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Synthesis of Dianionic β-Diketiminate Lanthanide Amides $L'LnN(SiMe_3)_2(THF)$ by Deprotonation of the β-Diketiminate Ligand L (L = $\{[(2,6\text{-}iPr_2C_6H_3)NC(CH_3)]_2CH\}^-$) and the Transformation with $[HNEt_3][BPh_4]$ to the Cationic Samarium Amide $[LSmN(SiMe_3)_2][BPh_4]$

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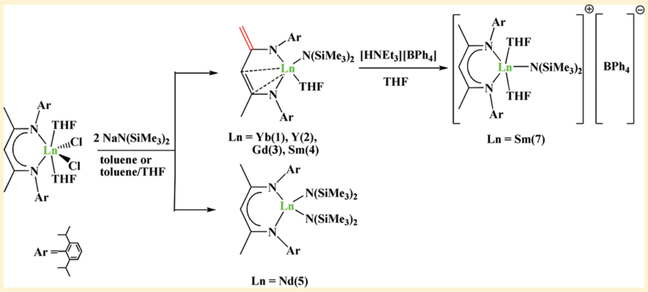
Supporting Information



ABSTRACT: Reaction of β-diketiminate lanthanide dichlorides $LLnCl_2(THF)_2$ (L = $\{[(2,6\text{-}iPr_2C_6H_3)NC(CH_3)]_2CH\}^-$) with 2 equiv of $NaN(SiMe_3)_2$ in toluene afforded lanthanide amide complexes supported by a dianionic β-diketiminate ligand L′, $L'LnN(SiMe_3)_2(THF)$ (L′ =$\{(2,6\text{-}iPr_2C_6H_3)NC(CH_2)CHC(CH_3)N(2,6\text{-}iPr_2C_6H_3)\}^{2-}$, Ln = Yb (**1**), Y (**2**), Gd (**3**), Sm (**4**)), in moderate yields via deprotonation of L. Addition of a small amount of THF led to an increase of the yields of **1**−**4**. Lanthanide metals have a great influence on the deprotonation of L. The same reaction with $LNdCl_2(THF)_2$ did not afford the analogous complex $L'NdN(SiMe_3)_2(THF)$, but the normal diamide complex $LNd[N(SiMe_3)_2]_2$ (**5**) was isolated instead. The metathesis reaction of the triply bridged dichlorides of Sm, $LSmCl(\mu\text{-}Cl)_3SmL(THF)$, with 2 equiv of $NaN(SiMe_3)_2$ yielded the diamide complexes $LSm[N(SiMe_3)_2]_2$ in toluene, while complex **4** was formed instead in a mixture of toluene and THF. In contrast, the same reactions with $LYbCl(\mu\text{-}Cl)_3YbL(THF)$ either in toluene or in a mixture of toluene and THF both afforded **1**. Treatment of **4** with $[HNEt_3][BPh_4]$ in THF at room temperature gave the novel cationic Sm β-diketiminate amide complex $[LSmN(SiMe_3)_2(THF)_2][BPh_4]$ (**7**) in good yield. Complexes **1**−**5** and **7** have been confirmed by single-crystal X-ray structural analyses. The mechanism of deprotonation of L was discussed.

■ INTRODUCTION

Monoanionic β-diketiminates have been widely used in organolanthanide chemistry as versatile spectator ligands, stabilizing various Ln-active groups due to their strong binding to the lanthanide metals and tunable electronic and steric factors.[1] However, these monoanionic β-diketiminate ligands themselves can participate in transformations under certain conditions, including deprotonation via an amine[2a] or an alkane elimination[2b−f] or an β-diketiminate elimination to a dianionic ligand,[3a,b] reduction to a di- or trianionic ligand,[4a−e] and oxidation to a dimer or a proligand.[4f] In particular, the dianionic β-diketiminate ligands formed are highly reactive.[3a,5] The reactivity of L′TmL toward ammonium borate led to the direct preparation of cationic β-diketiminate Tm complexes $[TmL_2][BPh_4]$ and $[TmL_2][B(C_6F_5)_4]$ in good yields via protonation of L′.[3a]

Cationic organometallic complexes of lanthanide have attracted increasing attention, as the reactivity of these complexes in catalytic and stoichiometric reactions has often led to improved activity with respect to their neutral analogues and in some cases allowed the development of completely new synthetic pathways.[6] However, the syntheses of cationic lanthanide amide complexes are still limited. The cationic species of lanthanide amides have been mentioned by abstraction of the amido ligand using ammonium borate[7a] and trityl borate,[7b] but no molecular structures were reported. Recently, the first structurally characterized cationic Sc amide complexes of $(2\text{-Me-Ind})Sc\{N(SiMe_3)_2\}(PhNMe_2)]^+[B(C_6F_5)_4]^-$ and $[(2\text{-Me-Ind})Sc\{N(SiMe_3)_2\}(THF)_2]^+[B(C_6F_5)_4]^-$ were formed via the unexpected abstraction of an indenyl group.[7c] Therefore, we attempted to synthesize isolable cationic lanthanide amides by protonation of a dianionic β-diketiminate lanthanide amide complex by ammonium borate with the aim of searching for a convenient route for the preparation of cationic β-diketiminate lanthanide amides.

The deprotonation of monoanionic β-diketiminate ligand by the highly hindered base $NaN(SiMe_3)_2$ was first described in 2001.[2a] In that case the dianionic β-diketiminate Sc amide formed was unstable and transferred immediately to a binuclear

