ORGANOMETALLICS

Bulky Formamidinate-Supported Lanthanoid Halides and Alkyls, Including a Rare Terminal La–Me Species

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S Supporting Information

ABSTRACT: The oxidation of $[Sm(DippForm)_2(thf)_2]$ (1; DippFormH = *N*,*N*'bis(2,6-diisopropylphenyl)formamidine) by *tert*-butyl chloride, 1,2-dibromoethane, and iodine, respectively, at ambient temperature led to the isolation of the light yellow crystalline samarium(III) halide complexes $[Sm(DippForm)_2X(thf)]$ (2, X = Cl; 3, X = Br; 4, X = I) in good yield. The subsequent metathesis reaction of $[Ln(DippForm)_2X(thf)]$ (2, Ln = Sm, X = Cl; Ln = La, X = F) with LiMe and $LiCH_2SiMe_3$ generated the samarium alkyl complexes $[Sm(DippForm)_2R(thf)]$ (5, R = Me; 6, R = CH_2SiMe_3) and the rare terminal La–Me complex [La-(DippForm)_2Me(thf)] (7). The attempted ligand exchange reaction of 7 with 1,2,3,4-tetraphenylcyclopentadiene gave, unexpectedly, the homoleptic tris-(formamidinato)lanthanum complex [La(DippForm)_3] (8) in very low yield. The redox transmetalation/protolysis (RTP) reaction from samarium metal with bis(2bromo-3,4,5,6-tetrafluorophenyl)mercury and DippFormH in thf yielded the



mono(formamidinato)samarium(III) complex $[Sm(DippForm)Br_2(thf)_3]$ (9) as a coproduct with the bis(formamidinate) 3. Redox reaction of the divalent samarium complex $[Sm(DippForm)_2(thf)_2]$ (1) with diphenylmercury resulted in the ethenolate complex $[Sm(DippForm)_2(OCH=CH_2)(thf)]$ (10) instead of the target Sm–Ph complex, the product resulting from the decomposition of Lewis base thf molecules.

INTRODUCTION

Organolanthanoid halides LnR_nX_{3-n} are often target molecules in synthetic organolanthanoid chemistry, since they are possible isolable products directly from metathesis reactions between lanthanoid trihalides and alkali-metal salts of anionic organic ligands.¹ Such organolanthanoid halides are key starting materials for derivatization to give other organolanthanoids, including alkyl, hydride, organoamide, and alkoxide complexes LnR_nZ_{3-n} (Z = R', H, NR'₂, OR'). Lanthanoid alkyl complexes, e.g., $LnCp_nR_{3-n}$ are generally highly reactive, and both halides and alkyl derivative complexes have found applications as catalysts or cocatalysts in some catalytic processes.² Over the course of organolanthanoid chemistry studies, cyclopentadienyl and related ligand systems have been dominant in the synthesis of lanthanoid halide, alkyl, and other relevant heteroleptic complexes.³ For non-cyclopentadienyl ligands,⁴ the syntheses of relevant heteroleptic lanthanoid halide derivatives are usually prerequisites before conversion into alkyl, organoamide, and related reactive species to establish the systems as alternatives to their cyclopentadienyl analogues.

1,3-Diazaallyl related ligand systems ($[RN=C(R')NR]^-$, R' = H, formamidinate; R' = alkyl, amidinate; R' = amine, guanidinate) have shown potential in stabilizing the coordination of lanthanoid metals.⁵ Two anionic 1,3-diazaallyl moieties bicapping a large Lewis acidic rare-earth-metal center in a mononuclear complex is a typical bonding mode for amidinate/ guanidinate ligand systems and is comparable to the ubiquitous sandwiching bonding modes of two cyclopentadienyl groups

and related ligand systems. The bonding mode $(\kappa^2(N,N'))$ encapsulates much of the coordination sphere of lanthanoid metals effectively and leaves the remaining coordination sphere accessible to a coligand such as halide/alkyl (overall formula $[Ln(RN=C(R')NR)_2L'(S)_n]$, L' = halide, alkyl, etc., solv, usually n = 0, 1). The catalytic studies of amidinato/ guanidinato rare-earth-metal complexes in various processes such as homogeneous polymerizations, though at an early stage, have proven to be promising.⁵

Our research in rare-earth-metal amidinate coordinaton chemistry focuses on formamidinate ([RN=C(H)NR]⁻) complexes, where the proton on the backbone carbon of the anionic heteroallyl group has minimal steric and electronic effects in comparison with other amidinates/guanidinates ([RN=C(R')NR]⁻, R' = alkyl/amine).^{6–9} The backbone proton is also an advantage in monitoring the reaction pathways or identifying the formation of new formamidinate complexes by NMR spectroscopy due to the resonances often appearing isolated from other protons of the molecule. Formamidines are readily prepared and can be tuned sterically and electronically. Previously, we have reported the synthesis of homoleptic tris(formamidinato) lanthanoid(III) complexes [Ln(RN=C(H)NR)₃(thf)_n] (R = aryl, n = 0-2) and heteroleptic bis(formamidinato)complexes [Ln(RN=C(H)-

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Article





^{*a*}Dipp = 2,6-diisopropylphenyl. Legend: (i) Ln = Sm, R = ^{*b*}Bu, X = Cl (2), R = BrC₂H₄ or 2-HC₆F₄, X = Br (3), X₂ = I₂ (4); (ii) Ln = Sm, X = Cl, R' = Me (5), R' = CH₂SiMe₃ (6), Ln = La, X = F, R' = Me (7).

NR)₂R'(thf)], (R = aryl, R' = F, CCPh),⁶⁻⁸ by the redox transmetalation/protolysis (RTP) method. We have also synthesized the divalent samarium formamidinate complex $[Sm(DippForm)_2(thf)_2]$ (1) and explored its reactivity with $Hg(C_6F_5)_2$, $Hg(CCPh)_2$, and carbodiimides, forming the trivalent samarium formamidinate complexes [Sm- $(\text{DippForm})_2(L')(\text{thf})_n$] (L' = F, CCPh, RN=C(R')NR (R = aryl, R' = H, CH₂Ph); n = 0, 1.^{6,8,9} Now we report new oxidation reactions of the samarium(II) complex to form new key reagents: viz., the structurally characterized samarium(III) halide complexes $[Sm(DippForm)_2X(thf)]$ (X = Cl, Br, I). These are potential reagents for the formation of the heteroleptic alkyl, aryl, hydride, organoamide, alkoxide, and aryloxide derivatives $[Sm(DippForm)_2Z(solv)]$ (Z = R, Ar, H, NR₂, OR, etc.), as foreshadowed by their conversion and that of $[La(DippForm)_2F(thf)]^8$ into alkyl derivatives, including a La complex with a rare terminal La-Me bond. In addition, [La(DippForm)₃], [Sm(DippForm)Br₂(thf)₃], and [Sm-(DippForm)₂(OCH=CH₂)(thf)] have been structurally characterized, even though they were not obtained in amounts allowing further characterization.

