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Lanthanide Complexes of Bulky Siloxide Ligands Incorporating Pendant Amine Donors: Synthesis and Structural Characterization of a Volatile Tris(siloxide) Complex of Yttrium(III) and a Novel Zwitterionic Tetrakis(siloxide) of Ytterbium(III)

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The silanol ligands $HOSi(t\text{-}Bu)_{3-n}[(CH_2)_3NMe_2]_n$ (**3**, $n = 2$; **4**, $n = 1$), were prepared from the appropriate chlorosilanes, $HSi(t\text{-}Bu)_{3-n}Cl_n$, in two steps. Reaction of 3 equiv of **3** or **4** with $Ln[N(SiMe_3)_2]_3$ allowed isolation of the tris(siloxide) complexes $Ln\{OSi(t\text{-}Bu)_{3-n}[(CH_2)_3NMe_2]_n\}_3$ (**5**, Ln = Y, $n = 2$; **6**, Ln = Y, $n = 1$; **7**, Ln = Ce, $n = 1$). Complexes **6** and **7** sublimed unchanged at 115 and 135 °C at 10^{-4} Torr, respectively. A single-crystal X-ray diffraction study of **6** revealed a trigonal bipyramidal geometry with the equatorial sites occupied by three siloxide O and the axial sites occupied by two NMe_2 groups. The third dimethylaminopropyl arm is not coordinated. [Crystal data: triclinic space group $P\bar{1}$, $a = 13.738(2)$ Å, $b = 15.940(3)$ Å, $c = 13.363(2)$ Å, $\alpha = 93.80(1)°$, $\beta = 116.77(1)°$, $\gamma = 74.55(1)°$, $V = 2513.5$ Å^3, $Z = 2$, $R = 0.0839$, and $R_w = 0.1081$.] Complex **6** is fluxional in solution to −80 °C; exchange of coordinated and dangling (dimethylamino)propyl arms is suggested as a possible mechanism. Reaction of 4 equiv of **4** with $Ln[N(SiMe_3)_2]_3$ produced novel zwitterionic tetrakis(siloxide) complexes, $Ln[OSi(t\text{-}Bu)_2(CH_2)_3NMe_2]_3[OSi(t\text{-}Bu)_2(CH_2)_3NMe_2H]$ (**8**, Ln = Y; **9**, Ln = Yb). An X-ray crystallographic study of **9** revealed a tetrahedral arrangement of siloxide O about Yb. One of the four dangling NMe_2 groups is protonated and hydrogen-bonded to a second NMe_2 unit. [Crystal data: monoclinic space group $P2_1/n$, $a = 13.266(3)$ Å, $b = 23.337(5)$ Å, $c = 21.914(3)$ Å, $\beta = 93.94(1)°$, $V = 6768.0$ Å^3, $Z = 4$, $R = 0.0684$, and $R_w = 0.0929$.] Complex **8** partially dissociates into **4** and **6** in toluene solution. A variable-temperature ^1H NMR study yielded $\Delta H° = 40 \pm 4$ kJ mol^{-1} and $\Delta S° = 124 \pm 10$ J mol^{-1} K^{-1} for this equilibrium. Reaction of **8** with $LiCH_2SiMe_3$ produced $Li^+\{Y[OSi(t\text{-}Bu)_2(CH_2)_3NMe_2]_4\}^-$ (**10**) in good yield.

Introduction

The alkoxide and siloxide chemistry of the group 2 and 3 and lanthanide elements has seen explosive growth in the last 5 years. Despite the pioneering work of Bradley and Mehrotra, relatively little structural information was available for this class of compounds prior to 1987.[1] Since that time, the discovery of high T_c superconductors based on $YBa_2Cu_3O_7$[2a] and more recent variants such as TBCCO (Tl–Ba–Ca–Cu–O)[2] and BSCCO (Bi–Sr–Ca–Cu–O)[2c] has led to intensive efforts to develop molecular precursors to these oxides.[3] These efforts have revealed a fascinating array of alkoxide structures from simple monomers to polymetallic clusters[4] and the fascinating cyclic decamer $[Y(OR)_3]_{10}$ (R = CH_2CH_2OMe).[5] A picture of the steric saturation requirements of these metals has emerged which allows design of soluble alkoxide complexes suitable for use in sol–gel processes.[6]

The current challenge is the development of volatile alkoxide compounds which can be employed in the growth of thin-film superconductors by MOCVD. One approach to this problem has been to use fluorinated β-diketonate or alkoxide complexes, which show greatly enhanced volatility when compared to their non-fluorinated analogs.[7] One disadvantage of this method, while not insurmountable, is the formation of metal fluorides during attempted thermal decomposition to the oxides.[7a] In this paper, we report our initial attempts to circumvent this problem by using bulky siloxide ligands with pendant amine functionality. Several recent reports have employed a similar strategy using chelating

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alkoxides in lanthanide,[5,6e,6g,8] transition,[9,10e] and main group[9c,10] metal chemistry. We report here the synthesis of soluble, monomeric aminosiloxides of yttrium, ytterbium, and cerium which show moderate volatility. The synthesis, structural characterization, and solution equilibria of a novel zwitterionic alkoxide is also presented.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere, with the rigorous exclusion of oxygen and water, using standard glovebox (Braun MB150-GII) or Schlenk techniques, except as noted. Tetrahydrofuran (THF), diethyl ether, hexane, and toluene were dried by distillation from sodium benzophenone ketyl under argon immediately prior to use. Trichlorosilane and (3-chloro-*N,N*-dimethylpropyl)amine hydrochloride were purchased from Aldrich and used without further purification. Anhydrous metal chlorides (Ce, Yb, and Y) were prepared from the hydrated salts by prolonged reflux in neat $SOCl_2$ followed by vacuum distillation and drying at 150 °C (10^{-2} Torr) for 16–20 h. Hexamethyldisilazane was purchased from Aldrich and dried by distillation from sodium metal. Lanthanide silylamides, $\mathrm{Ln}[\mathrm{N(SiMe_3)_2}]_3$ (Ln = Ce, Yb, Y), were prepared as reported in the literature.[11] The chlorosilanes $t\text{-BuSiCl}_2\text{H}$ and $t\text{-Bu}_2\text{SiClH}$ were prepared from the appropriate number of equivalents of *t*-BuLi and $HSiCl_3$ in THF, followed by short-path vacuum distillation.

^{1}H, ^{13}C, ^{29}Si, and ^{89}Y NMR spectra were recorded on a Bruker WM-250 MHz or a Bruker AMX-360 MHz spectrometer. Spectra were recorded in C_6D_6 or C_7D_8 solvent, previously distilled from sodium under argon, using 5-mm tubes fitted with a Teflon valve (Brunfeldt). ^{29}Si spectra were recorded using DEPT or INEPT pulse sequences as appropriate. ^{1}H and ^{13}C NMR spectra were referenced to residual solvent resonances; ^{29}Si and ^{89}Y NMR were referenced to external TMS and 3 M YCl_3 in D_2O, respectively. Mass spectra were recorded on a Finnegan 3300 or a Kratos Concept H spectrometer using chemical ionization and electron impact (70 eV) sources, respectively. Melting points were recorded using a Reichert hot stage and are not corrected. Infrared spectra were recorded on a Bruker IFS 25 FT instrument as Nujol mulls or neat oils on KBr disks. Elemental analyses were performed by Canadian Microanalytical, Delta, B.C.

