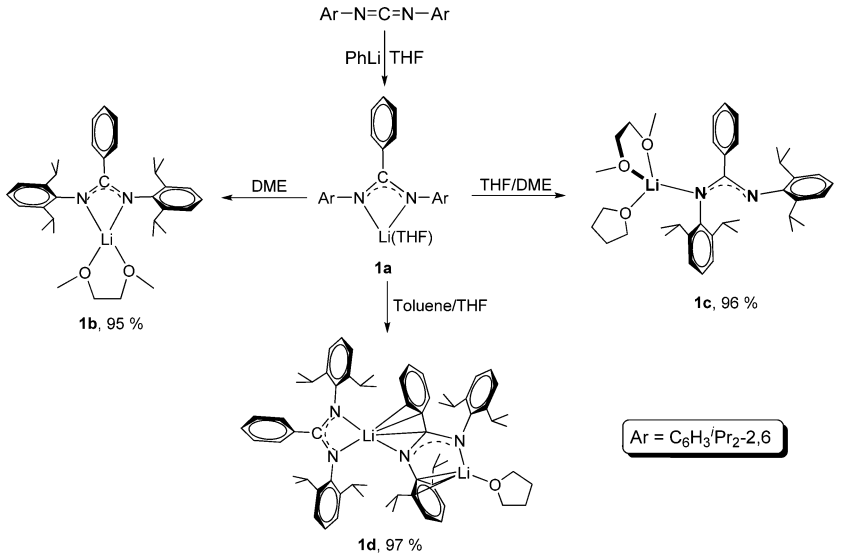
Scheme 1. Syntheses of Lithium Amidinates and Solvent Effects



RESULTS AND DISCUSSION

In this paper, we describe a "one pot" synthesis of rare-earth-metal bis(aminobenzyl) complexes bearing a bulky benzamidinate ligand from the sequential reaction of anhydrous $LnCl_3$ with lithium amidinate and 2 equiv of (aminobenzyl)lithium and their reaction behavior toward some small molecules such as carbon dioxide, isocyanate, amine, and sulfur. In addition, during the syntheses of lithium amidinate intermediates, three different bonding modes of *C*-phenyl-substituted amidinate to the lithium ion are observed.

Syntheses and Characterization of Lithium Amidinates. The reaction of $C(NC_6H_4{}^iPr_2\text{-}2,6)_2$ with 1 equiv of PhLi in THF at room temperature afforded the corresponding lithium amidinate $[PhC(NC_6H_4{}^iPr_2\text{-}2,6)_2)]Li(THF)$ (**1a**) quantitatively (Scheme 1). **1a** could be transformed into three new solvated complexes depending on the crystallization conditions. Recrystallization of **1a** in DME allowed the isolation of the adduct $[PhC(NC_6H_4{}^iPr_2\text{-}2,6)_2]Li(DME)$ (**1b**), while recrystallization of **1a** in mixed DME/THF gave $[PhC(NC_6H_4{}^iPr_2\text{-}2,6)_2]Li(DME)(THF)$ (**1c**).

Furthermore, recrystallization of **1a** in toluene formed $[PhC(NC_6H_4{}^iPr_2\text{-}2,6)_2]Li[\mu\text{-}\eta^4\text{:}\eta^4\text{-}PhC(NC_6H_4{}^iPr_2\text{-}2,6)_2]Li(THF)$ (**1d**).

Compounds **1a**−**d** were well characterized by NMR spectra. The signals of isopropyl groups in **1a** appeared at δ 3.58 (CH), 1.08 (Me), and 0.73 ppm (Me). The NMR spectra of **1b** showed that replacement of coordinated THF by DME led to the migration of isopropyl absorptions from high to low magnetic field at 3.75 (CH), 1.29 (Me), and 1.15 ppm (Me). It was unexpected that the two 2,6-diisopropylphenyl groups of **1c** would be equivalent, and absorptions appeared at 3.74 (CH), 1.28 (Me), and 1.13 ppm (Me) attributable to isopropyl, indicating that there may be a fast exchange between bonding N and nonbonding N. In the ^{1}H NMR spectrum of **1d**, the CH proton on the coordinated aryl ring appears as a multiplet at 3.23 ppm, while the corresponding resonance of the free aryl groups exists at 3.72 ppm as a multiplet peak.

The structures of complexes **1b**−**d** have been further confirmed by X-ray single-crystal diffraction analysis, wherein three different bonding modes of $PhC(NC_6H_4iPr_2\text{-}2,6)_2$ anion to Li^+ ion are observed (Figures 1 and 2). In **1b** the amidinate

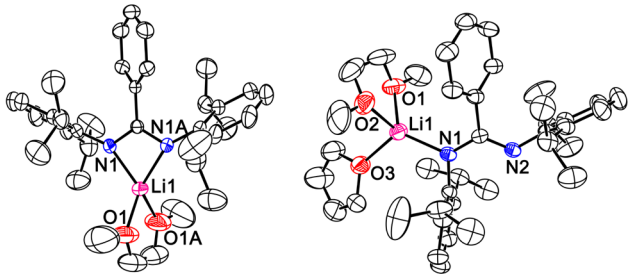


Figure 1. Molecular structure of complexes **1b** (left) and **1c** (right) with thermal ellipsoids at 30% probability. All of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows. **1b**: Li1−N1 1.98(1), Li1−O1 1.96(1); N1−Li1−N1A 68.9(3), N1−Li1−O1 123.1(2), N1−Li1−O1A 135.8(2), O1−Li1−O1A 80.2(5). **1c**: Li1−N1 2.00(1), Li1−O1 2.01(1), Li1−O2 2.00(1), Li1−O3 2.03(1); N1−Li1−O1 120.8(3), N1−Li1−O2 128.4(3), N1−Li1−O3 116.6(2), O1−Li1−O2 82.2(2).

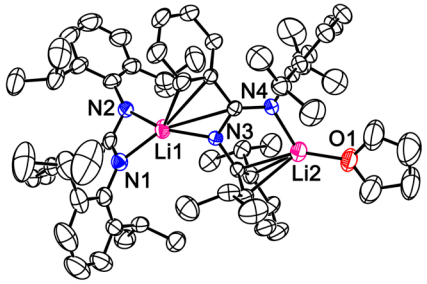


Figure 2. Molecular structure of complex **1d** with thermal ellipsoids at 30% probability. All of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Li1−N1 2.01(1), Li1−N2 2.05(1), Li1−N3 2.00(1), Li2−N4 1.94(1), Li2−O1 1.84(1); N1−Li1−N2 68.0(2), O1−Li2−N4 127.7(4).

is normally η^2-bonded to the metal through two N atoms. Surprisingly, the amidinate anion in **1c** coordinates to the lithium ion in a η^1 fashion, although the negative charge is delocalized to form two equivalent C−N bonds. The mismatch between negative charge distribution and bonding mode of the amidinate ligand is somewhat puzzling; a possible explanation would be a rapid intra- or intermolecular transmetalation

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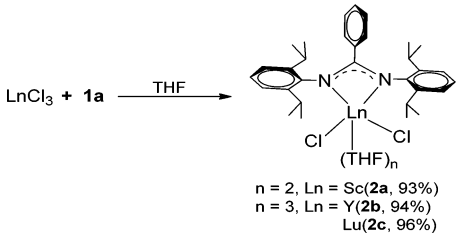
leading to the bonding equilibrium between two N atoms. As shown in Figure 2, **1d** is a THF-solvated dinuclear structure, in which one bidentate polyarylated amidinate ligand chelates one metal, while another acts as both a bridging and side-on chelating group to connect two metals in an unprecedented μ-η^4:η^4 bonding mode. The two Li atoms are located in two different coordinate environments. Li1 is coordinated by one chelating η^2-N,N unit and one η^4-azadiene from another amidinate to form a distorted-tetragonal-bipyramidal geometry, while Li2 is coordinated by one N atom, one η^3-aryl group, and one THF oxygen atom to form a distorted-tetrahedral geometry. The bond parameters indicate that the π electrons of C═N double bonds are delocalized over the amidinate skeleton. This type of bonding mode of C-aryl of amidinate to the metal center observed is a rare example, although amidinate complexes have been studied extensively.[7a,8b,13] The results indicate that the bonding mode of $PhC(NC_6H_4{}^iPr_2\text{-}2,6)_2$ to metal in the lithium series varies as a function of the coligand, which represents a good example that the change of the bonding mode of aryl-substituted amidinate to metal from monodentate, through bidentate, to multidentate can be finely tuned simply by changing the nature of the coordinating solvent.

Synthesis and Characterization of Mono(amidinate) Rare-Earth-Metal Dichloride Complexes. The reactions of $LnCl_3$ with **1** in THF afforded neutral amidinate rare-earth-metal dichlorides $(NCN^{dipp})LnCl_2(THF)_n$ (n = 2, Ln = Sc (**2a**, 93%); n = 3, Ln = Y (**2b**, 94%), Lu (**2c**, 96%)) in excellent yields (Scheme 2).

Scheme 2. Syntheses of Monoamidinate Rare-Earth-Metal Dichloride Complexes

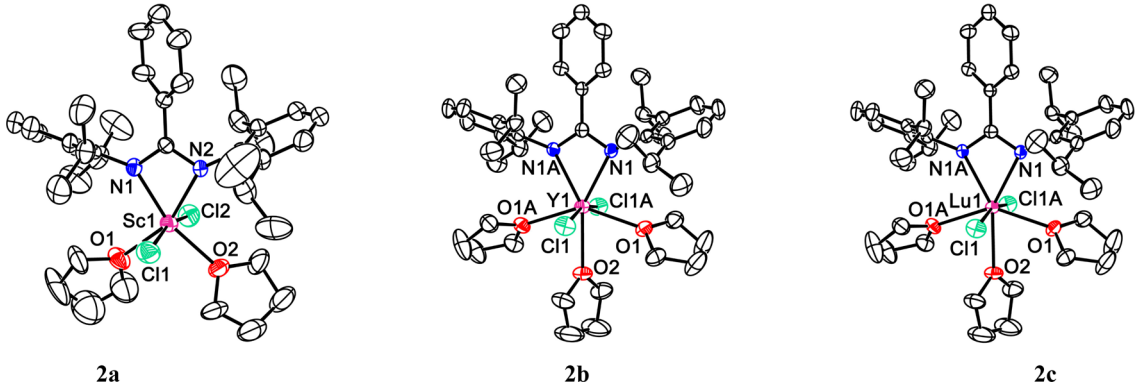


To avoid the formation of ligand distribution or salt-type byproducts, the dilute THF solution of **1a** generated in situ was dropped into the THF slush of $LnCl_3$ slowly. Then THF solvent was removed, the residue was extracted with toluene (3 × 20 mL), the extract was concentrated to about 5 mL, and recrystallization was carried out to give pale yellow crystals.

All complexes have been characterized by NMR spectroscopy, elemental analysis, and X-ray structural analysis. The results indicate that all three complexes are solvated monomeric structures. In contrast, the rare-earth dichloride complexes bearing Cp or substituted Cp ligands were obtained as dimers with two Cl bridges in many cases.[14] The Y−Cl bond (2.579 Å) is significantly shorter than Y−(μ-Cl) (2.614−2.776 Å),[15] but it is consistent with a bond found from yttrium to a terminal chlorine atom (2.58 Å).[16] The number of coordinated THF molecules in the solid-state structure of these complexes increases with an increase of the metal ionic radius (Figure 3). However, attempts to synthesize the analogues of the larger rare earth metals such as La, Nd, and Sm were unsuccessful; only oily complex products were obtained.