RESULTS AND DISCUSSION

Syntheses, Reactivity, and Analytical/Spectroscopic Characterization. The oxidation of the green divalent samarium complex $[Sm(DippForm)_2(thf)_2]$ (1) by *tert*-butyl chloride, 1,2-dibromoethane, and iodine, respectively, in toluene at ambient temperature led to isolation of the light yellow crystalline samarium(III) halide complexes $[Sm-(DippForm)_2X(thf)]$ (2, X = Cl; 3, X = Br; 4, X = I) in good yields (Scheme 1(i)). The samarium(III) bromide 3 was also isolated from a redox reaction of 1 with 1-bromo-2,3,4,5-tetrafluorobenzene, but with a yield lower than that from the reaction with 1,2-dibromoethane.

C, H, and N analyses for compounds $[Sm(DippForm)_2X-(thf)]$ were consistent with the proposed composition, and their molecular structures were further confirmed by singlecrystal X-ray crystallography (see below). Infrared spectra of the samarium(III) halides 2–4 are similar, as expected from their isomorphous structures, and some tentative assignments are provided in the Experimental Section.

The NMR spectra show resonances assignable to relevant protons of the molecules. Thus, the methyl protons of the isopropyl groups of 2–4 display two separate broad resonances (0.00-1.50 ppm) at 303 K, indicating steric hindrance hampering free rotation of the aryl group about the N–C(Ar) axis and/or the isopropyl group along C(ⁱPr)–C(Ar) axis. However, there is relatively free rotation at 333 K, as the resonances coalesce, as shown for 3. The CH(ⁱPr) resonances are broad at 2.85–3.13 ppm. Typical NC(H)N proton

resonances are observed with substantial paramagnetic shifting for X = Cl, Br, I and increase according to the sequence F $(6.90-7.32 \text{ ppm})^6 \rightarrow \text{Cl} (12.16 \text{ ppm}) \rightarrow \text{Br} (12.35 \text{ ppm}) \rightarrow \text{I}$ (13.07 ppm) (at 303 K).

The subsequent metathesis reactions of lanthanoid halides $[Ln(DippForm)_2X(thf)]$ (Ln = Sm, La; X = Cl, F) with the lithium reagents LiMe and LiCH₂SiMe₃ at ambient temperature in toluene yielded crystalline $[Ln(DippForm)_2Me(thf)]$ (Ln = Sm, 5, light yellow; Ln = La, 7, colorless) and light yellow $[Sm(DippForm)_2(CH_2SiMe_3)(thf)]$ (6) in moderate yields (Scheme 1(ii)). C, H, and N elemental analyses are consistent with the proposed molecular formulas. Their identities have been authenticated by their X-ray crystal structures (see below). IR absorption bands from formamidinate and coordinating thf ligands are evident at frequencies similar to those of the relevant metal halides 2–4.

In the ¹H NMR spectra, the typical sharp singlet resonances of NC(H)N protons in alkyl complexes 5–7 vary over a wide range, with paramagnetic 5 being at frequencies lower than those of 2–4 and that of 6 being near the value of the iodide 4. Diamagnetic 7 has the resonance shifted to higher frequency from the parent fluoride⁷ (see the Experimental Section). Sm–CH₃ (or –CH₂) proton resonances in 5 and 6 are observed as broad singlets, presumably due to the strong paramagnetic effect of the samarium atom in close proximity to the protons.¹⁰ In contrast, La–CH₃ protons of the diamagnetic lanthanum complex 7 show a sharp singlet at 0.22 ppm.

Alkyl complexes 5-7 are among the rare species of amidinate complexes incorporating direct Ln–C bonding.⁵ The lanthanum complex 7 is a rare case of a species with a terminal La–Me bond in organolanthanum chemistry.¹¹ The relatively high decomposition temperatures (ca. 250 °C) for alkyllanthanoid derivatives are attributable to the crowded structures (below). However, the precursor halides have even higher thermal stability, melting without decomposition at ca. 340 °C because of fewer possible decomposition paths in comparison to those for the alkyl derivatives.

Because of our current interest in lanthanoid complexes with bulky polyarylcyclopentadienyl ligands,¹² the ligand exchange reaction of $[La(DippForm)_2Me(thf)]$ (7) with 1,2,3,4tetraphenylcyclopentadiene (H₂C₅Ph₄) was attempted but failed to generate the direct ligand exchange product [La-(DippForm)₂(HC₅Ph₄)] (Scheme 2(i)). Instead, colorless crystalline [La(DippForm)₃] (8) was formed in low yield (Scheme 2(ii)). The formation of the congener of the previously reported samarium complex [Sm(DippForm)₃] is surprising, and the mechanism of the formation is not fully understandable at the current stage. A previous attempt from 3 equiv of the group 1 metal salt ([Na(DippForm)(thf)₃]) and 1 equiv of LnCl₃ failed to deliver the homoleptic complexes.⁶

Scheme 2. Formation of $[La(DippForm)_3]$ (8)



Likewise, the attempted alternative metathesis reaction between $[Ln(DippForm)_2X(thf)]$ (Ln = Sm, X = Cl; Ln = La; X = F) and $[Li(DippForm)(thf)_3]$ in C₆D₆ at 70 °C overnight did not generate the homoleptic complexes, nor did the attempted protolysis reactions between [Ln(DippForm)₂Me(thf)] (Ln = Sm, La) and DippFormH under the same conditions. The unsuccessful transformation to [Ln(DippForm)₃] obviously results from the bulky characteristics of the DippForm ligand. A similar situation was encountered previously in the reactions of [Sm(DippForm)₂(CCPh)(thf)] with carbodiimides, where the reaction goes smoothly with less bulky carbodiimides, giving [Sm(DippForm)₂(RNC(CCPh)NR] (R = mesityl, cyclohexyl), but no reaction occurs with the bulkier $N_i N'$ -bis(2,6diisopropylphenyl)carbodiimide.9 The molecular structures of $[Ln(DippForm)_3]$ (Ln = Sm,⁶ La) impressively display a sterically hindered coordination environment (see Molecular Structures). The bulky nature of the formamidinate ligand makes homoleptic [Ln(DippForm)₃] free of Lewis base molecule coordination. This is in contrast with the less bulky formamidinate complexes, e.g., [La(XylForm)₃(thf)], where a Lewis base molecule coordinates.⁸