***tert*-Butylbis((*N,N*-dimethylamino)propyl)silane, $\mathrm{HSi}(t\text{-Bu})[(\mathrm{CH_2})_3\mathrm{NMe_2}]_2$ (1).** A 10% solution of KOH in water (250 mL) was added dropwise to a solution of 25.0 g (157 mmol) of $\mathrm{ClCH_2CH_2CH_2NMe_2H^+Cl^-}$ cooled to 0 °C, over a period of 20 min. The aqueous layer was extracted with 2 × 250 mL of Et_2O and the combined ether phases dried over anhydrous $MgSO_4$. The free base was isolated as a colorless oil after removal of ether by rotary evaporation (water aspirator).

The Grignard reagent, $\mathrm{ClMgCH_2CH_2CH_2NMe_2}$, was prepared by dropwise addition of 15.6 g (127 mmol) of the free amine to 3.50 g (146 mmol) of Mg turnings in 300 mL of THF. The green-gray Grignard solution was then added rapidly by canula to a stirred solution of 8.30 g (52.9 mmol) $t\text{-BuSiHCl}_2$ in 100 mL of THF cooled to 0 °C with an ice bath. After addition was complete, the bath was removed and the reaction mixture heated at reflux for 24 h. The reaction mixture was quenched with $Na_2SO_4{\cdot}10H_2O$ and the THF removed under reduced pressure. The residue was extracted with 750 mL of Et_2O and the extract dried over anhydrous $MgSO_4$. Filtration and removal of Et_2O from the filtrate afforded **1** as a colorless oil. Yield: 9.3 g (36 mmol, 68%). Bp: 59 °C (10^{-2} Torr). ^{1}H NMR (C_6D_6): δ 3.65 (t, 1H, $\mathrm{Si}H$, $^3J_{\mathrm{HH}}$ = 3.2 Hz), 2.14 (t, 4H, $\mathrm{C}H_2\mathrm{N}$, $^3J_{\mathrm{HH}}$ = 7.1 Hz), 2.07 (s, 12H, $\mathrm{N}Me_2$), 1.52 (m, 4H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 0.92 (s, 9H, $\mathrm{C}Me_3$), 0.59 (m, 4H, $\mathrm{SiC}H_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 63.22 ($C\mathrm{H_2N}$), 45.61 ($\mathrm{N}Me_2$), 27.94 ($\mathrm{C}Me_3$), 23.79 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 16.93 ($C\mathrm{Me_3}$), 7.43 ($\mathrm{Si}C\mathrm{H_2}$). ^{29}Si{^{1}H} NMR ($C_6D_6$): δ 5.5 ppm. IR: 2095 cm^{-1} (vs, ν(Si–H)). MS (CI): *m/z* 258 (M^+), 201 (M^+ – *t*-Bu), 172 ($\mathrm{M^+ - CH_2CH_2CH_2NMe_2}$). Anal. Calcd for $C_{14}H_{34}N_2Si$: C, 65.04; H, 13.26; N, 10.84. Found: C, 64.96; H, 13.21; N, 10.53.

Bis(*tert*-butyl)((*N,N*-dimethylamino)propyl)silane, $\mathrm{HSi}(t\text{-Bu})_2(\mathrm{CH_2})_3\mathrm{NMe_2}$ (2). This compound was prepared from $t\text{-Bu}_2\text{SiHCl}$ by the procedure detailed above for **1** except that the reaction mixture was refluxed for 48 h following addition of the Grignard reagent. The product was isolated as a colorless air stable liquid. Yield: 58%. Bp: 41 °C (10^{-2} Torr) ^{1}H NMR (C_6D_6): δ 3.24 (t, 1H, Si-H, $^3J_{\mathrm{HH}}$ = 2.6 Hz), 2.18 (t, 2H, $\mathrm{C}H_2\mathrm{N}$, $^3J_{\mathrm{HH}}$ = 7.6 Hz), 2.14 (s, 6H, $\mathrm{N}Me_2$), 1.54 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 0.93 (s, 18H, $\mathrm{C}Me_3$), 0.53 (m, 2H, $\mathrm{SiC}H_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 63.41 ($C\mathrm{H_2N}$), 45.55 ($\mathrm{N}Me_2$), 28.87 ($\mathrm{C}Me_3$), 25.07 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 18.90 ($C\mathrm{Me_3}$), 6.54 ($\mathrm{Si}C\mathrm{H_2}$). ^{29}Si{^{1}H} NMR ($C_6D_6$): δ 14.4 ppm. IR: 2092 cm^{-1} (vs, ν(Si–H)). MS (CI): *m/z* 230 (M^+ +1), 171 (M^+ – *t*-Bu). Anal. Calcd for $C_{13}H_{31}NSi$: C, 68.04; H, 13.62; N, 6.10. Found: C, 68.11; H, 13.40; N, 6.07.

***tert*-Butylbis((*N,N*-dimethylamino)propyl)silanol, $\mathrm{HOSi}(t\text{-Bu})[(\mathrm{CH_2})_3\mathrm{NMe_2}]_2$ (3).** A 500-mL flask was charged with **1** (9.0 g, 35 mmol) and 100 mL of water and cooled to 0 °C with an ice bath. A solution of 10% aqueous HCl (100 mL) was added, and the now homogeneous mixture was refluxed for 40 h exposed to air. The reaction mixture was then neutralized with aqueous KOH, and the oily product which separated was extracted with diethyl ether. After removal of Et_2O, the residue was purified by sublimation to afford colorless crystals of silanol **3**. Yield: 8.2 g (30 mmol, 86%). Mp 43–44 °C. ^{1}H NMR (C_6D_6): δ 2.55 (m, 4H, $\mathrm{C}H_2\mathrm{N}$), 2.02 (s, 12H, $\mathrm{N}Me_2$), 1.67 (m, 4H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 1.12 (s, 9H, $\mathrm{C}Me_3$), 0.70 (m, 4H, $\mathrm{SiC}H_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 63.09 ($C\mathrm{H_2N}$), 45.24 ($\mathrm{N}Me_2$), 26.74 ($\mathrm{C}Me_3$), 22.21 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 18.81 ($C\mathrm{Me_3}$), 11.61 ($\mathrm{Si}C\mathrm{H_2}$). ^{29}Si{^{1}H} NMR ($C_6D_6$): δ 10.5 ppm. IR: 3349 cm^{-1} (br w, ν(SiO–H)). MS (CI): *m/z* 275 (M^+ + 1), 259 ($\mathrm{M^+ - CH_3}$), 217 (M^+ – *t*-Bu), 188 ($\mathrm{M^+ - CH_2CH_2CH_2NMe_2}$). Anal. Calcd for $C_{14}H_{34}N_2OSi$: C, 61.25; H, 12.48; N, 10.21. Found: C, 60.93; H, 12.06; N, 9.99.

Bis(*tert*-butyl)((*N,N*-dimethylamino)propyl)silanol, $\mathrm{HOSi}(t\text{-Bu})_2(\mathrm{CH_2})_3\mathrm{NMe_2}$ (4). This silanol was prepared by the procedure outlined above for **3** except the acidic solution was refluxed for 72 h prior to basic workup. Yield: 93%. Bp: 58–60 °C (10^{-2} Torr) ^{1}H NMR (C_6D_6): δ 1.93 (m, 2H, $\mathrm{C}H_2\mathrm{N}$), 1.85 (s, 6H, $\mathrm{N}Me_2$), 1.53 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 1.16 (s, 18H, $\mathrm{C}Me_3$), 0.65 (m, 2H, $\mathrm{SiC}H_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 62.56 ($C\mathrm{H_2N}$), 45.01 ($\mathrm{N}Me_2$), 27.98 ($\mathrm{C}Me_3$), 22.46 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 20.89 ($C\mathrm{Me_3}$), 10.85 ($\mathrm{Si}C\mathrm{H_2}$). ^{29}Si{^{1}H} NMR ($C_6D_6$): δ 8.0 ppm. IR: 3362 cm^{-1} (br m, ν(SiO–H)). MS (CI): *m/z* 246 (M^+ + 1), 230 ($\mathrm{M^+ - CH_3}$), 188 (M^+ – *t*-Bu). Anal. Calcd for $C_{13}H_{31}NOSi$: C, 63.60; H, 12.73; N, 5.71. Found: C, 62.45; H, 12.47; N, 5.80.