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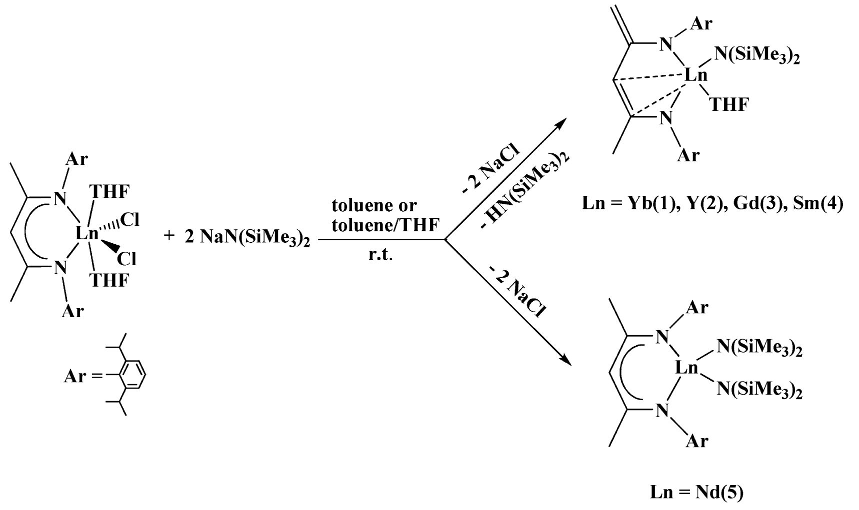
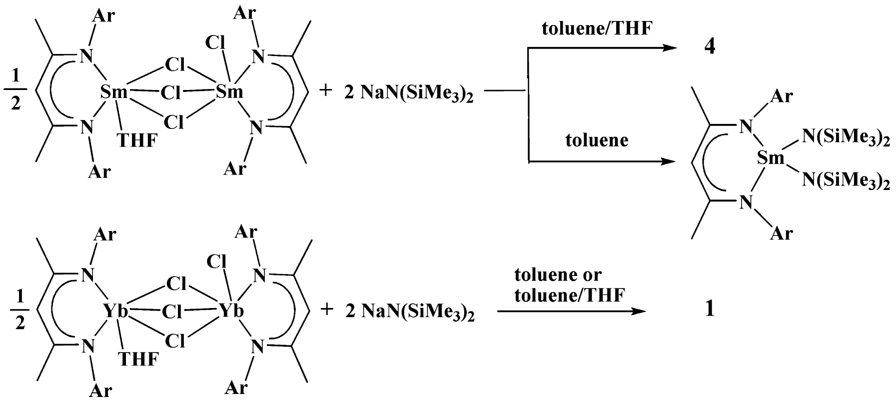
Scheme 1. Reaction of $LLnCl_2(THF)_2$ with $NaN(SiMe_3)_2$: Influence of Lanthanide Metals



Scheme 2. Reaction of $LLnCl(\mu\text{-}Cl)_3LnL(THF)$ with $NaN(SiMe_3)_2$: Influence of the Lanthanide Metals



Sc amide complex via dimerization of the newly formed highly reactive dianionic β-diketiminate ligand.[2a] Thus, no dianionic β-diketiminate lanthanide amide complex could be used to date.

In a continuation of our study on the reactivity of β-diketiminate ligands in a sterically demanding complex,[4e,8] we found that the dianionic β-diketiminate lanthanide amide complexes $L'LnN(SiMe_3)_2(THF)$ ($L' = \{(2,6\text{-}i\text{Pr}_2C_6H_3)NC(CH_2)CHC(CH_3)N(2,6\text{-}i\text{Pr}_2C_6H_3)\}^{2-}$, Ln = Yb (**1**), Y (**2**), Gd (**3**), Sm (**4**)) could be synthesized by the reaction of $LLnCl_2(THF)_2$ with 2 equiv of $NaN(SiMe_3)_2$, via deprotonation of the L ligand ($L = \{(2,6\text{-}i\text{Pr}_2C_6H_3)NC(CH_2)CHC(CH_3)N(2,6\text{-}i\text{Pr}_2C_6H_3)\}$ by the $-N(SiMe_3)_2$ group. The deprotonation reaction is greatly influenced by the size of the central metals. For the large Nd metal the deprotonation of L did not occur in any cases. In contrast, the deprotonation product **1** was isolated as the only product in all the cases with the small Yb metal. For the medium-sized Sm metal, the presence of THF molecules is crucial for the occurrence of a deprotonation reaction. The cationic amide complex $[LSmN(SiMe_3)_2(THF)_2]^+[BPh_4]^-$ (**7**) could be synthesized in high yield by the reaction of **4** with $[HNEt_3][BPh_4]$. Here we wish to report the results, and the pathway for the deprotonation of L is also discussed.

■ RESULTS AND DISCUSSION

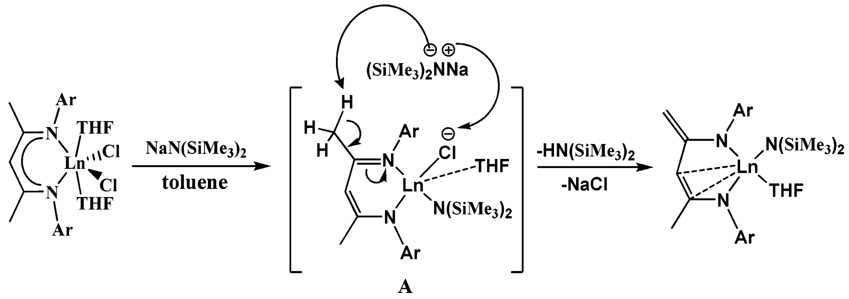
Synthesis and Molecular Structures of Dianionic β-Diketiminate Lanthanide Amide Complexes $L'LnN(SiMe_3)_2(THF)$ ($L' = \{(2,6\text{-}i\text{Pr}_2C_6H_3)NC(CH_2)CHC(CH_3)N(2,6\text{-}i\text{Pr}_2C_6H_3)\}^{2-}$; Ln = Yb (1), Y (2), Gd (3), Sm (4)): Influence of the Lanthanide Metals. The reaction of $LYbCl_2(THF)_2$ ($L = \{[(2,6\text{-}i\text{Pr}_2C_6H_3)NC(CH_3)]_2CH\}^-$) with 2 equiv of $NaN(SiMe_3)_2$ at room temperature was first tried in toluene solution. The solution changed gradually from red to dark green during the reaction period. After workup dark green crystals were isolated in 40% yield. Elemental analysis of the crystals is consistent with the formula of $L'YbN(SiMe_3)_2(THF)$ (**1**) (Scheme 1). Complex **1** was further confirmed by an X-ray crystal structure analysis. The formation of **1** indicates that the reaction proceeds with the elimination of a hydrogen atom from a methyl group of the ligand backbone by a $-N(SiMe_3)_2$ group and formation of a methylene moiety.

Further study revealed that an addition of a small amount of THF could result in an increase in the yield up to 70%.

To see the generality of the deprotonation reaction, the same reactions with the dichlorides of lanthanide metals of Y, Gd, and Sm were conducted in a mixture of toluene and THF. All reactions went smoothly and a color change for all the cases was observed (from yellow to orange for Y and Gd and yellow to red for Sm). After workup, the analogous complexes $L'LnN(SiMe_3)_2(THF)$ were prepared as pale yellow crystals for Y (**2**), orange crystals for Gd (**3**), and red crystals for Sm (**4**) in moderate yields (54% for **2**, 48% for **3**, and 43% for **4**) (Scheme 1).

Complexes **2**−**4** were further confirmed by single-crystal X-ray structural analyses.