The redox transmetalation/protolysis (RTP) reaction of samarium metal with bis(pentafluorophenyl)mercury and $N_{N'}$ bis(2,6-diisopropylphenyl)formamidine in thf also did not yield $[Sm(DippForm)_3]$ but led to the isolation of $[Sm-(DippForm)_2F(thf)]$.⁶ The reaction is considered to proceed through a pathway involving C-F activation, as shown in Scheme 3((i) and (iii); Ar = C_6F_5 ; X = F). The corresponding RTP reaction with bis(2-bromo-3,4,5,6-tetrafluorophenyl)mercury has now been found to yield $[Sm(DippForm)_2Br(thf)]$ (3) and the coproduct $[Sm(DippForm)Br_2(thf)_3]$ (9), both identified by single-crystal X-ray structural determinations from a cocrystallized mixture. The reaction probably involves the intermediate samarium 2-bromo-3,4,5,6-tetrafluorophenyl complex $[Sm(DippForm)_2(2-BrC_6F_4)(thf)]$ (Scheme 3(i), Ar = 2-BrC₆F₄), which undergoes C-Br activation to form [Sm- $(\text{DippForm})_2 \text{Br}(\text{thf})$ (3) (Scheme 3(iii), X = Br). Tetrafluorobenzyne has previously been trapped as an N-functionalized formamidine from analogous but high-yielding RTP reactions.⁸ The isolation of the dibromo(formamidinato)samarium(III) complex coproduct 9 from the RTP reaction is surprising, and it is considered to be formed by C-Br activation of the intermediate $[Sm(DippForm)(2-BrC_6F_4)_2(thf)_n]$ formed in the RTP reaction (Scheme 3(i,i), Ar = 2-BrC₆F₄). The dibromo product 9 is inseparable (apart from hand-picked

Scheme 3. Formation of $[Sm(DippForm)_2X(thf)]$ (3), $[Sm(DippForm)Br_2(thf)_3]$ (9), and $[Sm(DippForm)_2(OCH=CH_2)(thf)]$ (10)^{*a*}



^aLegend: (i) Ar = C_6F_5 ,⁶ 2-Br C_6F_4 , -Hg; (ii) Ar = 2-Br C_6F_4 , X = Br, -2" C_6F_4 "; (iii) Ar = C_6F_5 ,⁶ 2-Br C_6F_4 ; X = F,⁶ Br. -" C_6F_4 "; (iv) HgPh₂, PhMe, 110 °C, Ar = Ph, -Hg; (v) HgPh₂, PhMe, 110 °C, -Hg, -PhH, -CH₂=:CH₂; (vi) thf, Ar = Ph, -PhH, -CH₂=:CH₂.

crystals) from 3 in the mixture, which prohibited more characterization of 9.

As the redox reaction of $[Sm(DippForm)_2(thf)_2]$ (1) with the mercurial reagent $Hg(CCPh)_2$ at ambient temperature afforded the complex [Sm(DippForm)₂(CCPh)(thf)] in good yield (Scheme 3(iv), Ar = CCPh),⁸ the possible synthesis of the analogous [Sm(DippForm)₂Ph(thf)] was attempted (Scheme 3(iv), Ar = Ph). However, the reaction of 1 with HgPh₂ under similar conditions caused no color change from the green samarium(II) complex. Further, NMR spectrum monitoring of the reaction mixture confirmed that no reaction occurred. However, after the reaction mixture was heated to 110 °C, a gradual color change from green to light yellow occurred. Subsequent crystallization gave a mixture of crystals, some of them being identified by X-ray crystallography (see Molecular Structures) as $[Sm(DippForm)_2(OCH=CH_2)(thf)]$ (10) (Scheme 3(v)), in contrast to the isolation of $[Sm(C_5Me_5)_2Ph-$ (thf)] from the reaction of $[Sm(C_5Me_5)_2(thf)_2]$ with HgPh₂.¹³ The mixture was inseparable, prohibiting further characterization. The ethenolate ligand in **10** is plausibly formed through the formation of a reactive Sm–Ph intermediate (Scheme 3(iv), Ar = Ph) which abstracts a proton from thf at 110 $^{\circ}$ C (Scheme 3(vi)). The formation of 10 is not surprising, since similar decomposition processes of thf molecules by other M-C species have been observed previously.¹⁴

Molecular Structures. N_iN' -bis(2,6-diisopropylphenyl)formamidinate complexes $[Ln(DippForm)_2L'(thf)]$ (Ln = Sm, L' = Cl (2), Br (3), I (4), CH₃ (5), CH₂SiMe₃ (6), OC=CH₂ (10); Ln = La, L' = CH₃ (7)) are all mononuclear species, and their molecular structures are shown in Figure 1 (for 3), Figure 2 (for 6), Figure 3 (for 7), and Figure 4 (for 10). The lanthanoid metals are six-coordinate in these heteroleptic species. Both formamidinate ligands in each



Figure 1. (a) Molecular structure of 3 shown with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. (b) Depiction of the coordination core of 3 drawn as sticks with the equatorial Sm1C1C26 plane (marked by dashed lines) orthogonal to the page.



Figure 2. Molecular structure of 6 PhMe shown with 50% thermal ellipsoids. Lattice solvent molecules and hydrogen atoms (excluding those on C51) are omitted for clarity.

molecule are κ^2 -bonded to the metal atom through two nitrogen donor atoms. The coordination geometry of these complexes can be described by a distorted tetrahedron if the formamidinate ligand is considered to be a single-point donor located on the backbone carbon (NCN carbon). These complexes all crystallized in the $P\overline{1}$ space group with a shared isomorphism among samarium halide complexes 2–4 and



Figure 3. Molecular structure of 7 shown with 50% thermal ellipsoids. Hydrogen atoms (excluding those on C51) are omitted for clarity.



Figure 4. Molecular structure of 10 shown with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

samarium/lanthanum methyl complexes **5** and 7 (see the Experimental Section). This isomorphism, however, does not extend to complexes with the larger anionic ligands (trimethylsilyl)methyl (**6**) and ethenolate (**10**) and the smallest halide in the fluoride complex [Sm(DippForm)₂F(thf)] (space group $P2_1/n$ (No. 14), unit cell data a = 20.4714(2) Å, b = 12.1996(2) Å, c = 21.6593(3) Å, $\beta = 110.0650(10)$ Å, V = 5080.93(12) Å³).⁶

The N-aryl groups are nearly orthogonal to the NCN plane (e.g. torsion angles of the two planes for 3 range from 69.8(2)to $84.6(2)^\circ$), values typical of a coordinating amidinate such as DippForm.⁶⁻⁹ The negative charges of anionic formamidinates are delocalized on the NCN cores, as the C-N bond lengths are similar and intermediate between typical single bonds and double bonds (e.g. \sim 1.32 Å in 3). As a result, the two Ln–N bond lengths from the same formamidinate ligand can be very close (e.g., Sm1-N1 = 2.440(5) Å and Sm1-N2 = 2.460(4) Å in 2). However, Ln1-N1 and/or Ln1-N3 bond lengths are generally marginally shorter than values for Ln1-N2 and/or Ln1–N4 bonds (Tables 1 and 2), suggesting that the negative charge of each formamidinate may be slightly asymmetrically distributed. The N1C1N2 and N3C26N4 planes are both more or less perpendicular to the C1Sm1C26 plane according to the individual specific coordination environment (e.g., 75.9(2) and $44.8(2)^{\circ}$ in 3, Figure 1(b)). The mean Sm–N bond lengths are