Synthesis and Characterization of Mono(amidinate) Rare-Earth-Metal Bis(aminobenzyl) Complexes. Reactions of o-$Me_2NC_6H_4CH_2Li$ with the in situ generated $LLnCl_2(THF)_n$ at room temperature yielded the corresponding bis(o-aminobenzyl) complexes $LLn(CH_2C_6H_4NMe_2\text{-}o)_2$ (L = NCN^{dipp}, Ln = Sc (**3a**, 92%), Y (**3b**, 88%), Lu (**3c**, 90%); L = $NCN^{dipp\prime}$, Ln = Sc (**3d**, 84%), Lu (**3e**, 92%)) (Scheme 3 and Figure 4). However, treatment of **1a** with $SmCl_3$ (or $GdCl_3$) followed by reaction with $Me_2NC_6H_4CH_2Li$ under the same conditions gave an oily mixture.

Complexes **3** are stable under an N_2 atmosphere even at 80 °C. They are sparingly soluble in hexane but readily dissolve in THF and aromatic solvents. It is noteworthy that the ^1H NMR spectrum of **3a** shows broad signals in the ranges 4.56−3.16 and 1.80−0 ppm for the isopropyl group at ambient temperature. However, the signal at 3.87 ppm attributable to the methine proton becomes sharp when the measurement temperature is increased to 70 °C, and the corresponding methyl protons split into two groups of doublet signals at 1.36 and 0.94 ppm, respectively. Resonances for the alkyls of the aminobenzyl groups appear at 2.44 (−NMe_2) and 1.90 ppm



2a **2b** **2c**

Figure 3. Molecular structure of complexes **2** with thermal ellipsoids at 30% probability. All of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows. Sc (**2a**): Sc(1)−N(1) 2.171(3), Sc(1)−N(2) 2.172(3), Sc(1)−O(1) 2.193(3), Sc(1)−O(2) 2.193(3), Sc(1)−Cl(1) 2.430(2), Sc(1)−Cl(2) 2.427(2); N(1)−Sc(1)−N(2) 61.9(1), Cl(1)−Sc(1)−Cl(2) 164.5(1), O(1)−Sc(1)−O(2) 103.7(1). Y (**2b**): Y(1)−N(1) 2.384(3), Y(1)−O(1) 2.439(3), Y(1)−O(2) 2.506(3), Y(1)−Cl(1) 2.579(1); N(1)−Y(1)−N(1A) 55.4(1), Cl(1)−Y(1)−Cl(1A) 164.8(1), O(1)−Y(1)−O(1A) 143.7(1), O(1)−Y(1)−O(2) 71.8(1). Lu (**2c**): Lu(1)−N(1) 2.345(3), Lu(1)−O(1) 2.398(3), Lu(1)−O(2) 2.474(4), Lu(1)−Cl(1) 2.525(1); N(1)−Lu(1)−N(1A) 56.5(2), Cl(1)−Lu(1)−Cl(1A) 165.2(1), O(1)−Lu(1)−O(1A) 143.7(1), O(1)−Lu(1)−O(2) 71.8(1).

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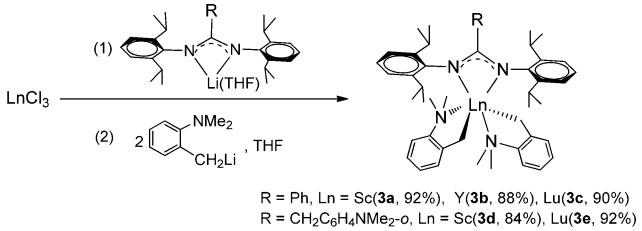
Scheme 3. Syntheses of Mono(amidinate) Rare-Earth-Metal Bis(aminobenzyl) Complexes



R = Ph, Ln = Sc(**3a**, 92%), Y(**3b**, 88%), Lu(**3c**, 90%)
R = $CH_2C_6H_4NMe_2$-*o*, Ln = Sc(**3d**, 84%), Lu(**3e**, 92%)

(CH_2). Complexes **3b,c** give well-resolved NMR spectra in C_6D_6 at ambient temperature. Methine and methyl protons of the isopropyl group split into two sets of broad signals and three groups of broad signals, indicating a loss of symmetry in these two complexes. Methine protons exhibit a multiplet signal at 3.81 ppm for complex **3d** and 3.73 ppm for complex **3e**. Methyl protons of isopropyl groups show two groups of doublets at 1.38 and 1.25 ppm for **3d** and 1.36 and 1.26 ppm for **3e**. The two $CH_2C_6H_4NMe_2$-*o* groups exhibit one NMe_2 signal and one CH_2 signal at δ 2.39 and 2.02 ppm for **3d** and at 2.37 and 1.83 ppm for **3e**, respectively.

The structures of complexes **3** were determined by single-crystal X-ray structural analysis. The rare-earth-metal ion in each of complexes **3** is six-coordinated by two nitrogen atoms from the amidinate ligand, two carbon atoms, and two amino nitrogen atoms, forming a distorted-octahedral geometry. Selected bond distances and angles are summarized in Table 1. The average distance of Ln−N_{alkyl} bonds in complex **3c** (2.538(6) Å) is in the normal range of Ln−N donating bonds.[17] It is noteworthy that two Ln−C bonds are almost the same in complex **3a**; however, in complex **3c** there is a difference of 0.037 Å since the greater size of Lu allows one of the phenyl rings of the aminobenzyl moieties to approach more closely to the metal ion center. This feature was also observed in complex **3b**.[8e]

Reactions of Bis(aminobenzyl) Complexes with CO_2. To explore the reactivity of these dialkyl complexes, the reactions of complexes **3a−c** with CO_2 were carried out. Introduction of CO_2 into a toluene solution of **3a−c** led to a color change from yellow to colorless immediately, forming the expected Ln−C bond insertion products $[(NCN^{dipp})Sc(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CCH_2C_6H_4NMe_2\text{-}o)_2]_2$ (**4a**) and $[(NCN^{dipp})Ln(\mu\text{-}\eta^1{:}\eta^2\text{-}O_2CCH_2C_6H_4NMe_2\text{-}o)(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CCH_2C_6H_4NMe_2\text{-}o)]_2$ (Ln = Y (**4b**), Lu (**4c**)) (Scheme 4). The X-ray crystallographic studies indicate that **4b,c** are isostructural (Figure 5, right).[18] It is interesting that the coordination modes of carboxyl groups in complexes **4** depend on the size of the metals. In **4a** all of the newly formed carboxyl ligands bridge two $(NCN^{dipp})Ln$ fragments through an $\mu\text{-}\eta^1{:}\eta^1$ bonding mode (Figure 5, left), while in **4b,c** the carboxyl bridges bear two different bonding modes: $\mu\text{-}\eta^1{:}\eta^1$ and $\mu\text{-}\eta^1{:}\eta^2$. The C−O bond distances in **4c**, ranging from 1.228(6) to 1.280(6) Å, are between the typical values for a C−O single bond and a C=O double bond, indicating that the negative charge is delocalized on the O=C=O unit.[19] The Lu−O bond distances are in the previously reported range of 2.210(9)−2.566(2) Å.[20]

Table 1. Selected Bond Lengths and Angles for 3a,c−e

	3a (Sc)	**3c** (Lu)	**3d** (Sc)	**3e** (Lu)
	Bond Lengths (Å)			
Ln−C1	2.287(3)	2.415(7)	2.287(6)	2.414(5)
Ln−C10	2.282(3)	2.378(7)	2.275(6)	2.413(6)
Ln−N1	2.227(2)	2.346(5)	2.198(5)	2.308(4)
Ln−N2	2.207(3)	2.352(5)	2.209(5)	2.344(5)
Ln−N3	2.483(3)	2.548(6)	2.432(6)	2.502(6)
Ln−N4	2.492(3)	2.527(6)	2.521(6)	2.581(4)
	Bond Angles (deg)			
C1−Ln−C10	153.3(1)	129.5(3)	156.4(2)	154.3(2)
N1−Ln−N2	60.4(1)	57.8(2)	61.2(2)	57.9(1)
N3−Ln−N4	103.5(1)	122.9(2)	96.4(2)	98.5(2)
C1−Ln−N3	70.4(1)	67.6(2)	72.4(2)	70.1(2)
C10−Ln−N4	70.7(1)	68.4(3)	69.4(2)	67.9(2)

Reactions of Bis(aminobenzyl) Complexes with PhNCO. To get more information about the reactivities of these dialkyl complexes, the reactions of complexes **3b,c** with PhNCO were examined as well. Treatment of **3b,c** with 2 equiv of PhNCO in THF at −15 °C gave the insertion products $(NCN^{dipp})Ln[OC(CH_2C_6H_4NMe_2\text{-}o)NPh]_2(THF)$ (Ln = Y (**5b**), Lu (**5c**)) in moderate yields (Scheme 5). Notably, when the reaction was carried out at room temperature, the cyclotrimerization byproduct $(PhNCO)_3$ was obtained. In the ^{1}H NMR spectrum, signals for the methylene of aminobenzyl groups partially overlap with the methine of the isopropyl group at around 3.85 (**5b**) and 3.84 (**5c**) ppm, but signals for *N*-methyls clearly appeared at 2.45 (**5b**) and 2.46 (**5c**) ppm.

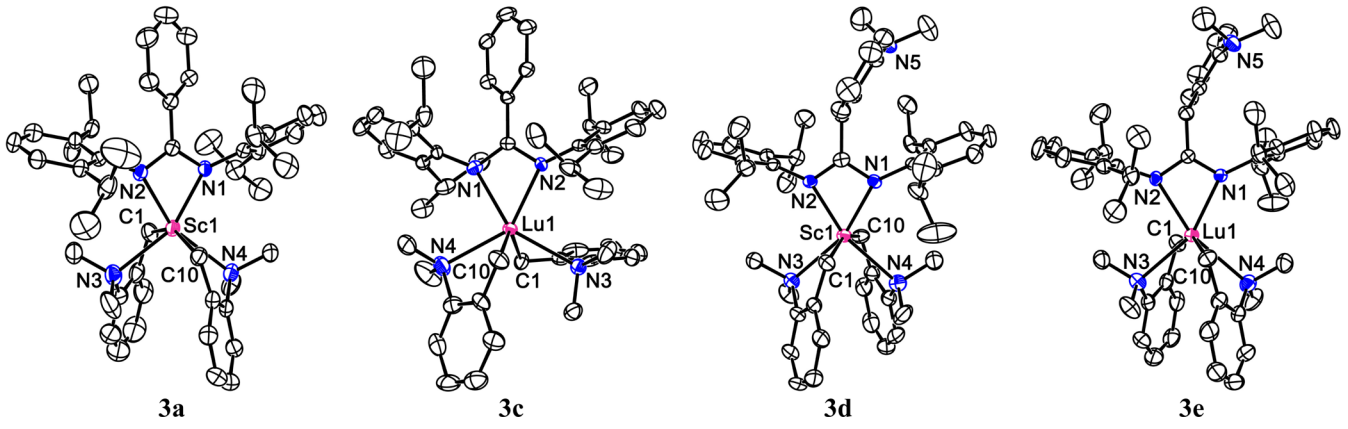


Figure 4. Molecular structure of complexes **3** (R = Ph, Ln = Sc (**3a**), Lu (**3c**); R = $CH_2C_6H_4NMe_2$-*o*, Ln = Sc (**3d**), Lu (**3e**)) with thermal ellipsoids at 30% probability. All of the hydrogen atoms are omitted for clarity.