Scheme 3. Proposed Mechanism for the Deprotonation of L



However, replacing the above dichlorides by the large Nd metal complex $LNdCl_2(THF)_2$ did not afford the analogous complex $L'NdN(SiMe_3)_2$ whether the solvent was toluene or a mixture of toluene and THF; the normal diamide complex $LNd[N(SiMe_3)_2]_2$ (**5**) was isolated instead (Scheme 1). Complex **5** was confirmed by elemental analysis, IR, and an X-ray structure analysis. Obviously, in the present case deprotonation of L could not occur. This might be because the ionic radius of Nd metal is the largest in comparison to the above metals, which makes the coordination environment around the Nd metal less crowded and the coordination of the second $-N(SiMe_3)_2$ group to the Nd metal is allowed. Therefore, a crowded coordination environment around the central metal might be required for the occurrence of deprotonation of L.

The formation of **4** is somewhat surprising, as a similar reaction with the triply bridged dichloride $LSmCl(\mu\text{-}Cl)_3SmL(THF)$ in toluene was reported to give the normal diamide complex $LSm[N(SiMe_3)_2]_2$.[9] Therefore, the metathesis reaction of $LSmCl(\mu\text{-}Cl)_3SmL(THF)$, which was prepared as yellow crystals according to the published procedure,[9] with 2 equiv of $NaN(SiMe_3)_2$ was carried out again in toluene. Indeed, only the diamide complex $LSm[N(SiMe_3)_2]_2$ was isolated in 48% yield and no complex **4** was detected (Scheme 2). However, addition of a small amount of THF into the above reaction solution led to the occurrence of deprotonation of L with the formation of **4** (Scheme 2), indicating that the presence of THF is the key point for the formation of **4**.

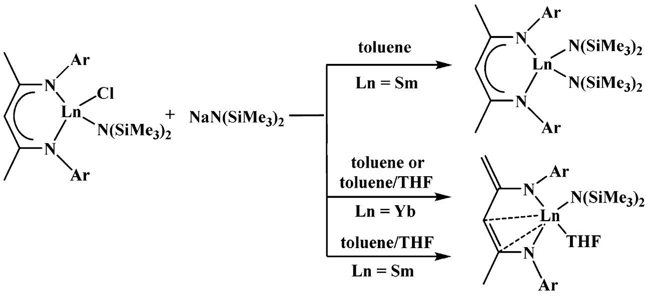
In contrast, a similar reaction with the small Yb metal analogue $LYbCl(\mu\text{-}Cl)_3YbL(THF)$ in toluene gave the deprotonation product **1** only. In this case the presence of THF is not necessary. The difference in outcome between the two reactions should be attributed to the smaller ionic radius of Yb metal, in comparison to the Sm metal, which makes the coordination sphere around the Yb metal more crowded, and the entrance of the second hindered $-N(SiMe_3)_2$ group becomes impossible even without the presence of a THF molecule.

Deprotonation of a *β*-diketiminate ligand by an alkyl or amide group in a thermally unstable complex is well documented.[2a,d] However, the diamide complexes $LNd[N(SiMe_3)_2]_2$ (**5**) and $LSm[N(SiMe_3)_2]_2$ are thermally stable. Heating a solution of $LSm[N(SiMe_3)_2]_2$ in THF at 60 °C for 72 h did not lead to deprotonation of L, and $LSm[N(SiMe_3)_2]_2$ was recovered completely, indicating complex **4** is formed by an intermolecular deprotonation process, not an intramolecular pathway.

Thus, the deprotonation of L in the present case proceeds by the following steps, as described previously.[2a] The first step is monosubstitution of one of the chlorine atoms in $LLnCl_2(THF)_2$ to form a monoamide with a loose THF molecule **A** (Scheme 3). The intermediate **A** reacts with another $NaN(SiMe_3)_2$ immediately by C−H bond breaking due to the steric congestion around the metal center, which favors the base-assisted dehydrochlorination via monodeprotonation of a methyl group on the backbone of L instead of a nucleophilic $Cl/N(SiMe_3)_2$ substitution (Scheme 3). The existence of the loosely coordinated THF molecule in the coordination sphere certainly makes the intermediate (**A**) more crowded in comparison with that without the THF, thereby favoring the occurrence of deprotonation. For the small Yb metal the presence of a loose coordinated THF in the intermediate might be not necessary.

To further confirm the assumption, monoamide complexes $LLn[N(SiMe_3)_2]Cl$ (Ln = Sm, Yb (**6**)) were synthesized by the reaction of $LLnCl_2(THF)_2$ with 1 equiv of $NaN(SiMe_3)_2$ and complex **6** was fully characterized including an X-ray diffraction as it is a novel one. Treatment of **6** with 1 equiv of $NaN(SiMe_3)_2$ either in toluene or in a mixture of toluene and THF at room temperature both afforded **1** as the only product (Scheme 4). In contrast, the reaction of $LSm[N(SiMe_3)_2]Cl$ with 1 equiv of $NaN(SiMe_3)_2$ yielded different outcomes depending on the reaction solvent used: the normal diamide complex $LSm[N(SiMe_3)_2]_2$ for toluene but complex **4** for a mixture of toluene and THF (Scheme 4).

Scheme 4. Reactions of $LLn[N(SiMe_3)_2]Cl$ with $NaN(SiMe_3)_2$



Molecular Structures of 1−6. Single crystals of complexes **1**−**4** suitable for X-ray diffraction analysis were obtained by recrystallization from a mixture of toluene and *n*-hexane at −10 °C. All the complexes crystallize in the orthorhombic space group $P2_1/n$ with a toluene molecule in the unit cell. The molecular structure of complexes **1**−**4** are shown in Figure 1 as they are isostructural. Selected bond lengths and angles are given in Table 1. All the complexes are THF-solvated monomers. The coordination of a THF molecule is not surprising, because of the low coordination number of 4 (see

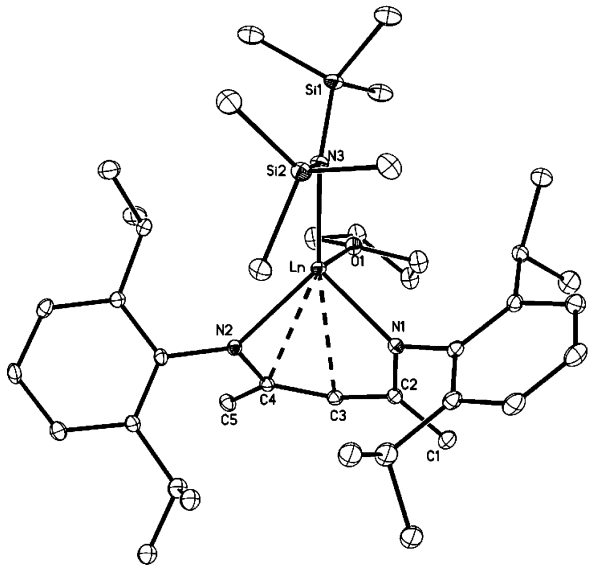


Figure 1. ORTEP diagram of L′LnN(SiMe$_3$)$_2$(THF) (Ln = Yb (**1**), Y (**2**), Gd (**3**), Sm (**4**)), showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes 1−4

