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Syntheses and Fluxional Behavior of Yttrium Complexes Containing the Bulky Arylsiloxide OSi^{t}BuAr$_2$ [Ar = o-C$_6$H$_4$(CH$_2$NMe$_2$)] and the X-ray Crystal Structure of Y[OSi^{t}BuAr$_2$][N(SiMe$_3$)$_2$]$_2$

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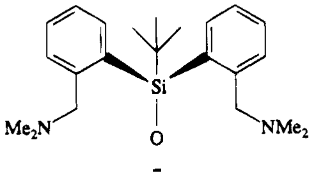
The silanol ligand HOSi^{t}BuAr$_2$ (**1**; Ar = o-C$_6$H$_4$(CH$_2$NMe$_2$)) was prepared from ^{t}BuSiCl$_3$ and 2 equiv of LiAr followed by aqueous workup. Reaction of **1** with Y[N(SiMe$_3$)$_2$]$_3$ provided the monosiloxide complex Y[OSi^{t}BuAr$_2$][N(SiMe$_3$)$_2$]$_2$ (**2**). A single crystal X-ray diffraction study of **2** revealed a highly distorted tetrahedral geometry at Y. Only one of the two 2-(N,N-dimethylaminomethyl)phenyl arms of the siloxide is coordinated. [Crystal data: monoclinic space group $I2/a$, a = 20.709(3) Å, b = 9.511(1) Å, c = 46.579(6) Å, β = 98.04(1)°, V = 9084.6 Å^3, Z = 8, R = 0.078 and R_w = 0.101]. Reaction of **2** with 2 equiv of HOC$_6$H$_3$^{t}Bu$_2$-2,6 afforded Y[OSi^{t}BuAr$_2$][OC$_6$H$_3$^{t}Bu$_2$-2,6]$_2$ (**3**) in good yield. Complexes **2** and **3** exhibit very similar fluxional behavior in solution. Two separate fluxional processes were distinguished by ^{1}H NMR: a lower temperature process involving restricted rotation of the silylamide (**2**, $\Delta G^*_{\text{rotation}} = 53 \pm 1$ kJ/mol) or phenoxide (**3**, $\Delta G^*_{\text{rotation}} = 57 \pm 1$ kJ/mol) groups and a higher temperature process involving exchange of free and coordinated 2-(N,N-dimethylaminomethyl)phenyl arms (**2**, $\Delta G^*_{\text{arm exchange}} = 72 \pm 1$ kJ/mol; **3**, $\Delta G^*_{\text{arm exchange}} = 75 \pm 1$ kJ/mol). Complex **3** reacts with 2 equiv of LiCH$_2$SiMe$_3$ to give Li$^+${Y[OSi^{t}BuAr$_2$][OC$_6$H$_3$^{t}Bu$_2$-2,6][CH$_2$SiMe$_3$]$_2$}$^-$ (**4**). Attempts to prepare a neutral dialkyl by elimination of the remaining LiOC$_6$H$_3$^{t}Bu$_2$-2,6 were not successful. Complex **4** exhibits complex fluxional behavior in solution by ^{1}H NMR.

Introduction

The organometallic chemistry of yttrium and the lanthanides has been dominated by pentamethylcyclopentadienyl (Cp*) as ancillary ligation.[1] While this ligand system has played a crucial role in the development of trivalent lanthanoid monoalkyl chemistry, Cp$^*_2$LnR, it has been employed with far less success in the preparation of dialkyl complexes, Cp*LnR$_2$.[2] Ligand redistribution and formation of oligomeric or polymeric products have been the major obstacles. The challenge now is to design monoanionic ancillary ligands of sufficient bulk to allow isolation of these rather elusive dialkyl complexes. In this contribution, we report the synthesis of a new chelating arylsiloxide (**I**, OSi^{t}BuAr$_2$, Ar = o-C$_6$H$_4$(CH$_2$NMe$_2$)) and two hydrocarbon soluble yttrium complexes which contain a single arylsiloxide in the metal coordination sphere: Y[OSi^{t}BuAr$_2$][N(SiMe$_3$)$_2$]$_2$ and Y[OSi^{t}BuAr$_2$][OC$_6$H$_3$^{t}Bu$_2$-2,6]$_2$. The latter compound was prepared as a precursor to yttrium dialkyl complexes. Our initial efforts to prepare yttrium dialkyls are also included here.