Lanthanide Complexes. The lanthanide complexes described below were all prepared in an argon-filled glovebox by dropwise addition (30 min) of the appropriate number of equivalents of silanol in toluene solution to $\mathrm{Ln}[(\mathrm{N(SiMe_3)_2}]_3$ in toluene. After the mixture was stirred for 1 h, the solvent was removed in vacuo and the residue recrystallized from toluene–hexane mixtures at –30 °C.

$\mathrm{Y[OSi}(t\text{-Bu})((\mathrm{CH_2})_3\mathrm{NMe_2})_2]_3$ (5). The complex was isolated as a viscous, hexane soluble oil which slowly crystallized on standing. Yield: 65%. Mp: 72–75 °C. ^{1}H NMR (C_6D_6): δ 2.32 (m, 12H, $\mathrm{C}H_2\mathrm{N}$), 2.27 (s, 36H, $\mathrm{N}Me_2$), 1.76 (m, 12H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 1.11 (s, 27H, $\mathrm{C}Me_3$), 0.69 (m, 12H, $\mathrm{SiC}H_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 64.32 ($C\mathrm{H_2N}$), 46.36 ($\mathrm{N}Me_2$), 27.52 ($\mathrm{C}Me_3$), 23.24 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 19.43 ($C\mathrm{Me_3}$), 12.52 ($\mathrm{Si}C\mathrm{H_2}$). ^{29}Si{^{1}H} NMR ($C_6D_6$): δ –1.7 ($^2J_{\mathrm{SiY}}$ = 5.8 Hz). MS (CI): *m/z* 909 (M^+), 852 (M^+ – *t*-Bu), 823 ($\mathrm{M^+ - CH_2CH_2CH_2NMe_2}$). Anal. Calcd for $C_{42}H_{99}N_6O_3Si_3Y$: C, 55.47; H, 10.97; N, 9.24. Found: C, 55.56; H, 10.51; N, 8.76.

$\mathrm{Y[OSi}(t\text{-Bu})_2(\mathrm{CH_2})_3\mathrm{NMe_2}]_3$ (6). Yield: 84%. Mp: 117–119 °C. ^{1}H NMR (C_6D_6): δ 2.36 (s, 18H, $\mathrm{N}Me_2$), 2.30 (t, 6H, $\mathrm{C}H_2\mathrm{N}$, $^3J_{\mathrm{HH}}$ = 6.5 Hz), 1.79 (m, 6H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 1.17 (s, 54H, $\mathrm{C}Me_3$), 0.65 (t, 6H, $\mathrm{SiC}H_2$, $^3J_{\mathrm{HH}}$ = 7.1 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 64.03 ($C\mathrm{H_2N}$), 47.54 ($\mathrm{N}Me_2$), 29.36 ($\mathrm{C}Me_3$), 23.62 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 21.34 ($C\mathrm{Me_3}$), 10.84 ($\mathrm{Si}C\mathrm{H_2}$). ^{29}Si{^{1}H} NMR ($C_6D_6$): δ –2.7 ($^2J_{\mathrm{SiY}}$ = 6.0 Hz). MS (CI): *m/z* 821 (M^+), 764 (M^+ – *t*-Bu). Anal. Calcd for $C_{39}H_{90}N_3O_3Si_3Y$: C, 56.96; H, 11.03; N, 5.11. Found: C, 56.31; H, 10.93; N, 5.06.

$\mathrm{Ce[OSi(t\text{-}Bu)_2(CH_2)_3NMe_2]_3}$ (7). Yield: 71%. Mp: 142–144 °C. ^{1}H NMR (C_6D_6, 30 °C): δ 3.04 (54H, $\mathrm{C}Me_3$, fwhm = 5 Hz), 2.18 (6H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$, 31 Hz), 1.48 (6H, $\mathrm{SiC}H_2$, 12 Hz), –4.31 (6H, $\mathrm{C}H_2\mathrm{N}$, 49

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Table 1. Summary of Crystallographic Data for **6** and **9**

	6	**9**
empirical formula	$C_{39}H_{90}N_3O_3Si_3Y$	$C_{52}H_{121}N_4O_4Si_4Yb$
fw	822.3	1151.9
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	13.738(2)	13.266(3)
b (Å)	15.940(3)	23.337(5)
c (Å)	13.363(2)	21.914(3)
α (deg)	93.80(1)	90
β (deg)	116.77(1)	93.94(1)
γ (deg)	74.55(1)	90
V (Å^3)	2513.3	6768.3
Z	2	4
ρ(calcd) (g cm^{-3})	1.087	1.130
μ (cm^{-1})	25.96	35.49
radiation, λ (Å)	Cu Kα, 1.542	Cu Kα, 1.542
T	ambient	ambient
$2\theta_{max}$ (deg)	60	55
no. of obsd reflcns	6850	8171
no. of unique reflcns	4395	7048
R^a	0.0839	0.0684
$R_w{}^b$	0.1081	0.0929

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

Hz), –4.8 (18H, N*Me*$_2$, 39 Hz). ^{1}H NMR (C_7D_8, –60 °C): δ 6.2 (18H, 120 Hz), 3.0 (9H, 65 Hz), 2.4 (9H, 200 Hz), 0.4 (9H, 140 Hz), –1.1 (9H, 110 Hz). MS (CI): *m/z* 873 (M$^+$), 816 (M$^+$ – *t*-Bu), 787 (M$^+$ – $CH_2CH_2CH_2NMe_2$), 760 (M$^+$ – 2*t*-Bu). Anal. Calcd for $C_{39}H_{90}CeN_3O_3Si_3$: C, 53.62; H, 10.38; N, 4.81. Found: C, 53.26; H, 10.30; N, 4.79.

Y[OSi(t-Bu)$_2$(CH$_2$)$_3$NMe$_2$]$_3$[OSi(t-Bu)$_2$(CH$_2$)$_3$NMe$_2$H] (8). Yield: 73%. Mp: 144–147 °C. ^{1}H NMR (C_6D_6): δ 1.88 (s, 24H, N*Me*$_2$), 1.32 (s, 72H, C*Me*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, –10 °C): δ 68.97 (*C*H$_2$N), 52.71 (N*Me*$_2$), 34.42 (C*Me*$_3$), 15.57 (Si*C*H$_2$). Other peaks in the ^{1}H and ^{13}C{^{1}H} NMR are obscured by equilibrium concentrations of Y[OSi(*t*-Bu)$_2$($CH_2CH_2CH_2NMe_2$)]$_3$ and HOSi(*t*-Bu)$_2$($CH_2CH_2CH_2NMe_2$) (*vide infra*). ^{29}Si{^{1}H} NMR (C_6D_6): δ –6.7 ($^2J_{SiY}$ = 6.8 Hz). MS (CI): *m/z* 952 (M$^+$ – 2*t*-Bu), 821 (M$^+$ – HOSi(*t*-Bu)$_2$$CH_2CH_2CH_2NMe_2$)). Anal. Calcd for $C_{52}H_{121}N_4O_4Si_4Y$: C, 58.49; H, 11.42; N, 5.25. Found: C, 58.09; H, 11.20; N, 5.23.

