Synthesis and Single-Crystal X-ray Diffraction Examination of a Structurally Homologous Series of Tetracoordinate Heteroleptic Anionic Lanthanide Complexes: $\mathbf{Ln\{\overline{N[Si(CH_3)_2CH_2CH_2Si}(CH_3)_2]\}_3(\mu\text{-}Cl)Li(L)_3}$ [Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb; $\mathbf{(L)_3 = (THF)_3, (Et_2O)_3, (THF)_2(Et_2O)}$]

Oliver Just[†,‡] **and William S. Rees, Jr.***[†,‡,§]

School of Chemistry and Biochemistry, School of Materials Science and Engineering, and Molecular Design Institute, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Received October 12, 1999

Anhydrous lanthanide(III) chlorides (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb) react with 3 equiv of lithium 2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentanide, $\mathrm{Li\{\overline{N[Si(CH_3)_2CH_2CH_2Si}(CH_3)_2]\}}$, in THF or Et_2O to afford the monomeric four-coordinate heteroleptic ate complexes $\mathrm{Ln\{\overline{N[Si(CH_3)_2CH_2CH_2Si}(CH_3)_2]\}_3(\mu\text{-}Cl)Li(THF/Et_2O)_3}$ (Ln = Sm (**1**), Eu (**2**), Gd (**3**), Tb (**4**), Dy (**5**), Ho (**6**), Er (**7**), Tm (**8**), Yb (**9**)), whose solid-state structures were determined by the single-crystal X-ray diffraction technique. All complexes additionally were characterized by melting point determination, elemental analyses, and mass spectrometry.

Introduction

Lanthanide tris(amide) derivatives represent an important area within f-element chemistry, because of their potential as starting materials for the convenient preparation of lanthanide alkoxides in the "silylamide route",[1] as main-element constituents in Metal-Organic Chemical Vapor Deposition (MOCVD) of superconducting metal oxides, and as volatile dopant sources in MOCVD processes with applications in the opto- and microelectronic industry.[2] Tricoordinate lanthanide amides initially were reported in 1973 by Bradley,[3] utilizing the bulky bis(trimethylsilyl)amide ligand. Crystal structure determinations of the Nd,[4] Yb,[5] Eu,[6] Sc,[6] Er,[7] Dy,[7] and Ce[8] derivatives, as well as gas-phase electron diffraction studies of the Ce, Pr, and Lu complexes,[9] have been conducted, confirming the monomeric, three-coordinate nature of the metal atom surrounded by the ligands in a nonplanar, trigonal-pyramidal fashion. This contrasts with the planar coordination sphere observed for numerous transition or main-group element compounds with this type of ligand.[5,9−12] Additionally, these structural investigations revealed disordered positions of the central metal atom leading to occupancies out of the N_3 plane.[6−8]

During one preparation of a neodymium tris(amide) derivative, an example of a tetracoordinate tris(amide), "ate" complex, $\mathrm{Nd[N(SiMe_3)_2]_3(\mu\text{-}Cl)Li(THF)_3}$, was isolated as a reaction byproduct and crystallographically characterized.[13] The propensity of lanthanide elements to acquire a coordination number higher than 3 by retaining alkali-metal-bearing solvent molecules or through bridging by one (or two) halide anions has been observed additionally in other ate complexes with amide,[13,14] alkoxide,[13,15] and σ- and π-bonding organic ligands.[16] Recently, an extensive exploration of the utility of employing the lithium

---

[†] School of Chemistry and Biochemistry.

[‡] Molecular Design Institute.

[§] School of Materials Science and Engineering.

(1) (a) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273. (b) Herrmann, W. A.; Anwander, R.; Kleine, M.; Scherer, W. *Chem. Ber.* **1992**, *125*, 1971. (c) Herrmann, W. A.; Anwander, R.; Denk, M. *Chem. Ber.* **1992**, *125*, 2399.

