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Synthesis and Structural Characterization of a Series of Lanthanide(II) Amides: Steric Effect of Amido Ligand

Liying Zhou,[†] Junfeng Wang,[†] Yong Zhang,[†] Yingming Yao,[†] and Qi Shen*,[†]

Key Laboratory of Organic Synthesis, Jiangsu Province, Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, PR China

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The synthesis and structures of a series of lanthanide(II) and lanthanide(III) complexes supported by the amido ligand $N(SiMe_3)Ar$ were described. Several lanthanide(III) amide chlorides were synthesized by a metathesis reaction of $LnCl_3$ with lithium amide, including $\{[(C_6H_5)(Me_3Si)N]_2YbCl(THF)\}_2{\cdot}PhCH_3$ (**1**), $[(C_6H_3\text{-}^{i}Pr_2\text{-}2,6)(SiMe_3)N]_2YbCl(\mu\text{-}Cl)Li(THF)_3{\cdot}PhCH_3$ (**4**), $[(C_6H_3\text{-}^{i}Pr_2\text{-}2,6)(SiMe_3)N]YbCl_2(THF)_3$ (**6**), and $[(C_6H_3\text{-}^{i}Pr_2\text{-}2,6)(SiMe_3)N]_2SmCl_3Li_2(THF)_4$ (**7**). The reduction reaction of **1** with Na–K alloy afforded bisamide ytterbium(II) complex $[(C_6H_5)(Me_3Si)N]_2Yb(DME)_2$ (**2**). The same reaction for Sm gave an insoluble black powder. An analogous samarium(II) complex $[(C_6H_5)(Me_3Si)N]_2Sm(DME)_2$ (**3**) was prepared by the metathesis reaction of SmI_2 with $NaN(C_6H_5)(SiMe_3)$. The reduction reaction of ytterbium chloride **4** with Na–K alloy afforded monoamide chloride $\{[(C_6H_3\text{-}^{i}Pr_2\text{-}2,6)(SiMe_3)N]Yb(\mu\text{-}Cl)(THF)_2\}_2$ (**5**), which is the first example of ytterbium(II) amide chloride, formed via the cleavage of the Yb–N bond. The same reduction reaction of **7** gave a normal bisamide complex $[(C_6H_3\text{-}^{i}Pr_2\text{-}2,6)(SiMe_3)N]_2Sm(THF)_2$ (**8**) via Sm–Cl bond cleavage. This is the first example for the steric effect on the outcome of the reduction reaction in lanthanide(II) chemistry. **5** can also be synthesized by the Na/K alloy reduction reaction of **6**. All of the complexes were fully characterized including X-ray diffraction for **1**–**7**.

Introduction

The nature of the ancillary ligand plays a crucial role in determining the reactivity/stability of lanthanide(II) complexes. For example, the lanthanide(II) complexes supported by cyclopentadienyl-based ligands have been proven to show rich chemical transformations because the unique versatility of the C_5R_5 ligand puts forth the electronic and steric requirements necessary for stabilizing a wide variety of complexes.[1] Therefore, great effort has been made to develop suitable ligands, other than cyclopentadienyl systems, for stabilizing the divalent complexes, which show unique reactivity in chemical transformations.[2−7] Amido ligands, as the alternatives, have recently attracted increasing attention because their electronic and steric properties can be changed conveniently by the variation of the substituents on the nitrogen atom.[8] Thus, quite a few lanthanide(II) complexes based on amido ligands have been developed. The pyrrolide-based lanthanide(II) complexes have been demonstrated to

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* To whom correspondence should be addressed. E-mail: qshen@suda.edu.cn.

[†] Suzhou University.

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possess unique reactivity.[6] The complexes $Ln[N(SiMe_3)_2]_2(Sol)$ are not only excellent precursors to a variety of lanthanide(II) complexes, but also are precatalysts for polymerization of polar monomers.[7b−g] Moreover, The bulky silylamido ligand, $[N(SiMe_3)_2]$, has been found to provide the steric, electrostatic, and solubility characteristics required for the divalent samarium halide, $[(Me_3Si)_2NSm(\mu\text{-}I)(DME)(THF)]_2$.[7a] However, the study on the steric effect of the amido ligand on the reactivity of lanthanide(II) amide complexes has been limited. However, whereas a variety of examples revealed the influence of metal size on reactivity/stability in lanthanide(III) complexes,[9] less attention has been paid to address the relationship between the stability/reactivity and the size of the metal in the chemistry of organolanthanide(II) complexes. This might be mainly because the oxidation potential of metals plays a crucial role in determining the structures and reactivity of lanthanide(II) complexes. For example, the reaction of metallocenes $(C_5Me_5)_2Ln(II)$ with $PhC{\equiv}CH$ afforded a trivalent complex $[(C_5Me_5)_2Sm]_2(PhC{=}C{=}C{=}CPh)$ for Sm,[10a] a mixed-valence complex $[(C_5Me_5)_2Yb^{III}]_2(\mu\text{-}C{\equiv}CPh)_4Yb^{II}$ for Yb, and a divalent complex $[(C_5Me_5)Eu(\mu\text{-}C{\equiv}CPh)(THF)_2]_2$ for Eu,[10b] depending on the reduction potentials of the metals. Moreover, the Sm(II) complexes show remarkable reactivity, which may not found for Yb(II) and Eu(II).[9a,10c,d]

During our study on the synthesis of a series of lanthanide(II) amides with different bulks of amido ligand, we found that the outcome of the reduction reaction of bisamide lanthanide chloride with Na/K depends both on the metal size and on the bulk of amido ligand. Here, we would like to report the results.

Experimental Section

General Procedures. All of the manipulations were performed under pure Ar with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl prior to use. Deuterated benzene (C_6D_6) was purchased from Acros, and was dried over sodium and vacuum-transferred. ϵ-CL was purchased from Acros, dried by stirring with CaH_2 for 48 h, and then distilled under reduced pressure. Anhydrous $LnCl_3$,[11] $HN(C_6H_5)(SiMe_3)$,[12] and $HN(C_6H_3\text{-}{}^iPr_2\text{-}2,6)(SiMe_3)$[12] were prepared according to the literature procedures. Melting points were determined in sealed Ar-filled capillary tubes and are uncorrected. Metal analyses were carried out by complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA = 1110 instrument. The IR spectra were recorded on a Magna-IR 550 spectrometer. ^1H NMR spectra were measured on a Unity Inova-400 spectrometer.

Synthesis of $\{[(C_6H_5)(Me_3Si)N]_2YbCl(THF)\}_2\cdot C_7H_8$ (1). A Schlenk flask was charged with $HN(C_6H_5)(SiMe_3)$ (2.66 mL, 17.60 mmol), hexane (10 mL), and a stir bar. The solution was cooled to 0 °C, and *n*-BuLi (15.04 mL, 17.60 mmol, 1.17 M in hexane) was added. The solution was slowly warmed to room temperature and stirred for 1 h. Then, this solution was added slowly to a pale-gray slurry of $YbCl_3$ (2.46 g, 8.80 mmol) in 20 mL of THF. The resulting solution was stirred for 48 h at room temperature. The solvent was removed under a vacuum, and the residue was extracted with toluene to remove LiCl by centrifugation. After the extracts were concentrated, red crystals (4.90 g, 85%, based on $YbCl_3$) were obtained at the room temperature for a few days. Mp 150−152 °C (dec). The ^1H NMR spectrum of this compound displayed very broad resonances and proved uninformative because of the paramagnetism of Yb metal. Anal. Calcd for $C_{51}H_{80}Cl_2N_4O_2Si_4Yb_2$ (1310.53): C 46.74, H 6.15, N 4.28, Yb 26.41. Found: C 46.53, H 6.02, N 4.30, Yb 26.16. IR (KBr pellet, cm^{-1}): 3040 (w), 2959 (m), 2901 (w), 1605 (s), 1501 (s), 1439 (w), 1385 (m), 1296 (m), 1254 (s), 1157 (m), 995 (w), 899 (s), 841 (s), 752 (m), 694 (m), 625 (w), 505 (m).