	1	2	3	4
	Bond Lengths			
Ln(1)−N(1)	2.151(9)	2.177(4)	2.223(7)	2.239(4)
Ln(1)−N(2)	2.196(9)	2.241(5)	2.283(7)	2.294(5)
Ln(1)−N(3)	2.179(9)	2.227(5)	2.262(7)	2.291(5)
Ln(1)−O(1)	2.273(8)	2.337(4)	2.412(7)	2.443(4)
Ln(1)−C(2)	2.874(12)	2.294(9)	2.922(9)	2.933(6)
Ln(1)−C(3)	2.899(12)	2.857(6)	2.887(9)	2.889(6)
Ln(1)−C(4)	2.780(11)	2.771(5)	2.775(8)	2.799(5)
N(1)−C(2)	1.382(15)	1.381(8)	1.386(11)	1.388(8)
N(2)−C(4)	1.407(13)	1.382(7)	1.355(10)	1.371(7)
C(1)−C(2)	1.373(16)	1.364(8)	1.333(11)	1.359(9)
C(2)−C(3)	1.474(17)	1.489(9)	1.493(12)	1.472(8)
C(3)−C(4)	1.390(16)	1.380(8)	1.411(12)	1.393(8)
C(4)−C(5)	1.518(16)	1.526(8)	1.522(11)	1.520(8)
	Bond Angles			
N(1)−Ln(1)−N(2)	94.6(4)	93.15(17)	90.8(3)	88.59(17)
N(1)−Ln(1)−N(3)	116.6(4)	116.07(19)	114.5(3)	114.54(18)
N(2)−Ln(1)−N(3)	131.6(4)	130.37(17)	128.5(3)	128.33(17)

below). Each Ln metal ion in **1**−**4** is four-coordinate and is bound to the two nitrogen atoms of the chelating *β*-diketiminate dianion (L′), one −N(SiMe$_3$)$_2$ ligand, and one coordinated THF molecule. The coordination geometry can be described as a distorted tetrahedron. The of Ln−N bond distances (Ln−N(1) and Ln−N(2) bonds) are 2.151(9) and 2.196(9) Å for **1**, 2.177(4) and 2.241(5) Å for **2**, 2.223(7) and 2.283(7) Å for **3**, 2.239(4) and 2.294(5) Å for **4**, which are quite comparable with each other, when the differences in ionic radii among the lanthanide metals are considered. The values are 0.058−0.103 Å (for **1**) and 0.040−0.095 Å (for **4**) shorter than those found in the corresponding lanthanide monoanionic *β*-diketiminate derivatives (2.254(6) Å in [LYbN(SiMe$_3$)$_2$(Cl)] (**6**) and 2.334(3) Å in [LSmN(SiMe$_3$)$_2$(Cl)][9]) but very close to the corresponding Ln−N$_{\text{amide}}$ distances. The bond parameters feature the dianionic nature of L′ in complexes **1**−**4**. Each Ln(L′) moiety in **1**−**4** is best described as η^3-1-azaallyl (C3−C4−N2) and amido (N1) centered bonds to the Ln atom. Thus, the Ln···C3 (2.899(12) Å for **1**, 2.857(6) Å for **2**, 2.887(9) Å for **3**, and 2.890(6) Å for **4**) and Ln···C4 contacts (2.780(11) Å for **1**, 2.771(5) Å for **2**, 2.775(8) Å for **3**, and 2.800(5) Å for **4**) are near the upper range of LnCp$_3$ distances (2.62(1)−2.79(1) Å, average 2.69 Å for Cp$_3$Yb(NC$_4$H$_4$N)-YbCp$_3$;[10a] 2.614(11)−2.859(14) Å, average 2.73 Å for [YCp$_3$];[10b] 2.766(2)−2.897(4) Å, average 2.80 Å for [GdCp$_3$];[10c] 2.78(2)−2.91(3) Å, average 2.82 Å for [SmCp$_3$][10d]), whereas the Ln···C3 contact is longer (2.899(12) Å for **1**, 2.857(6) Å for **2**, 2.887(9) Å for **3**, and 2.890(6) Å for **4**). The bite angle for L′ (N(1)−Ln−N(2) = 94.6(4)° for **1** and 88.59(17)° for **4**) is larger than those found for L (N(1)−Ln−N(2) = 85.9(2)° in **6** and 81.6(1)° in [LSmN(SiMe$_3$)$_2$(Cl)][9]). The wider ligand bite angle leads to facilitating the Ln···C(3,4) close contacts in theLn(L′) moiety.

Most notably, deprotonation of the methyl on the *β*-carbon is evident from shortening of the sp^3 H$_3$C−C bond to an sp^2 H$_2$C═C bond (1.518(16) Å (**1**), 1.526(8) Å (**2**), 1.522(11) Å (**3**), 1.520(8) Å (**4**) for an sp^3 CH$_3$−C bond vs 1.373(16) Å (**1**), 1.364(8) Å (**2**), 1.333(11) Å (**3**), 1.359(9) Å (**4**) for the sp^2 CH$_2$═C bond).