I

Siloxides are attractive as ligands because of the ease of preparation from commercially available (or easily prepared) precursors and the presence of ^{29}Si as a NMR probe. In addition, the strong Si−O bond is expected to make these ligands more robust by avoiding the C−O cleavage reactions sometimes observed with early transition metal and lanthanide alkoxides.[3] A multidentate ligand framework provides a flexible coordination environment and should help prevent formation of oligomeric species by blocking coordination sites at the metal center.

Thermochemical studies by Marks and co-workers have suggested that replacement of Cp* by alkoxide ligation strengthens the M−C bond and may help suppress β−H elimination in alkyl complexes.[4] Additionally, recent work by Schaverien has shown that Cp*Y[OAr][CH(SiMe$_3$)$_2$] and [Cp*Y(OAr)]$_2$(μ-H)(μ-R) (OAr = OC$_6$H$_3$^{t}Bu$_2$-2,6; R = H, alkyl) are stable toward

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ligand redistribution.[5] Benefits similar to those observed with alkoxide ligation may reasonably be expected to apply to the siloxide ligand system described here.

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. *tert*-Butyltrichlorosilane and 2,6-di-*tert*-butylphenol were purchased from Aldrich and used without further purification. Preparation of $Li[o\text{-}C_6H_4(CH_2NMe_2)]$ was carried out according to a published procedure.[6] Anhydrous yttrium trichloride was prepared from the hydrated salt by prolonged reflux in neat $SOCl_2$ followed by vacuum distillation and drying at 150 °C (10^{-2} Torr) for 16 h. Hexamethyldisilazane was purchased from Aldrich and dried by distillation from sodium metal. $Y[N(SiMe_3)_2]_3$ was prepared as reported in the literature.[7]

^1H, ^{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 or 10 mm tubes fitted with a Teflon valve (Brunfeldt). ^{29}Si spectra were recorded using an INEPT pulse sequence. ^1H 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. All spectra were recorded at room temperature unless otherwise noted. ^{13}C NMR assignments were made by comparisons between the spectra of compounds **1**–**4**, as well as by ^{13}C DEPT (attached proton test) and ^1H-^{13}C COSY experiments, whenever practical. Mass spectra were recorded on a Finnegan 3300 or a Kratos Concept H spectrometer using chemical ionization sources. Melting points were recorded using a Reichert hot stage and are not corrected. Elemental analyses were performed by Canadian Microanalytical, Delta, BC, Canada.

$HOSi^tBu[o\text{-}C_6H_4(CH_2NMe_2)]_2$ (1). A solution of $Li[o\text{-}C_6H_4(CH_2NMe_2)]$ (10.1 g, 71.5 mmol) in 80 mL of THF was added rapidly by canula to a 250 mL flask containing $t\text{-}BuSiCl_3$ (6.45 g, 33.7 mmol) in 50 mL of THF precooled to 0 °C. The reaction mixture was stirred overnight at room temperature and then quenched with $Na_2SO_4{\cdot}10H_2O$. The solids were filtered off and the filtrate was evaporated to an oily residue under reduced pressure. The oil was washed with a 100 mL portion of 10% aqueous KOH at 0 °C and extracted with 500 mL of diethyl ether. The ether extract was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed from the filtrate by rotary evaporation. The yellow oil was recrystallized from toluene to afford slightly yellow crystals of the silanol. Yield: 10.3 g (27.8 mmol, 82.5%). Mp: 63–65 °C. ^1H NMR (C_6D_6): δ 8.75 (s, 1H, *H*OSi), 7.17–8.10 (m, 8H, arylC*H*), 3.42 (d, 2H, $CH_aH_bNMe_2$, $^2J_{HH} = 12.8$ Hz), 3.05 (d, 2H, $CH_aH_bNMe_2$, $^2J_{HH} = 12.8$ Hz), 1.85 (s, 12H, NMe_2), 1.40 (s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 145.0, 139.0, 136.3, 130.8, 129.4, 126.4 (aryl*C*), 64.3 (CH_2N), 44.5 (NMe_2), 27.7 (CMe_3), 20.1 (CMe_3). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −6.86. MS(CI): *m/z* 371 ($M^+ + 1$), 355 ($M^+ - Me$), 313 ($M^+ - {}^tBu$), 236 ($M^+ - C_6H_4(CH_2NMe_2)$). Anal. Calcd for $C_{22}H_{34}N_2OSi$: C, 71.30; H, 9.25; N, 7.56. Found: C, 71.95; H, 9.15; N, 7.56.