Yb[OSi(t-Bu)$_2$(CH$_2$)$_3$NMe$_2$]$_3$[OSi(*t*-Bu)$_2$(CH$_2$)$_3$NMe$_2$H] (9). Yield: 76%. Mp: 140–141 °C. No signals were observable in the ^{1}H NMR spectrum of this paramagnetic complex. The highest mass fragment observed in the mass spectrum was *m/z* 892 (possibly M$^+$ – 3$CH_2CH_2CH_2NMe_2$). Anal. Calcd for $C_{52}H_{121}N_4O_4Si_4Yb$: C, 54.22; H, 10.59; N, 4.86. Found: C, 54.22: H, 10.41; N, 4.87.

Li$^+${Y[OSi(*t*-Bu)$_2$(CH$_2$)$_3$NMe$_2$]$_4$}$^-$ (10). Reaction of equimolar quantities of **8** and $LiCH_2SiMe_3$ in toluene–hexane mixtures afforded **10** as colorless crystals after concentration of the reaction mixture and cooling at –30 °C. Yield: 85%. Mp: 107–109 °C. ^{1}H NMR (C_7D_8): δ 2.29 (t, 8H, C*H*$_2$N, $^3J_{HH}$ = 6.9 Hz), 2.15 (s, 24H, N*Me*$_2$), 1.73 (m, 8H, CH$_2$C*H*$_2$CH$_2$), 1.21 (s, 72H, C*Me*$_3$), 0.72 (m, 8H, SiC*H*$_2$). ^{13}C{^{1}H} NMR (C_7D_8): δ 64.1 (*C*H$_2$N), 45.8 (N*Me*$_2$), 29.9 (C*Me*$_3$), 23.9 ($CH_2CH_2CH_2$), 21.6 (*C*Me$_3$), 12.6 (Si*C*H$_2$). ^{29}Si{^{1}H} NMR (C_7D_8): δ 1.2 ($^2J_{SiY}$ = 4.9 Hz). Anal. Calcd for $C_{52}H_{120}LiN_4O_4Si_4Y$: C, 58.17; H, 11.26; N, 5.22. Found: C, 57.65; H, 11.03; N, 4.95.

X-ray Crystallographic Studies. Crystallographic data for **6** and **9** are summarized in Table 1. Crystals of **6** (0.45 × 0.18 × 0.10 mm) and **9** (0.6 × 0.5 × 0.2 mm) were loaded into glass capillaries in the glove box and subsequently examined by photographic methods using Weissenberg and Precession (9) cameras. The space group of **9** was determined by the systematic absences and that of **6** by successful solution of the structure using a symmetry center. The crystals were transferred to a Nonius CAD4F diffractometer equipped with Ni-filtered Cu Kα radiation. The unit cell of **6** was refined using 23 reflections in the 2θ range 22–56° while that of **9** was refined using 25 reflections in the 2θ range 55–76°. Experimental densities were not obtained because of the air sensitivity of both compounds. Three standard reflections, measured periodically during data collection (for **6**, 6,6,0, –3,2,7, and 5,8,–4, and for **9**, –8,0,12, 0,4,17, and 0,18,0), showed a decline in combined intensity to 88 and 77% of their original value, for **6** and **9**, respectively. Intensity measurements were collected over one hemisphere for **6** and one-fourth of the sphere for **9**. After the usual data reduction procedures, including an absorption correction according to a measured ψ scan, the structures were solved using SHELX76 (**6**), SHELXS (**9**), and the Patterson function for both structures.[12] The refinements minimized $\sum w((|F_o| - |F_c|)^2)$ and proceeded normally using SHELX76. Criteria for inclusion of reflections were $I > 3\sigma(I)$ and $I > 2\sigma(I)$ for **6** and **9**, respectively. The weighting scheme was determined by counting statistics using $w = 1/(\sigma^2(F) + 0.001F^2)$. Convergence was satisfactory for both compounds: max shift/esd = 0.01 for **6**, and 0.04 for **9**. A total of 442 parameters (49 atoms × 9 parameters per atom + scale) were refined in two blocks for **6**. For **9**, 590 parameters (65 × 9 parameters per atom + 1 H atom (4 parameters) + scale) were refined in two blocks. No intermolecular contacts shorter than 3.5 Å were observed in either structure. The structural perspective plots were drawn using ORTEP.[13]

Results and Discussion

Ligand Synthesis. The (dimethylamino)silanol ligands used in this study were prepared in two steps from the appropriate chlorosilane and the Grignard reagent as shown in eqs 1 and 2.

$$(t\text{-Bu})_{3-n}HSiCl_n + nClMg(CH_2)_3NMe_2 \rightarrow (t\text{-Bu})_{3-n}HSi[(CH_2)_3NMe_2]_n + nMgCl_2 \quad (1)$$

1, $n = 2$
2, $n = 1$

$$\mathbf{1} \text{ or } \mathbf{2} + H_2O\ (H^+ \text{ catalyst}) \rightarrow (t\text{-Bu})_{3-n}(HO)Si[(CH_2)_3NMe_2]_n + {}^1/_2H_2(g) \quad (2)$$

3, $n = 2$
4, $n = 1$

The intermediate silanes **1** and **2** were isolated as very pure colorless oils after vacuum distillation. The purified silanes did not show any evidence of hydrolysis after exposure to air for several days. Indeed, conversion of the silanes to silanols, **3** and **4**, proved quite difficult as prolonged (>24 h) reflux in acidic water was necessary to effect reaction 2. Disiloxane condensation products of **3** and **4** were not observed, providing evidence for the steric congestion at silicon in these ligands. Additionally, the mass spectra of **1–4** all revealed a base peak corresponding to loss of a *tert*-butyl fragment with the more bulky di-*tert*-butyl compounds **2** and **4** showing the greatest relative intensity for this peak.

Tris(siloxide) Complexes. Reaction of **3** and **4** with Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = Ce and Y) in a 3:1 molar ratio allowed isolation of the tris(siloxide) complexes (eq 3). Complexes derived from the tridentate silanol **3** were found to be viscous oils of high hexane solubility. Yttrium complex **5** was isolated as a pure oil that slowly crystallized but the cerium analog could not be isolated in reasonable purity. In contrast **6** and **7**, derived from the bidentate silanol **4**, were isolated as crystalline compounds from toluene–hexane mixtures.

$$3 \text{ equiv of } \mathbf{3} \text{ or } \mathbf{4} + Ln[N(SiMe_3)_2]_3 \rightarrow Ln[OSi(t\text{-Bu})_{3-n}[(CH_2)_3NMe_2]_n]_3 + 3HN(SiMe_3)_2 \quad (3)$$

5, $n = 2$, Ln = Y
6, $n = 1$, Ln = Y
7, $n = 1$, Ln = Ce

The NMR spectra of **5–7** show only one type of siloxide ligand. The yttrium complexes, **5** and **6**, show a small $^2J(^{29}Si\text{–}^{89}Y)$ coupling of 6 Hz. The ^{29}Si resonance shifts ca. 10 ppm upfield relative to the free silanol (**3** and **4**, respectively) for both **5** and **6**. The ^{89}Y NMR shift of 269 ppm in **6** is similar to that reported for Y(OSiMe$_2$(*t*-Bu))$_3$(THF)$_3$ (266.6 ppm)[14] and Y(OC(i-Pr)$_2$CH$_2$OEt)$_3$ (277.1 ppm).[8c] With the exception of a small amount of broadening, the ^{1}H NMR spectra of **5** and **6** are invariant to –80 °C. Since these results are consistent with either a high symmetry static structure or rapid exchange of coordinated

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(12) Sheldrick, G. M.; SHELX76, Programs for Crystal Structure Determination. University of Cambridge, 1976.