Table 1. Selected Bond Lengths (Å) and Angles (deg) in 2-4 and 10

	2 , L' = Cl	3, L' = Br	4 , L' = I	10, L' = OCH= CH ₂
Ln1-N1	2.440(5)	2.394(3)	2.3784(15)	2.462(2)
Ln1-N2	2.460(4)	2.462(3)	2.4751(15)	2.472(2)
Ln1-N3	2.404(5)	2.436(4)	2.4238(16)	2.418(2)
Ln1-N4	2.456(4)	2.458(3)	2.4529(15)	2.495(2)
Ln1-X1 ^a	2.5977(16)	2.7508(5)	2.9851(1)	2.109(2)
Ln1-O(thf)	2.453(4)	2.454(3)	2.4535(13)	2.453(2)
O-Sm-X1 ^a	84.79(10)	84.95(7)	85.33(3)	85.46(10)
C1SmC26	132.61(16)	133.17(11)	133.30(5)	131.34(8)
^{<i>a</i>} For 10 , X1 = 0	OCH=CH ₂ .			

Table 2. Selected Bond Lengths (Å) and Angles (deg) in 5–7

	5, L' = Me	6 ·PhMe, $L' = CH_2SiMe_3$	7, $L' = Me$
Ln1-N1	2.436(3)	2.462(3)	2.534(2)
Ln1-N2	2.477(3)	2.502(3)	2.564(2)
Ln1-N3	2.460(2)	2.441(3)	2.506(2)
Ln1-N4	2.478(3)	2.536(3)	2.555(2)
Ln1-C(51)	2.475(3)	2.420(4)	2.508(3)
Ln1-O(thf)	2.467(2)	2.490(2)	2.553(2)
O-Sm-C51	84.19(9)	89.43(11)	84.34(9)
C1SmC26	135.06(9)	129.76(10)	134.33(7)

close in bis(formamidinato)samarium(III) complexes 2–5 (2, 2.44 Å; 3, 2.43 Å; 4, 2.43 Å; 5, 2.46 Å) and 10 (2.46 Å). They are all slightly shorter than in 6 (2.48 Å), a result of the steric effect of the relatively bulkier CH₂SiMe₃ group. These values are comparable to the mean Sm–N bond length in [Sm-(DippForm)₂F(thf)] (2.45 Å).⁶ As expected, they are all shorter than the mean La–N bond length (2.54 Å) in 7, consistent approximately with the different size of the two metals (six-coordinate La is 0.07 Å larger than Sm).¹⁵ The angle between the two bulky amidinates in terms of the nonbonding angle C1–Ln–C26 (e.g., 133.17° for 3) is much larger than the bond angle of the other two less bulky unidentate ligands (e.g., O–Ln–Br = 84.95° for 3).

The Sm-X bond length (X = F, 2.093(2) Å; 6 X = Cl, 2.5977(16) Å; X = Br, 2.7512(5) Å; X = I, 2.9851(1) Å) in these bis(formamidinate) complexes increases according to the size of each halide.¹⁵ The Sm-Cl bond length in 2 is in the range of those closely relevant mononuclear six-coordinate samarium complexes $[Sm(Ap')_2Cl(thf)]$ (2.5681(6) Å, Ap' = $(2,6-diisopropylphenyl)[6-(2,6-dimethylphenyl)pyridin-2-yl]-aminate)^{16}$ and $[Sm\{2-(2,6-^{i}Pr_2-C_6H_3N=CH)-5-^{t}BuC_4H_2N\}_2Cl(thf)]$ (2.625(2) Å).¹⁷ The Sm-Br bond length in 3 (2.7512(5) Å) is comparable with the reported values for seven-coordinate $[SmBr_3(thf)_4]$ (2.8083(4), 2.8314(4), 2.8582(4) Å)¹⁸ after allowing for coordination number differences. The Sm–I bond length in 4 (2.9851(1) Å) is shorter than that in the 1-azaallyl complex [Sm(Me₃SiCH= $C(^{t}Bu)NSiMe_{3}_{2}I(thf)]$ (3.092(1) Å),^{19¹} attributable to either different steric effects or trans influences of the respective chelating ligands. The terminal Sm1-C51(methyl) bond in 5 (2.476(3) Å) is comparable with that of the eight-coordinate $[Sm(C_5Me_5)_2Me(thf)]$ (2.484(14) Å),²⁰ despite the coordination number difference, while the Sm1-C51(methylene) bond distance in 6 (2.420(4) Å) is comparable with that of $[Sm\{2 (2_{1}6^{-i}Pr_{2}-C_{6}H_{3}N=CH)-5^{-i}BuC_{4}H_{2}N\}_{2}(CH_{2}SiMe_{3})(thf)]$

(2.455(4) Å).¹⁷ The La-C(methyl) bond length in 7 (2.508(3)) Å) is slightly longer than the Sm–C length in 5 (2.476(3) Å) but less than that expected for the different metal size, implying considerable steric strain in the Sm complex. However, there is no closely relevant reported terminal La-C(methyl) bond length for comparison.¹¹ The bond length is similar to that of a discrete cation in $[LaMe(thf)_6][B(C_6H_4F-4)_4]_2$ (2.456(6) Å).²¹ The Sm-O(thf) bond lengths of all bis(formamidinate) complexes are in the close range of 2.45-2.49 Å, and they are, as expected, longer than the Sm-OCH=CH₂ (anionic) bond in 10 (2.111(3) Å). The Sm-O bond length of the anionic ethenolate is comparable with that in Yb-O-(ethenolate) (2.069 Å) in the four-coordinate [Yb{N(SiMe3)- $C_6H_3^{i}Pr_2-2,6\}_2(OCHCH_2)ClLi(thf)_3]^{22}$ and Sc–O(ethenolate) (1.90 Å) in the four-coordinate diketiminate [Sc-{2,6-ⁱPr₂C₆H₃NC(Me)CHC(Me)N-C₆H₃ⁱPr₂-2,6}-(NHC₆H₃ⁱPr₂-2,6)(OCHCH₂)],²³ after consideration of metal size and coordination number differences.

The homoleptic tris(formamidinato)lanthanum complex $[La(DippForm)_3]$ (8) crystallized in space group $P2_1/n$ (Figure 5 and Table 3) and is isomorphous with its samarium congener



Figure 5. (a) Molecular structure of $8 \cdot 2C_6 D_6$. PhMe shown with 50% thermal ellipsoids. Isopropyl groups on arene rings are drawn as sticks, and hydrogen atoms and lattice solvent molecules are omitted for clarity. (b) Depiction of coordination core of 8 as sticks with the C1C26C51 plane in the plane of the page.