(2) (a) Rees, W. S., Jr.; Green, D. M.; Anderson, T. J.; Bretschneider, E. *Mater. Res. Soc. Symp. Proc.* **1992**, *242*, 281. (b) Luten, H.; Just, O.; Rees, W. S., Jr. *Chem. Commun.* **2000**, *9*, 735. (c) Bunge, S.; Just, O.; Rees, W. S., Jr. *Angew. Chem., Int. Ed.* **2000**, *39*, 3082. (d) Rees, W. S., Jr.; Just, O.; Castro, S. L.; Matthews, J. S. *Inorg. Chem.* **2000**, *39*, 3736. (e) Just, O.; Rees, W. S., Jr. *Adv. Mater. Opt. Electron.*, accepted for publication. (f) Gaul, D. A.; Just, O.; Rees, W. S., Jr. *Inorg. Chem.*, accepted for publication. (g) Just, O.; Gaul, D. A.; Rees, W. S., Jr. *Polyhedron*, accepted for publication. (h) Rees, W. S., Jr.; Just, O.; Schumann, H.; Weimann, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 419. (i) Gaul, D. A.; Rees, W. S., Jr. *Adv. Mater.* **2000**, *12*, 935. (j) Rees, W. S., Jr.; Just, O.; Kimerling, L.; Morse, M. T. *Proc. SPIE* **1998**, *3469*, 2. (k) Rees, W. S., Jr.; Green, D.; Hesse, W.; Anderson, T.; Pathangey, B.; Kim, J. *J. Electron. Mater.* **1992**, *21*, 361.

(3) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Chem. Commun.* **1973**, 1021.

(4) Andersen, R. A.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1978**, *17*, 2317.

(5) Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1.

(6) Ghotra, J. S.; Hursthouse, M. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1973**, 669.

(7) Herrmann, W. A.; Anwander, R.; Munck, F. C.; Scherer, W.; Dufaud, V.; Huber, N. W.; Artus, G. R. J. *Z. Naturforsch.* **1994**, *49b*, 1789.

(8) Rees, W. S., Jr.; Just, O.; Vanderveer, D. S. *J. Mater. Chem.* **1999**, *9*, 249.

(9) Fjeldberg, T.; Andersen, R. A. *J. Mol. Struct.* **1985**, *129*, 93.

(10) Sheldrick, G. M.; Sheldrick, W. S. *J. Chem. Soc.* **1969**, 2279.

(11) Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1972**, 2100.

(12) Ellison, J. J.; Power, P. P.; Shoner, S. C. *J. Am. Chem. Soc.* **1989**, *111*, 8044.

(13) Edelmann, F. T.; Steiner, A.; Stalke, D.; Gilje, J. W.; Jagner, S.; Håkansson, M. *Polyhedron* **1994**, *13*, 539.

(14) (a) Schumann, H.; Winterfeld, J.; Rosenthal, E. C. E.; Hemling, H.; Esser, L.; Kim, J. *Z. Anorg. Allg. Chem.* **1995**, *621*, 122. (b) Recknagel, A.; Steiner, A.; Noltmeyer, M.; Brooker, S.; Stalke, D.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *414*, 327. (c) Recknagel, A.; Knosel, F.; Gornitzka, H.; Noltmeyer, M.; D.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *417*, 363.

(15) Clark, D. L.; Watkin, J. G.; Huffman, J. C. *Inorg. Chem.* **1992**, *31*, 1554.

10.1021/ic9912023 CCC: $20.00

amide $Li[NSi(CH_3)_2CH_2CH_2Si(CH_3)_2]$ as a reactant with a diverse variety of metal halides has been initiated in these laboratories.[17] These experiments were inspired by a desire to probe the differences created by "tying back the arms" of the popular $[N(TMS)_2]^-$ ligand. In earlier research,[18] it was demonstrated that the cleavage of a N–Si bond during CVD experiments was one dominant pathway leading to premature vapor phase decomposition. Thus, it was decided to see if pinning the two silicon atoms on a given amide ligand together, in this example with an ethylene bridge, would have a positive influence in shutting off this disadvantageous decomposition route. As a result, it was set out to prepare the lanthanide series of this ligand. However, rather than the expected, neutral, three-coordinate amide compounds, the "ate" complexes were obtained. Results to date have not revealed the ability to procure a neutral ML_3 compound from the sublimate of the thermolysis of $[ML_3Cl][LiS_3]$ (S_3 = $(THF)_3$, $(Et_2O)_3$, $(THF)_2(Et_2O)$). Thus, herein, the synthesis and crystal structure determination of a series of lanthanide tris(amide) ate complexes containing the 2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentanide ligand—considerably less sterically hindered modification of the widely employed bis(trimethylsilyl)amide entity—is described.

Experimental Section

General Comments. Due to the extreme oxygen and moisture sensitivity of the lanthanide amides, all manipulations were performed either under a dried and purified argon atmosphere on a vacuum line by employing standard Schlenk techniques or in an inert-gas-filled glovebox. All solvents were degassed and freshly distilled from sodium or potassium/benzophenone prior to use. In this study, each compound was characterized by the single-crystal X-ray diffraction technique, satisfactory elemental analyses, melting point determination, and mass spectrometry. Handling and mounting of selected crystals on the diffractometer were carried out in a liquid-nitrogen-cooled argon stream to prevent the rapid quality deterioration which would occur at ambient temperature. All anhydrous lanthanide trichlorides were purchased from Alfa Aesar and employed in subsequent preparations as received, without additional purification.