(13) Johnson, C. K. *ORTEPII*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

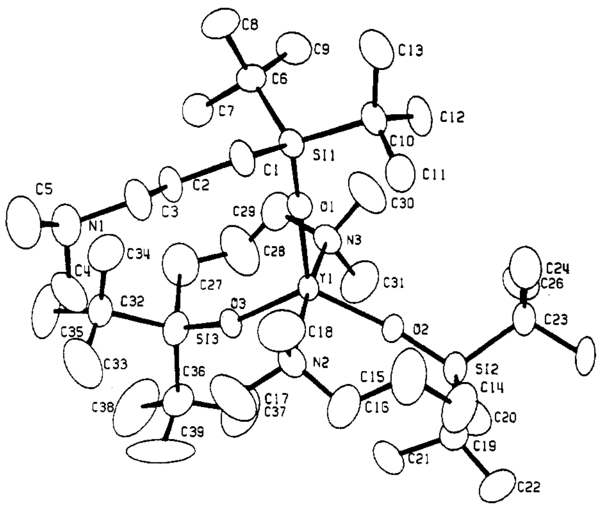

Figure 1. ORTEP diagram of $Y[OSi(t\text{-}Bu)_2(CH_2)_3NMe_2]_3$ (**6**).

and free (dimethylamino)propyl arms, an X-ray crystallographic study of **6** was carried out.

Solid-State Structure of 6. The structure of **6** is shown in Figure 1. Fractional atomic coordinates are given in Table 2, and selected bond lengths and angles are collected in Table 3. The X-ray crystal structure reveals that **6** possesses a trigonal bipyramidal geometry at the central yttrium atom with the bulkier siloxide groups occupying the equatorial positions (mean O–Y–O angle 120°) and the two coordinated dimethylamino donors occupying the axial sites (N–Y–N angle 169.2(4)°). The third (dimethylamino)propyl arm is not coordinated.

The Y–O distances are all equivalent within experimental error (mean 2.097 Å) and very similar to the terminal Y–O distances (mean 2.09 Å) for the five-coordinate Y center of $(ROH)(RO)_2Y(\mu\text{-}OR)_2Y(OR)_2$ (RO = t-$BuMe_2SiO$), **I**.[14a] The range of trivalent lanthanide–alkoxide oxygen bond distances reported in the literature is 2.03–2.12 Å[8a,14a,17] after correction for differences in metal ionic radii.[15] The Y–O distances in **6**, while nearer the upper extreme, are still well within the expected range. The Y–O–Si angles are nearly linear for all three ligands and fall within the typical range found in early metal siloxides.[14a,16] This angle is greatest (175.1(4)°) for the monodentate siloxide. The more pronounced bending of the bidentate Y–O–Si angles may reflect a requirement for chelation.

The observation of a trigonal bipyramidal geometry in the solid state indicates that **6** is fluxional in solution. The most likely dynamic process is the interchange of mono- and bidentate siloxides by the dissociation and reassociation of dimethylamino donors (an "arm on–arm off" process). The fact that this exchange occurs rapidly on the NMR time scale even at −80 °C is consistent with the well-known lability of lanthanide–Lewis base adducts.[18] It is also noteworthy that Lappert[8a] isolated and structurally characterized **II**. This is remarkable because the shorter C–O bond should result in increased steric pressure at Y in this compound. It is therefore probable that the considerably longer Y–P bond distances (3.045(2) Å) in **II** are important in allowing formation of a six-coordinate geometry. Additionally, the

Table 2. Fractional Atomic Coordinates[a] and Equivalent Isotropic Temperature[b] Factors for **6** (Estimated Standard Deviations in Parentheses)

atom	x	y	z	U_{eq}
Y(1)	40493(7)	26310(6)	17808(8)	543(4)
Si(1)	3566(3)	2936(2)	4320(2)	67(2)
Si(2)	6939(3)	2233(3)	2061(3)	95(2)
Si(3)	1499(3)	2814(3)	−834(3)	101(2)
O(1)	3752(5)	2852(4)	3193(5)	68(4)
O(2)	5636(5)	2562(4)	1875(5)	71(4)
O(3)	2671(5)	2531(4)	257(5)	68(3)
N(1)	1150(8)	517(6)	3269(9)	103(6)
N(2)	4632(7)	925(5)	2113(7)	83(5)
N(3)	3580(8)	4254(5)	1147(8)	81(5)
C(1)	3254(10)	1923(7)	4658(9)	80(6)
C(2)	2189(9)	1668(7)	3721(9)	79(6)
C(3)	2169(10)	786(7)	4144(10)	90(7)
C(4)	1316(14)	215(11)	2263(13)	134(11)
C(5)	926(13)	−164(9)	3790(14)	135(11)
C(6)	2311(10)	3949(7)	4127(10)	79(7)
C(7)	1355(10)	3957(8)	2914(10)	95(7)
C(8)	1822(12)	3858(10)	4962(12)	118(10)
C(9)	2603(13)	4829(8)	4238(13)	118(10)
C(10)	4965(11)	2984(8)	5591(10)	88(7)
C(11)	5849(11)	2095(9)	5732(12)	117(8)
C(12)	5429(11)	3705(9)	5355(12)	106(8)
C(13)	4858(13)	3174(11)	6719(10)	127(10)
C(14)	7548(13)	1024(11)	2748(15)	148(12)
C(15)	6727(15)	819(13)	3143(16)	177(13)
C(16)	5738(15)	533(10)	2172(20)	167(15)
C(17)	3779(19)	590(9)	1108(18)	205(16)
C(18)	4631(17)	577(10)	3118(16)	157(15)
C(19)	7065(12)	2099(9)	691(11)	98(8)
C(20)	6998(18)	2982(11)	199(14)	158(14)
C(21)	5997(13)	1823(11)	−224(12)	134(11)
C(22)	8155(14)	1459(13)	792(15)	166(13)
C(23)	7851(11)	2881(12)	3134(13)	127(10)
C(24)	7820(15)	2781(16)	4287(14)	189(15)
C(25)	9115(11)	2581(12)	3325(14)	141(10)
C(26)	7362(16)	3949(11)	2664(17)	166(14)
C(27)	867(15)	4073(11)	−880(17)	173(13)
C(28)	1681(18)	4676(12)	−604(17)	188(15)
C(29)	2333(12)	4780(10)	594(16)	133(10)
C(30)	4138(16)	4601(9)	2239(14)	159(13)
C(31)	4190(14)	4310(10)	461(15)	150(12)
C(32)	376(10)	2429(10)	−729(11)	107(8)
C(33)	702(19)	1364(14)	−742(18)	200(17)
C(34)	438(14)	2596(13)	458(14)	155(13)
C(35)	−836(11)	2748(14)	−1739(15)	187(13)
C(36)	1677(12)	2508(13)	−2152(10)	121(9)
C(37)	2697(21)	2742(25)	−2062(18)	309(28)
C(38)	673(17)	2814(25)	−3213(16)	308(24)
C(39)	1811(35)	1586(22)	−2358(30)	332(39)

[a] ×10^n where n = 5 for Y and n = 4 for Si, C, N, and O. [b] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*(a_i\cdot a_j)$ in $Å^2 \times 10^n$ where n = 4 for Y and n = 3 for Si, C, N, and O.

