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N-Substituted Guanidinate Anions as Ancillary Ligands in Organolanthanide Chemistry. Synthesis and Characterization of $\{CyNC[N(SiMe_3)_2]NCy\}_2SmCH(SiMe_3)_2$

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Addition of $N(SiMe_3)_2$ anion equivalents to CyN═C═NCy provided entry to a series of N-substituted guanidinate complexes of Sm(III) and Yb(III) with the general formula $M\{CyNC[N(SiMe_3)_2]NCy\}_2(\mu\text{-Cl})_2Li(S)_2$ (M = Sm, Yb; Cy = cyclohexyl; S = Et_2O, $^1/_2$ TMEDA). Substitution of the chloro ligands of these complexes using $LiCH(SiMe_3)_2$ or $LiN(SiMe_3)_2$ yields solvent-free, monomeric alkyl and amido compounds, respectively. Definitive evidence for the molecular structures of these products is provided through single-crystal X-ray analysis, and in particular, the results for $Sm\{CyNC[N(SiMe_3)_2]NCy\}_2CH(SiMe_3)_2$ (**7**) and $Yb\{CyNC[N(SiMe_3)_2]NCy\}_2N(SiMe_3)_2$ (**8**) are presented. These results provide the first reported example of an organolanthanide complex supported by a guanidinate ligand.

Organolanthanide chemistry is an area of vigorous research due largely to the marvelous catalytic abilities exhibited by many of these species.[1−7] The most successful ancillary ligands in this field have been derivatives of the cyclopentadienyl anion whose dominant presence in the organometallic chemistry of the lanthanides began with the preparation of the tris(cyclopentadienyl) compounds.[8] Among the most versatile materials for the preparation of catalytically active species have been complexes with the formula $(C_5Me_5)_2LnX$, where X is hydride or hydrocarbyl.

In an effort to develop alternatives to cyclopentadienyl-based ligands, we were attracted to N-substituted guanidinate anions, $[RNC(NR'_2)NR'']^-$, as potential bulky supporting ligands for organolanthanide complexes. These ligands, which have not been previously used in lanthanide chemistry, fall into a family of bidentate, three-atom bridging ligands with the general formula $RNXNR^-$ (X = CNR'_2,[9] CR',[10] or N[11]). One member of this family, *N*,*N'*-bis(trimethylsilyl)benzamidinate-based ligands $[Me_3SiNC(C_6H_{5-n}R_n)NSiMe_3]^-$, has recently been employed for preparation of inorganic complexes of the lanthanide elements[12−14] and organometallic complexes of yttrium.[15] Steric analysis of this ligand system places it intermediate between the Cp

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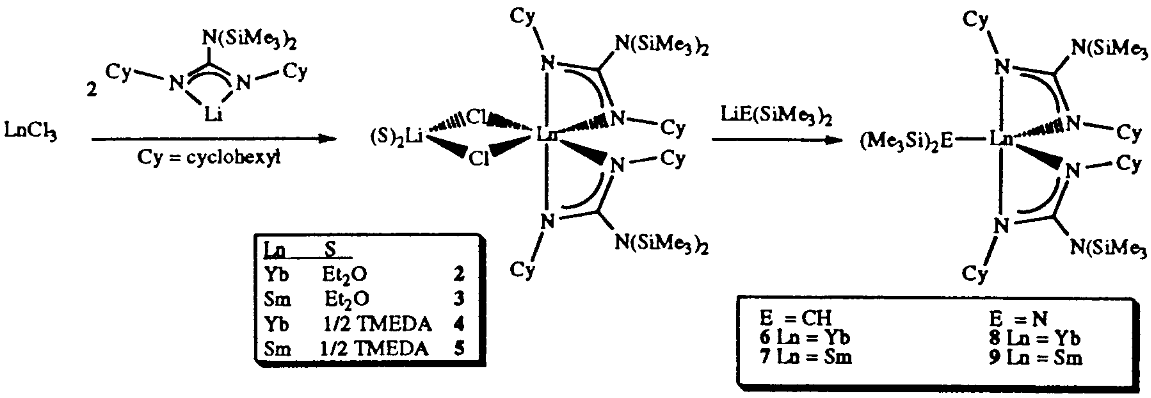
Scheme 1