$Y\{OSi^tBu[o\text{-}C_6H_4(CH_2NMe_2)]_2\}\{N(SiMe_3)_2\}_2$ (2). Silanol **1** (1.83 g, 4.95 mmol) and $Y[N(SiMe_3)_2]_3$ (2.82 g, 4.95 mmol) were weighed into a 250 mL Schlenk tube and dissolved in 200 mL of toluene. The reaction mixture was refluxed overnight and the volatiles removed under reduced pressure to yield a white solid. Recrystallization from toluene gave colorless crystals of **2**. Yield: 2.75 g (3.53 mmol, 71.3%). Mp: 158 °C. $^{13}C\{^1H\}$ NMR (C_7D_8, −40 °C): δ 149.8, 149.3, 143.3, 141.5, 141.1, 137.9, 134.6, 134.2, 132.3, 131.3 (aryl*C*, two resonances were not observed), 67.3, 63.6 (CH_2N), 49.7, 45.3 (coordinated NMe_2), 44.8 (noncoordinated NMe_2), 28.1 (CMe_3), 21.1 (CMe_3), 5.7, 5.1, 4.7, 3.9 ($SiMe_3$). $^{29}Si\{^1H\}$ NMR (C_7D_8, −40 °C): δ −8.4, −9.5, −12.9, −13.1 ($N(SiMe_3)_2$), −20.5 (OSi^tBuAr_2, $^2J_{SiY} = 4.9$ Hz). ^{89}Y NMR (C_6D_6): δ 479. MS(CI): *m/z* 778 (M^+), 763 ($M^+ - Me$), 721 ($M^+ - {}^tBu$), 644 ($M^+ - C_6H_4(CH_2NMe_2)$), 617 ($M^+ - N(SiMe_3)_2$). Anal. Calcd for $C_{34}H_{69}N_4OSi_5Y$: C, 52.40; H, 8.92; N, 7.19. Found: C, 51.95; H, 8.48; N, 6.72.