Synthesis of $[(C_6H_5)(Me_3Si)N]_2Yb(DME)_2$ (2). A Schlenk flask was charged with **1** (5.02 g, 3.83 mmol), THF (20 mL), and a stir bar. Then the Na−K alloy (0.18 g, 0.04 g, 5 mL of toluene) was added. The resulting solution was stirred for 72 h at 40 °C. The solvent was centrifugated and NaCl was removed. The solvent was removed under a vacuum and 15 mL of DME was added. After a few days, orange-red crystals (3.55 g, 68%) were obtained at room temperature. Mp 110 °C (dec). ^1H NMR (400 MHz, C_6D_6, 25 °C, δ): = 6.64−7.20 (m, 10H, *H*-Ph); 3.24 (m, 8H, *H*-DME); 3.11 (s, 12H, *H*-DME); 0.14 (s, 18H, $\text{-}Si(CH_3)_3$). Anal. Calcd for $C_{26}H_{48}N_2O_4Si_2Yb$ (681.88): C 45.80, H 7.09, N 4.11, Yb 25.38. Found: C 45.66, H 6.92, N 4.30, Yb 25.85. IR (KBr pellet, cm^{-1}): 3044 (w), 2955 (m), 2893 (m), 2824 (w), 1605 (s), 1501 (s), 1447 (w), 1385 (m), 1296 (s), 1250 (s), 1157 (s), 1107 (m), 1030(w), 995 (w), 903 (s), 841 (s), 752 (m), 694 (m), 637 (w), 556 (w), 505 (m).

Synthesis of $[(C_6H_5)(Me_3Si)N]_2Sm(DME)_2$ (3).

Path A: A solution of $LiN(C_6H_5)(SiMe_3)$ (2.79 mL, 15.82 mmol, 20 mL hexane) was added slowly to a slurry of $SmCl_3$ (2.03 g, 7.91 mmol) in THF (20 mL). The resulting solution was stirred for 48 h at room temperature. To the resulting yellow solution, the Na−K alloy (0.18 g, 0.04 g, 5 mL of toluene) was added. The mixture was stirred for 72 h at 40 °C. The color of the solution changed from yellow to dark brown, and an insoluble black solid separated out from the resulting solution.

Path B: A Schlenk flask was charged with SmI_2 (30.0 mL, 3.00 mmol, 0.10 M in THF) and a stir bar, then $NaN(C_6H_5)(SiMe_3)$ (12.25 mL, 6.00 mmol, 0.49 M in THF) was added by a syringe.

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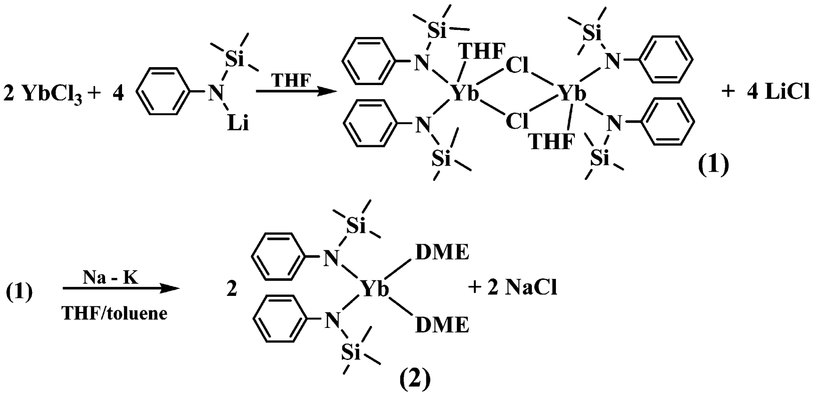
Scheme 1



The resulting solution was then stirred for another 24 h and removed under a vacuum. The residue was extracted with toluene to remove NaI by centrifugation. The solvent was removed under a vacuum and 15 mL of DME was added. Black crystals (1.54 g, 78%) were obtained at 0 °C for a few days. Mp 115−116 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C, δ): = 10.76 (br, 8H, *H*-DME); 7.42 (m, 4H, *H*-Ph); 6.79 (m, 2H, *H*-Ph); 6.58 (m, 4H, *H*-Ph); −0.28 (s, 18H, -Si(C*H*$_3$)$_3$); −1.26 (br, 12H, *H*-DME). Anal. Calcd for $C_{26}H_{48}N_2O_4Si_2Sm$ (659.19): C 47.37, H 7.34, N 4.25, Sm 22.81. Found: C 47.03, H 7.15, N 4.15, Sm 22.69. IR (KBr pellet, cm^{-1}): 2956 (s), 2902 (s), 2871 (s), 1574 (s), 1474 (s), 1335 (s), 1328 (s), 1204 (m), 1173 (m), 1120 (w), 1026 (m), 880(m), 841(m), 741 (m), 702 (w), 602 (w), 533 (m), 448 (m).

Synthesis of [(C_6H_3-^{i}Pr$_2$-2,6)(SiMe$_3$)N]2YbCl(μ-Cl)Li(THF)$_3$·PhCH$_3$ (4). A solution of LiN(C_6H_3-^{i}Pr$_2$-2,6)(SiMe$_3$) (18.26 mmol, 20 mL hexane) was added slowly to a slurry of YbCl$_3$ (2.55 g, 9.13 mmol) in THF (20 mL). The resulting solution was stirred for 48 h at room temperature. The solvent was removed under a vacuum, and proper toluene was added to remove LiCl by centrifugation. Orange crystals (8.68 g, 90%) were obtained at room temperature from the toluene solution. Mp 103−104 °C. The ^{1}H NMR spectrum of this compound displayed very broad resonances and proved uninformative because of the paramagnetism of Yb metal. Anal. Calcd for $C_{49}H_{84}Cl_2LiN_2O_3Si_2Yb$ (1056.24): C 55.72, H 8.02, N 2.65, Yb 16.38. Found: C 55.34, H 7.91, N 2.55, Yb 16.15. IR (KBr pellet, cm^{-1}): 2964(s), 2871(m), 1628(s), 1505(w), 1459(m), 1389(w), 1366(w), 1266(w), 1119(w), 1050(w), 749(m), 641(s).

Synthesis of {[(C_6H_3-^{i}Pr$_2$-2,6)(SiMe$_3$)N]Yb(μ-Cl)(THF)$_2$}$_2$ (5).

Path A: To a THF (20 mL) solution of **4** (7.98 mmol) was added the Na−K alloy (0.18 g, 0.04 g, 5 mL of toluene). The mixture was stirred for 72 h at 40 °C. The color of the solution changed from red to orange-yellow. The precipitate was separated by centrifugation. After removal of THF/toluene, extraction with toluene, and centrifugation to separate NaCl/KCl, a toluene solution was obtained, which gave yellow crystals (3.26 g, 68%) at room temperature. Mp 162−163 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C, δ): 6.90−7.10 (m, 6H, *H*-Ph); 3.44−4.02 (m, 20H, *H*-THF and −C*H*(CH$_3$)$_2$); 1.19−1.50 (m, 40H, *H*-THF and −CH(C*H*$_3$)$_2$), 0.46 (s, 18H, −Si(C*H*$_3$)$_3$). Anal. Calcd for $C_{46}H_{84}Cl_2N_2O_4Si_2Yb_2$ (1202.31): C 45.95, H 7.04, N 2.33, Yb 28.78. Found: C 45.72, H 6.91, N 2.54, Yb 28.87. IR (KBr pellet, cm^{-1}): 2962(s), 2871(w), 1622(s), 1462(w), 1438(m), 1385(w), 1251(m), 1156(m), 746(m), 505(m).