The molecular structures of **5** and **6** are shown in Figures 2 and 3, respectively. Both complexes are solvent-free monomers, but there is 0.5 toluene molecule in the unit cell for **5**. The four-coordinated central Nd atom in **5** is ligated by four nitrogen atoms from the L ligand and the two −N(SiMe$_3$)$_2$ groups, while the four-coordinated central Yb atom in **6** is ligated by two nitrogen atoms from the L ligand, one −N(SiMe$_3$)$_2$ group, and one chlorine atom. The coordination geometry around each metal can be described as a distorted tetrahedron. The solid-state structures of **5** and **6** are quite similar to those of

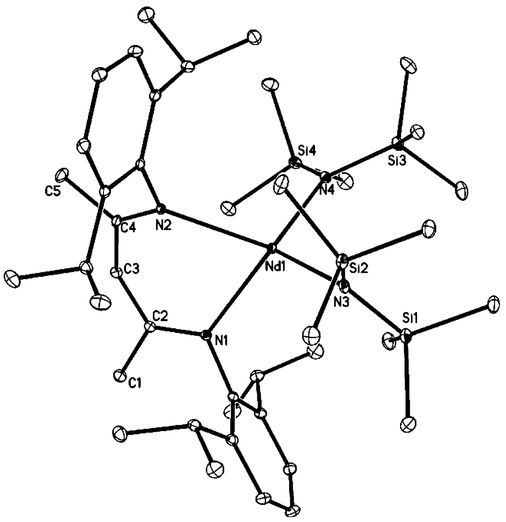


Figure 2. ORTEP diagram of LNd[N(SiMe$_3$)$_2$] (**5**) showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Nd(1)−N(1) = 2.163(3), Nd(1)−N(2) = 2.471(2), Nd(1)−N(3) = 2.327(2), Nd(1)−N(4) = 2.342(3), N(1)−C(2) = 1.344(4), C(2)−C(3) = 1.390(4), C(3)−C(4) = 1.403(4), C(4)−N(2) = 1.343(4); N(1)−Nd(1)−N(2) = 77.36(7).

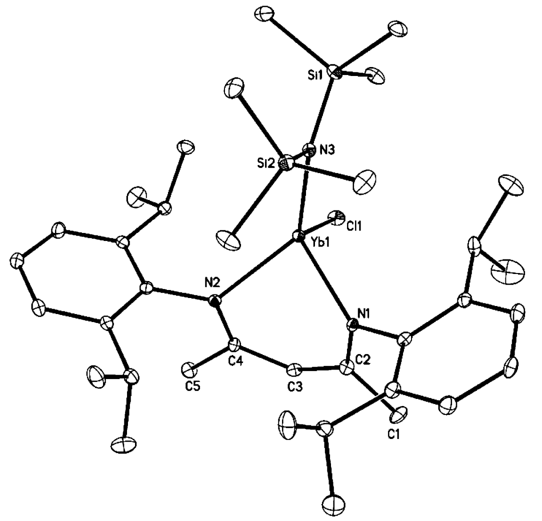


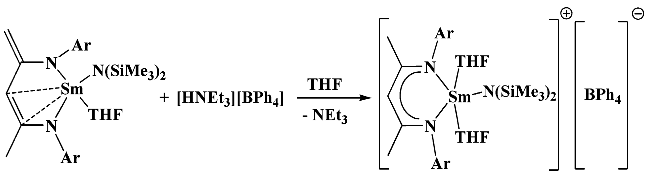
Figure 3. ORTEP diagram of LYb[N(SiMe$_3$)$_2$]Cl (**6**) showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Yb(1)−N(1) = 2.225(6), Yb(1)−N(2) = 2.254(6), Yb(1)−N(3) = 2.174(6), Yb(1)−Cl(1) = 2.489(2), N(1)−C(2) = 1.341(9), C(2)−C(3) = 1.417(9), C(3)−C(4) = 1.411(10), C(4)−N(2) = 1.333(9); N(1)−Yb(1)−N(2) = 85.9(2).

their analogous Sm complexes LSm[N(SiMe$_3$)$_2$]$_2$ and LSm[N(SiMe$_3$)$_2$]Cl[9] reported previously. The bond distances N(1)−C(2), C(2)−C(3), C(3)−C(4), C(4)−N(2) (1.344(4), 1.390(4), 1.403(4), 1.343(4) Å for **5**; 1.341(9), 1.417(9), 1.411(10), 1.333(9) Å for **6**) suggest significant delocalization within the π- ystem of the β-diketiminate ligand.

Synthesis and Characterization of the Cationic Samarium Amide Complex [LSmN(SiMe$_3$)$_2$(THF)$_2$]$^+$[BPh$_4$]$^-$ (7). The reaction of complex **4** with [HNEt$_3$][BPh$_4$] was tried with the aim of developing a useful route for the synthesis of cationic lanthanide amide complexes. Treatment of **4** with 1 equiv of [HNEt$_3$][BPh$_4$] in THF at room temperature resulted in an immediate color change of the reaction solution from red to yellow. Removing the volatiles, washing with hexane, and extracting with THF gave yellow crystals in 85% yield upon crystallization.

The elemental analysis of the crystals is consistent with the formula of the cationic amide complex [LSmN(SiMe$_3$)$_2$(THF)$_2$]$^+$[BPh$_4$]$^-$ (**7**) (Scheme 5). The IR spectra of complex **7** exhibited strong absorptions near 1551 cm^{-1}, indicating partial C═N double-bond character.[11] Complex **7** was further confirmed by an X-ray crystal structure analysis.

Scheme 5. Synthesis of Complex 7



Complex **7** is soluble in THF but not in nonpolar solvents such as hexane and toluene.

The molecular structure of **7** is shown in Figure 4. Complex **7** consists of separated ion pairs of the THF-solvated cationic species [LSmN(SiMe$_3$)$_2$(THF)$_2$]$^+$ and the anion of [BPh$_4$]$^-$. The five-coordinated central Sm atom in the cation is ligated by two nitrogen atoms from the L ligand, one nitrogen atom of the −N(SiMe$_3$)$_2$ group, and two oxygen atoms from the two THF molecules in a distorted-trigonal-bipyramidal geometry. The nitrogen N(1) of the β-diketiminate ligand and the O(2) of one THF ligand occupy the apical positions with the angle of N(1)−Sm−O(2) being 144.02(11)°, which deviates greatly from 180°. The nitrogen atom N(2), oxygen atom O(1), and the nitrogen N(3) of the amido group are located at the equatorial vertices, with the sum of these bond angles around the Sm atom of 359.98°. The bond distances N(1)−C(2) (1.343(5) Å), C(1)−C(2) (1.528(6) Å), C(2)−C(3) (1.385(6) Å), and N(2)−C(4) (1.420(6) Å) suggest significant delocalization within the π system of the β-diketiminate ligand. The Sm−C(2,3,4) distances are quite long, indicating a negligible π contribution to the β-diketiminate−Sm bonding in this complex. The bond parameters in the LSm part are quite comparable with those found in the cationic thulium β-diketiminate.[3a] The bond distance Sm−N(amide) = 2.280(3) Å can be compared to 2.005(2) Å found in the cationic amide complex,[7c] when the difference in ionic radii between Sm and Sc metals is considered.