Physical Measurements. X-ray diffraction data were acquired on a Siemens SMART CCD diffractometer, microanalyses were performed on a Perkin-Elmer 2400 Series II elemental analyzer, mass spectra were recorded on a VG Instruments 70SE spectrometer, and uncorrected melting points were determined in argon-sealed capillary tubes on a Mel-Temp II apparatus. Thermogravimetric analyses were recorded on a Perkin-Elmer TGA7 apparatus inside an inert-atmosphere glovebox. Between 5 and 20 mg of each compound, loaded into a platinum sample pan, was placed into the furnace with an Ar purge rate of 15 sccm. A temperature program consisting of a heating rate of 10 °C/min was used to collect the thermograms.

X-ray Data Collection and Structure Determination for 1–9. Suitable single crystals were selected and mounted under a continuous argon stream on an X-ray diffractometer at 173 K. Graphite-monochromated Mo Kα radiation was used (λ = 0.710 73 Å). In all cases, reflections were collected with a frame width of 0.3° in ω scans and a counting time of 30 s per frame at a crystal-to-detector distance of 4.911 cm. The double-pass method of scanning was used to exclude any noise. The first 50 frames of data were recollected at the conclusion of data collection to monitor crystal decay. All structures were solved by direct methods (SHELXS-97), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares calculations based on F^2 (SHELXL-97). Lorentzian polarization and absorption corrections (SADABS) were applied. Hydrogen atom coordinates were calculated with SHELXL using an appropriate riding model with varied thermal parameters, or the hydrogen atoms were assigned to calculated positions, riding on adjacent carbon atoms with $U(H) = 1.5U_{eq}(C)$ for hydrogen atoms on methyl groups and $U(H) = 1.2U_{eq}(C)$ for the remaining hydrogen atoms. Non-hydrogen atoms were refined with

Table 1. Crystal and Data Collection Parameters for $Ln\{N[Si(CH_3)_2CH_2CH_2Si(CH_3)_2]\}_3(\mu\text{-}Cl)Li(L)_3$ [Ln = Sm (**1**), Eu (**2**), Gd (**3**), Tb (**4**), Dy (**5**), Ho (**6**), Er (**7**), Tm (**8**), Yb (**9**); $(L)_3$ = $(THF)_3$ for **2** and **4**, $(Et_2O)_3$ for **5**–**9**, and $(THF)_2(Et_2O)$ for **1** and **3**]

	1	**2**	**3**
chemical formula	$C_{30}H_{74}N_3O_3Si_6ClLiSm$	$C_{30}H_{72}N_3O_3Si_6ClLiEu$	$C_{30}H_{74}N_3O_3Si_6ClLiGd$
fw, g·mol^{-1}	886.210	885.799	893.100
T, K	173(2)	173(2)	173(2)
λ, Å	0.710 73	0.710 73	0.710 73
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a, Å	11.39620(10)	25.6070(5)	11.4536(3)
b, Å	21.7309(3)	17.4284(4)	21.7727(5)
c, Å	19.6745(2)	21.2201(5)	19.7242(5)
β, deg	102.67	93.5390(10)	102.5270(10)
V, Å^3	4753.79(9)	9452.2(4)	4801.6(2)
Z	4	8	4
ρ_{calc}, g·cm^{-3}	1.238	1.245	1.235
μ, mm^{-1}	1.471	1.565	1.615
R,^{a} %	3.52	4.95	3.68
R_w,^{b} %	8.12	10.42	6.61

	4	**5**	**6**
chemical formula	$C_{30}H_{72}N_3O_3Si_6ClLiTb$	$C_{30}H_{78}N_3O_3Si_6ClLiDy$	$C_{30}H_{78}N_3O_3Si_6ClLiHo$
fw, g·mol^{-1}	892.759	902.382	904.812
T, K	173(2)	173(2)	173(2)
λ, Å	0.710 73	0.710 73	0.710 73
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a, Å	25.6729(4)	12.70820(10)	12.7352(5)
b, Å	17.4492(2)	20.72560(10)	20.7721(8)
c, Å	21.2795(3)	18.83340(10)	18.8634(7)
β, deg	93.6350(10)	98.4000(10)	98.3480(10)
V, Å^3	9513.4(2)	4907.22(5)	4937.2(3)
Z	8	4	4
ρ_{calc}, g·cm^{-3}	1.247	1.221	1.217
μ, mm^{-1}	1.723	1.752	1.830
R,^{a} %	5.06	2.86	3.26
R_w^{b} %	13.67	7.17	8.10