Path B: To a THF (20 mL) solution of **6** (6.00 mmol) was added the Na−K alloy (0.14 g, 0.03 g, 5 mL of toluene). The mixture was stirred for 72 h at 40 °C. The color of the solution changed from orange to yellow. After workup, yellow crystals (2.70 g, 75%) were obtained from the toluene solution.

Synthesis of [(C_6H_3-^{i}Pr$_2$-2,6)(SiMe$_3$)N]YbCl$_2$(THF)$_3$(6). A Schlenk flask was charged with LiN(C_6H_3-^{i}Pr$_2$-2,6)(SiMe$_3$) (10.67 mmol, 20 mL hexane) prepared freshly. Then, this solution was added slowly to a pale-gray slurry of YbCl$_3$ (2.98 g 10.67 mmol) in 20 mL THF. The resulting solution was stirred for 48 h at room temperature. The solvent was removed under a vacuum, and the residue was extracted with toluene to remove LiCl by centrifugation. After the extracts were concentrated, orange-yellow crystals (6.65 g, 88%) were obtained at room temperature for a few days. Mp 122 °C (dec). The ^{1}H NMR spectrum of this compound displayed very broad resonances and proved uninformative. Anal. Calcd for $C_{27}H_{50}Cl_2NO_3SiYb$ (708.71): C 45.76, H 7.11, N 1.98, Yb 24.42. Found: C 45.42, H 6.94, N 2.13, Yb 24.75. IR (KBr pellet, cm^{-1}): 2964(s), 2871(s), 2555(w), 1621(s), 1528(s), 1466(m), 1381(m), 1320(m), 1258(m), 1181(w), 1111(w), 1042(m), 880(m), 841(m), 795(m), 741(m), 664(m), 486(w).

Synthesis of [(C_6H_3-^{i}Pr$_2$-2,6)(SiMe$_3$)N]$_2$SmCl$_3$Li$_2$(THF)$_4$ (7). Following the procedure similar to the synthesis of **4**, using LiN(C_6H_3-^{i}Pr$_2$-2,6)(SiMe$_3$) (16.08 mmol, 20 mL hexane), SmCl$_3$ (2.06 g, 8.04 mmol) and THF (20 mL), followed by crystallization from toluene, yielded light-yellow crystals of **7** (7.21 g, 85%). Mp 73−74 °C. The ^{1}H NMR spectrum of this compound displayed very broad resonances and proved uninformative. Anal. Calcd for $C_{46}H_{84}Cl_3Li_2N_2O_4Si_2Sm$ (1055.91): C 52.33, H 8.02, N 2.65, Sm 14.24. Found: C 52.21, H 7.87, N 2.83, Sm 14.53. IR (KBr pellet, cm^{-1}): 3063(w), 2962(s), 2870(w), 1622(s), 1461(m), 1438(m), 1384(w), 1265(m), 1045(w), 788(m), 745(s), 592(m).

Synthesis of [(C_6H_3-^{i}Pr$_2$-2,6)(SiMe$_3$)N]$_2$Sm(THF)$_2$ (8). To a THF (20 mL) solution of **7** (6.80 g, 6.44 mmol) was added the Na−K alloy (0.15 g, 0.03 g, 5 mL toluene). The mixture was stirred for 48 h at 40 °C. The color of the solution changed from yellow to dark brown. Following the procedure similar to the synthesis of **5**, crystallization from toluene obtained the black crystals (3.67 g, 72%) at 0 °C for a few days. Mp 129−130 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C, δ): 12.10 (br, 8H, *H*-THF); 10.78 (br, 12H, CH(C*H*$_3$)$_2$); 8.05 (br, 2H, *H*-Ph); 6.76 (br, 4H, *H*-Ph); 5.58 (br, 8H, *H*-THF, *H*-Ph); −1.51 (br, 18H, Si(C*H*$_3$)$_3$); −2.04 (br, 12H, CH(C*H*$_3$)$_2$); −13.59 (br, 4H, CH(C*H*$_3$)$_2$). Anal. Calcd for $C_{38}H_{68}N_2O_2Si_2Sm$ (791.47): C 57.67, H 8.66, N 3.54, Sm 19.00. Found: C 57.48, H 8.49, N 3.65, Sm 19.23. IR (KBr pellet, cm^{-1}): 3071(w), 2963(s), 2870(w), 1624(s), 1462(m), 1439(m), 1385(m), 1250(s), 1215(m), 1157(s), 1046(w), 884(w), 841(w), 745(m), 637(w), 556(w), 505(m).

X-ray Structural Determination of 1−7: Suitable single crystals of **1**−**7** were each sealed in a thin-walled glass capillary,

Table 1. Details of the Crystallographic Data of **1**−**3** and **5**−**7**

	1	**2**	**3**	**5**	**6**	**7**
empirical formula	$C_{51}H_{80}Cl_2N_4O_2Si_4Yb_2$	$C_{26}H_{48}N_2O_4Si_2Yb$	$C_{26}H_{48}N_2O_4Si_2Sm$	$C_{46}H_{84}Cl_2N_2O_4Si_2Yb_2$	$C_{27}H_{50}Cl_2NO_3SiYb$	$C_{46}H_{84}Cl_3Li_2N_2O_4Si_2Sm$
fw	1310.53	681.88	659.19	1202.31	708.71	1055.91
cryst color	red	orange-red	black	yellow	orange-yellow	light-yellow
T (K)	193(2)	193(2)	153(2)	193(2)	193(2)	193(2)
wavelength (Å)	0.71070	0.71070	0.71070	0.71070	0.71070	0.71070
size (mm^3)	0.78 × 0.50 × 0.35	0.40 × 0.30 × 0.16	0.30 × 0.20 × 0.15	0.30 × 0.25 × 0.15	0.20 × 0.16 × 0.15	0.40 × 0.25 × 0.20
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$c2/c$	$P21/n$	$P21/n$	$P21/n$	$P21/n$	$P-1$
a (Å)	20.538(2)	8.6077(6)	8.5881(11)	9.832(3)	11.6025(14)	12.2771(7)
b (Å)	9.9638(7)	21.5836(19)	21.815(3)	15.097(4)	24.236(3)	13.2851(7)
c (Å)	29.368(3)	17.2281(15)	17.306(2)	18.925(5)	11.4942(11)	19.0245(16)
α (deg)	90	90	90	90	90	85.934(6)
β (deg)	102.125(4)	91.921(3)	91.856(3)	99.434(10)	91.401(3)	86.278(6)
γ (deg)	90	90	90	90	90	64.072(4)
V ($Å^3$)	5875.6(9)	3198.9(5)	3240.5(7)	2771.0(13)	3231.2(6)	2781.6(3)
Z	4	4	4	2	4	2
D_{calcd} ($mg\ m^{-3}$)	1.481	1.416	1.351	1.441	1.457	1.261
absorption coefficient (mm^{-1})	3.375	3.028	1.916	3.531	3.123	1.280
F (000)	2640	1392	1360	1216	1444	1106
θ (deg)	3.12−27.48	3.03−27.48	3.01−25.35	3.08−25.35	3.03−25.35	3.01−25.35
reflns collected	28 025	35 672	31 578	26 456	31 898	27 867
independent rflns	6567	7323	5926	5039	5902	10 113
params	295	327	327	270	333	534
$R\ [I > 2\sigma(I)]$	0.0451	0.0288	0.0363	0.0749	0.0556	0.0448
wR	0.1010	0.0563	0.0591	0.1400	0.0987	0.1010
GOF on F^2	1.316	1.153	1.196	1.238	1.142	1.103

and intensity data were collected on a Rigaku Mercury CCD equipped with graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation. Details of the intensity data collection and crystal data are given in Table 1. The crystal structures of these complexes were solved by direct methods and expanded by Fourier techniques. Atomic coordinates and thermal parameters were refined by full-matrix least-squares analysis on F^2. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically with assigned appropriate isotropic thermal parameters. The structures were solved and refined using the SHELXS-97 and SHELXL-97 programs.