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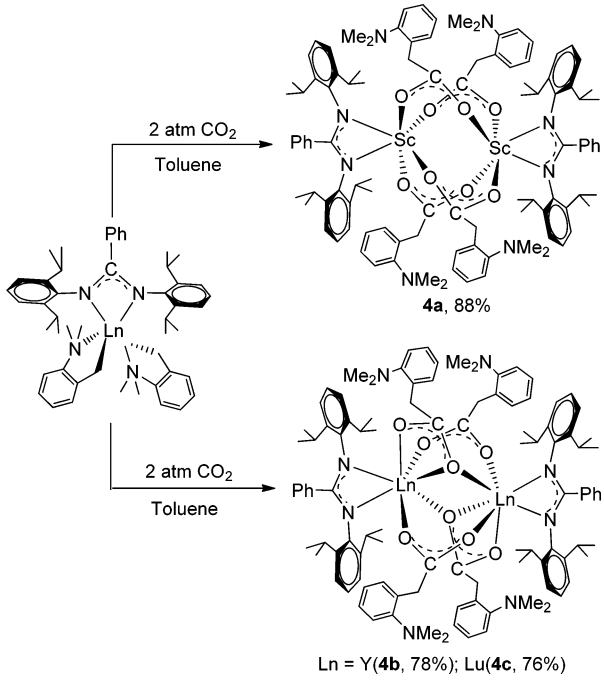
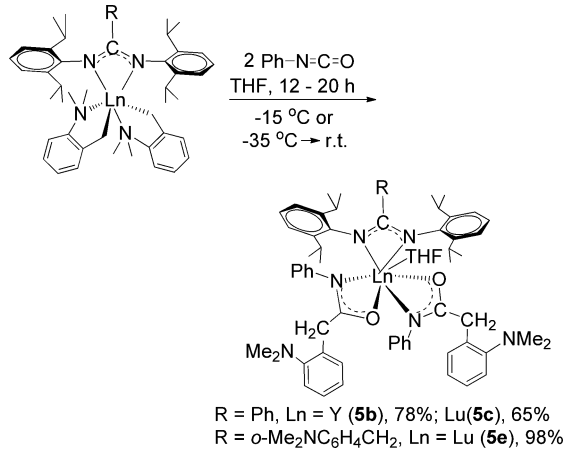
Scheme 4. Reactions of Rare-Earth-Metal Bis(aminobenzyl) Complexes with CO_2



Scheme 5. Reactions of 3 with PhNCO



Complexes **5b,c** are mononuclear (Figure 6). The metal ion is coordinated by one THF molecule, one η^2-amidinate ligand, and two η^2-amido ligands. The average Lu–$N_{amidinate}$ bond distance of 2.318(5) Å is in the normal bonding range. The average Lu–O and Lu–N bond lengths involving the amido moiety are 2.262(4) and 2.370(5) Å, respectively (Table 2). Taking account of the difference between metal ionic radii, they compare well with the corresponding values in $(C_5H_4Me)_2$Ho-[OC(ⁿBu)NPh].[21]

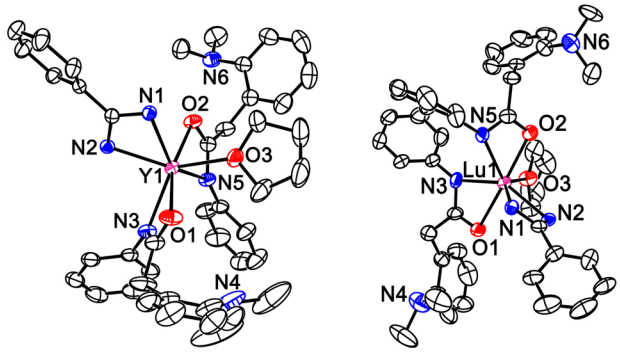


Figure 6. Molecular structures of complexes **5b** (left) and **5c** (right) with thermal ellipsoids at 30% probability. 2,6-Diisopropylphenyls of amidinate ligands and all of the hydrogen atoms are omitted for clarity.

In contrast to the case for **3c**, only the insertion product $(NCN^{dipp\prime})$Lu[OC($CH_2C_6H_4NMe_2$-*o*)NPh]$_2$(THF) (**5e**) was

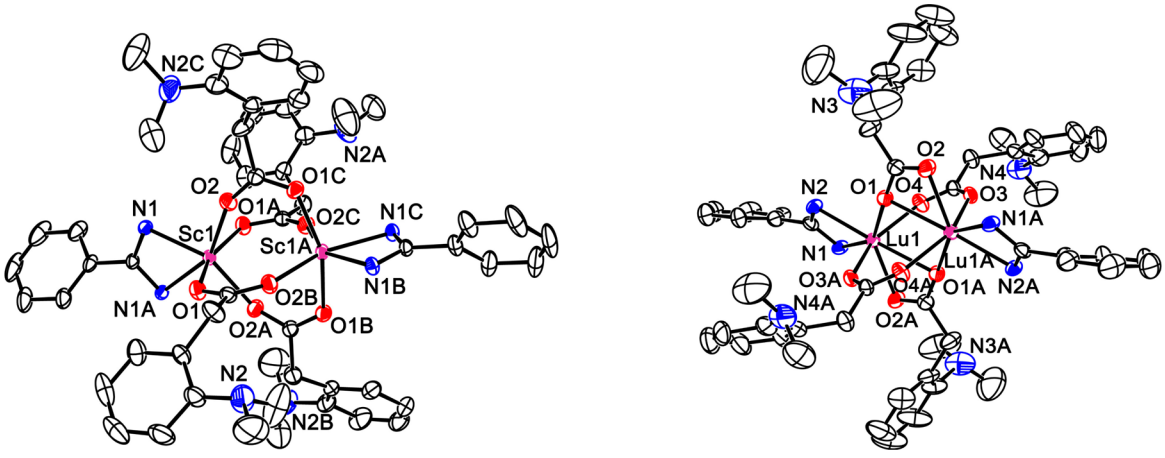


Figure 5. Molecular structures of complexes **4a** (left) and **4c** (right) with thermal ellipsoids at 30% probability. 2,6-Diisopropylphenyls of amidinate ligands and all of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows. **4a** (Sc): Sc(1)–O(1) 2.097(2), Sc(1)–O(2) 2.123(2), Sc(1)–N(1) 2.195(2), C(18)–O(1) 1.260(3), C(18A)–O(2) 1.256(3); N(1)–Sc(1)–N(1A) 60.7(1), O(1A)–Sc(1)–O(1) 158.0(1), O(1A)–Sc(1)–O(2) 85.0(1), O(1)–Sc(1)–O(2) 83.8(1), O(1A)–Sc(1)–O(2A) 83.8(1), O(1)–Sc(1)–O(2A) 85.0(1), O(2)–Sc(1)–O(2A) 118.1(1), O(1)–C(18)–O(2A) 123.5(2). **4c** (Lu): Lu(1)–O(1) 2.498(4), Lu(1)–O(1A) 2.231(4), Lu(1)–O(2) 2.288(4), Lu(1)–O(3) 2.249(4), Lu(1)–O(4A) 2.196(4), Lu(1A)–O(1) 2.231(4), Lu(1A)–O(4) 2.196(4), Lu(1)–N(1) 2.280(4), Lu(1)–N(2) 2.307(4), C(32)–O(1) 1.274(6), C(32)–O(2) 1.228(6), C(42)–O(3) 1.244(6), C(42)–O(4) 1.280(6); O(1)–Lu(1)–O(1A) 83.0(1), O(1)–Lu(1)–O(2) 54.2(1), O(1)–Lu(1)–O(3) 75.6(1), O(1)–Lu(1)–O(4A) 77.4(1), O(2)–Lu(1)–O(3) 80.7(1), O(1A)–Lu(1)–O(2) 136.0(1), O(2)–Lu(1)–O(4A) 99.7(2), O(1A)-Lu(1)–O(3) 79.1(1), O(3)–Lu(1)–O(4A) 146.1(1), O(1A)–Lu(1)–O(4A) 77.5 (1), N(1)–Lu(1)–N(2) 57.6(2), O(1)–C(32)–O(2) 122.1(6), O(3)–C(42)–O(4) 126.4(5).

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Table 2. Selected Bond Lengths and Angles for 5b,c,e

	5b	5c	5e
	Bond Lengths (Å)		
Ln−O1	2.289(2)	2.296(4)	2.287(6)
Ln−O2	2.330(2)	2.229(4)	2.264(6)
Ln−O3	2.367(2)	2.345(4)	2.368(9)
Ln−N1	2.404(2)	2.288(5)	2.355(6)
Ln−N2	2.338(2)	2.348(5)	2.350(7)
Ln−N3/N4	2.413(2)	2.391(6)	2.369(9)
Ln−N5/N6	2.418(2)	2.350(5)	2.375(9)
	Bond Angles (deg)		
N1−Ln−N2	55.8(1)	58.0(2)	56.4(5)
O1−Ln−N3/N4	56.2(1)	57.6(2)	55.5(4)
O2−Ln−N5/N6	55.2(1)	57.5(2)	57.2(5)
O1−C32−N3	118.3(3)	118.7(7)	
O2−C48−N5	116.3(2)	115.5(6)	
O1−C35−N4			114.6(10)
O2−C51−N6			115.6(9)

obtained when **3e** reacted with 2 equiv of PhNCO in THF at room temperature (Scheme 5), indicating that the greater steric crowding of **3e** in comparison with **3c** prevents PhNCO from cyclotrimerization. As shown in Figure 7, complex **5e** has a

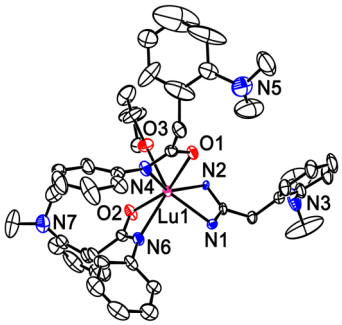
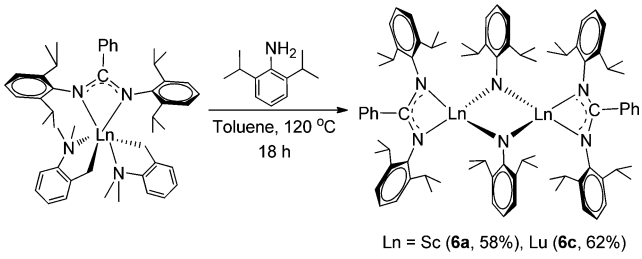


Figure 7. Molecular structure of complex **5e** with thermal ellipsoids at 30% probability. 2,6-Diisopropylphenyls of amidinate ligand and all of the hydrogen atoms are omitted for clarity.

conformation similar to that of complexes **5b,c**. The average Lu−$N_{amidinate}$ and Lu−O bond distances are 2.352(6) and 2.276(6) Å, respectively. All of the bond parameters involving the metal are consistent with the corresponding values in complex **5c**.

Reactions of Bis(aminobenzyl) Complexes with 2,6-Diisopropylaniline. Significantly, treatment of complexes **3a,c** with 1 equiv of 2,6-diisopropylaniline in toluene at 120 °C gave the corresponding imido lanthanide complexes $[(NCN^{dipp})Ln(\mu\text{-}NC_6H_4{}^iPr_2\text{-}2,6)]_2$ (Ln = Sc (**6a**), Lu (**6c**)) (Scheme 6).