	7	**8**	**9**
chemical formula	$C_{30}H_{78}N_3O_3Si_6ClLiEr$	$C_{30}H_{78}N_3O_3Si_6ClLiTm$	$C_{30}H_{78}N_3O_3Si_6ClLiYb$
fw, g·mol^{-1}	907.142	908.816	912.922
T, K	173(2)	173(2)	173(2)
λ, Å	0.710 73	0.710 73	0.710 73
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	12.700	12.6678(14)	12.6763(2)
b, Å	20.7277(3)	20.660(3)	20.6996(3)
c, Å	18.7914(2)	18.744(2)	18.7475(2)
β, deg	98.24	98.304(11)	98.2000(4)
V, Å^3	4895.48(11)	4854.2(10)	4868.95(12)
Z	4	4	4
ρ_{calc}, g·cm^{-3}	1.231	1.235	1.245
μ, mm^{-1}	1.944	2.059	2.152
R,^{a} %	3.18	2.69	3.49
R_w,^{b} %	7.67	6.48	8.30

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

---

(16) (a) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Holton, J.; McMeeking, J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 140. (b) Cotton, S. A.; Hart, F. A.; Hursthouse, M. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1225. (c) Atwood, J. L.; Lappert, M. F.; Smith, R. G.; Zhang, H. *J. Chem. Soc., Chem. Commun.* **1988**, 1308. (d) Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1980**, *19*, 2190. (e) Tilley, T. D.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3267. (f) Rausch, M. D.; Moriarty, K. J.; Atwood, J. L.; Weeks, J. A.; Hunter, W. E.; Brittain, H. G. *Organometallics* **1986**, *5*, 1281.

(17) For a report of the employment of this amide as a ligand on a main-group element, see: Westerhausen, M.; Greul, J.; Hausen, H.-D.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1295.

(18) (a) Gaul, D. Ph.D. Thesis, Georgia Institute of Technology, Atlanta, GA, 1998. (b) Gaul, D.; Just, O.; Rees, W. S., Jr. *Inorg. Chem.*, in press.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for: **1**−**9**[a]

compd	Ln−N(1) Ln−N(2) Ln−N(3)	Ln−Cl	Cl−Li	Li−Cl−Ln	Cl−Ln−N(1) Cl−Ln−N(2) Cl−Ln−N(3)	N(1)−Ln−N(2) N(1)−Ln−N(3) N(2)−Ln−N(3)
1	2.262(3)	2.686(9)	2.338(6)	170.2(2)	106.18(7)	109.96(10)
	2.263(3)				107.86(7)	113.28(10)
	2.268(3)				107.88(7)	111.38(10)
2	2.244(5)	2.658(2)	2.335(12)	163.5(3)	108.0(2)	112.2(2)
	2.267(5)				105.84(14)	111.9(2)
	2.252(2)				106.30(13)	112.1(2)
	2.240(5)	2.655(2)	2.332(11)	171.3(3)	106.83(13)	111.2(2)
	2.260(5)				106.49(12)	113.6(2)
	2.259(4)				105.59(12)	112.5(2)
3	2.257(3)	2.6602(9)	2.374(6)	170.6(2)	106.94(7)	109.91(10)
	2.257(3)				107.98(7)	112.49(10)
	2.259(3)				108.10(7)	111.21(10)
4	2.254(4)	2.633(2)	2.354(12)	161.8(3)	106.00(13)	112.3(2)
	2.238(4)				106.88(12)	111.5(2)
	2.226(5)				107.70(14)	112.0(2)
	2.243(4)	2.625(2)	2.404(6)	172.0(3)	106.59(12)	110.8(2)
	2.224(5)				106.88(13)	112.9(2)
	2.240(4)				105.59(11)	113.5(2)
5	2.228(3)	2.623(9)	2.404(6)	170.7(2)	105.54(8)	113.44(10)
	2.227(3)				108.16(8)	110.73(11)
	2.225(3)				106.60(9)	111.90(10)
6	2.220(3)	2.612(10)	2.414(7)	170.8(2)	108.22(8)	111.83(11)
	2.220(3)				106.90(9)	113.17(12)
	2.223(3)				105.91(9)	110.41(12)
7	2.206(3)	2.593(9)	2.408(6)	171.0(2)	108.19(8)	111.38(11)
	2.199(3)				107.19(9)	113.29(10)
	2.202(3)				105.64(8)	110.79(11)
8	2.191(2)	2.578(8)	2.396(6)	171.17(13)	104.96(7)	113.77(9)
	2.187(2)				107.61(6)	111.34(9)
	2.184(2)				106.42(7)	112.13(9)
9	2.189(3)	2.573(11)	2.411(7)	171.3(2)	107.21(9)	112.58(12)
	2.179(3)				106.23(10)	113.99(12)
	2.181(3)				104.61(9)	111.48(13)