Results and Discussion

Synthesis and characterization of Arylamide Lanthanide Complexes. To address the steric effect of the amido ligand on the synthesis, structures, and reactivity of lanthanide(II) amide complexes, the amido ligands $N(SiMe_3)$-Ar (Ar = (C_6H_5) and $(C_6H_3\text{-}^iPr_2\text{-}2,6)$) were chosen as they are available from the reaction of $ClSiMe_3$ with the corresponding arylamine or the reaction of $ClSiMe_3$ with lithium amide.[12] Reduction reactions of trivalent bisamide ytterbium chloride and bisamide samarium chloride with alkali metal were studied here in an attempt to understand the effect of metal size.

Thus, the trivalent bisamide ytterbium chloride was first synthesized. The reaction of $YbCl_3$ with the less bulky amide salt $LiN(C_6H_5)(SiMe_3)$, which was synthesized in situ by the reaction of $HN(C_6H_5)(SiMe_3)$ with n-BuLi in a mixture of hexane and THF, in a 1:2 molar ratio, followed by crystallization from toluene, yielded the red crystals in high yield. The full characterization by elemental analysis and X-ray structural determination revealed the crystals to be the dimer $\{[(C_6H_5)(Me_3Si)N]_2YbCl(THF)\}_2$ (**1**).

The reduction reaction of **1** with a slight excess of Na−K alloy went smoothly in THF/toluene. The color change from red to orange during the reaction indicates the formation of Yb(II) species. After workup, the bisamide ytterbium(II) complex $[(C_6H_5)(Me_3Si)N]_2Yb(DME)_2$ (**2**) was obtained as orange-red crystals from a DME solution in high yield (Scheme 1). The X-ray structural analysis revealed **2** to be a monomer. In comparison with the similar complex $\{Yb[N(C_6H_5)(SiMe_3)][\mu\text{-}N(C_6H_5)(SiMe_3)](THF)\}_2$, which has a dimeric structure previously reported by Lappert et al.,[13] the difference in structural motifs between the two ytterbium(II) complexes should be attributed to the presence of solvated DME molecules in **2**, which led to the prevention of the formation of amido bridges.

An attempt to synthesize the bisamide samarium(II) complex with the same amido ligand by the similar reduction reaction failed. The same reduction reaction of bisamide samarium chloride, which was synthesized in situ by the reaction of $SmCl_3$ with 2 equiv of $LiN(C_6H_5)(SiMe_3)$, by use of a slight excess of Na−K alloy afforded an insoluble black powder. The black powder could be an Sm(O) species or an insoluble Sm(II) oligomer because the demand of the higher coordination number is larger for the Sm(II) ion compared to that of Yb(II) ion. Whether it is the former or the latter is not clear because the insolubility of the black powder prevented further characterization. A similar situation

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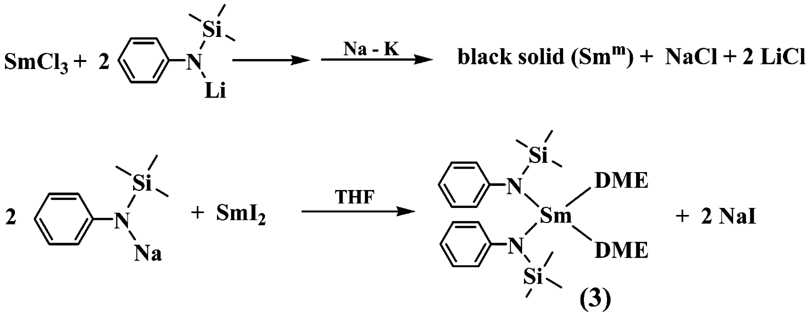
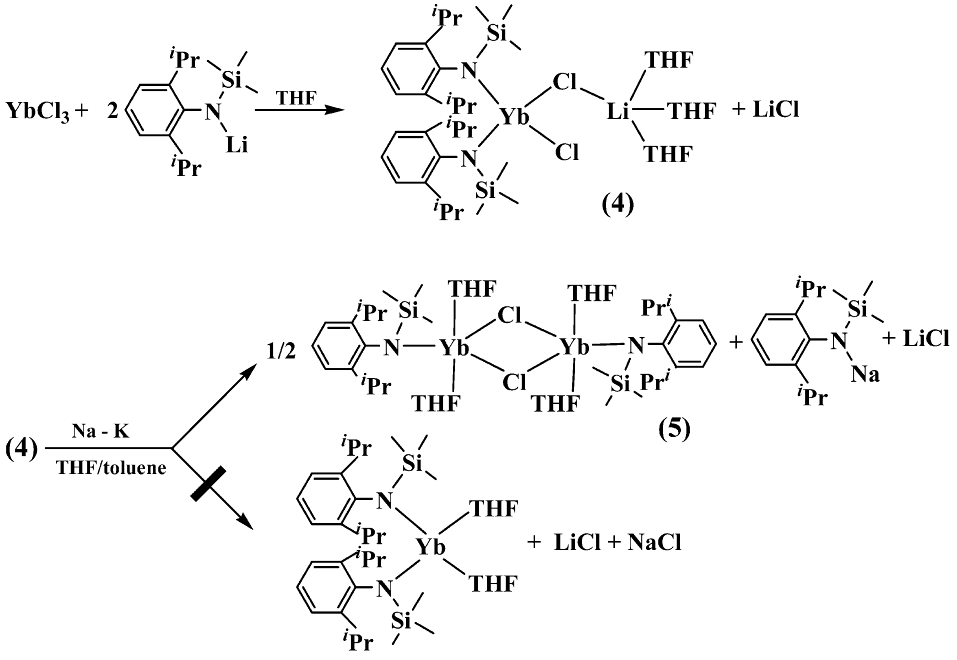
(13) Hitchcock, P. B.; Khvostov, A. V.; Lappert, M. F.; Protchenko, A. V. *J. Organomet. Chem.* **2002**, *647*, 198.

Scheme 2



Scheme 3



was also found in the reduction reaction of $[(Cy_2N)_2Sm(\mu\text{-}Cl)(THF)]_2$ with alkali metal reported by Gambarotta et al.[14]

Further study found that the bisamide samarium(II) complex could be successfully synthesized by the conventional salt metathesis approach. The reaction of SmI_2 with 2 equiv of $NaN(C_6H_5)(SiMe_3)$ proceeded smoothly in THF. After workup, black crystals of samarium(II) complex $[(C_6H_5)(Me_3Si)N]_2Sm(DME)_2$ (**3**) were isolated from DME solution (Scheme 2).