$Y\{OSi^tBu[o\text{-}C_6H_4(CH_2NMe_2)]_2\}\{OC_6H_3{}^tBu_2\text{-}2,6\}_2$ (3). Silylamide complex **2** (1.50 g; 1.92 mmol) and 2,6-di-*tert*-butylphenol (0.800 g, 3.88 mmol) were weighed into a Schlenk tube and dissolved in 100 mL of toluene. The solution was refluxed overnight and the solvent stripped under vacuum. The solid white residue was recrystallized from toluene to afford colorless crystals of **3**. Yield: 1.51 g (1.74 mmol, 90.5%). Mp: 240–243 °C. ^1H NMR (C_7D_8, −40 °C): δ 8.63 (d, 1H, arylC*H*, $J_{HH} = 6.8$ Hz), 8.01 (d, 1H, arylC*H*, $J_{HH} = 6.5$ Hz), 7.92 (d, 1H, arylC*H*, $J_{HH} = 7.3$ Hz), 7.0–7.45 (m, 8H, arylC*H*), 6.89 (t, 1H, arylC*H*, $J_{HH} = 7.7$ Hz), 6.74 (t, 1H, arylC*H*, $J_{HH} = 7.7$ Hz), 6.64 (d, 1H, arylC*H*, $J_{HH} = 8.5$ Hz), 4.18 (d, 1H, coordinated CH_2N, $^2J_{HH} = 12.3$ Hz), 3.33 (d, 1H, noncoordinated CH_2N, $^2J_{HH} = 13.2$ Hz), 2.88 (d, 1H, noncoordinated CH_2N, $^2J_{HH} = 13.2$ Hz), 2.20 (d, partially obscured, 1H, coordinated CH_2N), 2.18 (s, 3H, coordinated NMe_2), 1.99 (s, 9H, phenoxide CMe_3), 1.96 (s, 3H, coordinated NMe_2), 1.74 (s, 6H, noncoordinated NMe_2), 1.61 (s, 9H, phenoxide CMe_3), 1.41 (s, 9H, phenoxide CMe_3), 1.26 (s, 9H, $SiCMe_3$), 1.05 (s, 9H, phenoxide CMe_3). ^1H NMR (C_7D_8, 40 °C): δ 8.47 (br s, 1H, arylC*H*), 8.02 (br d, 1H, arylC*H*), 7.70 (br d, 1H, arylC*H*), 6.95–7.40 (m, 7H, arylC*H*), 6.76 (t, 2H, arylC*H*), 6.65 (t, 2H, arylC*H*), 4.22 (d, 1H, coordinated CH_2N), 3.20 (d, 1H, noncoordinated CH_2N), 2.83 (d, 1H, noncoordinated CH_2N), 2.32 (d, 1H, coordinated CH_2N), 2.28 (s, 3H, coordinated NMe_2), 2.13 (s, 3H, coordinated NMe_2), 1.74 (s, 6H, noncoordinated NMe_2), 1.65 (br s, 18H, phenoxide CMe_3), 1.29 (s, 18H, CMe_3), 1.22 (s, 9H, $SiCMe_3$). ^1H NMR (C_7D_8, 110 °C): δ 8.2 (br s, 2H, arylC*H*), 7.0–7.3 (m, 8H, arylC*H*), 6.64 (br s, 4H, arylC*H*), 2.85 (v br s, 2H, CH_2N), 2.02 (br s, 12H, NMe_2), 1.47 (s, 36H, phenoxide CMe_3), 1.22 (s, 9H, $SiCMe_3$). $^{13}C\{^1H\}$ NMR (C_7D_8, −40 °C): δ 161.9, and 161.0 (phenoxide *ipsoC*), 145.3, 144.5, 139.1, 138.3, 137.0, 136.5, 133.8, 129.8, 129.3, 129.1, 129.0, 128.5, 128.4, 127.9, 126.1, and 125.7 (aryl*C*), 117.6, and 117.3 (phenoxide aryl*C*), 67.9 (coordinated CH_2N), 63.8 (noncoordinated CH_2N), 48.3 (coordinated NMe_2), 44.8 (noncoordinated NMe_2), 44.3 (coordinated NMe_2), 35.5, 35.4, and 34.9 (phenoxide CMe_3), 32.6, 31.8, and 30.5 (phenoxide CMe_3), 27.5 ($SiCMe_3$), 20.5 ($SiCMe_3$). Four arylC resonances were not observed. $^{29}Si\{^1H\}$ NMR (50/50% C_7D_8 /THF): δ −14.8 ($^2J_{SiY} = 5.4$ Hz). ^{89}Y NMR (C_6D_6): δ 221 MS(CI): *m/z* 869 ($M^+ + 1$), 853 ($M^+ - Me$), 812 ($M^+ - {}^tBu$), 664 ($M^+ - OC_6H_3tBu_2$). Anal. Calcd for $C_{50}H_{75}N_2O_3SiY$: C, 69.10; H, 8.70; N, 3.22. Found: C, 68.96; H, 8.60; N, 2.99.

$\{Y\{OSi^tBu[o\text{-}C_6H_4(CH_2NMe_2)]_2\}\{OC_6H_3{}^tBu_2\text{-}2,6\}\cdot\{CH_2SiMe_3\}_2\}^- Li^+{\cdot}0.5\ C_6H_{14}$ (4). Complex **3** (1.67 g, 1.92 mmol) was dissolved in 50 mL of toluene and cooled to −30 °C. A solution of $LiCH_2SiMe_3$ (0.362 g, 3.85 mmol) in 20 mL of toluene was added dropwise and the reaction mixture was allowed to warm to room temperature with stirring overnight. Insoluble $LiOC_6H_3{}^tBu_2$ was filtered off and the toluene was removed from the filtrate under vacuum to yield a white powder. Recrystallization from hexane produced colorless crystals of **4** as a hexane solvate. Exposure of the crystals to vacuum resulted in loss of hexane and formation of a white microcrystalline powder. Yield: 1.57 g (1.69 mmol, 88%). $^{13}C\{^1H\}$ NMR (C_7D_8, −10 °C): δ 162.8 (phenoxide *ipsoC*, $^2J_{YC} = 4.5$ Hz), 142.0, 141.4, 139.1, 138.5, 137.8, 137.7, 135.9, 134.4, 133.0, 129.7, 129.2, 128.4, 127.4, 127.2, 125.6, 124.9, and 116.6 (aryl*C*), 66.1, and 66.0 (coordinated CH_2N), 50.5, 47.8, 45.7, and 45.1 (coordinated NMe_2), 35.1 (phenoxide CMe_3), 31.9 (phenoxide CMe_3), 27.9 ($SiCMe_3$), 21.3 ($SiCMe_3$), 4.6, and 4.4 (CH_2SiMe_3) $^{29}Si\{^1H\}$ NMR (C_7D_8): δ −4.0 (CH_2SiMe_3), and −9.8 (OSi^tBuAr_2). ^{89}Y NMR (C_7D_8): δ 758. ^{89}Y NMR (C_7D_8, −70 °C): δ 765 and 755 (ca. 2:1 relative intensity). Anal. Calcd for $C_{47}H_{83}LiN_2O_2Si_3Y$: C, 63.55; H, 9.42; N, 3.15. Found: C, 62.97; H, 9.45; N, 3.17.