[a] The second set of data for **2** and **4** includes corresponding interatomic distances and angles for the second crystallographically unique molecule present in the unit cells of each.

anisotropic displacement coefficients to convergence (in isolated cases, when their refinement became unstable, disordered carbon atoms were refined isotropically). Hydrogen atoms were refined isotropically. No attempts were made to assign hydrogen atoms to disordered carbon positions. All software sources are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI). Crystal and data collection parameters for **1**−**9** are summarized in Table 1; key interatomic distances and angles are compiled in Table 2.

Synthesis of Lithium 2,2,5,5-Tetramethyl-2,5-disila-1-azacyclopentanide. A 35.2 mL portion of a *n*-BuLi/hexane solution (1.69 M) was added at 0 °C to a THF solution of 9.47 g (59.47 mmol) of 2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane over a period of 30 min. The pale yellow solution that formed was refluxed for 1 h and, after attaining ambient temperature on its own, was stirred for an additional hour at this temperature and used as such in the ensuing experiments.

Lithium 2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentanide samples utilized in subsequent syntheses of **2**−**9** were prepared accordingly.

General Procedure for the Preparation of 1. To a suspension consisting of 5.09 g (19.82 mmol) of anhydrous $SmCl_3$ in 100 mL of THF in a 250 mL Schlenk flask was added dropwise over a period of 1 h at 0 °C a solution of 9.83 g (59.47 mmol) of lithium 2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentanide in 100 mL of THF. After overnight stirring, the resulting clear, pale yellow solution was reduced to dryness under vacuum. Following extraction from boiling hexane and removal of lithium chloride by Schlenk filtration, the solvent was removed at reduced pressure and the crude reaction product was redissolved in diethyl ether (∼30 mL). From this clear, pale yellow solution pale yellow crystals were grown overnight at −40 °C. Yield = 8.43 g (48%). MS (CI, 70 eV): $[M^+]$, $[M^+] - Me$, $[M^+]$-2Me, $[M^+] - L$; $M = Sm[\overline{NSi(CH_3)_2CH_2CH_2Si}(CH_3)_2]_3$. Anal. Calcd for $C_{30}H_{74}N_3O_3Si_6LiClSm$: C, 40.65; H, 8.41; N, 4.74. Found: C, 40.29; H, 8.75; N, 4.77.

Table 3. Melting Points and Colors for **1**−**9**

compd	Ln	color	mp, °C
1	Sm	pale yellow	87−89
2	Eu	yellow	90−95
3	Gd	colorless	80−85
4	Tb	colorless	95−99
5	Dy	colorless	88−92
6	Ho	yellow-orange	71−75
7	Er	pink	80−82
8	Tm	colorless	85−87
9	Yb	pale yellow	69−73

The syntheses of complexes **2**−**9** were accomplished similarly.

2: Yield = 1.27 g (36%). Anal. Calcd for $C_{30}H_{72}N_3O_3Si_6LiClEu$: C, 40.67; H, 8.19; N, 4.74. Found: C, 40.40; H, 8.49; N, 5.23.

3: Yield = 2.80 g (41%). Anal. Calcd for $C_{30}H_{74}N_3O_3Si_6LiClGd$: C, 40.34; H, 8.35; N, 4.70. Found: C, 40.08; H, 8.54; N, 5.14.

4: Yield = 1.18 g (47%). Anal. Calcd for $C_{30}H_{74}N_3O_3Si_6LiClTb$: C, 40.36; H, 8.12; N, 4.70. Found: C, 40.03; H, 8.47; N, 4.87.

5: Yield = 1.21 g (38%). Anal. Calcd for $C_{30}H_{78}N_3O_3Si_6LiClDy$: C, 39.93; H, 8.71; N, 4.68. Found: C, 40.13; H, 8.82; N, 4.94.

6: Yield = 1.83 g (55%). Anal. Calcd for $C_{30}H_{78}N_3O_3Si_6LiClHo$: C, 39.82; H, 8.68; N, 4.64. Found: C, 40.00; H, 8.64; N, 4.86.