 $[Sm(DippForm)_3]$.⁶ If the amidinate ligand is treated as a single donor ligand located on the backbone carbon (NCN), the geometry of the coordination of samarium can be described as almost perfectly trigonal planar ($\sum(C-Sm-C \text{ angles}) = 359.9^\circ$). As seen previously for the structure of $[Sm-(DippForm)_3]$, the sterically hindered coordination environ-

Table 3. Selected Bond Lengths (Å) and Angles (deg) in 8 and 9

[La(DippForm) ₃] (8)		[Sm(DippForm)Br ₂ (thf) ₃] (9·PhMe)		
Ln1-N1	2.538(2)	Ln1-N1	2.434(3)	
Ln1-N2	2.558(2)	Ln1-N2	2.465(3)	
Ln1-N3	2.541(2)	Ln1-Br1	2.8331(4)	
Ln1–N4	2.546(2)	Ln1-Br2	2.8395(4)	
Ln1-N5	2.544(2)	Ln1–O1(thf)	2.449(2)	
Ln1–N6	2.562(2)	Ln1-O2(thf)	2.514(2)	
		Ln1-O3(thf)	2.476(2)	
C1…La1…C26	119.00(7)	Br1-Sm1-Br2	166.614(13)°	
C26…La1…C51	121.20(7)	O1-Sm1-O3	$148.00(8)^{\circ}$	
C1…La1…C51	119.79(7)	O2-Sm1…C1	177.23(8)°	

ment results in a dramatic deviation of the arene rings from perpendicular to the metallacycle NCNLn, e.g. the torsion angles of two planes for 8 range from 57.1(1) to $63.0(2)^{\circ}$, in contrast with the bis(amidinate) complexes 2–7 and 10, where the *N*-aryl rings are nearly orthogonal to the NCNLn plane. The mean La–N bond length (2.54 Å) is similar to the mean distances of $[La({}^{t}BuNC(Me)NBu^{t})_{3}]$ (2.54 Å)²⁴ and $[La(2,6-Et_{2}C_{6}H_{3}NC(H)NC_{6}H_{3}-Et_{2}2,6)_{3}]$ (2.52 Å)⁸ and the bis(amidinato)lanthanum complex 7 (2.54 Å).

The mono(formamidinate) samarium dibromide complex $[Sm(DippForm)Br_2(thf)_3]$ (9) crystallized in the *Pbca* space group. The seven-coordinate samarium complex also adopts a mononuclear form (Figure 6 and Table 3). As can be seen from



Figure 6. Molecular structure of 9 shown with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

the aforementioned bis(formamidinato)lanthanoid complexes, the formamidinate in this complex is similarly κ^2 bonded to the metal atom through two nitrogen donor atoms. The mean Sm– N bond length (2.45 Å) is close to that in the six-coordinate monobromo samarium complex 3 (2.43 Å), but the mean Sm– Br bond length (2.84 Å) is longer than in 3 (2.7512(5) Å), and the former is in the range of Sm–Br bond lengths of [SmBr₃(thf)₄] (2.8083(4), 2.8314(4), 2.8582(4) Å).¹⁸ If the amidinate ligand is treated as a single donor ligand located on the backbone carbon (NCN), the geometry of the coordination of samarium can be described as distorted octahedral with two bromides occupying two vertices in a near-trans array (Br1– Sm1–Br2 = 166.614(13)°). The Br₂(thf)₃ array is similar to that of the $[LnCpBr_2(thf)_3]$ complexes,²⁵ suggesting an analogy between tridentate Cp and the bulky bidentate DippForm ligand.

CONCLUSION

Rare species of alkyl samarium/lanthanum amidinate complexes with an uncommon terminal La-Me bond have been synthesized in satisfactory yields. The very bulky anionic N_iN' bis(2,6-diisopropylphenyl)formamidinate ligand has shown the ability to stabilize bis(formamidinato)samarium/lanthanum halide (2-4) and alkyl (5-7) complexes, where two amidinate ligands are capping the metal atom each through κ^2 bonding from two nitrogen donors. The bonding modes act effectively so that the remaining coordination sites of the lanthanoid metal are occupied by either a halide or an alkyl ligand and an additional Lewis base molecule (thf). A very low yield of the homoleptic tris(formamidinato)lanthanum complex 8 was isolated, and the molecule shows a sterically hindered coordination environment. The synthesis of bulky 8 has proven to be a challenge, as several alternative attempts (including metathesis reactions) were unsuccessful. The mono-(formamidinato)samarium dibromide complex 9 was identified from an RTP reaction, and the complex incorporates a sevencoordinate metal atom rather than the six-coordinate metals seen in bis- or tris(formamidinate) complexes 2-8.

EXPERIMENTAL SECTION

General Considerations. The compounds described herein were prepared and handled under dinitrogen with conventional techniques. IR spectra were recorded as Nujol mulls between NaCl plates using either a Perkin-Elmer 1600 Series FTIR instrument or a Perkin-Elmer Spectrum RX I FTIR spectrometer within the range 4000-600 cm⁻¹. ¹H NMR spectra were recorded on a Bruker DPX 300 spectrometer, and chemical shifts were referenced to the residual ¹H resonances of the deuterated solvents. Melting points were determined in sealed glass capillaries under nitrogen and are uncalibrated. Microanalyses were determined by the Campbell Microanalytical Service, University of Otago (New Zealand). Toluene, hexane, and thf were predried over sodium metal and distilled over sodium (for toluene) or sodium benzophenone ketyl (hexane and thf) before being stored under an atmosphere of nitrogen. C₆D₆ was dried over sodium and stored under an atmosphere of nitrogen. tert-Butyl chloride, 1,2-dibromoethane, MeLi (1.60 M in diethyl ether), LiCH₂SiMe₃ (1.0 M in pentane), and HgPh₂ were purchased from Aldrich, and iodine was obtained from Merck; all were used as supplied. Lanthanoid metals were purchased from Santoku (America Int.) or Tianjiao (Baotou, People's Republic of China) as ingots, powders, or rods and stored under nitrogen in a glovebox. $[Sm(DippForm)_2(thf)_2]$ (1),⁹ $[La(DippForm)_2F(thf)]$,⁷ tetraphenylcyclopentadiene, ²⁶ $[Li(DippForm)(thf)_3]$, ²⁷ Dipp-FormH, ²⁸ and Hg(2-BrC₆F₄), ²⁹ were prepared by literature methods.