X-ray Crystallographic Studies. Crystallographic data for **2** is summarized in Table 1. Crystals of **2** (0.63 × 0.22 × 0.08 mm) were loaded into glass capillaries in the glove box and subsequently examined by photographic methods using Weissenberg and Precession cameras. The space group was determined 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 **2** was refined using 25 reflections in the 2θ range 36–72°. The experimental density was not obtained because of the air sensitivity

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Table 1. Summary of Crystallographic Data for **2**

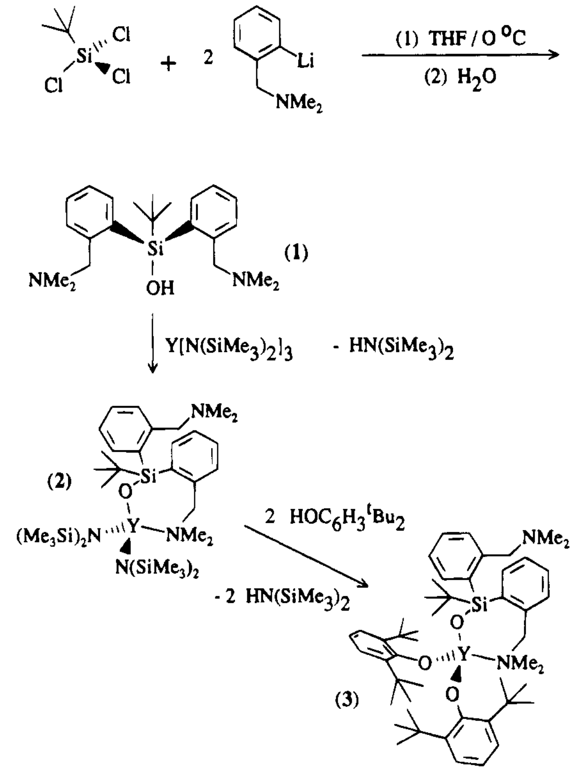
empirical formula	$C_{34}H_{69}N_4OSi_5Y$	Z	8
fw	779.3	ϱ(calcd) (g cm^{-3})	1.139
cryst syst	monoclinic	μ (cm^{-1})	33.34
space group	$I2/a$ (No. 15)	radiation, λ (Å)	Cu Kα, 1.542
a (Å)	20.709(3)	T	295 K
b (Å)	9.511(1)	$2\theta_{max}$ (deg)	60
c (Å)	46.579(6)	no. of obsd reflcns	5986
α (deg)	90	no. of unique reflcns	3543
β (deg)	98.04(1)	R^a	0.078
γ (deg)	90	$R_w{}^b$	0.101
V (Å^3)	9084.6		

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

of **2**. Three standard reflections, measured periodically during data collection (12,2,6; −8,5,11; −2,2,30), showed a decline in combined intensity to 90% of their original value. Intensity measurements were collected over one hemisphere. After the usual data reduction procedures, including an absorption correction according to a measured Ψ scan, the structure was solved using SHELX76 and direct methods.[8] The refinement minimized $\Sigma w((|F_o| - |F_c|)^2)$ and proceeded normally using SHELX76. The criterion for inclusion of reflections was $I > 3\sigma(I)$. The weighting scheme was determined by counting statistics using $w = 1/(\sigma^2(F) + 0.001F^2)$. Convergence was satisfactory with a max shift/esd = 0.005. A total of 406 parameters (45 atoms × 9 parameters per atom + scale) were refined in two blocks. No intermolecular contacts shorter than 3.5 Å were observed. The structural perspective plot was drawn using ORTEP.[9]