To see the influence of a bulk of amido ligand on the reduction reaction, the bisamide ytterbium chloride with a more bulky amido ligand, $N(C_6H_3\text{-}{}^iPr_2\text{-}2,6)(SiMe_3)$, was synthesized by the metathesis reaction of $YbCl_3$ with $LiN(C_6H_3\text{-}{}^iPr_2\text{-}2,6)(SiMe_3)$ in a 1:2 molar ratio. The chloride was characterized by an X-ray structural determination. Although the quality of the refinement is low, the overall structure of the molecule was clearly established to be an "ate" complex $[(C_6H_3\text{-}{}^iPr_2\text{-}2,6)(SiMe_3)N]_2YbCl(\mu\text{-}Cl)Li(THF)_3\cdot PhCH_3$ (**4**) (Supporting Information), which is similar to the anionic lanthanide methyl complex $[(C_6H_3\text{-}{}^iPr_2\text{-}2,6)(SiMe_3)N]_2YbCH_3(\mu\text{-}CH_3)_2Li(THF)_3\cdot PhCH_3$ in the structural motif.[15] The formation of an ate complex is not surprising because lithium readily affords ate salt adducts in synthetic lanthanide chemistry.[16]

The reduction reaction of the ytterbium chloride with Na−K alloy was then conducted in THF/toluene. The color changed from red to orange-yellow gradually during the reaction. After workup, yellow crystals were isolated in high yield. To our surprise, the full characterization by elemental analysis and X-ray structural determination revealed the crystals isolated to be monoamide ytterbium(II) chloride $\{[(C_6H_3\text{-}{}^iPr_2\text{-}2,6)(SiMe_3)N]Yb(\mu\text{-}Cl)(THF)_2\}_2$ (**5**), not the expected bisamide complex $[(C_6H_3\text{-}{}^iPr_2\text{-}2,6)(SiMe_3)N]_2Yb(THF)_2$ (Scheme 3). **5** can be reproduced. **5** is very sensitive to air and moisture, but more stable compared to $[(Me_3Si)_2NSm(\mu\text{-}I)(DME)(THF)]_2$, which tends toward ligand redistribution to SmI_2 and $Sm[N(SiMe_3)_2]_2$.[7a]

5 can also be obtained by Na/K alloy reduction of the monoamide ytterbium dichlorides $[(C_6H_3\text{-}{}^iPr_2\text{-}2,6)(SiMe_3)N]$-

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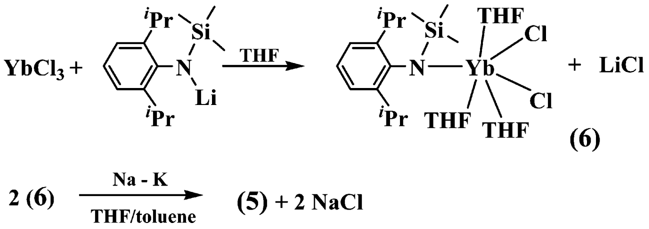
(14) Minhas, R. K.; Ma, Y.; Song, J. I. and Gambarotta, S. *Inorg. Chem.* **1996**, *35*, 1866.

(15) Luo, Y. J.; Yao, Y. M.; Li, W. J.; Chen, J. L.; Zhang, Z. Q.; Zhang, Y.; Shen, Q. *J. Organomet. Chem.* **2003**, *679*, 125.

(16) (a) Edelmann, F. T.; Freckmann, D. M. M. and Schumann, H. *Chem. Rev.* **2002**, *102*, 1851. (b) Hou, Z. M.; Wakatsuki, Y. *Coord. Chem. Rev.* **2002**, *231*, 1.

Scheme 4



$YbCl_2(THF)_3$ (**6**), which was prepared by the reaction of $YbCl_3$ with $LiN(C_6H_3\text{-}{}^i\!Pr_2\text{-}2,6)(SiMe_3)$ in a 1:1 molar ratio and characterized by X-ray crystal structural analysis (Scheme 4).

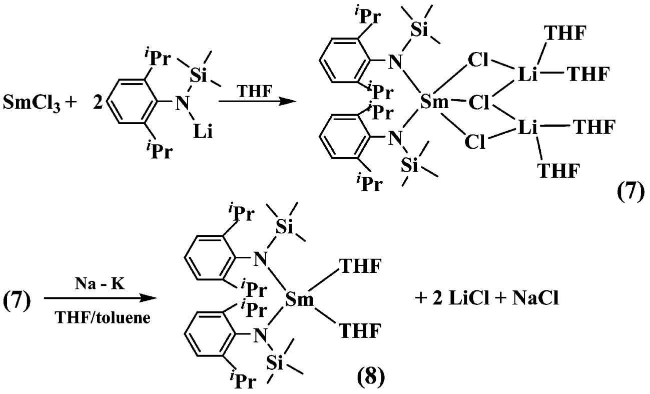
However, the metathesis reaction of YbI_2 with 1 equiv of $NaN(C_6H_3\text{-}{}^i\!Pr_2\text{-}2,6)(SiMe_3)$ in THF did not occur, from which only the starting materials were recovered.

Generally, the reduction of lanthanide(III) chloride by alkali metal often gives the corresponding Ln(II) complex and a precipitate of alkali metal chloride.[17] The result obtained from Scheme 3 indicates that the reduction reaction takes place via the cleavage of the Ln−N bond, not the Ln−Cl bond. The cleavage of the Ln−N bond prior to the Ln−Cl bond in the reduction reaction has never been found before. To see whether this is a special case for Yb, the same reduction reaction with samarium chloride was further tried. Even the divalent Sm complex $[(C_6H_3\text{-}{}^i\!Pr_2\text{-}2,6)(SiMe_3)N]_2Sm(THF)_2$ has already been synthesized by the redox transmetallation reaction of metal Sm with mercury(II) complex $Hg[N(C_6H_3\text{-}{}^i\!Pr_2\text{-}2,6)(SiMe_3)]_2$.[18] Thus, the precursor, samarium(III) chloride, was synthesized by the reaction of $SmCl_3$ with 2 equiv of $LiN(C_6H_3\text{-}{}^i\!Pr_2\text{-}2,6)(SiMe_3)$ because no such complex was reported previously. The reaction occurred in a mixture of hexane and THF and after workup, yielded the ate complex $[(C_6H_3\text{-}{}^i\!Pr_2\text{-}2,6)(SiMe_3)N]_2SmCl_3Li_2(THF)_4$ (**7**) in high yield as yellow crystals, which was characterized by elemental analysis and X-ray crystal structural analysis.

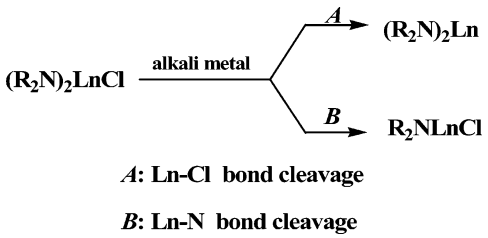
The reduction reaction of **7** with Na−K alloy yielded indeed a normal reduction product $[(C_6H_3\text{-}{}^i\!Pr_2\text{-}2,6)(SiMe_3)N]_2Sm(THF)_2$ (**8**) via the cleavage of the Ln−Cl bond as black crystals in high yield, not the chloride as in the case of ytterbium(II) (Scheme 5).

The preparation of **5** and **8** by the similar reaction indicated that the reduction reaction of a bisamide lanthanide(III) chloride by alkali metal may take place according to two modes: mode **A** via the cleavage of Ln−Cl bond and mode **B** via the cleavage of Ln−N bond (Scheme 6). Normally, mode **A** is preferable to mode **B**. In contrast, when the steric repulsion is as large as the steric demand of the ligand, mode **B** will be taken. So, for metal Yb, the reduction reaction of bisamide chloride with the less bulky amido $N(C_6H_5)(SiMe_3)$ gave the bisamide complex by mode **A**, whereas an amide chloride proceeded by mode **B** with the more bulky amido $N(C_6H_3\text{-}{}^i\!Pr_2\text{-}2,6)(SiMe_3)$. For a given bulky amido ligand, the reduction reaction afforded a bisamide complex for Sm(II), whereas a monoamide chloride for the smaller metal Yb(II) compared to Sm(II), as the coordination sphere around Yb, is more crowded than that around Sm for the complex with the same coordination numbers. To the best of our knowledge, this is the first example of metal size and steric demand of amido dependence determining the reduction reaction pathway in the chemistry of lanthanide(II) complexes.

Scheme 5



Scheme 6



The examples presented here show that substantial differences in outcome and reactivity can be achieved by using the bulky ancillary ligand attached and using metals of different size. The result may provide a platform for further study of the relationship between the steric effect and reactivity/stability of divalent complexes.