Synthesis of $[Sm(DippForm)_2Cl(thf)]$ (2). A solution of *tert*-butyl chloride (0.10 g, 1.1 mmol) in toluene (10 mL) was added with stirring at ambient temperature to a green solution of $[Sm(DippForm)_2(thf)_2]$ (1; 1.02 g, 1.0 mmol) in toluene (40 mL). The solution turned light yellow in 5 min, and the mixture was stirred continuously for $^{1}/_{2}$ h. The solution was reduced in volume to 5 mL under vacuum and stored at -30 °C for 2 days, during which time light yellow crystalline 2 precipitated and was collected (yield: 0.83 g, 91%). Mp: 330–334 °C. Anal. Calcd for C₅₄H₇₈ClN₄OSm (985.04): C, 65.84; H, 7.98; N, 5.69. Found: C, 65.66; H, 7.84; N, 5.55. IR (Nujol, cm⁻¹): 1666 w (ν (CN)), 1592 w, 1520 w and 1506 w (ν (CC)), 1316 m, 1278 m, 1192 w (β (CH)), 1109 w, 1098 w, 1056 w (ν (C–O), thf), and 1016 m (β (CH)), 943 w, 862 w (ring mode, thf), 800 w, 775 w, 757 m (γ (CH)). ¹H NMR (C₆D₆, 303 K, ppm): 0.50 (s, broad, 24H, CH₃), 1.39 (s, broad, 28H, CH₃ + thf), 3.15 (m, broad,

Table 4. Crystal Data and Structure Refinement Details for Complexes 2-10

	$ \begin{bmatrix} Sm(DippForm)_2 \\ Cl(thf) \end{bmatrix} (2) $	$\begin{bmatrix} Sm(DippForm)_2 \\ Br(thf) \end{bmatrix} (3)$		$\begin{bmatrix} Sm(DippForm)_2 \\ Me(thf) \end{bmatrix} (5)$	[Sm(DippForm) ₂ (CH ₂ SiMe ₃) (thf)]·PhMe (6 ·PhMe)
formula	C54H78ClN4OSm	$\mathrm{C}_{54}\mathrm{H}_{78}\mathrm{BrN}_{4}\mathrm{OSm}$	C54H78IN4OSm	$\mathrm{C}_{55}\mathrm{H}_{81}\mathrm{N}_{4}\mathrm{OSm}$	C ₆₅ H ₉₇ N ₄ OSiSm
$M_{ m r}$	985.00	1029.46	1076.45	964.64	1128.91
space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a (Å)	11.283(2)	11.4129(2)	11.6940(2)	11.238(2)	12.858(3)
b (Å)	14.597(3)	14.5854(3)	14.5418(2)	14.685(3)	13.488(3)
c (Å)	16.373(3)	16.3356(3)	16.2892(3)	16.382(3)	18.772(4)
α (deg)	84.14(3)	83.9810(10)	83.4130(10)	83.97(3)	108.51(3)
β (deg)	77.90(3)	77.8760(10)	77.4830(10)	77.94(3)	93.48(3)
γ (deg)	80.80(3)	80.5180(10)	79.7300(10)	80.91(3)	95.08(3)
V (Å ³)	2596.1(9)	2615.31(9)	2652.49(8)	2603.4(9)	3061.4(11)
Ζ	2	2	2	2	2
$\mu \text{ (mm}^{-1})$	1.222	1.926	1.727	1.167	1.021
$ ho_{ m calcd}~(m g~cm^{-3})$	1.260	1.307	1.348	1.231	1.225
$N_{ au}$	24021	29084	40351	28121	46141
$N(R_{int})$	9124 (0.1229)	11910 (0.0766)	12012 (0.0313)	11914 (0.0667)	14001 (0.0945)
$\frac{\text{R1/wR2}}{2\sigma(I)} (I > 1)$	0.0659/0.0825	0.0458/0.0958	0.0225/0.0466	0.0442/0.0839	0.0508/0.1078
R1/wR2 (all data)	0.0971/0.1335	0.0766/0.1092	0.0280/0.0487	0.0666/0.0904	0.0806/0.1191
GOF	0.965	1.017	1.033	1.005	1.013
$\max/\min_{\text{\AA}^{-3}} \Delta e$ (e	0.967/-0.777	1.410/-1.825	0.426/-0.490	1.253/-0.953	0.127/-1.007
	[La(DippForm) ₂ Me(thf)] (7)	$ [La(DippForm)_3] \cdot (8 \cdot 2C_6 D_6 \cdot P_6)] $	2C ₆ D ₆ ∙PhMe hMe)	$ \begin{matrix} [Sm(DippForm)Br_2(thf)_3] \cdot PhMe \\ (9 \cdot PhMe) \end{matrix} $	$ \begin{array}{c} [Sm(DippForm)_2(OCH=CH_2) \\ (thf)] (10) \end{array} $
formula	$\mathrm{C}_{55}\mathrm{H}_{81}\mathrm{N}_4\mathrm{OLa}$	C ₉₄ H ₇₇ D ₄₈	N ₆ La	$C_{44}H_{67}Br_2N_2O_3Sm$	$C_{56}H_{81}N_4O_2Sm$
$M_{ m r}$	953.15	1477.98		982.17	992.60
space group	$P\overline{1}$	$P2_1/n$		Pbca	$P\overline{1}$
a (Å)	11.2278(2)	13.033(3)		19.5632(3)	12.2755(3)
b (Å)	14.7760(3)	37.741(8)		19.1357(3)	14.0703(3)
c (Å)	16.4311(3)	16.757(3)		23.8446(4)	17.8816(5)
α (deg)	83.683(1)	90		90	78.3150(10)
β (deg)	77.954(1)	96.42(3)		90	69.9430(10)
γ (deg)	80.980(1)	90		90	67.8920(10)
$V(Å^3)$	2624.51(9)	8191(3)		8926.4(2)	2678.30(11)
Ζ	2	4		8	2
$\mu ({\rm mm^{-1}})$	0.853	0.570		3.144	1.138
$\rho_{\rm calcd} \ ({\rm g \ cm^{-3}})$	1.206	1.208		1.462	1.231
N_{τ}	32704	89472		63397	62130
$N(R_{\rm int})$	12055 (0.0554)	18757 (0.0	663)	10226 (0.0959)	12287 (0.0401)
$\frac{\text{R1/wR2}}{2\sigma(I)} (I > 2\sigma(I))$	0.0408/0.0720	0.0464/0.1	058	0.0379/0.0822	0.0367/0.0780
R1/wR2 (all data)	0.0582/0.0764	0.0730/0.1	130	0.0724/0.0936	0.0432/0.0825
GOF	1.014	1.019		0.978	1.068
$\max/\min_{\text{\AA}^{-3}} \Delta e \ (e$	0.093/-0.693	0.086/-0.7	711	1.314/-0.979	1.314/-0.979

8H, CH, Pr^i), 3.70 (s, 4H, thf), 7.20–7.48 (m, 12H, C_6H_3), 12.16 (s, 2H, NC(H)=N).