Table 3. Selected Distances (Å) and Angles (deg) for **6**[a]

	Distances		
Y(1)–O(1)	2.093(8)	Y(1)–O(2)	2.099(8)
Y(1)–O(3)	2.098(5)	Y(1)–N(2)	2.629(8)
Y(1)–N(3)	2.595(9)	O(1)–Si(1)	1.630(9)
O(2)–Si(2)	1.631(8)	O(3)–Si(3)	1.583(6)
	Angles		
O(1)–Y(1)–O(2)	121.5(3)	O(1)–Y(1)–O(3)	116.9(3)
O(2)–Y(1)–O(3)	121.6(3)	O(1)–Y(1)–N(2)	93.6(3)
O(1)–Y(1)–N(3)	97.2(3)	O(2)–Y(1)–N(2)	89.5(3)
O(2)–Y(1)–N(3)	84.1(3)	O(3)–Y(1)–N(2)	88.9(2)
O(3)–Y(1)–N(3)	87.0(3)	N(2)–Y(1)–N(3)	169.2(4)
Y(1)–O(1)–Si(1)	175.1(4)	Y(1)–O(2)–Si(2)	164.3(5)
Y(1)–O(3)–Si(3)	159.5(4)		

[a] Estimated standard deviation in parentheses.

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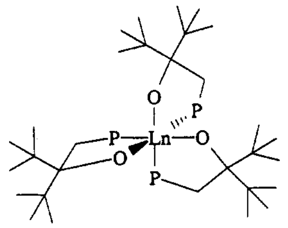
(18) DeCola, L.; Smailes, D. L.; Vallarino, L. M. *Inorg. Chem.* **1986**, *25*, 1729 and references therein.

presence of five-membered chelate rings in **II**, versus seven-membered rings in **6** should favor formation of a six-coordinate geometry.

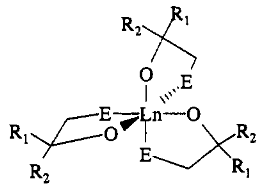


II

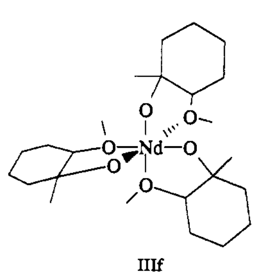
Ln = Nd, Y

P = PMe_2

Herrmann has recently reported the synthesis of a number of closely related chelating alkoxide complexes of the lanthanides, **III**.[8c] Interestingly, these complexes also show a single type of alkoxide in the room temperature NMR and a nearly identical ^{89}Y NMR shift to **6**. A six coordinate geometry was assumed on the basis of the similarity in ^{89}Y chemical shift to $Y(OSiMe_2(t\text{-Bu}))_3(THF)_3$,[14] but since a structural determination was not carried out, it is also possible that **IIIa–f** contain dangling donor arms which are in rapid exchange with coordinated donors. The shorter C–O bonds of these ligands should increase the steric crowding within the coordination sphere although this may be partially offset by the smaller size of OEt versus NMe_2.

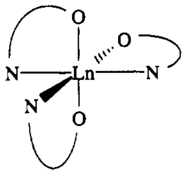


	R_1	R_2	E	Ln
III a	H	t-Bu	OEt	Nd
b	H	t-Bu	NEt_2	Nd
c	t-Bu	t-Bu	OEt	Nd
d	i-Pr	i-Pr	OEt	Nd
e	i-Pr	i-Pr	OEt	Y

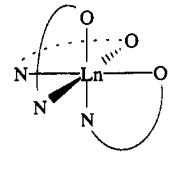


IIIf

Paramagnetic complex **7** exhibits very different ^{1}H NMR behavior compared with its Y analog **6**. When a sample of **7** is cooled from room temperature to –60 °C, the single set of resonances collapse and are finally replaced by a complex spectrum containing five large resonances (2:1:1:1:1 ratio) and several very broad peaks of smaller integrated intensity. Presumably, the five large resonances represent inequivalent *tert*-butyl groups. This pattern is consistent with a *mer*-octahedral geometry (C_1 symmetry) as shown in **IVa** assuming the accidental overlap of two *tert*-butyl resonances. A *fac*-octahedral geometry (C_3 symmetry, **IVb**) can be ruled out since this can, at most, result in two inequivalent *tert*-butyl goups. A five-coordinate structure similar to **6** should give rise to three *tert*-butyl resonances (assuming free rotation about the Ce–O bond) and seems unlikely in view of the rapid fluxional behavior of **6** at low temperature. A six-coordinate geometry may be possible for **7**, the solid state structure of **6** notwithstanding, because the ionic radius of Ce^{3+} is approximately 0.11 Å larger than that of Y^{3+} in this coordination number.[15] On the basis of these considerations, a *mer*-octahedral geometry (**IVa**) seems most reasonable. The structure of **5** is not known but a fluxional six- or seven-coordinate geometry is reasonable given the smaller size of the $^{-}OSi(t\text{-Bu})[(CH_2)_3NMe_2]_2$ ligand.



IVa
mer



IVb
fac

Volatility. Complexes **5**–**7** sublime at 115–135 °C (5×10^{-4} Torr) without decomposition. Sublimation at 10^{-2} Torr did result in some decomposition due to the higher temperatures required. The volatility of **6** is very similar to **IIIb–d** and higher than that of lanthanide complexes derived from less bulky monodentate ligands such as $OCMe_2(i\text{-Pr})$,[19a] OCMe(Et)(i-Pr),[19a] $OCEt_3$,[19a] $OC(t\text{-Bu})_2(i\text{-Pr})$,[17f] $OCH(t\text{-Bu})_2$,[17f] $O(t\text{-Bu})_3$,[19a] and $O(t\text{-Am})$[19a] (135–240 °C at 10^{-3} Torr). Lanthanide complexes of the fluorinated alkoxide $OCMe(CF_3)_2$ are more volatile than the compounds presented in this paper (80–130 °C at 10^{-2} Torr).[19b]

Zwitterionic Tetrakis(siloxide) Complexes. During the initial synthesis of **6**, we isolated a small amount of well-formed crystals which gave a more complex ^{1}H NMR spectrum. This impurity was traced to the presence of a slight excess of silanol **4** relative to $Y[N(SiMe_3)_2]_3$. Repeating the reaction using a 4:1 molar ratio of silanol to Y reproduced compound **8** in good yield (eq 4).

$$4\text{ equiv of }\mathbf{4} + \mathrm{Ln[N(SiMe_3)_2]_3} \rightarrow \underset{\substack{\mathbf{8},\ \mathrm{Ln = Y}\\ \mathbf{9},\ \mathrm{Ln = Yb}}}{\mathrm{Ln[OSi(\mathit{t}\text{-}Bu)_2(CH_2)_3NMe_2]_3[OSi(\mathit{t}\text{-}Bu)_2(CH_2)_3NMe_2H]}} + 3\mathrm{HN(SiMe_3)_2} \quad (4)$$

The ^{1}H NMR spectrum clearly showed the presence of free silanol **4** and complex **6** as well as a third component. Our initial assumption was that **8** represented a simple silanol adduct of **6**. The elemental analysis was consistent with this formulation, but a crystal structure was deemed desirable. We were unable to obtain X-ray quality crystals of **8**, but preparation of the ytterbium analog **9** provided crystals suitable for a structural study. Given the fact that Yb^{3+} is only 0.03 Å smaller than Y^{3+},[15] it is reasonable to assume that **9** and **8** have very similar structures.

Solid-State Structure of 9. The structure of **9** is shown in Figure 2. Fractional atomic coordinates are given in Table 4, and selected bond distances and angles are presented in Table 5. Surprisingly, the crystal structure of **9** does not show a simple silanol adduct of **6**. It is very clear that all four silanols have been deprotonated and bind to the central ytterbium atom as a regular tetrahedron of siloxides (O–Yb–O angles range from 107.5(2) to 111.2(2)° with an mean of 109.5°). All four Yb–O distances are similar (mean 2.076 Å). The best comparisons available in the literature are the terminal siloxide Y–O distances for the

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(19) (a) Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Motevalli, M. *Polyhedron* **1991**, *10*, 1049. (b) Bradley, D. C.; Chudzynska, H.; Hammond, M. E.; Hursthouse, M. B.; Motevalli, M.; Ruowen, W. *Polyhedron* **1992**, *11*, 375.