Crystal Structural Analyses. The molecular structures of **1**−**7** were determined by X-ray diffraction. Crystals of **2** and **3** suitable for X-ray diffraction were grown in a DME solution, whereas others were grown in a toluene solution. The molecular structures of **1**−**7** are shown in Figures 1−6, respectively. The details of the crystallographic data are given in Table 1 and selected bond lengths and angles are given in Tables 2−6, respectively.

X-ray structural analysis revealed that **1** is a dimer (Figure 1) in which each $[(C_6H_5)(SiMe_3)N]_2YbCl(THF)$ moiety is bonded together by two unsymmetrical chloro bridges with Yb−Cl bond lengths of 2.6600(13) and 2.6864(4) Å, respectively. The two chlorine atoms and two ytterbium atoms are coplanar (sum of angles, 360°). Each ytterbium ion is bound to two nitrogen atoms of two amido groups, one oxygen atom from the THF molecule, and two chlorine atoms, to form a formal coordination number of five in a distorted trigonal bipyramidal geometry. The Yb−N bond lengths (2.149(4) and 2.184(4) Å) are comparable to those

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(17) (a) Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, *102*, 1953. (b) Yao, Y. M.; Zhang, Y.; Zhang, Z. Q.; Shen, Q. and Yu, K. B. *Organometallics* **2003**, *22*, 2876.

(18) Deacon, G. B.; Fallon, G. D.; Forsyth, C. M.; Schumann, H.; Weimann, R. *Chem. Ber.* **1997**, *130*, 409.

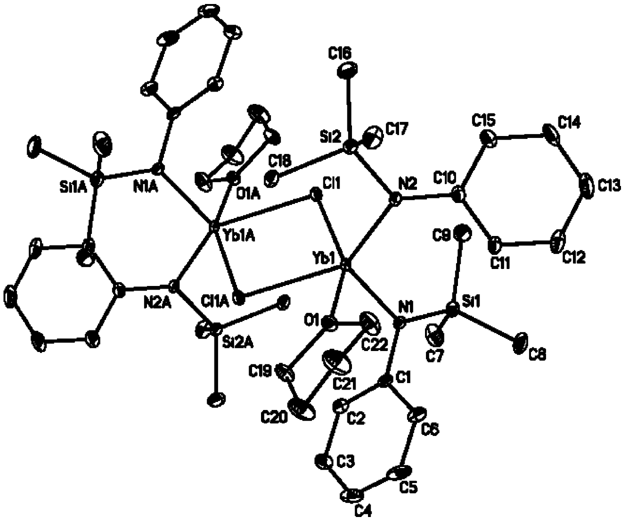

Figure 1. Molecular structure of **1**.

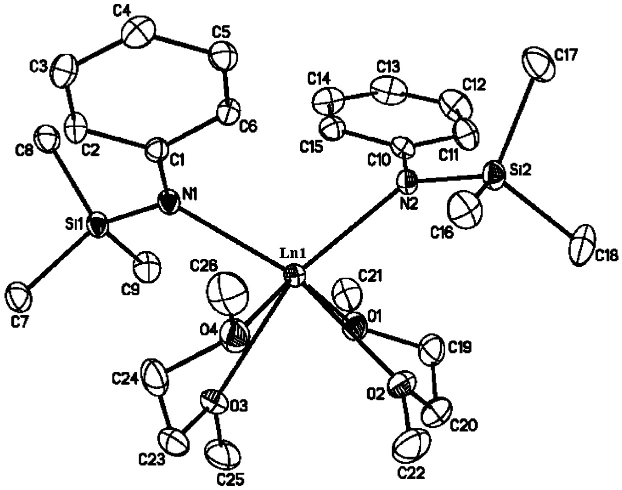

Figure 2. Molecular structure of **2** and **3**.

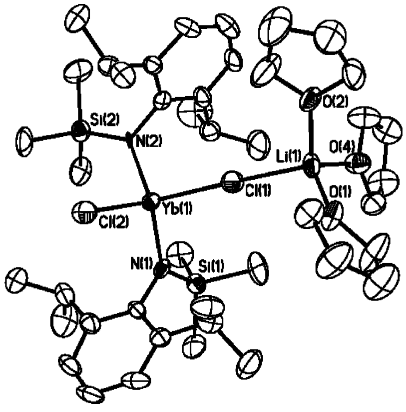

Figure 3. Molecular structure of **4**.

in $[(C_6H_3\text{-}^iPr_2\text{-}2,6)(SiMe_3)N]_2NdCl(THF)$ (2.276(2) and 2.264(2) Å),[19] when the difference in the ionic radii between Yb and Nd is considered.[20] The N−Yb−N angle is 112.69(16)°.

2 and **3** have analogous solid structures and they both are monomers with a six-coordinate lanthanide center ligated by two nitrogen atoms of two amido ligands and four oxygen atoms from two DME molecules as shown in Figure 2. The coordination geometry around the lanthanide ion for each complex is best described as a distorted octahedral geometry. The average Ln−N bond lengths for **2** and **3** are 2.427(2) and 2.525(3) Å, respectively. The average Ln−O bond lengths for **2** and **3** are 2.540(2) and 2.661(3) Å, respectively. These values are comparable when the ionic radii difference between Yb(II) and Sm(II) is considered. The N−Ln−N

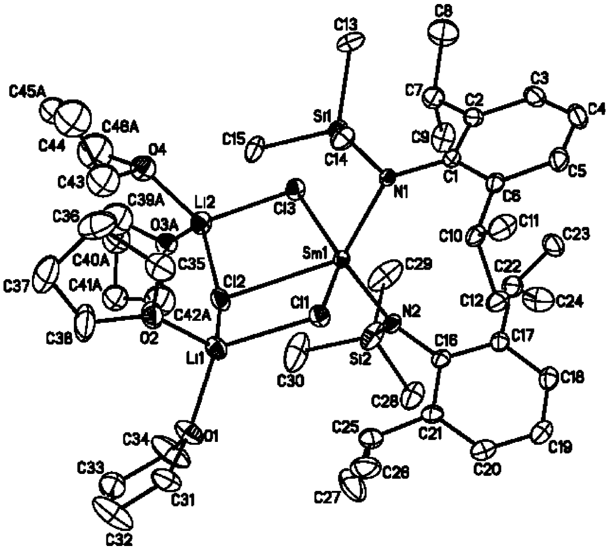

Figure 4. Molecular structure of **7**.

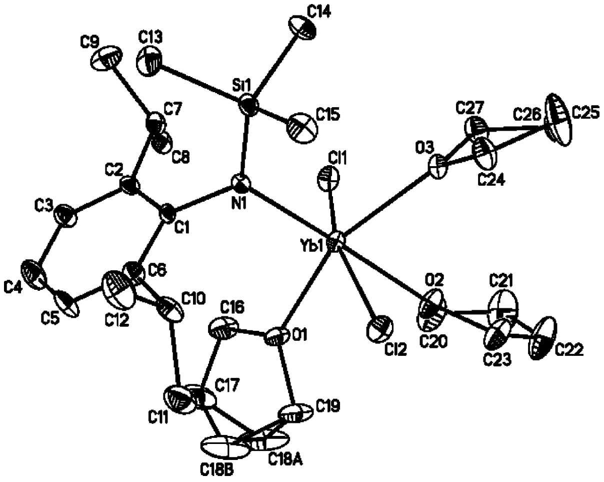

Figure 5. Molecular structure of **6**.

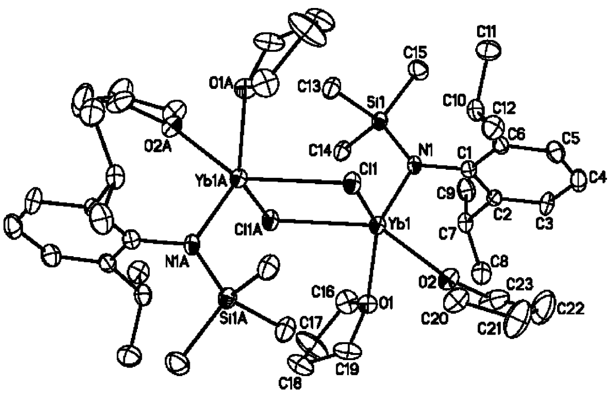

Figure 6. Molecular structure of **5**.