Synthesis of [Sm(DippForm)₂Br(thf)] (3). (a) A solution of 1,2dibromoethane (0.10 g, 0.50 mmol) in toluene (10 mL) was added with stirring at ambient temperature to a green solution of $[Sm(DippForm)_2(thf)_2]$ (1; 1.02 g, 1.0 mmol) in toluene (40 mL). The solution turned light yellow gradually, and the mixture was stirred continuously for $^{1}/_{2}$ h. The solution was reduced in volume to 3 mL under vacuum and stored at ambient temperature for 2 days, during which time light yellow crystalline **3** precipitated and was collected (yield: 0.80 g, 78%). Mp: 336–340 °C. Anal. Calcd for $C_{54}H_{78}BrN_4OSm$ (1029.46): C, 63.00; H, 7.64; N, 5.44. Found: C, 62.95; H, 7.75; N, 5.56. IR (Nujol, cm⁻¹): 1667 w, 1592 w, 1518 m, 1316 m, 1276 m, 1191 w, 1108 w, 1055 w, 1043 w, 1014 m, 942 w, 860 w, 800 m, 757 s, 670 w. ¹H NMR (C_6D_{6} , 303 K, ppm): 0.11 (s, broad, 24H, CH₃), 1.11 (s, broad, 24H, CH₃), 1.34 (s, broad, 4H, thf), 2.91 (m, broad, 8H, CH, Prⁱ), 3.86 (s, 4H, thf), 7.27–6.85 (m, 12H) C₆H₃), 12.35 (s, 2H, NC(H)=N). ¹H NMR (C₆D₆, 333 K, ppm): 0.68 (s, broad, 48H, CH₃), 1.36 (s, 4H, thf), 2.85 (s, broad, 8H, CH, Prⁱ), 4.46 (s, 4H, thf), 7.04–7.50 (m, 12H, C₆H₃), 12.51 (s, 2H, NC(H)=N). The unit cell was determined and is similar to that of **3** given in Table 4: space group $P\overline{1}$, a = 11.4407 Å, b = 14.6045 Å, c = 16.3514 Å, $\alpha = 83.876^{\circ}$, $\beta = 77.848^{\circ}$, $\gamma = 80.520^{\circ}$, V = 2627.04 Å³.

(b) A solution of 1-bromo-2,3,4,5-tetrafluorobenzene in thf (0.008 M, 45 mL, 0.36 mmol) was added dropwise with stirring to a dark green solution of $[Sm(DippForm)_2(thf)_2]$ (1; 0.37 g, 0.36 mmol) in thf (30 mL), at ambient temperature. After 1 h, the resulting light yellow solution was filtered, dried in vacuo, and extracted into the minimum volume of toluene (ca. 2 mL). Light yellow blocks of 3 deposited after standing for several days (yield 0.16 g, 43%), and the X-ray crystal structure was determined.

Synthesis of $[Sm(DippForm)_2](thf)]$ (4). A solution of iodine (0.13 g, 1.0 mmol) in toluene (10 mL) was added with stirring at ambient temperature to a green solution of $[Sm(DippForm)_2(thf)_2]$

(1; 1.02 g, 1.0 mmol) in toluene (40 mL). The solution turned light yellow gradually, and the mixture was stirred continuously for $1/_2$ h. The solution was reduced in volume to 10 mL under vacuum and stored at -30 °C for 2 days, during which time light yellow crystalline 4 precipitated and was collected (yield: 0.87 g, 81%). Mp: 338–342 °C. Anal. Calcd for C₅₄H₇₈IN₄OSm (1076.51): C, 60.25; H, 7.30; N, 5.20. Found: C, 60.20; H, 7.37; 5.22. IR (Nujol, cm⁻¹): 1667 w, 1592 w, 1519 s, 1361 w, 1316 m, 1277 m, 1235 w, 1191 m, 1108 w, 1055 w, 1043 w, 1013 w, 943 w, 859 w, 800 m, 775 w, 757 m. ¹H NMR (C₆D₆, 303 K, ppm): 0.16 (s, broad, 24H, CH₃), 1.20 (s, broad, 24H, CH₃), 1.80 (s, 4H, thf), 3.03 (m, broad, 8H, CH, Prⁱ), 4.63 (s, 4H, thf), 7.14–7.50 (m, 12H, C₆H₃), 13.07 (s, 2H, NC(H)=N). ¹H NMR (C₆D₆, 333 K, ppm): 0.71 (s, broad, 48H, CH₃), 1.73 (s, 4H, thf), 2.98 (s, broad, 8H, CH, Prⁱ), 4.46 (s, 4H, thf), 7.14–7.50 (m, 12H, C₆H₃), 13.15 (s, 2H, NC(H)=N).

Synthesis of [Sm(DippForm)₂Me(thf)] (5). A solution of methyllithium in diethyl ether (1.6 M, 0.80 mL, 1.3 mmol) was added to a solution of [Sm(DippForm)₂Cl(thf)] (2; 0.91 g, 1.0 mmol) in toluene (20 mL) with stirring at ambient temperature. The mixture was stirred continuously for 1/2 h. The solvent was removed under vacuum and replaced by toluene (30 mL). The insoluble precipitate was filtered off, and the volume of the solution was reduced to 5 mL under vacuum. The solution was stored at -30 °C for 2 days, during which time bright yellow crystalline 5 precipitated and was collected (yield: 0.48 g, 50%). Dec pt: 258 °C. Anal. Calcd for C55H81N4OSm (964.62): C, 68.48; H, 8.46; N, 5.81. Found: C, 68.21; H, 8.19; N, 5.66. IR (Nujol, cm⁻¹): 1667 w, 1592 w, 1522 s, 1361 w, 1315 m, 1280 m, 1192 m, 1109 w, 1098 w, 1056 w, 1044 w, 1024 w, 942 w, 868 w, 801 m, 774 w, 757 s, 728 w, 671 w. ¹H NMR (C₆D₆, 303 K, ppm): 0.33 (s, 4H, thf), 1.03 (s, 48H, CH₃, Prⁱ), 1.91 (s, br, 3H, CH₃), 2.16 (s, 4H, thf), 3.16 (s, 8H, CH, Prⁱ), 6.95-7.32 (m, 12H, C₆H₃), 10.83 (s, 2H, NC(H)=N).