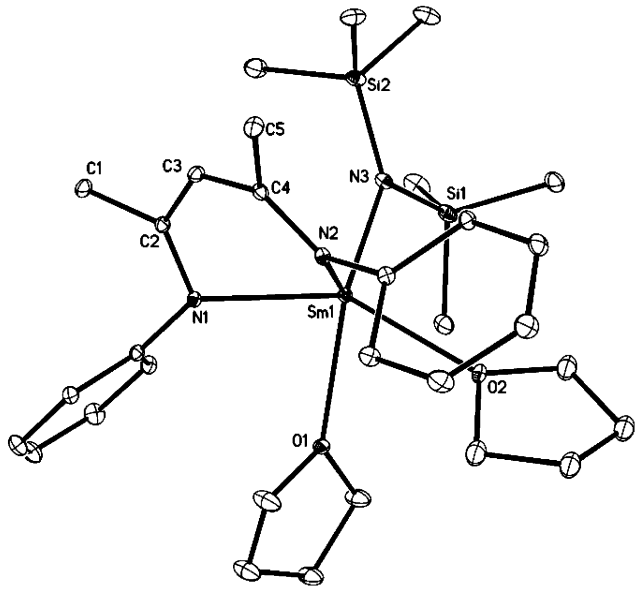


Figure 4. ORTEP diagram of [LSmN(SiMe$_3$)$_2$(THF)$_2$]$^+$[BPh$_4$]$^-$ (**7**) showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, *i*Pr substituent of L and BPh$_4$ are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sm(1)−N(1) = 2.380(3), Sm(1)−N(2) = 2.384(3), Sm(1)−N(3) = 2.280(3), Sm(1)−O(1) = 2.490(3), Sm(1)−O(2) = 2.506(3), Sm(1)−C(2) = 3.087(4), Sm(1)−C(3) = 3.274(4), Sm(1)−C(4) = 3.162(4), N(1)−C(2) = 1.343(5), N(2)−C(4) = 1.326(5), C(1)−C(2) = 1.528(6), C(2)−C(3) = 1.385(6), C(3)−C(4) = 1.420(6); O(1)−Sm(1)−N(2) = 112.99(11), O(1)−Sm(1)−N(3) = 137.65(11), O(2)−Sm(1)−N(1) = 144.02(11), N(2)−Sm(1)−N(3) = 109.34(12).

■ CONCLUSION

A series of dianionic β-diketiminate lanthanide monoamide complexes, L′LnN(SiMe$_3$)$_2$(THF) (Ln = Yb (**1**), Y (**2**), Gd (**3**), Sm (**4**)), were prepared via deprotonation of L by an −N(SiMe$_3$)$_2$ group, which represents the first examples of lanthanide amides supported by a dianionic β-diketiminate ligand. The size of the lanthanide metal has a profound influence on the deprotonation reaction of L, indicating that an overcrowded coordination environment around the central metal is necessary for deprotonation of L. By virtue of the high reactivity of the dianionic β-diketiminate ligand, the corresponding cationic Sm amide complex $[LSmN(SiMe_3)_2(THF)_2]^+[BPh_4]^-$ (**7**) was synthesized in high yield by the reaction of **4** with $[HNEt_3][BPh_4]$ and structurally characterized. The reactivity of dianionic β-diketiminate ligands in lanthanide derivatives toward small molecules is ongoing in our laboratory.

EXPERIMENTAL SECTION

Materials and Methods. All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques. Solvents were degassed and distilled from sodium benzophenone ketyl before use. Anhydrous $LnCl_3$ was prepared according to the literature procedure.[12] The proligand LH (L = $\{[(2,6\text{-}i\text{Pr}_2C_6H_3)NC(CH_3)]_2CH\}^-$)[13] and the complexes $LLnCl_2(THF)_2$ (Ln = Yb, Y, Gd, Sm),[14] $LLnCl(\mu\text{-}Cl)_3LnL(THF)$ (Ln = Yb,[14] Sm[9]), and $LSm[N(SiMe_3)_2]Cl$[9] were prepared by the methods reported. $[HNEt_3][BPh_4]$ was prepared according to the literature method.[15] ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz instrument and processed using MestReNova software. Elemental analyses were performed by direct combustion using a Carlo-Erba EA 1110 instrument. The IR spectra were recorded on a Nicolet-550 FT-IR spectrometer as KBr pellets. The uncorrected melting points of crystalline samples were determined in sealed Ar-filled capillaries.

$L'YbN(SiMe_3)_2(THF)\cdot(toluene)$ (1). To a slurry of $LYbCl_2(THF)_2$ (2.19 g, 3.00 mmol) in about 30 mL of toluene was added a solution of $NaN(SiMe_3)_2$ in toluene (20.0 mL, 6.00 mmol) as soon as possible, and about 5 mL of THF was added to the reaction mixture. The reaction mixture was stirred at room temperature for 24 h, and the undissolved portion was then removed by centrifugation. The dark green solution obtained was concentrated to about 2 mL, and 4 mL of *n*-hexane was then added. The solution was cooled to −10 °C for crystallization to give dark green crystals of **1** in 70% yield (1.92 g). Mp: 145−148 °C dec. Anal. Calcd for $C_{46}H_{74}N_3OSi_2Yb$ (914.3): C, 60.43; H, 8.16; N, 4.60. Found: C, 59.98; H, 8.02; N, 5.42. IR (KBr, cm^{-1}): 3064 (w), 2962 (s), 2868 (m), 2318 (w), 1622 (s), 1550 (s), 1252 (s), 1156 (m), 935 (m), 840 (m), 503 (m).

$L'YN(SiMe_3)_2(THF)\cdot(toluene)$ (2). The synthesis of complex **2** was carried out in the same way as that described for complex **1**; pale yellow crystals of **2** suitable for X-ray crystal structure analysis were obtained (1.34 g, 54%). Mp: 155−158 °C dec. ^1H NMR (400 MHz, C_6D_6): δ 7.16−6.99 (m, 6 H), 5.09 (s, 1 H), 3.74 (m, 4 H), 3.09 (s, 2 H), 1.57 (d, 3 H), 1.49 (m, 4 H), 1.41 (d, 3 H), 1.33 (d, 18 H), 1.06 (m, 4 H), 0.00 (s, 18 H); ^{13}C NMR (101 MHz, C_6D_6): 168.2, 153.9, 147.8, 147.4, 145.1, 144.7, 143.9, 142.7, 142.1, 141.8, 138.1, 129.5, 128.7, 124.7, 123.1, 98.0, 32.1, 30.8, 30.7, 28.6, 28.3, 27.3, 26.8, 26.4, 26.3, 26.0, 25.8, 25.5, 25.2, 24.9, 24.5, 24.3, 23.2, 21.6. Anal. Calcd for $C_{46}H_{74}N_3OSi_2Y$ (830.17): C, 66.55; H, 8.98; N, 5.06. Found: C, 66.13; H, 8.64; N, 4.89. IR (KBr, cm^{-1}): 3062 (w), 2961 (s), 2868 (m), 2361 (w), 1623 (s), 1551 (s), 1252 (s), 935 (m), 788 (m), 758 (s).