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(19) Schumann, H.; Winterfeld, J.; Rosenthal, E. C. E.; Hemling, H.; Esser, L. *Z. Anorg. Allg. Chem.* **1995**, *621*, 122.

(20) Shannon, R. D. *Acta Crystallogr. Sect. A* **1976**, *32*, 751.

Table 2. Selected Bond Distances (Angstroms) and Angles (Degrees) for **1**

bond	(angstroms)	bond	(angstroms)
Yb(1)−N(1)	2.149(4)	Si(1)−C(7)	1.872(7)
Yb(1)−N(2)	2.184(4)	Si(2)−N(2)	1.734(4)
Yb(1)−O(1)	2.318(4)	Si(2)−C(17)	1.872(6)
Yb(1)−Cl(1)	2.6600(13)	Si(2)−C(16)	1.877(7)
Yb(1)−Cl(1)#1	2.6864(12)	Si(2)−C(18)	1.880(6)
Yb(1)−Yb(1)#1	4.1777(5)	O(1)−C(22)	1.454(7)
Cl(1)−Yb(1)#1	2.6864(12)	O(1)−C(19)	1.470(7)
Si(1)−N(1)	1.729(4)	N(1)−C(1)	1.425(6)
Si(1)−C(9)	1.855(7)	N(2)−C(10)	1.412(6)
Si(1)−C(8)	1.863(7)		
Angle	(Degrees)	Angle	(Degrees)
N(1)−Yb(1)−N(2)	112.69(16)	N(1)−Yb(1)−Yb(1)#1	107.94(12)
N(1)−Yb(1)−O(1)	98.42(15)	N(2)−Yb(1)−Yb(1)#1	124.23(11)
N(2)−Yb(1)−O(1)	90.57(15)	O(1)−Yb(1)−Yb(1)#1	119.57(9)
N(1)−Yb(1)−Cl(1)	101.94(12)	Cl(1)−Yb(1)−Yb(1)#1	38.84(3)
N(2)−Yb(1)−Cl(1)	95.41(12)	Cl(1)#1−Yb(1)−Yb(1)#1	38.39(3)
O(1)−Yb(1)−Cl(1)	154.58(10)	Yb(1)−Cl(1)−Yb(1)#1	102.78(4)
N(1)−Yb(1)−Cl(1)#1	105.91(12)	N(1)−Si(1)−C(9)	108.5(3)
N(2)−Yb(1)−Cl(1)#1	141.38(11)	N(1)−Si(1)−C(8)	112.6(3)
O(1)−Yb(1)−Cl(1)#1	82.70(10)	C(9)−Si(1)−C(8)	109.1(3)
Cl(1)−Yb(1)−Cl(1)#1	77.22(4)		

Table 3. Selected Bond Distances (Angstroms) and Angles (Degrees) for **2** and **3**

bond (angstroms)	**2**	**3**	bond (angstroms)	**2**	**3**
Ln(1)−N(1)	2.431(2)	2.528(3)	Ln(1)−O(1)	2.538(2)	2.631(3)
Ln(1)−N(2)	2.422(2)	2.521(3)	Ln(1)−O(2)	2.524(2)	2.671(3)
Si(1)−N(1)	1.711(2)	1.704(3)	Ln(1)−O(3)	2.521(2)	2.627(3)
Si(2)−N(2)	1.709(2)	1.701(3)	Ln(1)−O(4)	2.578(2)	2.714(3)
Angle (Degrees)	**2**	**3**	Angle (Degrees)	**2**	**3**
N(2)−Ln(1)−N(1)	110.09(7)	109.74(9)	N(1)−Ln(1)−O(4)	85.41(7)	86.37(9)
N(1)−Ln(1)−O(3)	87.36(7)	87.70(8)	Si(1)−N(1)−Ln(1)	126.37(11)	125.06(14)
N(1)−Ln(1)−O(2)	163.46(7)	121.14(9)	O(2)−Ln(1)−O(1)	66.03(8)	62.75(9)
N(1)−Ln(1)−O(1)	119.95(7)	164.01(8)	O(3)−Ln(1)−O(4)	66.31(8)	63.02(8)
N(2)−Ln(1)−O(3)	161.43(7)	162.09(8)	N(2)−Ln(1)−O(4)	119.76(7)	120.39(8)
N(2)−Ln(1)−O(1)	84.78(7)	85.62(9)	N(2)−Ln(1)−O(2)	85.27(7)	85.69(8)

Table 4. Selected Bond Distances (Angstroms) and Angles (Degrees) for **7**

bond	(angstroms)	bond	(angstroms)
Sm(1)−N(1)	2.285(3)	Cl(3)−Li(2)	2.322(9)
Sm(1)−N(2)	2.308(4)	Si(1)−N(1)	1.733(3)
Sm(1)−Cl(1)	2.7368(11)	Si(2)−N(2)	1.744(4)
Sm(1)−Cl(2)	2.8470(11)	O(1)−Li(1)	1.916(9)
Sm(1)−Cl(3)	2.7360(11)	O(2)−Li(1)	1.907(9)
Cl(1)−Li(1)	2.326(8)	O(3A)−Li(2)	1.894(13)
Cl(2)−Li(2)	2.342(9)	O(3B)−Li(2)	1.948(13)
Cl(2)−Li(1)	2.357(8)	O(4)−Li(2)	1.908(10)
Angle	(Degrees)	Angle	(Degrees)
N(1)−Sm(1)−N(2)	123.53(12)	N(1)−Sm(1)−Li(2)	114.47(16)
N(1)−Sm(1)−Cl(3)	93.16(8)	N(2)−Sm(1)−Li(2)	108.85(17)
N(2)−Sm(1)−Cl(3)	99.49(10)	N(1)−Sm(1)−Li(1)	115.57(15)
N(1)−Sm(1)−Cl(1)	89.04(9)	N(2)−Sm(1)−Li(1)	109.33(16)
N(2)−Sm(1)−Cl(1)	108.42(10)	Li(1)−Cl(1)−Sm(1)	96.4(2)
Cl(3)−Sm(1)−Cl(1)	144.80(4)	Li(2)−Cl(2)−Li(1)	151.9(3)
N(1)−Sm(1)−Cl(2)	133.05(9)	Li(2)−Cl(2)−Sm(1)	91.3(2)
N(2)−Sm(1)−Cl(2)	103.41(10)	Li(1)−Cl(2)−Sm(1)	92.8(2)
Cl(3)−Sm(1)−Cl(2)	76.90(4)	Li(2)−Cl(3)−Sm(1)	94.6(2)
Cl(1)−Sm(1)−Cl(2)	76.10(4)		

angles in **2** (110.09(7)°) and **3** (109.74(9)°) are almost identical and smaller than that of **8** (121.5(2)°),[18] indicating that the nonsubstituent arylamido ligand provides a more-open coordination environment. The Ln−N bond lengths for **2** are similar with an average value of $\{Yb[N(C_6H_5)(SiMe_3)][\mu\text{-}N(C_6H_5)(SiMe_3)](THF)\}_2$ (2.340 Å),[13] when the difference in the ionic radii between six- and four-coordinated Yb is considered. The N−Ln−N angle (110.09(7)°) in **2** is larger than that of $\{Yb[N(C_6H_5)(SiMe_3)][\mu\text{-}N(C_6H_5)(SiMe_3)](THF)\}_2$, showing that the coordination environment around the Yb in **2** is less crowded than that in $\{Yb[N(C_6H_5)(SiMe_3)][\mu\text{-}N(C_6H_5)(SiMe_3)](THF)\}_2$.