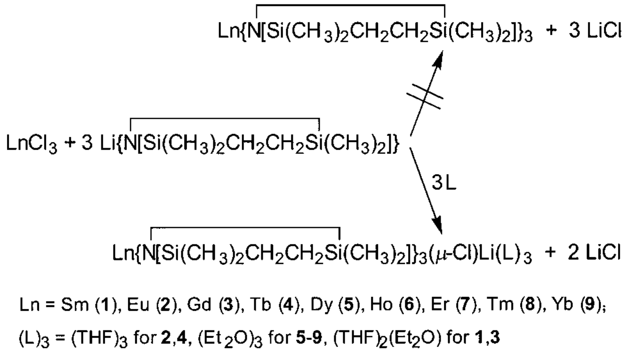
7: Yield = 3.10 g (42%). Anal. Calcd for $C_{30}H_{78}N_3O_3Si_6LiClEr$: C, 39.72; H, 8.66; N, 4.63. Found: C, 39.88; H, 8.43; N, 5.19.

8: Yield = 1.11 g (68%). Anal. Calcd for $C_{30}H_{78}N_3O_3Si_6LiClTm$: C, 39.64; H, 8.65; N, 4.62. Found: C, 39.84; H, 8.56; N, 5.05.

9: Yield = 11.94 g (45%). Anal. Calcd for $C_{30}H_{74}N_3O_3Si_6LiClSm$: C, 39.46; H, 8.61; N, 4.60. Found: C, 39.53; H, 8.73; N, 4.75.

Melting points and colors of compounds **1**−**9** are given in Table 3.

Scheme 1



Results and Discussion

Lanthanide tris[bis(trimethylsilyl)amide] complexes initially were synthesized by the stepwise addition of small portions of solid $LnCl_3$ to 3 equiv of lithium bis(trimethylsilyl)amide in THF, followed by repeated crystallization from pentane and subsequent careful purification by sublimation.[3] In an attempt to prepare lanthanide tris(2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentanide) analogues of the tris[bis(trimethylsilyl)amide] compounds, a similar procedure was attempted, following the transmetalation path in Scheme 1. This preparative procedure consisted of the addition of THF or Et_2O solutions of lithium 2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentanide to $LnCl_3$ in THF (**1**−**5**) or Et_2O (**6**−**9**) at 0 °C, removal of the reaction solvent under reduced pressure, extraction of the residue with hexane, and, finally, filtration to remove the insoluble, ionic LiCl precipitate.

Elemental analyses indicated the formation of materials compositionally different from the desired homoleptic lanthanide tris(2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentanide) compounds, while silver nitrate experiments and flame tests confirmed the incorporation of chloride and lithium, respectively, in isolated reaction products. On the basis of these data, it was hypothesized that formation of ate complexes, rather than the desired neutral, tricoordinate homoleptic derivatives, had occurred. This was confirmed by X-ray diffraction experiments.

Suitable crystals were obtained in each case from saturated hexane (**2**−**4**, **8**, **9**) or diethyl ether (**1**, **5**−**7**) solutions at −40 °C. The solid-state structures of all complexes, determined by single-crystal X-ray diffraction, were examined and found, apart from the varying type of coordinated solvent molecules on lithium, to be isostructural (see Figure 1). The europium (**2**) and terbium (**4**) complexes each contain two crystallographically independent molecules in the asymmetric unit; whereas, the samarium (**1**) and gadolinium (**3**) derivatives exhibit a displacement of one coordinated THF by an Et_2O molecule. In the structures of **1** and **7**−**9**, some disorder present in the solvent molecules was registered with the following site occupancies. **1**: C19:C19′ = 612:388; C29:C29′ and C30:C30′ = 43:57. **7**: C19:C19′ and C21:C21′ = 810:190, C23:C23′ and C25:C25′ = 768:232. **8**: C24:C24′ and C25:C25′ = 697:303, C28:C28′ and C29:C29′ = 726:274. **9**: C28:C28′ = 674:326, C29:C29′ and C30:C30′ = 667:333.