and Cp* ligands.[12,15] Substituted guanidinate ligands ($X = NR'_2$, $R \neq H$) present an ideal system for exploring the effects of making rational modifications to both the steric bulk and electronic properties of the supporting ligands through changes to the organic substituents on the nitrogen atoms.

Herein we report the synthesis and characterization of a novel series of guanidinate complexes of Sm and Yb including the first reported alkyl and amido lanthanide complexes with this family of ancillary ligands. We also provide a preliminary account of the use of these ligands in the preparation of Yb(II) complexes. These efforts complement work with alkylamidinates ligands and the main group and transition metals.[16,17]

Results and Discussion

Guanidinate anion **1** was generated by the direct reaction of 1,3-dicyclohexylcarbodiimide with 1 equiv of $LiN(SiMe_3)_2$ in diethyl ether. Although the lithium salt could be isolated in pure form by simple removal of the solvent, in most cases metathesis reactions with lanthanide halide salts can be carried out with freshly prepared solutions of lithium guanidinate. Thus, reaction of a 2:1 ratio of lithium salt of *N*,*N*′-dicylohexyl-*N*″-bis(trimethylsilyl)guanidinate with either $YbCl_3$ or $SmCl_3$ produced, after crystallization from diethyl ether, the new "ate" complexes $M\{CyNC[N(SiMe_3)_2]NCy\}_2(\mu\text{-}Cl)_2Li(Et_2O)_2$ (M = Sm (**2**), Yb (**3**)) (Scheme 1) in 79% and 88% yield, respectively. We propose the structures in Scheme 1 on the basis of the results of crystallographic characterization described below and analogy with the reported complex $[(CF_3)_3C_6H_2C(NSiMe_3)_2]Nd(\mu\text{-}Cl)_2LiTHF_2$.[13] Compounds **2** and **3** are monochloro bis(guanidinate) complexes in which 1 equiv of LiCl is retained in the coordination sphere of the lanthanide center. Diethyl ether completes the coordination sphere of the Li cation. The ether molecules in **2** and **3** can be displaced easily by reaction with other coordinating species such as *N*,*N*′-tetramethylethylenediamine to yield **4** and **5**.

These paramagnetic compounds represent a novel class of precursors for soluble organolanthanide species free of cyclopentadienyl ligands. Furthermore, these disubstituted complexes are important for the design of new complexes with potential in catalysis as they represent potential analogues of the well-known species $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Li(solvent)_2$, which are important starting materials for the synthesis of alkyl and hydride complexes.

The metathesis reaction of **2** and **3** with $LiCH(SiMe_3)_2$ or $LiN(SiMe_3)_2$ allowed for the replacement of chloride and the production of the solvent-free complexes **6**−**9** in excellent yields (73−87%). Although ^1H NMR provided evidence for the presence of the substituents, the paramagnetic nature of these complexes hindered full interpretation of the spectra.

Definitive formulation of the structural features of **7** and **8** was provided by single-crystal X-ray diffraction analysis (Figures 1 and 2).[18,19] These studies establish the coordination geometry of the metal center and the connectivity of the ligand for these compounds and provide the first reported structural characterization of alkyl or amido lanthanide complexes with guanidinate or amidinate ligands.

Consistent with our proposals, the structural analysis of **7** (Figure 1)[20] revealed a monomeric species with the coordination sphere of the Sm(III) center composed of the four nitrogen atoms of two chelating guanidinate anions and the bulky alkyl. The coordination geometry of **7** is best described as trigonal planar with the bisector of the guanidinate ligands (Sm−C(13) and Sm−C(32) vectors) defining two vertexes and the alkyl carbon (C(39)) the third. The angles defined by these vectors sum to 360°. This analysis emphasizes that fact that the molecular structure of **7** resembles that of the bent metallocene derivatives containing $(C_5Me_5)_2Ln$ units.