Scheme 6. Reactions of Bis(aminobenzyl) Complexes 3 with 2,6-Diisopropylaniline



Complexes **6** are sensitive to air and moisture and are readily soluble in THF and aromatic solvents but sparingly soluble in hexane. The structure of **6a** was determined by single-crystal X-ray diffraction. As shown in Figure 8, complex **6a** adopts a

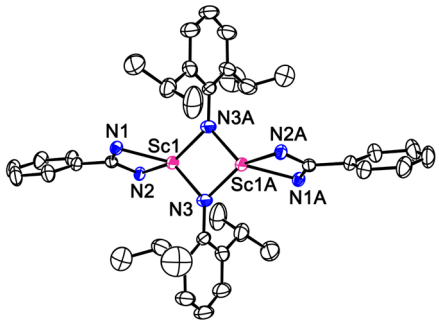


Figure 8. Molecular structure of complex **6a** with thermal ellipsoids at 30% probability. 2,6-Diisopropylphenyls of amidinate ligand and all of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc(1)−N(1) 2.197(2), Sc(1)−N(2) 2.222(2), Sc(1)−N(3) 2.017(2), Sc(1)−N(3A) 2.010(2); N(1)−Sc(1)−N(2) 61.2(1), N(1)−Sc(1)−N(3) 137.4(1), N(1)−Sc(1)−N(3A) 118.1(1), N(2)−Sc(1)−N(3) 121.7(1), N(2)−Sc(1)−N(3A) 140.9(1), N(3)−Sc(1)−N(3A) 86.2(1), Sc(1)−N(3)−Sc(1A) 93.8(1), N(1)−C(1)−N(2) 114.2(2).

Sc_2N_2 quadrilateral core structure via μ-imido bridges. The Sc−N_{imido} bond lengths ranging from 2.010(2) to 2.017(2) Å are consistent with those in the imido−scandium complex $\{[C_5H_4(CH_2)_2NMe_2]Sc[\mu\text{-}NC(Ph)C_6H_{10}]\}_2$.[22] The Sc−$N_{amidinate}$ bond lengths are in the range 2.197(2)−2.222(2) Å, which are quite comparable with the corresponding values of **3a**.

Reactions of Bis(aminobenzyl) Complex 3e with S_8. Reaction of complex **3e** with $^1/_8$ equiv of S_8 afforded the single-insertion product $[o\text{-}Me_2NC_6H_4CH_2C(NC_6H_4{}^iPr_2\text{-}2,6)_2]Lu(CH_2C_6H_4NMe_2\text{-}o)(SCH_2C_6H_4NMe_2\text{-}o)(THF)$ (**7e**) in high yield.[23] The double-insertion product $[o\text{-}Me_2NC_6H_4CH_2C(NC_6H_4{}^iPr_2\text{-}2,6)_2]Lu(SCH_2C_6H_4N\text{-}Me_2\text{-}o)_2(THF)_2$ (**7f**) was obtained in good yield when complex **3e** was treated with $^1/_4$ equiv of S_8 (Scheme 7). In previous studies carried out by us, on the sulfur insertion into the Ln−C bond of alkyl and benzyl complexes, the results obtained showed that the resulting thiolate ligands were easily oxidized by S_8 at room temperature, forming sulfide and disulfide complexes. However, no metal sulfide byproduct was obtained in the present cases.

It is clear that the presence of the amino group at the ortho position of the benzene ring improves the chemoselectivity of the reaction of lanthanide benzyls with elemental sulfur.[23] Single-crystal X-ray diffraction analysis determined the coordination number of complexes **7** to be 6. The metal in **7e** is surrounded by one amidinate ligand, one aminobenzyl, one thiolate and a THF molecule, to form a distorted-octahedral geometry. Interestingly, in contrast to **3**, in **7e,f** the NMe_2 group of the resulting $SCH_2C_6H_4NMe_2\text{-}o$ ligand is free; instead, the vacated coordination sites are occupied by THF molecules (Figure 9). This difference may be attributed to the larger ring strain of the six-membered ring in comparison with that of the five-membered ring, preventing the NMe_2 group from forming the intramolecular chelating coordination competitively. The newly formed Lu−S bond distance is 2.641(1) Å, which is remarkably shorter than the average Er−S distance of 2.732(2) Å found in $(C_5H_5)Er[SC_6H_4NC$-

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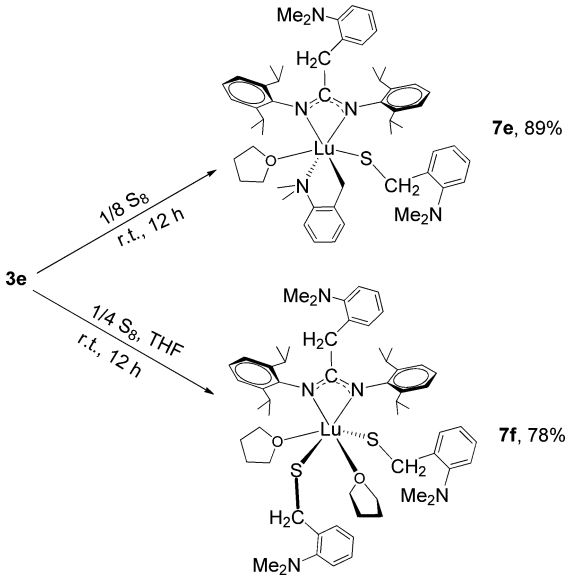
Scheme 7. Reactions of 3e with S_8



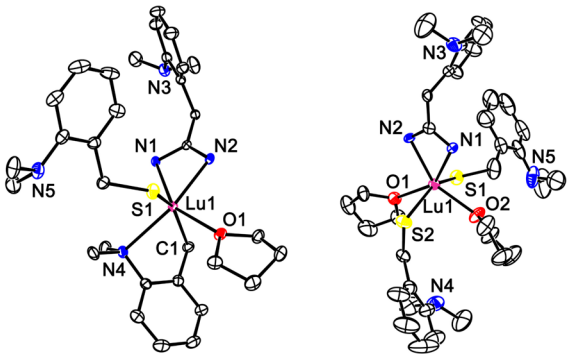


Figure 9. Molecular structures of complexes **7e,f** with thermal ellipsoids at 30% probability. 2,6-Diisopropylphenyls of amidinate ligands and all of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows. **7e** (Lu): Lu(1)–N(1) 2.342(3), Lu(1)–N(2) 2.308(3), Lu(1)–N(4) 2.542(3), Lu(1)–C(1) 2.393(4), Lu(1)–S(1) 2.641(1), Lu(1)–O(1) 2.321(2), S(1)–C(10) 1.813(4); N(1)–Lu(1)–N(2) 58.0(1), C(1)–Lu(1)–N(4) 70.1(1), C(1)–Lu(1)–S(1) 151.40(9), N(4)–Lu(1)–S(1) 93.70(7). **7f** (Lu): Lu(1)–N(1) 2.320(6), Lu(1)–N(2) 2.305(5), Lu(1)–S(1) 2.634(2), Lu(1)–S(2) 2.629(2), Lu(1)–O(1) 2.386(5), Lu(1)–O(2) 2.332(5), S(1)–C(1) 1.75(1), S(1)–C(10) 1.834(8); N(1)–Lu(1)–N(2) 57.8(2), S(1)–Lu(1)–S(2) 146.67(8).

$(NH^iPr)_2]_2$·THF,[24] taking into account the 0.029 Å difference between the metal ionic radii.[25] The residual Lu–C distance of 2.393(4) Å is slightly shorter than the average Lu–C distance of 2.414(6) Å observed in the precursor **3e**. The solid-state structure of complex **7f** shows that Lu^{3+} is coordinated to another $-SCH_2C_6H_4NMe_2$-*o* ligand instead of an aminobenzyl group in complex **7e**, and one more THF molecule fulfills the steric saturation of the coordination around the metal ion.

CONCLUSIONS

In summary, a series of lanthanide bis(*o*-aminobenzyl) complexes with a bulky amidinate coligand have been synthesized by treatment of $LnCl_3$ with amidinate lithium in THF followed by reaction with *o*-$Me_2NC_6H_4CH_2Li$. Stoichiometric reactions of these bis(*o*-aminobenzyl) complexes with small molecules have been investigated. The reactions of bis(aminobenzyl) complexes with CO_2 produces the corresponding lanthanide carboxylate complexes. Furthermore, ligand and temperature effects were observed in the reactions of bis(*o*-aminobenzyl) complexes with PhNCO. The reactions of bis(*o*-aminobenzyl) complexes with 2,6-diisopropylaniline offer a straightforward route to μ_2-imido lanthanide complexes which are potential precursors for the synthesis of other organolanthanide derivatives.

EXPERIMENTAL SECTION

General Procedures and Materials. All manipulations were performed with rigorous exclusion of air and water, using Schlenk techniques or an Mbraun glovebox (Unilab Mbraun; <1 ppm of O_2, <1 ppm of H_2O). Toluene, THF, and hexane were distilled from sodium strip/benzophenone ketyl, degassed, dried over fresh Na chips, and stored in the glovebox. Bis(2,6-diisopropylphenyl)carbodiimide was obtained from Tokyo Chemical Industry Co., Ltd., and used without purification. $CH_3C_6H_4NMe_2$-*o*, ^{n}BuLi (1.6 mol/L in hexane), and PhLi (2.0 mol/Lin dibutyl ether) were purchased from Acros and used without purification. 2,6-Diisopropylaniline was purchased from Alfa Aesar and dried with CaH_2. C_6D_6 and THF-d_8 were obtained from Cambridge Isotope and dried with sodium chips. Highly pure CO_2 (99.99%) was purchased from Pujiang Gas and dried by passing through activated 4 Å molecular sieves. Phenyl isocyanate was obtained from Alfa Aesar and dried with P_2O_5. $LnCl_3$ complexes (Ln = Sc, Y, Lu, etc.) were prepared according to literature procedures.[26] ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL ECA-400 NMR spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) in C_6D_6 or THF-d_8 at room temperature.

Synthesis of [PhC(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]Li(THF) (1a). A 0.5 mL portion of PhLi/dibutyl ether solution (2 M, 1 mmol) was added slowly to a stirred solution of bis(2,6-diisopropylphenyl)carbodiimide (0.363 g, 1 mmol) in THF (10 mL). Complex **1a** was obtained quantitatively after the reaction mixture was stirred for 2 h at ambient temperature. ^{1}H NMR (400 MHz, THF-d_8, room temperature): δ 6.73 (m, 9H, Ar), 6.59 (t, J = 7.6 Hz, 2H, Ar), 3.58 (m, 4H, THF), 3.46 (m, 4H, $-CHMe_2$), 1.74 (m, 4H, THF), 1.04 (d, J = 6.8 Hz, 12H, $-CHMe_2$), 0.73 (d, J = 6.8 Hz, 12H, $-CHMe_2$). ^{13}C NMR (100 MHz, THF-d_8, room temperature): δ 167.4 (s, NCN), 148.9 (s, Ar), 141.0 (s, Ar), 137.0 (s, Ar), 131.1 (s, Ar), 126.8 (s, Ar), 126.7 (s, Ar), 122.8 (s, Ar), 120.4 (s, Ar), 68.0 (s, THF), 28.3 (s, $-CHMe_2$), 26.1 (s, THF), 25.1 (s, $-CHMe_2$), 23.0 (s, $-CHMe_2$).