$L'GdN(SiMe_3)_2(THF)\cdot(toluene)$ (3). The synthesis of complex **3** was carried out in the same way as that described for complex **1**; orange crystals of **3** suitable for X-ray crystal structure analysis were obtained (1.29 g, 48%), Mp: 158−160 °C dec. Anal. Calcd for $C_{46}H_{74}N_3OSi_2Gd$ (898.51): C, 61.49; H, 8.30; N, 4.68. Found: C, 61.12; H, 8.21; N, 4.42. IR (KBr, cm^{-1}): 3062 (w), 2961 (s), 2868 (m), 2356 (w), 1623 (s), 1552 (s), 1252 (s), 935 (m), 844 (m), 758 (s), 504 (m).

$L'SmN(SiMe_3)_2(THF)\cdot(toluene)$ (4). *Method 1.* The synthesis of complex **4** was carried out in the same way as that described for complex **1**, red crystals **4** suitable for X-ray crystal structure analysis were obtained (1.15 g, 43%), Mp: 160−162 °C dec. ^1H NMR (400 MHz, C_6D_6): δ 7.45−6.96 (m, 6 H), 5.64 (s, 1 H), 3.87 (s, 3 H), 3.05 (s, 2 H), 2.68−2.62 (d, 9 H), 2.11 (s, 3 H), 1.27 (s, 3 H), 0.89−0.79 (d, 6 H), −0.22 (s, 3 H), −1.78 (s, 18 H). ^{13}C NMR (101 MHz, C_6D_6): 153.2, 152.0, 140.7, 139.2, 138.2, 137.7, 126.0, 125.4, 124.2, 123.8, 83.5, 63.6, 36.4, 35.3, 30.7, 29.8, 28.4, 27.3, 27.1, 26.1, 25.7, 25.2, 24.2, 21.8, 20.9. Anal. Calcd for $C_{46}H_{74}N_3OSi_2Sm$ (891.61): C, 61.97; H, 8.37; N, 4.71. Found: C, 61.52; H, 8.12; N, 4.88. IR (KBr, cm^{-1}): 3062 (w), 2962 (m), 2869 (w), 1623 (s), 1550(vs), 1378 (s), 1233 (s), 1065 (m), 1058 (m), 633 (m), 505 (s).

Method 2. A solution of $NaN(SiMe_3)_2$ in toluene (20.0 mL, 6.00 mmol) was added to a slurry of $LSmCl(\mu\text{-}Cl)_3SmL(THF)$ (1.54 g, 1.50 mmol) in about 25 mL of toluene as soon as possible, and about 5 mL of THF was added to the reaction mixture. The reaction mixture was stirred at room temperature for 24 h, and the undissolved portion was then removed by centrifugation. The red solution obtained was concentrated to about 2 mL, and 4 mL *n*-hexane was then added. The solution was cooled to −10 °C for crystallization to give red crystals of **4** in 45% yield (1.20 g).

$LNd[N(SiMe_3)_2]_2\cdot 0.5(toluene)$ (5). To a slurry of $LNdCl_2(THF)_2$ (2.19 g, 3.00 mmol) in about 30 mL of toluene was added a solution of $NaN(SiMe_3)_2$ in toluene (20.0 mL, 6.00 mmol). The reaction mixture was stirred at room temperature for 24 h, and the undissolved portion was then removed by centrifugation. The yellow-green solution obtained was concentrated to about 5 mL. The solution was cooled to −10 °C for crystallization to give yellow-green crystals of **7** in 52% yield (1.45 g). Mp: 263−266 °C. Anal. Calcd for $C_{44.50}H_{81}N_4NdSi_4$ (928.73): C, 57.55; H, 8.79; N, 6.03. Found: C, 57.83; H, 8.62; N, 5.85. IR (KBr, cm^{-1}): 3064 (w), 2360 (m), 2340 (m), 1622 (s), 1550 (s), 1306 (s), 1252 (s), 1156 (m), 935 (m), 924 (s), 840 (m), 790 (m), 771 (m), 731 (m), 665 (s), 605 (m).

$LYb[N(SiMe_3)_2]Cl$ (6). A solution of $NaN(SiMe_3)_2$ in toluene (10.0 mL, 3.00 mmol) was added dropwise to a slurry of $LYbCl_2(THF)_2$ (2.41 g, 3.00 mmol) in about 20 mL of toluene. The reaction mixture was stirred at room temperature for 12 h. The undissolved portion was then removed by centrifugation. The red solution was concentrated to about 5 mL. The solution was cooled at −10 °C for crystallization to give red crystals of **6** in 45% yield (1.06 g). Mp: 225−228 °C dec. Anal. Calcd for $C_{35}H_{59}Cl\ N_3Si_2Yb$ (786.52): C, 53.45; H, 7.56; N, 5.34. Found: C, 53.18; H, 7.65; N, 5.42. IR (KBr, cm^{-1}): 3053 (w), 2961 (s), 2926 (w), 2673 (m), 1621 (s), 1551(vs), 1488 (m), 1367 (m), 1324 (m), 1220 (m), 789 (m), 759 (m), 611 (w).

Reaction of $LYb[N(SiMe_3)_2]Cl$ (6) with $NaN(SiMe_3)_2$. To a slurry of $LYb[N(SiMe_3)_2]Cl$ (2.36 g, 3.00 mmol) in about 30 mL of toluene was added a solution of $NaN(SiMe_3)_2$ in toluene (10.0 mL, 3.00 mmol), and about 4 mL of THF was added to the reaction mixture. The reaction mixture was stirred at room temperature for 24 h. The undissolved portion was then removed by centrifugation. The dark green solution was concentrated to about 2 mL, and 4 mL of *n*-hexane was then added. The solution was cooled to −10 °C for crystallization to give dark green crystals of **1** in 73% yield (2.00 g).

Reaction of $LSm[N(SiMe_3)_2]Cl$ with $NaN(SiMe_3)_2$ in Toluene. To a slurry of $LSm[N(SiMe_3)_2]Cl$ (2.29 g, 3.00 mmol) in about 30 mL of toluene was added a solution of $NaN(SiMe_3)_2$ in toluene (10.0 mL, 3.00 mmol). The reaction mixture was stirred at room temperature for 24 h. The undissolved portion was removed by centrifugation. The yellow solution was concentrated to about 6 mL and then cooled to −10 °C for crystallization to give yellow crystals of $LSm[N(SiMe_3)_2]_2$ in 46% yield (1.68 g).