The bonding parameters within the two guanidinate ligands are not dramatically different, and the two nitrogens and bridging carbon atoms for each lie in a plane which includes the Sm atom. This results in an

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(18) $C_{45}H_{99}N_6Si_6Sm\cdot 0.33O(SiC_3H_9)_2$, space group = $P\bar{1}$, $a = 14.157(3)$ Å, $b = 24.952(5)$ Å, $c = 28.115(6)$ Å, $\alpha = 74.78(3)°$, $\beta = 76.74(3)°$, $\gamma = 82.14(3)°$, $V = 9297(3)$ Å^3, $Z = 6$, $T = 293$ K; R for 46 631 reflections $[I > 2\sigma(I)]$, $R(F) = 0.0616$, $wR(F^2) = 0.1046$, GOF on $F^2 = 1.061$.

(19) $C_{44}H_{98}N_7Si_6Yb\cdot THF$, space group = $P2_1/c$, $a = 13.303(5)$ Å, $b = 19.602(4)$ Å, $c = 2.932(5)$ Å, $\beta = 91.741(2)°$, $V = 7019.77(2)$ Å^3, $Z = 4$; R for 6224 reflections $[I > 2.5\sigma(I)]$, $R(F) = 0.066$, $wR(F^2) = 0.102$.

(20) For conciseness, the discussion of the structural parameters of **7** and the ORTEP shown in Figure 1 are confined to one of the three molecules that constitute the asymmetric unit in the crystal structure. Full data are provided in the Supporting Information.

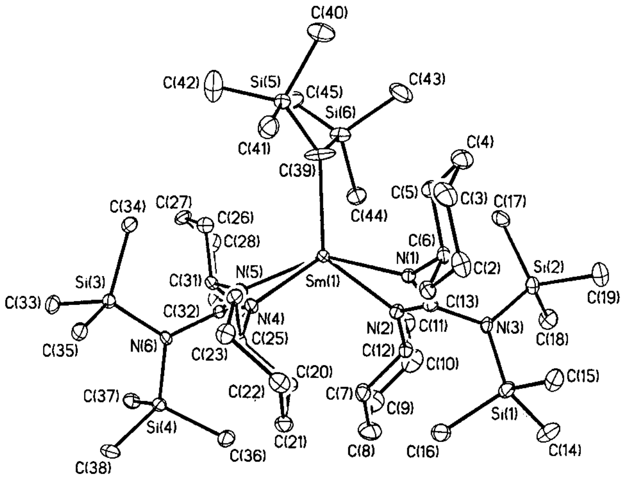

Figure 1. ORTEP diagram for one of the three symmetry unique molecules of **7**. Thermal ellipsoids are drawn at 30% probability. Selected bond distances (Å) and angles (deg): Sm(1)−N(4) 2.395(4), Sm(1)−N(1) 2.424(4), Sm(1)−N(2) 2.424(4), Sm(1)−N(5); 2.426(4), Sm(1)−C(39) 2.472(5); N(1)−Sm(1)−N(2) 55.06(13), N(4)−Sm(1)−N(5) 55.59(13), N(1)−Sm(1)−C(39) 104.7(2), N(2)−Sm(1)−C(39) 124.2(2), N(5)−Sm(1)−C(39) 106.9(2), N(4)−Sm(1)−C(39) 119.3(2), C(13)−N(1)−Sm(1) 95.3(3), C(13)−N(2)−Sm(1) 95.4(3), C(13)−N(3)−Si(1) 119.9(3), C(13)−N(3)−Si(2) 117.6(3), Si(1)−N(3)−Si(2) 122.5(2), C(32)−N(4)−Sm(1) 96.1(3), C(32)−N(5)−Sm(1) 94.6(3), N(3)−C(13)−Sm(1) 174.2(3).