Synthesis of [PhC(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]Li(DME) (1b). A DME solution of complex **1a** was concentrated under vacuum to a 2 mL saturated solution, and on crystallization at −35 °C, 0.510 g (95%) of colorless crystals of **1b** was obtained. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 7.20–7.12 (m, 6H, Ar), 7.03 (t, J = 7.6 Hz, 2H, Ar), 6.82 (t, J = 7.6 Hz, 2H, Ar), 6.72 (t, J = 7.0 Hz, 1H, Ar), 3.75 (m, 4H, $-CHMe_2$), 3.06 (s, 6H, $-CH_2OMe$), 2.77 (s, 4H, $-CH_2OMe$), 1.29 (d, J = 6.8 Hz, 12H, $-CHMe_2$), 1.15 (d, J = 6.8 Hz, 12H, $-CHMe_2$). ^{13}C NMR (100 MHz, C_6D_6, room temperature): δ 168.0 (s, NCN), 148.2 (s, Ar), 140.7 (s, Ar), 136.2 (s, Ar), 130.0 (s, Ar), 126.8 (s, Ar), 126.5 (s, Ar), 122.7 (s, Ar), 120.9 (s, Ar), 69.7 (s, $-CH_2OMe$), 58.9 (s, $-CH_2OMe$), 28.1 (s, $-CHMe_2$), 24.8 (s, $-CHMe_2$), 22.7 (s, $-CHMe_2$). Anal. Calcd for $C_{35}H_{49}N_2O_2Li$: C, 78.32; H, 9.20; N, 5.22. Found: C, 78.70; H, 9.03; N, 5.42.

Synthesis of [PhC(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]Li(DME)(THF) (1c). Recrystallization of complex **1a** in a DME/THF mixed solvent gave **1c** as colorless crystals (0.516 g, 96%). ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 7.17–7.11 (m, 6H, Ar), 7.01 (t, J = 7.2 Hz, 2H, Ar), 6.81 (t, J = 7.6 Hz, 2H, Ar), 6.72 (t, J = 7.0 Hz, 1H, Ar), 3.74 (m, 4H, $-CHMe_2$), 3.55 (br s, 4H, THF), 3.07 (s, 6H, $-CH_2OMe$), 2.83 (br d, 4H, $-CH_2OMe$), 1.39 (br s, 4H, THF), 1.28 (d, J = 6.8 Hz, 12H, $-CHMe_2$), 1.13 (d, J = 6.8 Hz, 12H, $-CHMe_2$). ^{13}C NMR (100 MHz, C_6D_6, room temperature): δ 167.9 (s, NCN), 148.2 (s, Ar), 140.7 (s, Ar), 136.3 (s, Ar), 130.0 (s, Ar), 126.7 (s, Ar), 126.5 (s, Ar), 122.7 (s, Ar), 120.9 (s, Ar), 69.9 (s, $-CH_2OMe$), 67.7 (s, THF), 58.8 (s, $-CH_2OMe$), 28.1 (s, $-CHMe_2$), 25.4 (s, THF), 24.8 (s, $-CHMe_2$),

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22.7 (s, −CHMe_2). Anal. Calcd for $C_{39}H_{57}N_2O_3Li$: C, 76.94; H, 9.44; N, 4.60. Found: C, 76.59; H, 9.06; N, 4.49.

Synthesis of [PhC(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]Li[μ-η^4:η^4-PhC(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]Li(THF) (1d). Complex **1d** was obtained as a yellow crystalline product (0.468 g, 97%), similarly to the preparation of **1c** described above only with a slight change of mixed solvent to toluene/THF. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 7.68 (m, 2H, Ar), 7.21 (d, J = 7.6 Hz, 2H, Ar), 7.12−7.07 (m, 6H, Ar), 7.00−6.90 (m, 8H, Ar), 6.84 (t, J = 7.6 Hz, 1H, Ar), 6.77 (t, J = 7.6 Hz, 2H, Ar), 6.67 (t, J = 7.4 Hz, 1H, Ar), 3.72 (m, 6H, −C*H*Me$_2$), 3.23 (m, 2H, −C*H*Me$_2$), 2.51 (br m, 4H, THF), 1.31 (d, J = 7.2 Hz, 12H, −CH*Me*$_2$), 1.24 (d, J = 6.8 Hz, 6H, −CH*Me*$_2$), 1.14 (br m, 24H, −CH*Me*$_2$), 0.90 (br m, 12H, −CH*Me*$_2$), 0.79 (br m, 4H, THF). ^{13}C NMR (100 MHz, C_6D_6, room temperature): δ 169.2 (s, NCN), 167.9 (s, NCN), 149.6 (s, Ar), 148.4 (s, Ar), 146.7 (s, Ar), 143.4 (s, Ar), 141.4 (s, Ar), 141.3 (s, Ar), 138.8 (s, Ar), 137.1 (s, Ar), 130.4 (s, Ar), 129.0 (s, Ar), 128.7 (s, Ar), 128.5 (s, Ar), 126.7 (s, Ar), 126.5 (s, Ar), 125.2 (s, Ar), 124.2 (s, Ar), 123.3 (s, Ar), 123.1 (s, Ar), 122.7 (s, Ar), 120.9 (s, Ar), 68.1 (s, THF), 28.2 (s, −*C*HMe$_2$), 28.1 (s, −*C*HMe$_2$), 27.5 (s, −*C*HMe$_2$), 25.6 (s, −CH*Me*$_2$), 25.4 (s, −CH*Me*$_2$), 24.8 (s, −CH*Me*$_2$), 24.6 (s, −CH*Me*$_2$), 23.4 (s, THF), 23.2 (s, −CH*Me*$_2$), 23.1 (s, −CH*Me*$_2$). Anal. Calcd for $C_{66}H_{86}N_4OLi_2$: C, 82.12; H, 8.98; N, 5.80. Found: C, 81.92; H, 8.46; N, 5.56.

Synthesis of [PhC(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]ScCl$_2$(THF)$_2$ (2a). A 0.5 mL portion of an ether solution (2 M, 1 mmol) of PhLi/dibutyl was added slowly to a stirred solution of bis(2,6-diisopropylphenyl)carbodiimide (0.362 g, 1 mmol) in THF (15 mL). After 2 h, the reaction mixture was added slowly via glass pipet to a THF (20 mL) suspension of $ScCl_3$ (0.151 g, 1 mmol). After 8 h, all volatiles were removed under vacuum, and then 60 mL of toluene was added to the residue. The resulting colorless suspension was filtered, the filtrate was concentrated under vacuum to 5 mL, and colorless crystals of **2a** (0.651 g, 93%) were harvested after the solution stood at −35 °C for 5 days. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.22 (m, 2H, Ar), 7.09−7.02 (m, 6H, Ar), 6.71 (m, 3H, Ar), 4.10 (m, 4H, −C*H*Me$_2$), 3.56 (br m, 8H, THF), 1.45 (m, 20H, THF and −CH*Me*$_2$), 0.98 (d, J = 7.2 Hz, 12H, −CH*Me*$_2$). ^{13}C NMR (100 MHz, C_6D_6, room temperature): δ 173.0 (s, NCN), 147.4 (s, Ar), 143.5 (s, Ar), 142.7 (s, Ar), 131.0 (s, Ar), 129.4 (s, Ar), 127.0 (s, Ar), 125.0 (s, Ar), 123.9 (s, Ar), 67.7 (s, THF), 27.8 (s, −CHMe$_2$), 25.8 (s, −CH*Me*$_2$), 25.6 (s, THF), 23.7 (s, −CH*Me*$_2$). Anal. Calcd for $C_{39}H_{55}N_2O_2Cl_2Sc$: C, 66.94; H, 7.92; N, 4.00. Found: C, 65.79; H, 7.73; N, 3.91.

Synthesis of [PhC(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]YCl$_2$(THF)$_3$ (2b). Complex **2b** was obtained as a colorless crystalline product (0.767 g, 94%), similarly to the preparation of **2a** described above. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 6.99 (d, J = 8.4 Hz, 2H, Ar), 6.92−6.88 (m, 7H, Ar), 6.71 (t, J = 7.6 Hz, 2H, Ar), 3.84 (m, 4H, −C*H*Me$_2$), 3.62 (br s, THF), 1.76 (br s, THF), 1.21 (d, J = 6.4 Hz, 12H, −CH*Me*$_2$), 0.71 (d, J = 6.8 Hz, 12H, −CH*Me*$_2$). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ 172.3 (s, NCN), 146.0 (s, Ar), 142.2 (s, Ar), 132.2 (s, Ar), 131.8 (s, Ar), 128.1 (s, Ar), 125.9 (s, Ar), 123.1 (br s, Ar), 122.9 (s, Ar), 67.3 (s, THF), 27.4 (s, −CHMe$_2$), 25.4 (s, THF), 24.5 (s, −CH*Me*$_2$), 23.3 (s, −CH*Me*$_2$). Anal. Calcd for $C_{43}H_{63}N_2O_3Cl_2Y$: C, 63.31; H, 7.78; N, 3.43. Found: C, 63.04; H, 7.58; N, 3.54.

Synthesis of [PhC(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]LuCl$_2$(THF)$_3$ (2c). Complex **2c** was obtained as a colorless crystalline product (0.866 g, 96%), similarly to the preparation of **2a** described above. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.32 (br d, 2H, Ar), 7.08 (br s, 7H, Ar), 6.68 (br m, 2H, Ar), 4.08 (br s, 4H, −C*H*Me$_2$), 3.65 (br s, 12H, THF), 1.52 (b d, J = 5.6 Hz, 12H, −CH*Me*$_2$), 1.36 (br s, 12H, THF), 1.11 (bd, J = 6.4 Hz, 12H, −CH*Me*$_2$); ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 6.96 (d, J = 8.4 Hz, 2H, Ar), 6.91−6.84 (m, 7H, Ar), 6.71 (t, J = 7.6 Hz, 2H, Ar), 3.82 (m, 4H, −C*H*Me$_2$), 3.59 (br s, 12H, THF), 1.73 (br s, 12H, THF), 1.18 (d, J = 6.4 Hz, 12H, −CH*Me*$_2$), 0.68 (d, J = 6.4 Hz, 12H, −CH*Me*$_2$). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ 171.5 (s, NCN), 145.3 (s, Ar), 142.6 (s, Ar), 142.3 (s, Ar), 132.3 (s, Ar), 131.6 (s, Ar), 128.4 (s, Ar), 126.0 (s, Ar), 123.3 (br s, Ar), 123.2 (s, Ar), 67.4 (s, THF), 27.3 (s, −CHMe$_2$), 25.4 (s, THF), 24.6 (s, −CH*Me*$_2$) 23.3 (s, −CH*Me*$_2$). Anal. Calcd for $C_{43}H_{63}N_2O_3Cl_2Lu$: C, 57.27; H, 7.04; N, 3.11. Found: C, 56.98; H, 6.86; N, 3.23.

Synthesis of [PhC(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$ (3a). To a THF suspension of complex **2a** generated in situ was added a THF (10 mL) solution of *o*-Me$_2$NC$_6$H$_4$CH$_2$Li (0.565 g, 4 mmol). After 12 h, all volatiles were removed under vacuum, and then 60 mL of toluene was added to the residue. The resulting brown-red suspension was filtered, and the filtrate was concentrated under vacuum to 5 mL. After the concentrated solution stood at ambient temperature for 3 days, yellow crystals of **3a** (1.638 g, 92%) were harvested. ^{1}H NMR (500 MHz, C_6D_6, 70 °C): δ 7.19 (m, 1H, Ar), 7.07 (br s, 7H, Ar), 6.95 (m, 2H, Ar), 6.86 (m, 2H, Ar), 6.68 (m, 3H, Ar), 6.57 (m, 2H, Ar), 6.52 (m, 2H, Ar), 3.87 (br m, 4H, −C*H*Me$_2$), 2.44 (s, 12H, −N*Me*$_2$), 1.90 (s, 4H, −CH_2−), 1.36 (d, J = 7.0 Hz, 12H, −CH*Me*$_2$), 0.94 (d, J = 4 Hz, 12H, −CH*Me*$_2$), ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 173.8 (s, NCN), 147.5 (s, Ar), 146.9 (s, Ar), 144.7 (s, Ar), 141.9 (s, Ar), 131.6 (s, Ar), 130.6 (s, Ar), 129.3 (s, Ar), 128.6 (s, Ar), 128.0 (s, Ar), 126.7 (s, Ar), 125.8 (s, Ar), 124.9 (s, Ar), 124.1 (s, Ar), 120.8 (s, Ar), 116.7 (s, Ar), 47.4 (br s, −N*Me*$_2$), 47.1 (s, −CH_2−), 28.1 (br s, −CHMe$_2$), 24.6 (br s, −CHMe$_2$), 23.4 (br s, −CH*Me*$_2$). Anal. Calcd for $C_{49}H_{63}N_4Sc$: C, 78.16; H, 8.43; N, 7.44. Found: C, 78.28; H, 8.59; N, 7.12.