Compound **3** was also subjected to an X-ray crystallographic investigation. There were 4 molecules of the complex and 4 molecules of hexane in the unit cell. Clear and reasonable images of the complex were obtained using two space groups: $P1$ and $P2_1/n$. The gross structural features of **3** are very similar to **2** with only one arm of the siloxide ligand coordinated to the yttrium center. The hexane molecules were disordered. The sum of the intensity standard reflections declined by 20% during data collection. The best R value was approximately 0.10 (triclinic). The angle α seemed to be 90.17(1)°, but systematic absences conformed to $P2_1/n$. In view of our indecision as to the crystal system, and the hexane disorder problem, we have decided not to publish any crystallographic details.

Scheme 1



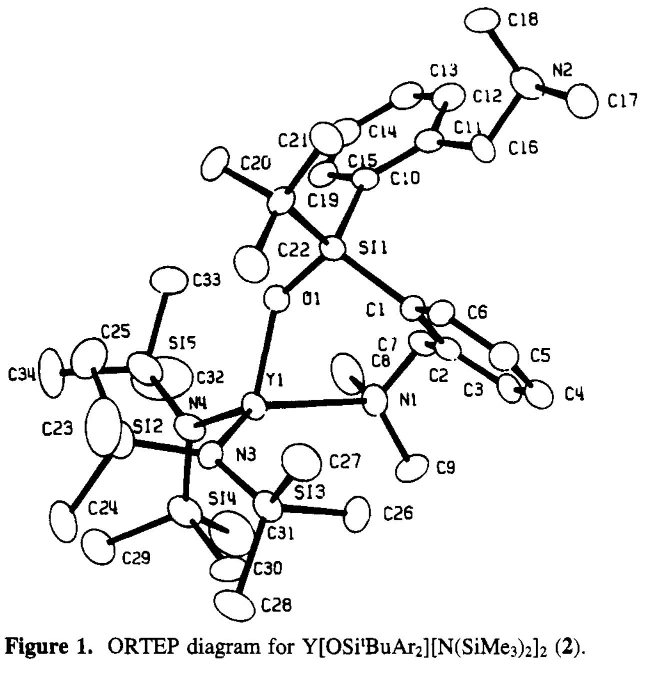


Figure 1. ORTEP diagram for $Y[OSi^tBuAr_2][N(SiMe_3)_2]_2$ (**2**).

Results and Discussion

Synthesis. The arylsilanol ligand **1** was isolated in high yield as yellow crystals by the procedure shown in Scheme 1. As anticipated for a bulky silanol,[10] condensation of **1** to the disiloxane was not observed. Reaction of 1 equiv of **1** with $Y[N(SiMe_3)_2]_3$ proceeded smoothly at toluene reflux to produce the mono(siloxide) **2** in good yield (Scheme 1). Complex **2** showed no tendency toward ligand redistribution and reacted very sluggishly (toluene reflux, several days) with excess **1** to yield impure bis- and tris(siloxide) products. However, replacement of the remaining silylamide ligands was achieved cleanly using 2,6-di-*tert*-butylphenol ($HOC_6H_3{}^tBu_2$-2,6) producing the bis(phenoxide) complex **3**.[11] Protonolysis of the arylsiloxide ligand by $HOC_6H_3{}^tBu_2$-2,6 to give the known $Y(OC_6H_3{}^tBu_2$-$2,6)_3$ was not observed provided only 2 equiv of the phenol were used.[12]

Solid-State Structure of 2. The complex NMR behavior of **2** and **3** (*vide infra*) prevented unambiguous structural assignments to be made by this technique alone. Therefore, **2** was subject to an X-ray crystallographic investigation. The structure of **2** is shown in Figure 1. Fractional atomic coordinates are given in Table 2, and selected bond distances and angles are collected in Table 3. The X-ray structure reveals that **2** is monomeric and contains a four-coordinate yttrium center. One of the 2-(*N*,*N*-dimethylaminomethyl)phenyl arms of the siloxide ligand is not coordinated to the yttrium center. As might be expected, the geometry at yttrium is severely