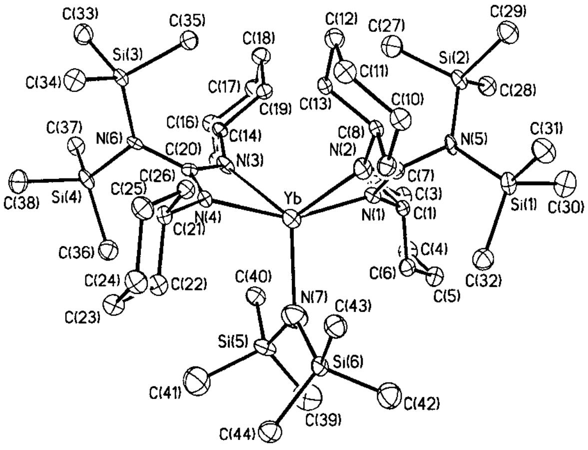

Figure 2. ORTEP diagram for **8**. Thermal ellipsoids are drawn at 30% probability. Selected bond distances (Å) and angles (deg): Yb−N(1) 2.329(13), Yb−N(2) 2.301(15), Yb−N(3) 2.311(13), Yb−N(4) 2.328(12), Yb−N(7) 2.343(19), N(1)−Yb−N(2) 58.0(5), N(3)−Yb−N(4) 57.9(4), N(1)−Yb−N(7) 100.6(6), N(2)−Yb−N(7) 119.4(6), N(3)−Yb−N(7) 124.6(6), N(4)−Yb−N(7) 104.6(6), C(7)−N(1)−Yb 94.5(10), C(7)−N(2)−Yb 93.7(11), C(7)−N(5)−Si(1) 118.7(11), C(7)−N(5)−Si(2) 118.5(11), Si(1)−N(5)−Si(2) 122.7(8), C(20)−N(3)−Yb 92.7(10), C(20)−N(3)−Yb 92.7(10).

approximately C_2 symmetric molecular geometry in which the pseudo-2-fold axis lies along the Sm−C(39) bond.

Characteristically, the alkyl carbon is nearly planar and the Sm−C distance of 2.472(5) Å compares favorably with the closely related yttrium species $[C_6H_5C(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (Y−C 2.431(5) Å)[15] and falls within the range reported for $SmCH(SiMe_3)_2$-containing compounds.[21]

The dihedral angle formed by the planar $N(SiMe_3)_2$ function and the SmNCN plane (average for all molecules 82.5°) militates against π-overlap between these two moieties. The nearly perpendicular disposition is likely the result of steric interactions between the cyclohexyl functions and the bulky trimethylsilyl groups. This orientation of the bulky $N(SiMe_3)_2$ group effectively adds a third dimension to the steric bulk of the otherwise essentially planar guanidinate ligand.

The structural analysis of **8** (Figure 2) revealed a monomeric species with general features similar to **7** with $CH(SiMe_3)_2$ replaced by $N(SiMe_3)_2$. Again, the coordination geometry of Yb in this species is best described as trigonal planar with the bisector of the guanidinate ligands (Yb−C(7)) and Yb−C(20) vectors) defining two vertexes subtending an angle of 130.5°. The metal−amido linkage defines the third vertex. These three vectors lie in a plane. As was observed for **7**, the two coordinated nitrogen atoms and bridging carbon atoms of the guanidinate ligands are planar. The amido nitrogen atom, N(7), is also planar as are the $N(SiMe_3)_2$ groups of the guanidinate ligands. The possibility of a π interaction between these $N(SiMe_3)_2$ functions and the bidentate NCN fragments can be ruled out on the basis of the observed dihedral angles of 100.8 and 100.1°.