Synthesis of [PhC(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]Y(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$ (3b). Complex **3b** was obtained as a yellow crystalline product in 88% yield (1.403 g) from the treatment of [PhC(NC$_6$H$_4$*i*Pr$_2$-2,6)$_2$)]YCl$_2$(THF)$_3$ (2 mmol) with 10 mL of a THF solution of *o*-Me$_2$NC$_6$H$_4$CH$_2$Li (0.565 g, 4 mmol), similarly to the preparation of **3a** described above. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.26 (br s, 1H, Ar), 7.07 (br s, 7H, Ar), 6.93 (m, 4H, Ar), 6.62 (m, 7H, Ar), 4.23 (br s, 2H, −C*H*Me$_2$), 3.05 (br s, 2H, −C*H*Me$_2$), 2.33 (br s, 12H, −N*Me*$_2$), 1.95 (br s, 4H, −CH_2−), 1.62 (b m, 12H, −CH*Me*$_2$), 0.93 (br s, 6H, −CH*Me*$_2$), 0.11 (br s, 6H, −CH*Me*$_2$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 172.8 (s, NCN), 144.5 (s, Ar), 144.0 (s, Ar), 142.1 (s, Ar), 141.2 (s, Ar),133.9 (s, Ar), 131.6 (s, Ar), 130.6 (s, Ar), 128.9 (s, Ar), 128.7 (s, Ar), 128.3 (s, Ar), 127.8 (s, Ar), 127.6 (s, Ar), 126.7 (s, Ar), 124.6 (s, Ar), 124.4 (s, Ar), 123.4 (s, Ar), 120.1 (s, Ar), 118.5 (s, Ar), 47.1 (d, J_{Y-C} = 15 Hz, −CH$_2$−), 45.4 (br s, −N*Me*$_2$), 29.8 (br s, −CHMe$_2$), 27.8 (br s, −CHMe$_2$), 24.8 (br s, −CH*Me*$_2$), 23.0 (br s, −CH*Me*$_2$). Anal. Calcd for $C_{49}H_{63}N_4Y$: C, 73.85; H, 7.97; N, 7.03. Found: C, 73.57; H, 8.13; N, 7.18.

Synthesis of [PhC(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]Lu(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$ (3c). Complex **3c** was obtained as a colorless crystalline product (1.589 g, 90%), similarly to the preparation of **3a** described above. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.28 (br s, 1H, Ar), 7.09 (br s, 7H, Ar), 6.94 (m, 4H, Ar), 6.58 (m, 7H, Ar), 4.42 (br s, 2H, −C*H*Me$_2$), 3.13 (br s, 2H, −C*H*Me$_2$), 2.51 (br s, 6H, −N*Me*$_2$), 2.23 (br s, 6H, −N*Me*$_2$), 1.98 (br s, 4H, −CH_2−), 1.60 (b m, 12H, −CH*Me*$_2$), 0.97 (br s, 6H, −CH*Me*$_2$), 0.13 (br s, 6H, −CH*Me*$_2$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 172.9 (s, NCN), 144.8 (s, Ar), 144.7 (s, Ar), 143.6 (s, Ar), 141.6 (br s, Ar), 131.6 (s, Ar), 131.0 (s, Ar), 129.1 (s, Ar), 128.9 (s, Ar), 126.7 (s, Ar), 126.5 (s, Ar), 124.8 (br s, Ar), 124.7 (s, Ar), 123.3 (br s, Ar), 120.5 (s, Ar), 117.7 (s, Ar), 51.8 (s, −CH$_2$−), 47.2 (br s, −N*Me*$_2$), 45.0 (br s, −N*Me*$_2$), 29.2 (br s, −CHMe$_2$), 27.5 (br s, −CHMe$_2$), 24. Seven (br s, −CHMe$_2$), 23.6 (br s, −CH*Me*$_2$), 23.2 (br s, −CH*Me*$_2$), 22.8 (br s, −CH*Me*$_2$). Anal. Calcd for $C_{49}H_{63}N_4Lu$: C, 66.65; H, 7.19; N, 6.34. Found: C, 66.39; H, 7.32; N, 6.22.

Synthesis of [*o*-Me$_2$NC$_6$H$_4$CH$_2$C(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]Sc-(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$ (3d). To a stirred THF (20 mL) solution of bis(2,6-diisopropylphenyl)carbodiimide (1.813 g, 5 mmol) was added slowly a THF (10 mL) solution of *o*-Me$_2$NC$_6$H$_4$CH$_2$Li (0.706 g, 5 mmol). After 2 h, the reaction mixture was added slowly via glass pipet to a THF (20 mL) suspension of $ScCl_3$ (0.757g, 5 mmol). The yellow suspension was then stirred for 12 h, and a THF (10 mL) solution of *o*-Me$_2$NC$_6$H$_4$CH$_2$Li (1.411 g, 10 mmol) was added to the resulting mixture. All volatiles were removed under vacuum after the reaction mixture was stirred overnight, and then 60 mL of toluene was added to the residue. The brown-red suspension was filtered, and then the filtrate was concentrated under reduced pressure to 5 mL. Yellow crystals of **3d** (3.402 g, 84%) were obtained after the solution stood at ambient temperature for 5 days. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.05 (m, 9H, Ar), 6.92 (m, 4H, Ar), 6.65 (m, 3H, Ar), 6.53 (m, 2H, Ar), 4.05 (s, 2H, *o*-Me$_2$NPhCH_2−$_{amidinate}$), 3.81 (m, 4H, −C*H*Me$_2$),

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2.39 (s, 12H, $-CH_2C_6H_4NMe_2$-o_{alkyl}), 2.02 (s, 4H, $-CH_2C_6H_4NMe_2$-o_{alkyl}), 1.91 (s, 6H, o-$Me_2NPhCH_2-_{amidinate}$), 1.38 (d, J = 6.4 Hz, 12H, $-CHMe_2$), 1.25 (d, J = 6.8 Hz, 12H, $-CHMe_2$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 178.7 (s, NCN), 152.3 (s, Ar), 149.3 (s, Ar), 148.0 (s, Ar), 143.7 (s, Ar), 143.1 (s, Ar), 131.1 (s, Ar), 129.6 (s, Ar), 129.5 (s, Ar), 126.9 (s, Ar), 125.8 (s, Ar), 125.1 (s, Ar), 124.3 (s, Ar), 121.1 (s, Ar), 120.1 (s, Ar),117.3 (s, Ar), 47.7 (s, $-CH_2C_6H_4NMe_2$-o_{alkyl}), 46.9 (s, o-$Me_2NPhCH_2-_{amidinate}$), 44.3 (s, o-$Me_2NPhCH_2-_{amidinate}$), 30.1 (s, $-CH_2C_6H_4NMe_2$-o_{alkyl}), 28.0 (br s, $-CHMe_2$), 26.5 (br s, $-CHMe_2$), 25.1 (s, $-CHMe_2$). Anal. Calcd for $C_{52}H_{70}N_5Sc$: C, 77.10; H, 8.71; N, 8.65. Found: C, 76.84; H, 8.87; N, 8.47.

Synthesis of [o-$Me_2NC_6H_4CH_2C(NC_6H_4{}^iPr_2$-2,6)$_2$]Lu-($CH_2C_6H_4NMe_2$-$o$)$_2$ (3e). Complex **3e** was obtained as a colorless crystalline product (2.594 g, 92%), similarly to the preparation of **3d** described above. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.20 (m, 1H, Ar), 7.06 (m, 8H, Ar), 6.92 (m, 4H, Ar), 6.59 (m, 3H, Ar), 6.51 (m, 2H, Ar), 4.00 (s, 2H, o-$Me_2NPhCH_2-_{amidinate}$), 3.73 (m, 4H, $-CHMe_2$), 2.37 (s, 12H, $-CH_2C_6H_4NMe_2$-o_{alkyl}), 1.93 (s, 6H, o-$Me_2NPhCH_2-_{amidinate}$), 1.83 (s, 4H, $-CH_2C_6H_4NMe_2$-o_{alkyl}), 1.36 (d, J = 6.4 Hz, 12H, $-CHMe_2$), 1.26 (d, J = 6.4 Hz, 12H, $-CHMe_2$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 178.3 (s, NCN), 152.3 (s, Ar), 146.6 (s, Ar), 145.5 (s, Ar), 143.4 (s, Ar), 143.3 (s, Ar), 130.6 (s, Ar), 130.1 (s, Ar), 129.2 (s, Ar), 126.8 (s, Ar), 126.1 (s, Ar), 124.9 (s, Ar), 124.0 (s, Ar), 123.6 (s, Ar), 120.4 (s, Ar), 119.7 (Ar), 117.5 (s, Ar), 51.6 (s, $-CH_2C_6H_4NMe_2$-o_{alkyl}), 46.6 (s, $-CH_2C_6H_4NMe_2$-o_{alkyl}), 44.3 (s, o-$Me_2NPhCH_2-_{amidinate}$), 30.9 (s, o-$Me_2NPhCH_2-_{amidinate}$), 28.2 (s, $-CHMe_2$), 26.1 (s, $-CHMe_2$), 24.9 (s, $-CHMe_2$). Anal. Calcd for $C_{52}H_{70}N_5Lu$: C, 66.43; H, 7.51; N, 7.45. Found: C, 66.19; H, 7.65; N, 7.31.

Synthesis of {[PhC($NC_6H_4{}^iPr_2$-2,6)$_2$]Sc(μ-η^1:η^1-$O_2CCH_2C_6H_4NMe_2$-o)$_2$}$_2$ (4a). A toluene (10 mL) solution of complex **3a** (0.188 g, 0.25 mmol) was placed in a tube with a Teflon stopcock and degassed by a freeze−pump− thaw cycle. Two atmospheres of CO_2 was introduced into the tube, and a color change from yellow to colorless was observed within 10 min. The solution was concentrated under reduced pressure to saturation, and colorless crystals of **4a** (0.196 g, 93%) were harvested after the solution stood at ambient temperature for 4 days. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.45 (d, J = 7.6 Hz, 4H, Ar), 7.18 (t, J = 6.8 Hz, 4H, Ar), 7.07 (t, J = 7.0 Hz, 4H, Ar), 6.97−6.87 (m, 20H, Ar), 6.68−6.57 (m, 6H, Ar), 3.76 (m, 8H, $-CHMe_2$), 3.68 (s, 8H, $-OOCCH_2C_6H_4NMe_2$-o), 2.41 (s, 24H, $-OOCCH_2C_6H_4NMe_2$-o), 1.19 (d, J = 6.0 Hz, 24H, $-CHMe_2$), 1.08 (d, J = 6.4 Hz, 24H, $-CHMe_2$), ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 182.4 (s, $-OOCCH_2C_6H_4NMe_2$-o), 176.6 (s, NCN), 152.5 (s, Ar), 143.0 (s, Ar), 142.7 (s, Ar), 131.3 (s, Ar), 130.5 (s, Ar), 130.0 (s, Ar), 129.9 (s, Ar), 129.1 (s, Ar), 127.1 (s, Ar), 126.7 (s, Ar), 124.4 (s, Ar), 123.5 (s, Ar), 123.2 (s, Ar), 119.1 (s, Ar), 44.8 (br s, $-OOCCH_2C_6H_4NMe_2$-o), 37.3 (s, $-OOCCH_2C_6H_4NMe_2$-o), 28.0 (s, $-CHMe_2$), 25.1 (s, $-CHMe_2$), 23.1 (s, $-CHMe_2$). Anal. Calcd for $C_{102}H_{126}N_8O_8Sc_2$: C, 72.83; H, 7.55; N, 6.66. Found: C, 73.05; H, 7.75; N, 6.51.