Reaction of $LSm[N(SiMe_3)_2]Cl$ with $NaN(SiMe_3)_2$ in a Toluene/THF Mixture. To a slurry of $LSm[N(SiMe_3)_2]Cl$ (2.29 g, 3.00 mmol) in about 30 mL of toluene were added a solution of $NaN(SiMe_3)_2$ in toluene (10.0 mL, 3.00 mmol) and about 4 mL of THF. The reaction mixture was stirred at room temperature for 24 h. The undissolved portion was removed by centrifugation. The red solution was concentrated to about 2 mL, and 4 mL of *n*-hexane was then added. The solution was cooled to −10 °C for crystallization to give red crystals of **4** in 50% yield (0.89 g).

$[LSmN(SiMe_3)_2(THF)_2]^+[BPh_4]^-$ (7). Into a red solution of **4** (0.89 g, 1.00 mmol) in THF (20 mL) was added dropwise a THF (10 mL) solution of $[HNEt_3][BPh_4]$ (0.42 g, 1.00 mmol) at room temperature with stirring. During this period, the reaction mixture was changed color from red to yellow. The reaction mixture was stirred for another 4 h. The volatiles were removed under reduced pressure, and the residues were washed three times with about 10 mL portions of *n*-

Table 2. Crystallographic Data for Complexes 1−4

	1	2	3	4
empirical formula	$C_{46}H_{74}N_3OSi_2Yb$	$C_{46}H_{74}N_3OSi_2Y$	$C_{46}H_{74}N_3OSi_2Gd$	$C_{46}H_{74}N_3OSi_2Sm$
formula wt	914.3	830.17	898.51	891.61
temp (K)	223(2)	223(2)	223(2)	223(2)
cryst syst	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
cryst size (mm)	0.50 × 0.10 × 0.10	0.60 × 0.25 × 0.20	0.55 × 0.15 × 0.10	0.30 × 0.30 × 0.20
a (Å)	11.7551(13)	11.7778(8)	11.7938(11)	11.7896(12)
b (Å)	18.556(2)	18.5593(12)	18.5139(18)	18.507(2)
c (Å)	21.673(3)	21.6903(15)	21.713(2)	21.740(3)
α (deg)	90	90	90	90
β (deg)	90	90	90	90
γ (deg)	90	90	90	90
V (Å^3)	4727.48(90)	4741.2(6)	4741.0(8)	4743.6(9)
Z	4	4	4	4
D_{calcd} (mg cm^{-3})	1.285	1.163	1.259	1.248
abs coeff (mm^{-1})	2.063	1.315	1.484	1.323
F(000)	1908	1784	1884	1876
θ range (deg)	3.03−25.50	3.02−25.50	3.02−25.50	3.02−25.50
no. of collected/unique rflns	19 628/8629	24 485/8798	14 324/8365	17 378/8477
R(int)	0.0824	0.0678	0.0646	0.0380
no. of data/restraints/params	8629/27/432	8798/27/432	8365/49/444	8477/28/445
goodness of fit on F^2	1.106	1.079	1.105	1.084
final R1 ($I > 2\sigma(I)$)	0.0791	0.0936	0.0745	0.0542
wR2 (all data)	0.1483	0.1713	0.1229	0.1118

Table 3. Crystallographic Data for Complexes 5−7

	5	6	7
empirical formula	$C_{44.50}H_{81}N_4NdSi_4$	$C_{35}H_{59}ClN_3Si_2Yb$	$C_{67}H_{95}BN_3O_2Si_2Sm$
formula wt	928.73	786.52	1191.80
temp (K)	223(2)	223(2)	223(2)
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
cryst size (mm)	0.60 × 0.60 × 0.50	0.25 × 0.20 × 0.07	0.40 × 0.40 × 0.20
a (Å)	11.7324(3)	17.156(5)	12.9937(18)
b (Å)	11.7814(2)	18.248(5)	13.2278(19)
c (Å)	20.5952(6)	13.096(4)	18.722(3)
α (deg)	75.163(3)	90	87.865(7)
β (deg)	79.407(3)	104.166(4)	84.872(6)
γ (deg)	68.293(3)	90	82.374(7)
V (Å^3)	2544.08(11)	3975.3(18)	3175.6(8)
Z	2	4	2
D_{calcd} (mg cm^{-3})	1.212	1.314	1.246
abs coeff (mm^{-1})	1.146	2.505	1.006
F(000)	984	1620	1258
θ range (deg)	3.08−25.50	3.14−25.50	3.15−25.50
no. of collected/unique rflns	12 138/8630	17 901/7373	27 301/11 741
R(int)	0.0678	0.0824	0.0563
no. of data/restraints/params	8630/8/496	7373/0/396	11 741/22/672
goodness of fit on F^2	1.064	1.164	1.120
final R1 ($I > 2\sigma(I)$)	0.0303	0.0767	0.0529
wR2 (all data)	0.0764	0.1046	0.1127

hexane. The solids were dissolved in THF, and the solution was kept at −10 °C for crystallization. Complex **7** was isolated as yellow crystals after several days. Yield: 1.01 g (85%). Mp: 168−170 °C dec. Anal. Calcd for $C_{67}H_{95}BN_3O_2Si_2Sm$ (1191.80): C, 67.52; H, 8.03; N, 3.53. Found: C, 67.28; H, 7.84; N, 3.65. IR (KBr, cm^{-1}): 3215 (m), 3057 (m), 2960 (s), 2867 (m), 1621 (s), 1551(vs), 1383 (m), 1276 (m), 1254 (m), 1058 (m), 743 (s), 714 (s), 601 (m).

X-ray Crystallography. Suitable single crystals of complexes **1**−**7** were sealed in thin-walled glass capillaries, to determine the single-crystal structures. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo Kα radiation (λ = 0.710 70 Å). The diffracted intensities were corrected for Lorentz−polarization effects and empirical absorption corrections. Details of the data collection and crystal data for complexes **1**−**7** are given in Tables 2 and 3. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically (C−H bond lengths fixed at 0.95 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined by using the SHELXL-97 program. CCDC-820930 (for **1**), -820929 (for **2**), -835065 (for **3**), -820927 (for **4**), -846319 (for **5**), -846318 (for **6**), and -835064 (for **7**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information

CIF files giving X-ray crystallographic data of complexes **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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