We have some evidence that the reported guandinate anions were also able to function as supporting ligands for soluble Yb(II) complexes (Scheme 2). Entry to $\{CyNC[N(SiMe_3)_2]NCy\}_2Yb(TMEDA)$ (**10**) is provided by either reduction of **4** with Na/K alloy or by direct reaction of YbI_2 with the $\{CyNC[N(SiMe_3)_2]NCy\}^-$ anion. In the first case the solvated complex, **10**, is generated directly due to the presence of TMEDA in the starting material. Both preparations proceed in excellent yield. The diamagnetic nature of divalent Yb allowed definitive characterization of these materials by NMR spectroscopy. Equivalence of the Cy groups in the NMR spectra, as exemplified by the single resonance (3.47 ppm) for the cyclohexyl protons α to nitrogen and corresponding carbon (57.5 ppm), indicates a symmetrical and/or fluxional structure for **10** and is a point of future investigation. These compounds are analogues of the reported Yb(II) benzamidinates (e.g. p-$PhC_6H_4C(NSiMe_3)_2]_2Yb$), which were prepared from YbI_2.[14]

Through a combination of X-ray crystallographic and spectroscopic studies, we have confirmed that substituted guanidinate anions can function as ligands for the preparation of a novel family of lanthanide complexes. These results contribute to revealing the steric and electronic features that influence the reactivity of metal guanidinate compounds. The alkyl complexes **6** and **7** are certainly interesting species; they are readily soluble nonpolar solvents and reactive with a variety of substrates. Their use as precursors to catalytically active species, and the reactivity of the reported Yb(II) complexes is currently under investigation.

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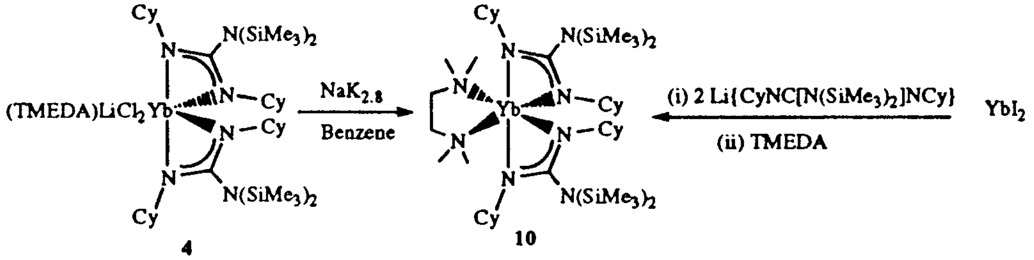
Scheme 2



Experimental Section

General Considerations. All manipulations were carried out in either a nitrogen-filled drybox or under nitrogen using standard Schlenk-line techniques. Solvents were distilled under nitrogen from Na/K alloy. Deuterated benzene was dried by vacuum transfer from potassium. Ytterbium, ICH_2CH_2I, and 1,3-dicyclohexylcarbodiimide were purchased from Aldrich and used without further purification. ^1H NMR spectra were run on a Gemini 200 MHz spectrometer with deuterated benzene or toluene as a solvent and internal standard. All elemental analyses were run on a Perkin-Elmer PE CHN 4000 elemental analysis system.

$Li[C_6H_{11}NC(N(SiMe_3)_2)NC_6H_{11}]$ (1). A Schlenk flask was charged with dicyclohexylcarbodiimide (1.00 g, 4.85 mmol), lithium bis(trimethylsilyl)amide (0.77 g, 4.85 mmol), diethyl ether (30 mL), and a stir bar. The mixture was stirred overnight at room temperature. Removal of solvent under oil pump vacuum gave **1** as white solid in quantitative yield. ^1H NMR (C_6D_6, ppm): 3.38 (br, 2H, C_6H_{11}), 2.07−1.05 (m, 20H, C_6H_{11}), 0.36 (s, 18H, $SiMe_3$).