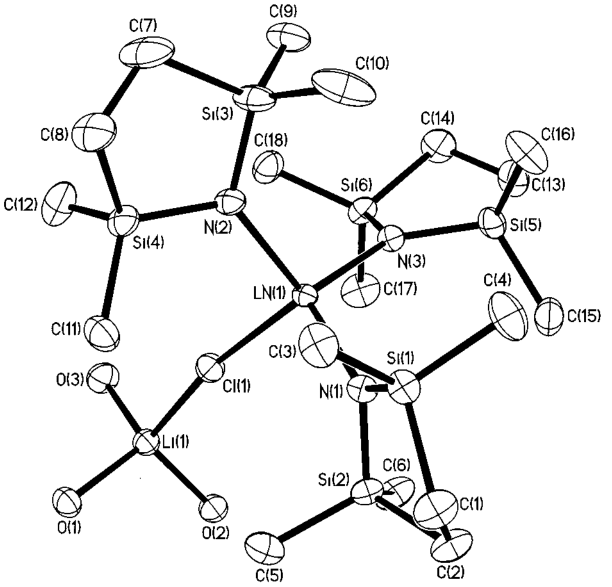


Figure 1. Generic ORTEP representation for the isostructural ate complexes $Ln\{N[Si(CH_3)_2CH_2CH_2Si(CH_3)_2]\}_3(\mu\text{-}Cl)Li(L)_3$ [Ln = Sm (**1**), Eu (**2**), Gd (**3**), Tb (**4**), Dy (**5**), Ho (**6**), Er (**7**), Tm (**8**), Yb (**9**); $(L)_3$ = $(THF)_3$ for **2** and **4**, $(Et_2O)_3$ for **5**−**9**, and $(THF)_2(Et_2O)$ for **1** and **3**]. The numbering scheme is consistent for all complexes. All hydrogen atoms throughout, as well as all carbon atoms of $(L)_3$, have been omitted for clarity in viewing of the representation.

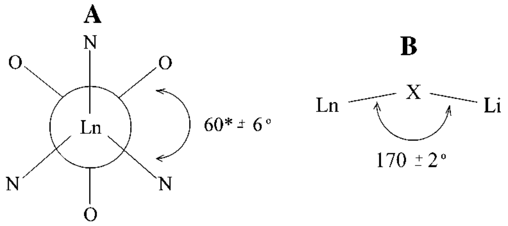


Figure 2. (A) An end-on view of the Ln−Cl−Li interaction present in **1**−**9**. The oxygen of the THF or Et_2O bound to Li is depicted in the back plane of this view. * This value is not valid for the second molecule found in the asymmetric unit for compounds **2** (Eu) and **4** (Tb). In these molecules, which are subjected to crystal lattice packing related distortions, the angles vary substantially (92 and 29°, respectively). (B) A side-on view of the Ln−Cl−Li interaction present in **1**−**9**.

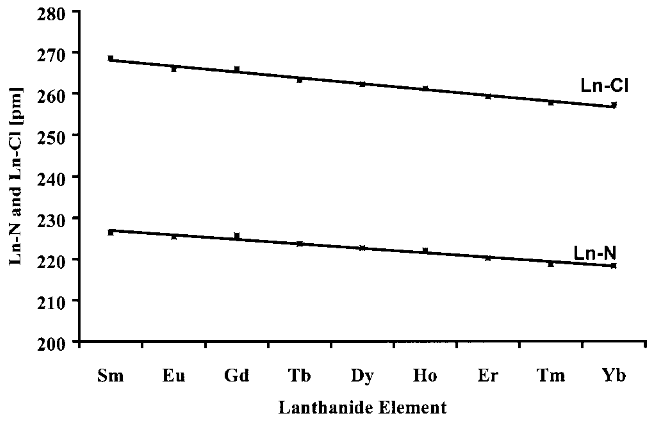


Figure 3. Interatomic Ln−N and Ln−Cl distances in **1**−**9**. The lines are guides for viewing the trends.

A key feature of all structures determined herein is that three amide nitrogens and a chlorine atom surround the metal atom in a slightly distorted tetrahedral coordination sphere. The angles formed around the metal center Cl−Ln−N(1), Cl−Ln−N(2), and Cl−Ln−N(3) range for all complexes between 104 and 108° (Table 2), and the angles N(1)−Ln−N(2), N(2)−Ln−N(3), and N(1)−Ln−N(3) at 110−113° (Table 2) differ only slightly from each other and from an ideal tetrahedral angle, as well. In the comparable $Nd[N(SiMe_3)_2]_3(\mu\text{-}Cl)Li(THF)_3$[13] ate complex, the respective angles, however, are more acute (97−98°) and more obtuse (115−120°). Analogous trends supporting a well-

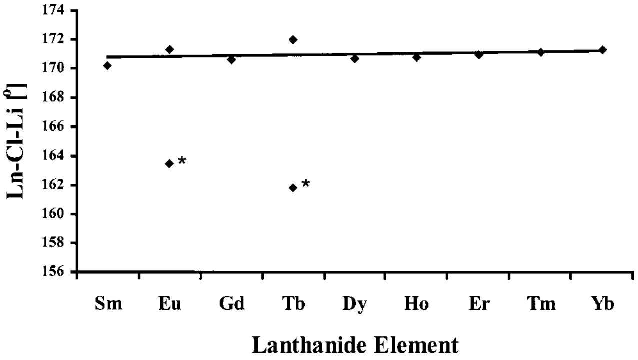


Figure 4. Interatomic Ln−Cl−Li angles in **1**−**9**. The line is a guide for viewing the trend. Asterisks signify data for the second molecules found in the asymmetric units, which are subjected to crystal lattice packing related distortions.

documented[17] bulkiness displayed by the $^{-}N(TMS)_2$ ligand as opposed to the $^{-}N[Si(CH_3)_2CH_2CH_2Si(CH_3)_2]$ cyclic arrangement, employed in this work, have been verified in related crystallographic studies.