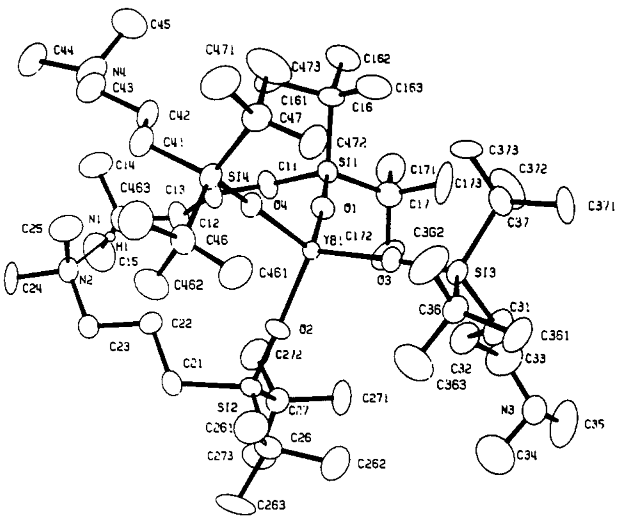

Figure 2. ORTEP diagram of Yb[OSi(t-Bu)$_2$(CH$_2$)$_3$NMe$_2$]$_3$[OSi(t-Bu)$_2$(CH$_2$)$_3$NMe$_2$H] (**9**).

four-coordinate Y in **I**.[14a] The distances of 2.046(20) and 2.060(19) Å observed in this compound predict Yb–O distances in **9** of 2.02 Å after correction for the ca. 0.03 Å smaller ionic radius of Yb^{3+} versus Y^{3+}.[15] The Yb–O distance in **9** compares well with that in the crowded Ce^{4+} alkoxide [(tritox)$_3$Ce]$_2$(μ-p-C$_6$H$_4$O$_2$).[17c] The nearly linear Yb–O–Si angles are typical for lanthanide siloxide complexes and similar to those observed in **6**.

The most unique structural feature of **9** is the location of the proton which has been removed from the fourth siloxide ligand. Initial refinement showed that two of the four dangling dimethylamino groups were in close proximity. The hydrogen atom was therefore placed between these two N atoms and refined isotropically in the final structure. Complex **9** is a zwitterion containing a discrete Y(OR)$_4^-$ core and a pendant, hydrogen-bonded ammonium counterion. One silanol ligand has therefore been deprotonated by an internal RNMe$_2$ base. To our knowledge this is the first example of self-deprotonation to form a zwitterionic complex for a lanthanide siloxide or alkoxide. Although the structural details are considerably different, **9** is reminiscent of the tetrakis(aryloxide) "ate" complex K[Nd(O-2,6-i-PrC$_6$H$_4$)$_4$],[20] where H$^+$ is replaced by K$^+$. Indeed, reaction of **8** with Me$_3$SiCH$_2$Li produces an "ate" complex **10** as shown in eq 5.

$$\mathbf{8} + \mathrm{LiCH_2SiMe_3} \rightarrow \underset{\mathbf{10}}{\mathrm{Li^+\{Y[OSi(\mathit{t}\text{-}Bu)_2(CH_2)_3NMe_2]_4\}^-}} + \mathrm{SiMe_4} \quad (5)$$

The deprotonation of a silanol by an amine has precedence in Al chemistry. Chisholm and co-workers[21] have isolated and structurally characterized [Me$_2$NH$_2$]$^+$[Al(OSiMe$_3$)$_4$]$^-$ (**V**, eq 6).

$$\mathrm{HNMe_2 + HOSiMe_3 + {}^1/_2Al_2(OSiMe_3)_6} \rightleftharpoons \underset{\mathbf{V}}{\mathrm{[Me_2NH_2]^+[Al(OSiMe_3)_4]^-}} \quad (6)$$

Complex **V** differs from **8** and **9** in that the Me$_2$NH$_2^+$ cation is hydrogen bonded to a siloxide oxygen rather than to another amine. No examples of zwitterionic alkoxide complexes have been reported, presumably reflecting the lower acidity of alcohols relative to silanols (pK_a in water: Et$_3$SiOH, 13.6;[22a] t-BuOH, 19[22b]). Caulton[14a] isolated **I**, which contains a coordinated silanol, in the absence of any deprotonating base, and it seems likely that addition of an amine to this complex will produce a salt similar to **V**, **8** and **9**.

Table 4. Fractional Atomic Coordinates[a] and Equivalent Isotropic Temperature Factors[b] for **9** (Estimated Standard Deviations in Parentheses)

atom	x	y	z	U_{eq}
Yb(1)	1115.3(3)	2049.2(2)	3354.6(2)	354(2)
Si(1)	2300(2)	3461.2(10)	3464.9(12)	523(8)
Si(2)	180(2)	1839.0(11)	1756.9(10)	501(8)
Si(3)	3007(2)	948.2(11)	3805.6(12)	577(9)
Si(4)	−1005(2)	1952.1(11)	4325.7(12)	592(10)
O(1)	1820(4)	2837(2)	3389(3)	59(2)
O(2)	580(4)	1908(3)	2455(3)	58(2)
O(3)	2135(4)	1410(3)	3659(3)	64(2)
O(4)	−102(4)	2091(3)	3900(3)	62(2)
C(11)	1528(7)	3987(4)	2968(5)	73(4)
C(12)	378(7)	3916(4)	2893(5)	72(4)
C(13)	6(8)	4280(5)	2345(7)	103(6)
N(1)	−1112(7)	4366(4)	2264(4)	73(4)
C(14)	−1542(12)	4722(6)	2753(8)	136(8)
C(15)	−1314(12)	4642(7)	1633(7)	151(9)
C(16)	2316(9)	3678(5)	4304(5)	85(5)
C(17)	3618(8)	3472(5)	3158(5)	80(4)
C(161)	1131(11)	3763(7)	4435(6)	128(7)
C(162)	2889(12)	4252(5)	4458(7)	124(7)
C(163)	2733(15)	3176(6)	4705(5)	137(8)
C(171)	4070(9)	4092(5)	3119(7)	106(6)
C(172)	3539(12)	3182(7)	2535(8)	137(8)
C(173)	4378(11)	3111(7)	3558(8)	141(8)
C(21)	−1139(7)	2151(4)	1610(4)	67(4)
C(22)	−1342(8)	2673(5)	2020(5)	71(4)
C(23)	−2372(8)	2936(5)	1802(5)	76(4)
N(2)	−2547(6)	3471(4)	2179(4)	72(3)
C(24)	−3462(8)	3758(6)	1884(7)	106(6)
C(25)	−2746(11)	3321(6)	2820(5)	109(6)
C(26)	72(8)	1038(4)	1569(5)	74(4)
C(27)	1048(7)	2258(4)	1259(4)	64(4)
C(261)	−519(11)	746(5)	2073(6)	107(6)
C(262)	1163(11)	749(5)	1564(7)	120(7)
C(263)	−490(13)	925(6)	933(6)	133(7)
C(271)	2165(8)	2088(5)	1398(7)	96(5)
C(272)	947(11)	2905(4)	1403(7)	101(6)
C(273)	766(11)	2186(6)	556(5)	106(6)
H(1)	−145(6)	404(4)	228(4)	5(3)[c]
C(31)	3933(10)	888(6)	3173(6)	114(6)
C(32)	3787(10)	1370(5)	2688(5)	101(5)
C(33)	4718(14)	1471(8)	2322(8)	150(9)
N(3)	5092(8)	1001(4)	1994(4)	88(4)
C(34)	4288(17)	825(10)	1554(9)	181(11)
C(35)	5918(14)	1150(9)	1658(9)	201(11)
C(36)	2423(9)	203(4)	3868(5)	80(4)
C(37)	3785(8)	1175(5)	4537(5)	87(5)
C(361)	3172(10)	−286(5)	3903(6)	102(6)
C(362)	1770(12)	170(6)	4417(8)	135(8)
C(363)	1750(15)	103(6)	3283(9)	172(10)
C(371)	4611(9)	739(5)	4747(7)	110(6)
C(372)	4389(13)	1728(7)	4337(9)	171(10)
C(373)	3118(12)	1331(8)	5039(6)	163(9)
C(41)	−1941(8)	2566(5)	4370(5)	82(5)
C(42)	−1504(9)	3180(5)	4327(6)	86(5)
C(43)	−2365(10)	3609(6)	4400(5)	102(6)
N(4)	−2044(9)	4198(4)	4258(5)	108(5)
C(44)	−2991(12)	4562(6)	4188(7)	140(8)
C(45)	−1295(14)	4435(7)	4725(8)	148(8)
C(46)	−1779(7)	1327(5)	3970(5)	80(5)
C(47)	−427(9)	1779(5)	5131(5)	84(5)
C(461)	−1137(10)	791(5)	3931(7)	113(6)
C(462)	−2134(11)	1527(6)	3304(6)	121(7)
C(463)	−2745(11)	1172(7)	4305(8)	139(8)
C(471)	−1230(12)	1641(7)	5595(6)	135(8)
C(472)	294(12)	1305(7)	5132(6)	134(7)
C(473)	105(16)	2343(8)	5374(7)	166(9)