$[C_6H_{11}NC(N(SiMe_3)_2)NC_6H_{11}]_2Yb[Cl_2Li(C_2H_5OC_2H_5)_2]$ (2). A Schlenk flask was charged with **1** (2.65 g, 7.24 mmol), $YbCl_3$ (1.00 g, 3.62 mmol), and THF (90 mL). The reaction mixture was stirred overnight at room temperature. Solvent was removed under vacuum, and the yellow residue was extracted with diethyl ether and filtered to remove LiCl. The diethyl ether solution was concentrated to 30 mL and cooled to −30 °C. Bright yellow crystals of **2** were collected in two crops by filtration (3.61 g, 2.28 mmol, 88%). The product was subsequently recrystallized from diethyl ether, mp (sealed) 135 °C dec. IR (Nujol, cm^{-1}): 1635 (w), 1435 (s), 1344 (s), 1260 (s), 1183 (s), 1004 (s), 954 (s), 846 (s), 665 (m). Anal. Calcd for $C_{46}H_{100}Cl_2LiN_6O_2Si_4Yb$: C, 48.78; H, 8.90; N, 7.42. Found: C, 48.93; H, 8.67; N, 7.22.

$[C_6H_{11}NC(N(SiMe_3)_2)NC_6H_{11}]_2Sm[Cl_2Li(C_2H_5OC_2H_5)_2]$ (3). Following a procedure similar to the synthesis of **2**, using 2.85 g of **1** (7.79 mmol), 1.00 g of $SmCl_3$ (3.90 mmol), and 90 mL of THF followed by crystallization from diethyl ether yielded bright yellow crystals of **3** (3.42 g, 2.22 mmol, 79%), mp (sealed) 157 °C dec. IR (Nujol, cm^{-1}): 1637 (w), 1448 (s), 1355 (s), 1260 (s), 1177 (s), 1065 (s), 963 (s), 836 (s) 662 (m). ^1H NMR (toluene-d_8, ppm): 1.43 (br); 3.30, 1.17 (br). Anal. Calcd for $C_{46}H_{100}Cl_2LiN_6O_2Si_4Sm$: C, 49.78; H, 9.08; N, 7.57. Found: C, 49.82; H, 9.06; N, 7.60.

$[C_6H_{11}NC(N(SiMe_3)_2)NC_6H_{11}]_2Yb[Cl_2Li(Me_2NCH_2CH_2NMe_2]$ (4). Complex **2** (1.00 g, 0.88 mmol) was dissolved in 20 mL of diethyl ether, and excess of TMEDA was added. The reaction mixture stood at room temperature for 1 day. The resulting bright yellow crystals were collected by filtration, washed with hexane, and dried under vacuum (0.94 g, 0.83 mmol, 94%), mp (sealed) 224 °C dec. IR (Nujol, cm^{-1}): 1639 (w), 1448 (s), 1355 (s), 1257 (s), 1091 (s), 1016 (s), 952 (s), 835 (s) 642 (m). Anal. Calcd for $C_{44}H_{96}Cl_2LiN_8Si_4Yb$: C, 48.02; H, 8.79; N, 10.18. Found: C, 48.22; H, 9.00; N, 10.25.

$[C_6H_{11}NC(N(SiMe_3)_2)NC_6H_{11}]_2Sm[Cl_2Li(Me_2NCH_2CH_2NMe_2]$ (5). Complex **3** (1.00 g, 0.93 mmol) was dissolved in 15 mL of diethyl ether, and excess of TMEDA was added. The reaction mixture stood at room temperature for 1 day. The resulting pale yellow crystals were collected by filtration, washed with hexane, and dried under vacuum (0.91 g, 0.84 mmol, 91%), mp (sealed) 200 °C dec. IR (Nujol, cm^{-1}): 1635 (w), 1445 (s), 1350 (s), 1256 (s), 1182 (s), 1071 (s), 965 (s), 838 (s) 657 (m). ^1H NMR (toluene-d_8, ppm): 3.00 (br); 2.33 (br, s) 2.19 (br, s); 2.00−1.10 (br, m); −1.8 (br, m). Anal. Calcd for $C_{44}H_{96}Cl_2LiN_8Si_4Sm$: C, 49.03; H, 8.98; N, 10.40. Found: C, 49.30; H, 9.09; N, 10.60.