Synthesis of {[PhC($NC_6H_4{}^iPr_2$-2,6)$_2$]Y(μ-η^1:η^2-$O_2CCH_2C_6H_4NMe_2$-o)(μ-η^1:η^1-$O_2CCH_2C_6H_4NMe_2$-o)}$_2$ (4b). A toluene (10 mL) solution of complex **3b** (0.199 g, 0.25 mmol) was placed in a tube with a Teflon stopcock and degassed by a freeze−pump−thaw cycle. Two atmospheres of CO_2 was introduced into the tube, and a color change from yellow to colorless was observed within 5 min. The solution was concentrated under reduced pressure to 2 mL, and colorless crystals of **4b** (0.172 g, 78%) were harvested after the solution stood at ambient temperature for 3 days. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.40 (b m, 4H, Ar), 7.18−7.09 (m, 7H, Ar), 7.02−6.82 (m, 21H, Ar), 6.67 (m, 4H, Ar), 6.60 (m, 2H, Ar), 3.69 (m, 16H, $-OOCCH_2C_6H_4NMe_2$-o and $-CHMe_2$), 2.44 (s, 24H, $-OOCCH_2C_6H_4NMe_2$-o), 1.21 (d, J = 6.8 Hz, 24H, $-CHMe_2$), 1.13 (d, J = 6.8 Hz, 24H, $-CHMe_2$), ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 184.6 (s, $-OOCCH_2C_6H_4NMe_2$-o), 176.5 (s, NCN), 153.0 (s, Ar), 143.1 (s, Ar), 142.2 (s, Ar), 132.5 (s, Ar), 130.9 (s, Ar), 130.4 (s, Ar), 129.6 (s, Ar), 128.6 (s, Ar), 126.6 (s, Ar), 124.0 (s, Ar), 123.6 (s, Ar), 123.0 (s, Ar), 119.7 (s, Ar), 45.2 (br s, $-OOCCH_2C_6H_4NMe_2$-o), 37.8 (s, $-OOCCH_2C_6H_4NMe_2$-o), 28.3 (s, $-CHMe_2$), 25.1 (s, $-CHMe_2$), 22.9 (s, $-CHMe_2$). Anal. Calcd for $C_{102}H_{126}N_8O_8Y_2$: C, 69.22; H, 7.18; N, 6.33. Found: C, 68.96; H, 7.33; N, 6.17.

Synthesis of {[PhC($NC_6H_4{}^iPr_2$-2,6)$_2$]Lu(μ-η^1:η^2-$O_2CCH_2C_6H_4NMe_2$-o)(μ-η^1:η^1-$O_2CCH_2C_6H_4NMe_2$-o)}$_2$ (4c). Complex **4c** was obtained as a colorless crystalline product (0.368 g, 76%), similarly to the preparation of **4b** described above. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.41 (br m, 4H, Ar), 7.20−6.93 (m, 24H, Ar), 6.86 (m, 4H, Ar), 6.67 (m, 4H, Ar), 6.60 (m, 2H, Ar), 3.73 (s, 16H, $-CHMe_2$ and $-OOCCH_2C_6H_4NMe_2$-o), 2.43 (s, 24H, $-OOCCH_2C_6H_4NMe_2$-o), 1.22 (d, J = 6.4 Hz, 24H, $-CHMe_2$), 1.12 (d, J = 6.8 Hz, 24H, $-CHMe_2$). ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 7.05−6.97 (br m, 12H, Ar), 6.89 (br d, 6H, Ar), 6.82−6.70 (br m, 20H, Ar), 3.47−3.38 (br m, 16H, $-CHMe_2$ and $-OOCCH_2C_6H_4NMe_2-$), 2.42 (br s, 24H, $-OOCCH_2C_6H_4NMe_2$-o), 0.95 (d, J = 6.8 Hz, 24H, $-CHMe_2$), 0.87 (d, J = 6.0 Hz, 24H, $-CHMe_2$), ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ 184.5 (s, $-OOCCH_2C_6H_4NMe_2$-o), 175.7 (s, NCN), 152.8 (s, Ar), 142.9 (s, Ar), 142.4 (s, Ar), 132.6 (s, Ar), 130.6 (s, Ar), 130.0 (s, Ar), 129.7 (s, Ar), 128.5 (s, Ar), 127.0 (s, Ar), 126.3 (s, Ar), 123.6 (s, Ar), 123.2 (s, Ar), 122.6 (s, Ar), 119.2 (s, Ar), 44.8 (br s, $-OOCCH_2C_6H_4NMe_2$-o), 37.4 (s, $-OOCCH_2C_6H_4NMe_2$-o), 27.9 (s, $-CHMe_2$), 24.8 (s, $-CHMe_2$), 22.4 (s, $-CHMe_2$). Anal. Calcd for $C_{102}H_{126}N_8O_8Lu_2$: C, 63.08; H, 6.54; N, 5.77. Found: C, 62.85; H, 6.67; N, 5.64.

Synthesis of [PhC($NC_6H_4{}^iPr_2$-2,6)$_2$]Y[OC($CH_2C_6H_4NMe_2$-o)-NPh]$_2$(THF) (5b). Complex **5b** was obtained as a pure colorless powder (0.393 g, 78%, based on complex **3b**) when complex **3b** (0.399 g, 0.5 mmol) was reacted with 2 equiv of PhNCO (0.108 mL, 1 mmol) at −15 °C for 20 h, and the solvent was subsequently removed under reduced pressure. Single crystals suitable for X-ray diffraction analysis were grown from THF/hexane at −35 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.48 (d, J = 8.0 Hz, 2H, Ar), 7.22 (d, J = 8.0 Hz, 2H, Ar), 7.11−6.91 (m, 18H, Ar), 6.71 (m, 3H, Ar), 6.44 (d, J = 7.6 Hz, 4H, Ar), 3.85 (br m, 8H, $-CH_2C_6H_4NMe_2$-o, and $-CHMe_2$), 3.59 (br s, 4H, THF), 2.45 (s, 12H, $-CH_2C_6H_4NMe_2$-o), 1.21 (br d, 16H, THF and $-CHMe_2$), 1.05 (d, J = 6.8 Hz, 12H, $-CHMe_2$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 182.0 (s, NCO), 173.6 (s, NCN), 153.1 (s, Ar), 147.6 (s, Ar), 144.6 (s, Ar), 142.1 (s, Ar), 133.0 (s, Ar), 132.3 (s, Ar), 131.0 (s, Ar), 130.5 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 126.9 (s, Ar), 126.8 (s, Ar), 124.6 (s, Ar), 123.5 (s, Ar), 122.9 (s, Ar), 122.8 (s, Ar), 119.3 (s, Ar), 69.2 (br s, THF), 44.8 (s, $-CH_2C_6H_4NMe_2$-o), 33.5 (s, $-CH_2C_6H_4NMe_2$-o), 28.1 (s, $-CHMe_2$), 25.1 (s, $-CHMe_2$), 25.0 (s, THF), 23.4 (s, $-CHMe_2$). Anal. Calcd for $C_{67}H_{81}N_6O_3Y$: C, 72.67; H, 7.37; N, 7.59. Found: C, 72.04; H, 7.55; N, 7.37.

Synthesis of [PhC($NC_6H_4{}^iPr_2$-2,6)$_2$]Lu[OC($CH_2C_6H_4NMe_2$-o)-NPh]$_2$(THF) (5c). At −15 °C, a THF (8 mL) solution of PhNCO (0.108 mL, 1 mmol) was added slowly to a stirred THF (15 mL) solution of complex **3c** (0.883 g, 1 mmol). After 20 h of workup, all of the volatiles were removed under vacuum. Single crystals suitable for X-ray diffraction analysis (0.776 g, 65%) were grown from THF/hexane at −35 °C over 4 days. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.48 (d, J = 7.2 Hz, 2H, Ar), 7.24 (d, J = 7.2 Hz, 2H, Ar), 7.11−6.88 (m, 18H, Ar), 6.70 (m, 3H, Ar), 6.40 (d, J = 8.0 Hz, 4H, Ar), 3.84 (br m, 8H, $-CH_2C_6H_4NMe_2$-o, and $-CHMe_2$), 3.61 (br s, 4H, THF), 2.46 (s, 12H, $-CH_2C_6H_4NMe_2$-o), 1.20 (br d, 18H, THF and $-CHMe_2$), 1.04 (d, J = 6.4 Hz, 12H, $-CHMe_2$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 181.5 (s, NCO), 172.9 (s, NCN), 153.1 (s, Ar), 147.4 (s, Ar), 144.7 (s, Ar), 142.4 (s, Ar), 133.2 (s, Ar), 132.2 (s, Ar), 131.1 (s, Ar), 130.7 (s, Ar), 128.6 (s, Ar), 128.3 (s, Ar), 127.0 (s, Ar), 126.8 (s, Ar), 124.9 (s, Ar), 123.6 (s, Ar), 123.5 (s, Ar), 123.0 (s, Ar), 122.8 (s, Ar), 119.3 (s, Ar), 69.9 (s, THF), 44.8 (s, $-CH_2C_6H_4NMe_2$-o), 33.7 (s, $-CH_2C_6H_4NMe_2$-o), 27.9 (s, $-CHMe_2$), 25.1 (s, $-CHMe_2$), 25.0 (s, THF), 23.6 (s, $-CHMe_2$). Anal. Calcd for $C_{67}H_{81}N_6O_3Lu$: C, 67.43; H, 6.84; N, 7.04. Found: C, 67.14; H, 6.90; N, 7.03.