Synthesis of [Sm(DippForm)₂(CH₂SiMe₃)(thf)] (6). A solution of ((trimethylsilyl)methyl)lithium in pentane (1.0 M, 1.2 mL, 1.2 mmol) was added to a solution of [Sm(DippForm)₂Cl(thf)] (2; 0.91 g, 1.0 mmol) in toluene (30 mL) with stirring at ambient temperature. The mixture was stirred continuously for $1/_{2}$ h. The precipitate was filtered off, and the solution was reduced in volume to 5 mL under vacuum. The solution was stored at -30 °C for 2 days, during which time yellow crystals of 6.PhMe precipitated and were collected (yield: 0.60 g, 53%). Dec pt: 256 °C. Anal. Calcd for C₆₅H₉₇N₄OSiSm (1128.94): C, 69.15; H, 8.66; N, 4.96. Found: C, 69.04; H, 8.74; N, 5.33. IR (Nujol, cm⁻¹): 1666 m (ν (CN)), 1593 w and 1526 s $(\nu(CC))$, 1362 w, 1317 m, 1286 s, 1251 w, 1238 m, 1187 m $(\beta(CH))$, 1108 w, 1054 w (ν (CO, thf)), 1044 w, and 1022 m (β (CH)), 940 m, 866 m (ring mode, thf), 800 m, 768 m, 755 m (γ(CH)), 728 m, 694 w, 673 w. ¹H NMR (C₆D₆, 333 K, ppm): -0.01 (s, br, 2H, CH₂Si), 0.11 (s, 9H, SiCH₃), 0.68 (s, 48H, CH₃, Prⁱ), 1.04 (s, 4H, thf), 2.11 (s, 3H, CH₃, PhMe), 2.71 (s, 8H, CH, Prⁱ), 3.29 (s, 4H, thf), 6.75-7.13 (m, 17H, $C_6H_3 + C_6H_5$), 12.92 (s, br, 2H, NC(H)=N).

Synthesis of [La(DippForm)₂Me(thf)] (7). A solution of methyllithium in diethyl ether (1.6 M, 0.8 mL, 1.3 mmol) was added to a solution of [La(DippForm)₂F(thf)] (0.96 g, 1.0 mmol) in toluene (20 mL) with stirring at ambient temperature. The mixture was stirred continuously for 1/2 h. The solvent was removed under vacuum and replaced by toluene (30 mL). The precipitate was filtered off, and the solution was reduced in volume to 5 mL under vacuum. The solution was stored at -30 °C for 2 days, during which time colorless crystals of 7 precipitated and were collected (0.46 g, 48%). Anal. Calcd for C555H81N4OLa (953.16): C, 69.30; H, 8.57; N, 5.88. Found: C, 68.41; H, 8.61; N, 5.78. IR (Nujol, cm⁻¹): 1667 w $(\nu(CN))$, 1592 w and 1518 s $(\nu(CC))$, 1361 w, 1314 m, 1284 s, 1233 w, 1190 s (β (CH)), 1108 w, 1098 w, 1056 w (ν (CO), thf), 1043 w and 1025 w (β (CH)), 1013 w, 940 m, 868 m (ring mode, thf), 822 w, 800 m, 774 m, 757 m (γ (CH)), 728 w, 669 w. ¹H NMR (C₆D₆, 303 K, ppm): 0.22 (s, 3H, CH₃), 0.98 (m, br, 4H, thf), 1.24 (d, 48H, CH₃, Pr^{i}), 3.55 (m, 12H, CH(Pr^{i}) + CH₂(thf)), 6.98–7.12 (m, 12H, C₆H₃), 8.21 (s, 2H, NC(H)=N).

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mL) in a J. Young valve equipped NMR tube. The mixture was heated to 70 $^{\circ}$ C and kept at this temperature overnight. The mixture was stored for 1 week at ambient temperature, during which time colorless rod-shaped crystals deposited that were sufficient for an X-ray crystal structure determination.

Attempted Reaction of $[Sm(DippForm)_2Cl(thf)]$ (2) or $[La-(DippForm)_2F(thf)]$ with $[Li(DippForm)(thf)_3]$. C_6D_6 (0.7 mL) was added to a J. Young valve equipped NMR tube charged with $[Sm(DippForm)_2Cl(thf)]$ (2) or $[La(DippForm)_2F(thf)]$ (0.030 g) and $[Li(DippForm)(thf)_3]$ (0.030 g). The mixture was heated to 70 °C and kept at this temperature overnight. ¹H NMR spectroscopy showed only two starting compounds and no appreciable new species formed.

Attempted Reaction of $[Sm(DippForm)_2Me(thf)]$ (5) or $[La(DippForm)_2Me(thf)]$ (7) with DippFormH. C_6D_6 (0.7 mL) was added to a J. Young valve equipped NMR tube charged with $[Sm(DippForm)_2Me(thf)]$ (5) or $[La(DippForm)_2Me(thf)]$ (7) (0.030 g) and DippFormH (0.030 g). The mixture was heated to 70 °C and kept at this temperature overnight. ¹H NMR spectroscopy showed only the two starting compounds and no appreciable new species formed.

Synthesis of [Sm(DippForm)Br₂(thf)₃] (9). Tetrahydrofuran (20 mL) was added to a Schlenk flask charged with freshly filed Sm metal (0.09 g, 0.60 mmol), Hg(2-BrC₆F₄)₂ (0.20 g, 0.30 mmol), and DippFormH (0.22 g, 0.60 mmol). The resulting slurry was stirred overnight to give a light burgundy reaction mixture. Filtration followed by removal of reaction volatiles in vacuo afforded an oily brown solid that was extracted into toluene (10 mL); the extract was concentrated to the point of crystallization and left to stand at ambient temperature. Light yellow prisms of $9 \cdot C_7 H_8$ and blocks of 3 codeposited after standing for several days. The mixture is inseparable, which prohibited the isolation of a bulk amount of 9 and its further characterization.

Synthesis of $[Sm(DippForm)_2(OCH=CH_2)(thf)]$ (10). A Schlenk flask was charged with $[Sm(DippForm)_2(thf)_2]$ (1; 0.50 g, 0.50 mmol), diphenylmercury (0.090 g, 0.25 mmol), and toluene (20 mL). The mixture was heated to 110 °C and kept at this temperature overnight. The volume of the solution was reduced to 2 mL under vacuum and stored for 1 week, during which time light yellow solid products precipitated. The precipitate contains light yellow crystals of 10, which were identified by X-ray crystallography. However, 10 was inseparable from the rest of the mixture, which prohibited other characterization.

X-ray Crystal Structure Determinations. Crystals were mounted in paraffin oil on glass fibres or cryoloops. Intensity data were collected on an Enraf-Nonius Kappa CCD diffractometer (3, 5, 6, and 9) or a Bruker X8 APEX II CCD diffractometer (2, 4, 7, and 10) using Mo K α radiation at 123 K ($\lambda = 0.71073$ Å). The data sets were empirically corrected for absorption with SORTAV³⁰ or SADABS.³¹ The data of compound 8 were collected on the Australian Synchrotron MX1 beamline at 100 K with wavelength $\lambda = 0.712$ Å using the BlueIce³² GUI and processed with the XDS³³ software package. All structures were solved by conventional methods and refined by fullmatrix least squares on all F^2 data using SHELX97,³⁴ in conjunction with the X-Seed graphical user interface.³⁵ Anisotropic thermal parameters were refined for non-hydrogen atoms, and hydrogen atoms on carbons were calculated and refined with a riding model. Crystal data collection and refinement details are given in Table 4.

ASSOCIATED CONTENT

Supporting Information

CIF files giving crystal data for 2-10. 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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