$[C_6H_{11}NC(N(SiMe_3)_2)NC_6H_{11}]_2YbCH(SiMe_3)_2$ (6). A Schlenk flask was charged with **2** (2.00 g, 1.77 mmol) and toluene (50 mL). The solution was cooled to −78 °C, and $LiCH(SiCH_3)_2$ (0.29 g, 1.77 mmol) was added. The reaction mixture was stirred overnight, during which time it slowly warmed to room temperature. The solvent was removed under vacuum, and the residue was extracted with hexane (50 mL). Concentration to 15 mL and cooling to −30 °C yielded orange crystals of **6** (1.47 g, 1.38 mmol, 78%), mp (sealed) 95−97 °C. IR (Nujol, cm^{-1}): 1632 (w), 1443 (s), 1344 (s), 1253 (s), 1180 (s), 1131 (s), 1065(m), 1010 (s), 963 (s), 945 (s), 863 (s), 838 (s), 758 (m), 637 (m). ^1H NMR (C_6D_6, ppm): 11.9 (br), 1.23 (s), 0.92 (s), −2.24 (br), −7.1 (br), −11.5 (br), −22.7 (br), −23.5 (br). Anal. Calcd for $C_{45}H_{99}N_6Si_6Yb$: C, 50.71; H, 9.36; N, 7.88. Found: C, 50.66; H, 9.22; N, 7.63.

$[C_6H_{11}NC(N(SiMe_3)_2)NC_6H_{11}]_2SmCH(SiMe_3)_2$ (7). Following a procedure similar to the synthesis of **6**, **3** (2.00 g, 1.86 mmol) was dissolved in toluene (50 mL) and $LiCH(SiCH_3)_2$ (0.31 g, 1.86 mmol) was added at −78 °C. After stirring overnight and workup, **7** was isolated as a crude material. Crystals were obtained by dissolving the crude material in hexamethyldisiloxane (approximately 30 mL) and cooling −30 °C. Bright yellow crystals were collected by filtration (1.64 g, 1.36 mmol, 73%). This compound can also be crystallized from diethyl ether, mp (sealed) 64−65 °C. IR (Nujol, cm^{-1}): 1635 (w), 1435 (s), 1344 (s), 1256 (s), 1177 (s), 1135 (s), 1065 (m), 1004 (s), 963 (s), 941 (s), 863 (s), 846 (s), 758 (m), 639 (m). ^1H NMR (C_6D_6, ppm): 15.83 (s), 3.20 (br, m), 1.87 (br), 0.88 (m), 0.585 (br) −1.32 (m), −2.19 (s) −5.36 (br s). Anal. Calcd for $C_{45}H_{99}N_6Si_6Sm$: C, 51.81; H, 9.57; N, 8.06. Found: C, 52.11; H, 9.89; N, 8.11.

$[C_6H_{11}NC(N(SiMe_3)_2)NC_6H_{11}]_2YbN(SiMe_3)_2$ (8). A Schlenk flask was charged with **2** (1.00 g, 0.88 mmol), $LiN(SiCH_3)_2$ (0.14 g, 0.88 mmol), and diethyl ether (25 mL). The reaction mixture was stirred overnight at room temperature. Filtration to remove LiCl and removal of solvent gave a yellow solid (0.78 g, 0.73 mmol, 83%). The product was subsequently recrystallized from diethyl ether at −30 °C, mp (sealed) 193 °C dec. IR (Nujol, cm^{-1}): 1633 (w), 1450 (s), 1350 (s), 1252 (s), 1184 (s), 1137 (s), 1071 (m), 1004 (s), 965 (s), 937 (s), 863 (s), 838 (s), 756 (m), 665 (m), 642 (m). Anal. Calcd for $C_{44}H_{98}N_7Si_6Yb$: C, 49.54; H, 9.26; N, 9.19. Found: C, 49.23; H, 9.25; N, 8.87.