The molecular structures of **4** and **7** are shown in Figures 3 and 4, respectively. Although the quality of the refinement for **4** is low, the overall structure of the molecule was clearly established. Both **4** and **7** are ate complexes; however, the

Table 5. Selected Bond Distances (Angstroms) and Angles (Degrees) for **6**

bond	(angstroms)	bond	(angstroms)
Yb(1)−N(1)	2.218(5)	Yb(1)−Cl(1)	2.5498(18)
Yb(1)−O(1)	2.300(5)	Yb(1)−Cl(2)	2.5436(19)
Yb(1)−O(2)	2.439(5)	Si(1)−N(1)	1.721(6)
Yb(1)−O(3)	2.325(5)	Si(1)−C(13)	1.871(8)
Angle	(Degrees)	Angle	(Degrees)
N(1)−Yb(1)−O(1)	100.30(19)	Cl(1)−Yb(1)−Cl(2)	163.40(6)
N(1)−Yb(1)−O(3)	103.50(18)	O(1)−Yb(1)−Cl(2)	89.18(13)
N(1)−Yb(1)−O(2)	178.4(2)	O(3)−Yb(1)−Cl(2)	87.05(13)
O(1)−Yb(1)−O(3)	156.20(18)	O(2)−Yb(1)−Cl(2)	81.33(14)
O(1)−Yb(1)−O(2)	78.1(2)	O(1)−Yb(1)−Cl(1)	89.85(13)
O(3)−Yb(1)−O(2)	78.11(19)	O(3)−Yb(1)−Cl(1)	87.17(12)
N(1)−Yb(1)−Cl(2)	98.64(14)	O(2)−Yb(1)−Cl(1)	82.26(14)
N(1)−Yb(1)−Cl(1)	97.83(14)	Si(1)−N(1)−Yb(1)	124.1(3)

Table 6. Selected Bond Distances (Angstroms) and Angles (Degrees) for **5**

bond	(angstroms)	bond	(angstroms)
Yb(1)−N(1)	2.302(8)	Yb(1)−O(1)	2.402(7)
Yb(1)−Cl(1)	2.718(2)	Yb(1)−O(2)	2.397(7)
Yb(1)−Cl(1)#1	2.724(2)	N(1)−C(1)	1.401(11)
Yb(1)−Yb(1)#1	4.0630(12)	Si(1)−N(1)	1.687(8)
Angle	(Degrees)	Angle	(Degrees)
N(1)−Yb(1)−O(2)	109.7(2)	N(1)−Yb(1)−Cl(1)#1	107.21(19)
N(1)−Yb(1)−O(1)	107.3(2)	O(1)−Yb(1)−Cl(1)#1	82.15(18)
N(1)−Yb(1)−Cl(1)	113.3(2)	Cl(1)−Yb(1)−Cl(1)#1	83.40(7)
O(2)−Yb(1)−Cl(1)	87.67(16)	Cl(1)−Yb(1)−C(1)	113.33(18)
O(1)−Yb(1)−Cl(1)	139.31(17)	Cl(1)#1−Yb(1)−C(1)	132.52(18)

difference in the molecular structure between them is observed. In **4**, two moieties, that is, $[(C_6H_3\text{-}^i Pr_2\text{-}2,6)(SiMe_3)N]_2YbCl$ and $LiCl(THF)_3$, are bonded together through a μ_2-Cl bridge. The coordination geometry around the Yb atom is best described as a distorted pseudo-tetrahedron with two nitrogen atoms of amide ligands and two Cl atoms. In **7**, three moieties, $[(C_6H_3\text{-}^i Pr_2\text{-}2,6)(SiMe_3)N]_2SmCl$ and two $LiCl(THF)_2$, are connected together by two μ_2-Cl and one μ_3-Cl bridges. The central metal Sm atom is coordinated by two double-bridging Cl atoms, one triple-bridging Cl atom, and two nitrogen atoms of amido ligands, resulting in a distorted trigonal bipyramidal geometry, which is similar to the structure of $[(^i Pr_2N)_2SmCl_3(Li(TMEDA))_2]$.[14] Two N atoms and one Cl2 define the equatorial plane, whereas the other two Cl atoms are placed at the axial positions. The differences observed between the structural motifs of **4** and **7** may result from the difference in metal sizes. The Sm−N bond lengths of 2.285(3) and 2.308(4) Å in **7** are longer than 2.218(5) and 2.202(5) Å in $[(^i Pr_2N)_2SmCl_3(Li(TMEDA))_2]$, which may be attributed to the more bulky silylaryl amido group compared to $^i Pr_2N$.

6 is crystallized in the monoclinic spaces. The coordination geometry around the Yb ion is best described as a distorted octahedral geometry with one nitrogen atom of an amido ligand, two Cl atoms, and three oxygen atoms from three THF molecules as shown in Figure 5. The Yb(1)−N(1) bond length is 2.218(5) Å. The bond angles of N(1)−Yb(1)−Cl(1) and N(1)−Yb(1)−Cl(2) are 98.64(14) and 97.83(14)°, respectively. The bond angle of Cl(1)−Yb(1)−Cl(2) is 163.40(6)°.

The crystal structural determination reveals **5** to be a centrosymmetric chloro-bridged dimer with trans-disposed amido groups as shown in Figure 6. The structure is similar to those found in metallocene ytterbium iodides $[Yb(\eta^5\text{-}C_5Me_5)(\mu\text{-}I)(THF)_2]_2$[21] and $[Yb(\eta^5\text{-}C_5Me_4SiMe_2NH^tBu)(\mu\text{-}I)(THF)_2]_2$,[22] when Cp* is regarded to occupy one position. Each ytterbium atom coordinates to an amido group, two bridged chlorines, and two THF molecules to form a distorted trigonal bipyramid. The Yb−Cl bond lengths of 2.718(2) and 2.724(2) Å are comparable to 3.134 (1) and 3.175 (1) Å of Yb−I distances in $[Yb(\eta^5\text{-}C_5Me_5)(\mu\text{-}I)(THF)_2]_2$, when the differences in ion radius between Cl and I, and five- and seven-coordinated Yb are considered. The bond length of Yb−N, 2.302(8) Å, is very close to 2.326(4) and 2.353(4) Å observed for the complex $\{Yb[N(C_6H_5)(SiMe_3)][\mu\text{-}N(C_6H_5)(SiMe_3)](THF)\}_2$.[13]

Conclusion

In summary, we have successfully synthesized a series of di- and trivalent lanthanide complexes supported by silylarylamido ligands. It was found that the reduction reaction of bisamide lanthanide chloride with Na/K depends on both the metal size and the steric bulk of the amido ligand. The same reduction reaction of bisamide ytterbium chloride with Na−K alloy afforded bisamide complex $\{[(C_6H_5)(Me_3Si)N]_2Yb(DME)_2\}$ (**2**) via the normal cleavage of the Ln−Cl bond with the less bulky amido, whereas monoamide chloride $\{[(C_6H_3\text{-}^i Pr_2\text{-}2,6)(SiMe_3)N]Yb(\mu\text{-}Cl)(THF)_2\}_2$ (**5**) was formed via the cleavage of the Ln−N bond prior to the Ln−Cl bond with a bulky amido group. The similar reduction reaction with the same bulky amido group for the larger metal Sm(II) compared to Yb(II) gave bisamide complex $[(C_6H_3\text{-}^i Pr_2\text{-}2,6)(SiMe_3)N]_2Sm(THF)_2$ (**8**) via the normal cleavage

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of the Ln−Cl bond. Further work on the steric effect on the stability/reactivity of lanthanide(II) complexes is proceeding in our laboratory.

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Supporting Information Available: Supporting Information Available: X-ray crystallographic data for **1**−**7** in CIF format. Detailed crystallographic data, selected bond lengths, and angles for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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