Another characteristic structural feature of the compounds presented herein is that the halide atoms bridge alkali-metal and lanthanide atoms in a slightly bent fashion, which deviates by about 10° (Figure 2B) from an exact linear array (170−171°) and shows good agreement with commensurate structures.[13,14a] The N_3 and O_3 planes are disposed at 60° to each other (Figure 2A). Presumably crystal packing forces cause the second crystallographically independent molecule present in the asymmetric unit—in the case of the europium (**2**) and terbium (**4**) derivatives—to display a higher degree of linear deviation for the Ln−Cl−Li entity (163 and 161° for **2** and **4**, respectively). The metal−nitrogen interatomic distances vary from 2.26 Å for the samarium complex (**1**), decreasing progressively with diminishing size of the lanthanide atoms, to 2.18 Å for the ytterbium representative (**9**) (Figure 3). The Ln−chloride interatomic distances exhibit a similar trend and decrease successively from 2.68 Å for **1** to 2.57 Å for **9** (Figure 3). Ln−N interatomic distances displayed by homoleptic tris(amide) compounds vary only insignificantly from those formed here: Nd, 2.29 Å;[4] Yb, 2.15 Å;[5] Er, 2.21 Å;[7] Dy, 2.21 Å;[7] Eu, 2.25 Å.[6] The trend for the interatomic Ln−Cl−Li angles in complexes **1**−**9** is illustrated in Figure 4.

In some instances, “ate” complexes may be converted thermally to a volatile neutral metal compound and an ionic residue. To date, such transformations have not been observed for the species examined in this study; however, MS data indicate that, under CI conditions, fragmentation to neutral tricoordinate species, revealed by the highest observed masses, may be possible for **1** and **7**. A representative TGA trace is given in Figure 5. All examined compounds behave similarly and give no indication, at one atmosphere, of being capable of expelling both the lithium-bound solvent (THF or Et_2O) and the free three-coordinate Ln tris(amide). The feature observed at ~120 °C represents the loss of solvent, with subsequent thermolytic decomposition of the $Li[Ln(amide)_3Cl]$ salt at 250 °C.

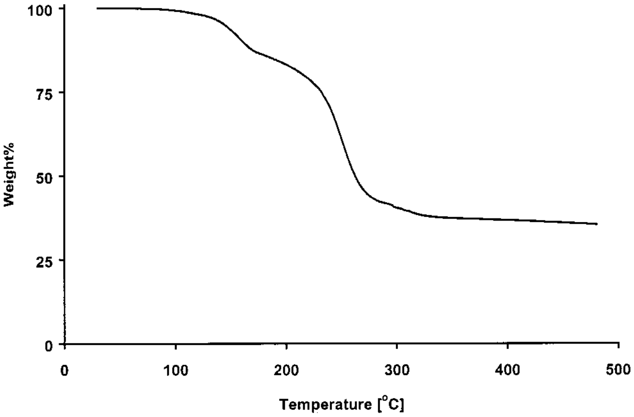


Figure 5. Thermogravimetric analysis plot for $Sm\{N[Si(CH_3)_2CH_2CH_2Si(CH_3)_2]\}_3(\mu\text{-}Cl)Li(THF)_2(Et_2O)$ (**1**).

Acknowledgment. We gratefully acknowledge financial support of this project from the Office of Naval Research, DARPA and the Georgia Institute of Technology Molecular Design Institute. W.S.R. was the recipient of an Alexander von Humboldt Award with Prof. Dr. H. Schumann at the Technische Universität Berlin (1998−1999).

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of $Ln\{N[Si(CH_3)_2CH_2CH_2Si(CH_3)_2]\}_3(\mu\text{-}Cl)Li(L)_3$ (Ln = Sm (**1**), Eu (**2**), Gd (**3**), Tb (**4**), Dy (**5**), Ho (**6**), Er (**7**), Tm (**8**), Yb (**9**); $(L)_3 = (THF)_3$ for **2** and **4**, $(Et_2O)_3$ for **5**−**9**, $(THF)_2(Et_2O)$ for **1** and **3**). This material is available free of charge via the Internet at http://pubs.acs.org.

IC9912023