[a] $\times 10^4$. [b] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*(a_i \cdot a_j)$ in Å$^2 \times 10^n$ where $n = 4$ for Yb and Si, $n = 3$ for C, N, and O, and $n = 2$ for H. [c] Refined isotropically.

Solution Behavior of 8. As noted earlier, the ^{1}H NMR spectrum of **8** shows the presence of free silanol **4**, tris(siloxide) **6**, and a

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(21) Chisholm, M. H.; Huffman, J. C.; Wesemann, J. L. *Polyhedron* **1991**, *10*, 1367.

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Table 5. Selected Distances (Å) and Angles (deg) for **9**[a]

	Distances		
Yb(1)–O(1)	2.062(6)	Yb(1)–O(2)	2.074(6)
Yb(1)–O(3)	2.092(6)	Yb(1)–O(4)	2.077(6)
Si(1)–O(1)	1.594(6)	Si(2)–O(2)	1.593(6)
Si(3)–O(3)	1.597(6)	Si(4)–O(4)	1.600(7)
	Angles		
O(1)–Yb(1)–O(2)	107.5(2)	O(1)–Yb(1)–O(3)	110.1(2)
O(1)–Yb(1)–O(4)	107.8(2)	O(2)–Yb(1)–O(3)	111.2(2)
O(2)–Yb(1)–O(4)	109.0(2)	O(3)–Yb(1)–O(4)	111.2(2)
Yb(1)–O(1)–Si(1)	174.7(4)	Yb(1)–O(2)–Si(2)	176.5(4)
Yb(1)–O(3)–Si(3)	171.3(4)	Yb(1)–O(4)–Si(4)	165.6(4)

[a] Estimated standard deviation in parentheses.

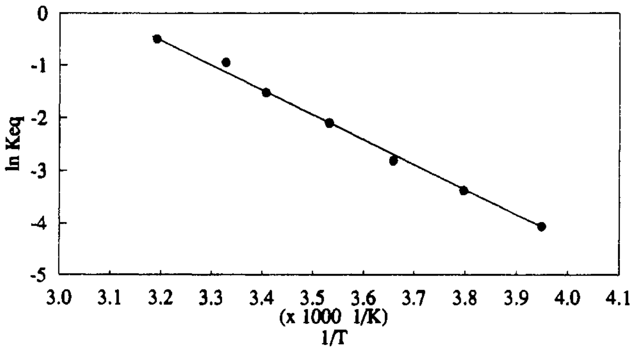
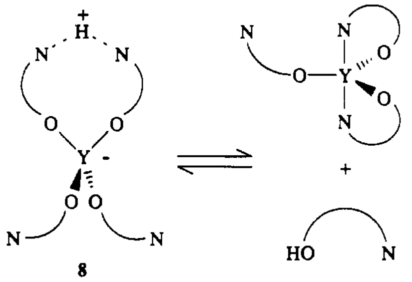


Figure 3. Plot of ln K_{eq} versus T^{-1} for the equilibrium **8** ⇌ **4** + **6** (eq 7).

third component which is assumed to be intact **8**. Cooling the sample results in an increase in intensity of the resonances assigned to **8** and a corresponding decrease for those resonances due to **4** and **6**, consistent with the equilibrium illustrated schematically in eq 7. A plot of ln K_{eq} versus T^{-1} (Figure 3) for this equilibrium is a good straight line giving $\Delta H° = 40 \pm 4$ kJ mol^{-1} and $\Delta S° = 124 \pm 10$ J mol^{-1} K^{-1}. The large positive value of $\Delta S°$ is consistent with dissociation of **8** into **4** and **6**. In comparison to V, **8** is more dissociated in solution which is further evidence for a high degree of steric crowding within the metal coordination sphere.



8 **6** **4** (7)

The observation of all three components of the equilibrium shown in eq 7 requires slow exchange of free silanol and coordinated siloxide. This fact rules out exchange of trace free silanol with coordinated siloxide as a possible explanation for the rapid fluxional behavior of **6** at low temperature. Further, observation of a single set of siloxide resonances for **8** at low temperature indicates that proton migration between all four dangling dimethylamino groups is a low-energy process. Paramagnetic line broadening precludes assignment of any ^{1}H NMR resonances for **9** but it is reasonable to assume that this compound exhibits solution behavior analogous to that for **8**.

Concluding Remarks

The use of bulky, chelating siloxides allows isolation of moderately volatile, monomeric lanthanide complexes without ligand fluorination. Incorporation of pendant donors was intended to decrease intermolecular interactions by satisfying the coordination requirements of the metal center. This goal was achieved for the tris(siloxides) without coordination of all three ligands in a multidentate mode. In addition, the dimethylamino groups used here were found to function as internal bases thus allowing isolation of novel zwitterionic tetrakis(siloxide) complexes. These compounds are obvious candidates for formation of heteropolymetallics by replacement of H$^+$ by metals such as copper. The possibility of using **8** as a building block for discrete and possibly volatile heterobimetallics is being actively pursued.

Acknowledgment. We thank Mrs. C. Greenwood for assistance in recording the ^{89}Y NMR spectra, Mrs. Kathy Beveridge for help with the X-ray structural studies, and Dr. D. McGillivray and Mr. L. Shallig for recording the mass spectra. D.J.B. thanks Dr. S. R. Stobart and Mr. R. Gossage for helpful discussions. This research was supported by the NSERC (Canada) and a University of Victoria Internal Research Grant (to D.J.B.).

Supplementary Material Available: Full tables of distances (Table S1), angles (Table S2) and anisotropic thermal parameters (Table S3) for **6** and distances (Table S4), angles (Table S5), anisotropic thermal parameters (Table S6) and hydrogen atom parameters (coordinates (Table S7), distances (Table S8) and angles (Table S9)) for **9** (9 pages). Ordering information is given on any current masthead page.