Synthesis of [o-$Me_2NC_6H_4CH_2C(NC_6H_4{}^iPr_2$-2,6)$_2$]Lu[OC-($CH_2C_6H_4NMe_2$-$o$)NPh]$_2$(THF) (5e). At −35 °C, a THF (10 mL) solution of PhNCO (0.22 mL, 2 mmol) was added slowly to a stirred THF (15 mL) solution of complex **3e** (0.94 g, 1 mmol). The solution was warmed to room temperature and stirred for 12 h. The solvent was removed under reduced pressure, leaving **5e** as a colorless powder (1.225 g, 98%, based on complex **3e**). Single crystals suitable for X-ray

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diffraction analysis were grown from THF/hexane mixed solvent at −35 °C for 6 days. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.76 (d, J = 7.2 Hz, 1H, Ar), 7.53 (d, J = 7.2 Hz, 2H, Ar), 7.12 (m, 7H, Ar), 7.07−6.96 (m, 11H, Ar), 6.84 (t, J = 7.2 Hz, 2H, Ar), 6.66 (d, J = 7.6 Hz, 1H, Ar), 6.53 (d, J = 7.6 Hz, 4H, Ar), 3.90 (m, 10H, *o*-$Me_2NPhCH_2-_{amidinate}$, $-CH_2C_6H_4NMe_2$-o_{alkyl}, and $-CHMe_2$), 2.62 (m, 4H, THF), 2.51 (s, 12H, $-CH_2C_6H_4NMe_2$-o_{alkyl}), 1.91 (s, 6H, *o*-$Me_2NPhCH_2-_{amidinate}$), 1.31 (d, J = 6.4 Hz, 12H, $-CHMe_2$), 1.23 (d, J = 6.8 Hz, 12H, $-CHMe_2$), 1.15 (m, 4H, THF). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 182.1 (s, NCO), 177.2 (s, NCN), 153.4 (s, Ar), 152.5 (s, Ar), 147.4 (s, Ar), 144.0 (s, Ar), 132.6 (s, Ar), 132.1 (s, Ar), 131.3 (s, Ar), 129.4 (s, Ar), 128.4 (s, Ar), 127.2 (s, Ar), 126.6 (s, Ar), 124.9 (s, Ar), 124.2 (s, Ar), 124.1 (s, Ar), 123.6 (s, Ar), 123.1 (s, Ar), 123.0 (s, Ar), 119.9 (s, Ar), 119.7 (s, Ar), 70.2 (s, THF), 45.1 (s, $-CH_2C_6H_4NMe_2$-o_{alkyl}), 44.3 (s, *o*-$Me_2NPhCH_2-_{amidinate}$), 34.0 (s, $-CH_2C_6H_4NMe_2$-o_{alkyl}), 30.4 (s, *o*-$Me_2NPhCH_2-_{amidinate}$), 28.0 (s, $-CHMe_2$), 26.2 (s, $-CHMe_2$), 24.9 (s, THF), 24.5 (s, $-CHMe_2$). Anal. Calcd for $C_{70}H_{88}N_7O_3Lu$: C, 67.24; H, 7.09; N, 7.84. Found: C, 66.96; H, 7.04; N, 7.88.

Synthesis of {[PhC(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]Sc(μ-NC$_6$H$_4$^{i}Pr$_2$-2,6)}$_2$ (6a). In a tube with a Teflon stopcock, a toluene (10 mL) solution of 2,6-diisopropylaniline (94 μL, 0.5 mmol) was added slowly to a stirred toluene solution of complex **3a** (0.376 g, 0.5 mmol). The tube was taken out of the glovebox and placed in a 120 °C oil bath. The mixture was stirred for 12 h, and the solvent was removed under reduced pressure. The residue was washed with hexane and dried, leaving **6a** as a yellow powder (0.191 g, 58%, based on complex **3a**). Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization of **3a** in toluene. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.14 (m, 8H, Ar), 6.96 (br m, 10H, Ar), 6.65 (m, 5H, Ar), 6.50 (m, 5H, Ar), 4.11−2.62 (br m, 12H, $-CHMe_2$), 1.74−1.51 (m, 24H, $-CHMe_2$), 1.27 (br s, 12H, $-CHMe_2$), 0.90−0.81 (m, 18H, $-CHMe_2$), 0.26−0.12 (m, 18H, $-CHMe_2$). Anal. Calcd for $C_{86}H_{112}N_6Sc_2$: C, 78.26; H, 8.55; N, 6.37. Found: C, 78.45; H, 8.66; N, 6.23.

Synthesis of {[PhC(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]Lu(μ-NC$_6$H$_4$^{i}Pr$_2$-2,6)}$_2$ (6c). Complex **6c** was obtained as a yellow crystalline product in 62% yield (0.244 g, based on complex **3c**) by treating complex **3c** (0.442 g, 0.5 mmol) with 2,6-diisopropylaniline (94 μL, 0.5 mmol) in toluene (30 mL), similarly to the preparation of **6a** described above. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.24 (d, J = 7.6 Hz, 1H, Ar), 7.14−7.06 (m, 5H, Ar), 7.00−6.81 (m, 8H, Ar), 6.74−6.52 (m, 13H, Ar), 4.84 (s, 1H, $-CHMe_2$), 4.49 (m, 1H, $-CHMe_2$), 4.05 (m, 2H, $-CHMe_2$), 3.83 (m, 1H, $-CHMe_2$), 3.65 (m, 1H, $-CHMe_2$), 2.86−2.65 (m, 6H, $-CHMe_2$), 2.12−1.24 (m, 36H, $-CHMe_2$), 0.89−0.11 (m, 36H, $-CHMe_2$). Anal. Calcd for $C_{86}H_{112}N_6Lu_2$: C, 65.38; H, 7.14; N, 5.32. Found: C, 65.03; H, 7.24; N, 5.11.

Synthesis of [*o*-Me$_2$NC$_6$H$_4$CH$_2$C(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]Lu(CH$_2$C$_6$H$_4$NMe$_2$-*o*)(SCH$_2$C$_6$H$_4$NMe$_2$-*o*)(THF) (7e). A THF (5 mL) solution of S_8 (0.016g, 0.0625 mmol) was added slowly to a stirred THF (15 mL) solution of complex **3e** (0.470 g, 0.5 mmol). After it was stirred at room temperature for 12 h, the solution was concentrated under vacuum and colorless crystals of **7e** (0.496 g, 89%) formed after the solution stood for 2 days. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 8.17 (d, J = 7.2 Hz, 1H, Ar), 7.79 (d, J = 7.6 Hz, Ar), 7.20−6.84 (m, 14H, Ar), 6.70−6.62 (m, 2H, Ar), 4.41 (s, 2H, *o*-$Me_2NPhSCH_2-$), 3.94 (br s, 6H, *o*-$Me_2NPhCH_2-_{amidinate}$ and $-CHMe_2$), 3.56 (br s, 4H, THF), 2.71 (br s, 12H, $-CH_2C_6H_4NMe_2$-o_{alkyl} and *o*-$Me_2NPhSCH_2-$), 1.94 (s, 2H, $-CH_2C_6H_4NMe_2$-o_{alkyl}), 1.87 (s, 6H, *o*-$Me_2NPhCH_2-_{amidinate}$), 1.46 (br s, 18H, $-CHMe_2$), 1.04 (br s, 10H, $-CHMe_2$ and THF). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 179.3 (s, NCN), 152.7 (s, Ar), 152.2 (s, Ar), 145.4 (br s, Ar), 144.9 (s, Ar), 143.5 (br s, Ar), 142.7 (s, Ar), 141.3 (s, Ar), 140.9 (s, Ar), 132.0 (s, Ar), 131.8 (s, Ar), 129.4 (s, Ar), 128.4 (s, Ar), 127.2 (s, Ar), 126.9 (s, Ar), 126.5 (s, Ar), 125.1 (s, Ar), 125.0 (s, Ar), 124.3 (s, Ar), 123.5 (s, Ar), 120.5 (s, Ar), 119.4 (Ar), 119.3 (Ar), 118.7 (s, Ar), 71.2 (s, THF), 47.7 (s, $-CH_2C_6H_4NMe_2$-o_{alkyl}), 47.5 (s, *o*-$Me_2NPhSCH_2-$), 45.5 (s, $-CH_2C_6H_4NMe_2$-o_{alkyl}), 44.6 (s, *o*-$Me_2NPhCH_2-_{amidinate}$), 30.4 (s, *o*-$Me_2NPhCH_2-_{amidinate}$), 28.3 (s, $-CHMe_2$), 28.1 (s, *o*-$Me_2NPhSCH_2-$), 27.2 (s, $-CHMe_2$), 25.5 (s, THF), 25.4 (s, $-CHMe_2$). Anal. Calcd for $C_{56}H_{78}N_5OSLu$: C, 64.41; H, 7.53; N, 6.71. Found: C, 64.29; H, 7.70; N, 6.81.

Synthesis of [*o*-Me$_2$NC$_6$H$_4$CH$_2$C(NC$_6$H$_4$^{i}Pr$_2$-2,6)$_2$]Lu(SCH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$(THF)$_2$ (7f). To a stirred THF (20 mL) solution of complex **3e** (0.470 g, 0.5 mmol) was added slowly a THF (8 mL) solution of S_8 (0.032 g, 0.125 mmol). After it was stirred at room temperature for 12 h, the solution was concentrated under vacuum to saturation and colorless crystals of **7f** (0.448 g, 78%) were obtained. ^{1}H NMR (500 MHz, C_6D_6, 60 °C): δ 7.88 (s, 2H, Ar), 7.57 (s,1H, Ar), 7.07 (t, J = 7.2 Hz, 3H, Ar), 7.02−6.83 (m, 11H, Ar), 6.59 (s, 1H, Ar), 4.41 (s, 2H, *o*-$Me_2NPhSCH_2-$), 3.94 (br s, 6H, *o*-$Me_2NPhCH_2-_{amidinate}$ and $-CHMe_2$), 3.56 (br s, 4H, THF), 2.71 (br s, 12H, $-CH_2C_6H_4NMe_2$-o_{alkyl} and *o*-$Me_2NPhSCH_2-$), 1.94 (s, 2H, $-CH_2C_6H_4NMe_2$-o_{alkyl}), 1.87 (s, 6H, *o*-$Me_2NPhCH_2-_{amidinate}$), 1.46 (br s, 18H, $-CHMe_2$), 1.04 (br s, 10H, $-CHMe_2$ and THF). ^{13}C NMR (125 MHz, C_6D_6, 60 °C): δ 180.6 (s, NCN), 152.0 (s, Ar), 143.6 (s, Ar), 141.9 (s, Ar), 136.8 (s, Ar), 130.8 (s, Ar), 130.5 (s, Ar), 128.5 (s, Ar), 126.4 (s, Ar), 126.0 (s, Ar), 124.6 (s, Ar), 123.9 (s, Ar), 123.5 (s, Ar), 122.8 (s, Ar), 119.6 (Ar), 117.9 (s, Ar), 68.4 (s, THF), 44.6 (s, *o*-$Me_2NPhSCH_2-$), 43.7 (s, *o*-$Me_2NPhCH_2-_{amidinate}$), 31.8 (s, o-$Me_2NPhCH_2-_{amidinate}$), 29.9 (s, *o*-$Me_2NPhSCH_2-$), 28.2 (s, $-CHMe_2$), 26.8 (s, $-CHMe_2$), 25.1 (s, THF), 23.7 (s, $-CHMe_2$). Anal. Calcd for $C_{60}H_{86}N_5O_2S_2Lu$: C, 64.41; H, 7.53; N, 6.71. Found: C, 64.29; H, 7.70; N, 6.81.

X-ray Crystallographic Analysis. Suitable crystals were sealed in thin-walled glass capillaries under a microscope in the glovebox. Data collections were performed on a Bruker SMART APEX or Bruker SMART APEX II (at 293 or 296 K) diffractometer with CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell was carried out by the SMART program package. The raw frame data were processed using SAINT[27] and SADABS[28] to yield the reflection data file. The structure was solved by using the SHELXTL program.[29] Refinement was performed on F^2 anisotropically by full-matrix least-squares methods for all non-hydrogen atoms. Analytical scattering factors for neutral atoms were used throughout the analysis. Except for the hydrogen atoms on bridging carbons, hydrogen atoms were placed at calculated positions and included in the structure calculation without further refinement of the parameters. The hydrogen atoms on bridging carbons were located by difference Fourier syntheses, and their coordinates and isotropic parameters were refined. The residual electron densities were of no chemical significance.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files, text, tables, and figures giving crystal data and processing parameters, selected NMR spectra, and additional experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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