$[C_6H_{11}NC(N(SiMe_3)_2)NC_6H_{11}]_2SmN(SiMe_3)_2$ (9). A Schlenk flask was charged with **3** (1.00 g, 0.93 mmol), $LiN(SiCH_3)_2$ (0.15 g, 0.93 mmol), and diethyl ether (20 mL). The reaction mixture was stirred overnight at room temperature. Filtration to remove LiCl and removal of solvent gave a colorless solid (0.85 g, 0.81 mmol, 87%). The product was subsequently recrystallized from ether at −30 °C, mp (sealed) 200 °C dec. IR (Nujol, cm^{-1}): 1636 (w), 1444 (s), 1344 (s), 1298 (m), 1250 (s), 1174 (s), 1137 (s), 1061(m), 1004 (s), 965 (s), 941 (s), 863 (s), 804 (s), 756 (m), 642 (m). ^{1}H NMR (C_6D_6, ppm): 1.85 (s); −3.38 (s). Anal. Calcd for $C_{44}H_{98}N_7Si_6Sm$: C, 50.61; H, 9.46; N, 9.39. Found: C, 50.80; H, 9.89; N, 9.65.

$[C_6H_{11}NC(N(SiMe_3)_2)NC_6H_{11}]_2Yb[Me_2NCH_2CH_2NMe_2]$ (10). In a drybox, a flask was charged with **4** (1.00 g, 0.91 mmol), excess $NaK_{2.8}$, and benzene (15 mL). The reaction mixture was stirred at room temperature for 5 days. The solvent was removed under vacuum, and the residue was extracted with hexane. Filtration and removal of solvent gave deep red **10** (0.60 g, 0.58 mmol, 64%), mp (sealed) 50−53 °C dec. IR (Nujol, cm^{-1}): 1545 (s), 1477 (s), 1290 (s), 1249 (s), 1168 (s), 1122 (s), 1068 (s), 994 (s), 945 (s), 889 (s), 863 (s), 838 (s), 755 (m), 695 (m), 639 (m). ^{1}H NMR (benzene-d_6, ppm): 3.58 (br, 4H, C_6H_{11}), 2.38 (s, 12H, NMe_2), 2.10−1.20 (m, 44H, C_6H_{11} and NCH_2), 0.37 (s, 36H, $SiMe_3$). ^{13}C NMR (C_6D_6, ppm): 168.2 (s, CN_3); 57.5, 39.0, 26.8, 26.7 (4s, C_6H_{11}) 55.7 (NCH_3), 45.6 (NCH_2), 3.32 ($SiCH_3$). Anal. Calcd for $C_{44}H_{96}N_8Si_4Yb$: C, 51.68; H, 9.46; N, 10.96. Found: C, 51.60; H, 9.35; N, 10.87. MS: m/z 1022 (M^+).

Crystallographic Study of 7. A suitable crystal of **7** was mounted on a glass fiber. Systematic absences and the unit-cell parameters are uniquely consistent for the reported space group. No absorption correction was required. The structure was solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. All computations used the SHELXTL (5.03) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Crystallographic Study of 8. Intensity data were collected on a Rigaku diffractometer at −153 °C using the $\theta-2\theta$ scan technique for crystals mounted on glass fibers. The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with $I > 2.5\sigma(I)$. Anomalous dispersion effects were included in the F_c. All calculations were performed using the NRCVAX package. Full details of the data collection, refinement, and final atomic coordinates are reported in the Supporting Information.

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Supporting Information Available: Listings providing complete descriptions of the structural solutions and ORTEP drawings for compounds **7** and **8** (44 pages). Ordering information is given on any current masthead page.

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