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(11) The pK_a of **1** and $HOC_6H_3{}^tBu_2$-2,6 are not known but may be estimated using the procedures outlined in: Perrin, D. D.; Dempsey, B.; Serjeant, E. P. *pK$_a$ Predictions for Organic Acids and Bases*; Chapman and Hall: London, 1981. A reasonable estimate for the pK_a of **1** is 10−11 based on the calculated value of 14.2 for $Ph_2{}^tBuCOH$ and the observation that silanols are typically about 4−5 pK_a units more acidic than alcohols (see ref 10 and: Arm, H.; Hochstramer, K.; Schindler, P. W. *Chimia* **1974**, *28*, 237). The calculated pK_a of $HOC_6H_3{}^tBu_2$-2,6 is 12.2. It would appear from these calculations that **1** is roughly as acidic as 2,6-di-*tert*-butylphenol. (All pK_a values are based on water as solvent).

(12) Lappert, M. F.; Singh, A.; Smith, R. G. *Inorg. Synth.* **1990**, *27*, 164.

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

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Y(1)	8012(5)	20650(12)	10505(2)	466(4)
Si(1)	831(2)	3450(4)	1747(1)	46(1)
Si(2)	−821(2)	2403(5)	772(1)	72(2)
Si(3)	−398(2)	−269(4)	1089(1)	58(1)
Si(4)	1231(2)	1592(5)	396(1)	82(2)
Si(5)	1388(2)	4565(5)	584(1)	89(2)
O(1)	85.8(3)	344.1(8)	140.4(1)	49(3)
N(1)	189.8(4)	112.6(1)	133.0(2)	59(4)
N(2)	168.7(5)	382.2(12)	273.9(2)	65(4)
N(3)	−23.3(4)	132.9(10)	96.2(2)	49(4)
N(4)	117.8(5)	283.7(11)	65.6(2)	60(4)
C(1)	94.5(5)	155.5(12)	187.3(2)	43(4)
C(2)	148.8(6)	74.2(14)	181.5(2)	48(5)
C(3)	159.6(7)	−59(2)	192.5(3)	62(6)
C(4)	115.5(7)	−125(2)	208.6(3)	66(6)
C(5)	60.5(7)	−51(2)	213.8(3)	65(6)
C(6)	50.0(6)	86.7(14)	203.4(3)	54(5)
C(7)	200.1(5)	142.6(14)	164.7(2)	52(5)
C(8)	237.6(6)	217(2)	121.0(3)	92(7)
C(9)	207.2(7)	−39(2)	126.8(3)	84(7)
C(10)	156.1(6)	452.4(12)	192.9(2)	46(5)
C(11)	184.5(6)	440.3(13)	221.9(3)	52(5)
C(12)	241.7(6)	518.3(14)	232.6(3)	65(6)
C(13)	270.9(6)	600(2)	213.2(3)	67(6)
C(14)	243.5(7)	614.4(14)	183.7(3)	64(6)
C(15)	185.3(6)	538.3(13)	173.7(3)	56(5)
C(16)	157.0(6)	338.3(13)	2433(2)	57(5)
C(17)	146.1(7)	270(2)	291.4(3)	76(6)
C(18)	135.6(7)	520(2)	278.2(3)	76(6)
C(19)	3.0(6)	433.5(13)	181.2(3)	56(5)
C(20)	3.2(7)	577(2)	165.9(3)	75(6)
C(21)	−4.5(7)	458(2)	213.6(3)	77(6)
C(22)	−57.2(6)	341(2)	165.7(3)	73(6)
C(23)	−163.9(7)	233(2)	92.1(4)	127(9)
C(24)	−98.1(9)	188(2)	37.3(3)	116(8)
C(25)	−53.6(8)	423(2)	79.2(4)	113(8)
C(26)	43.7(6)	−110(2)	123.8(3)	72(6)
C(27)	−86.8(7)	−26(2)	141.4(3)	77(6)
C(28)	−84.0(8)	−151(2)	81.2(3)	100(7)
C(29)	80.1(12)	203(2)	2.4(3)	150(11)
C(30)	85.3(8)	−11.6(14)	51.1(3)	84(7)
C(31)	208.7(8)	101(2)	35.4(4)	133(10)
C(32)	222.3(12)	468(2)	45.6(6)	182(13)
C(33)	143.4(10)	565(2)	91.2(3)	109(8)
C(34)	77.3(12)	548(2)	30.4(4)	180(13)

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

Table 3. Selected Distances (Å) and Angles (deg) for **2**[a]

	Distances		
Y(1)−O(1)	2.093(7)	N(3)−Si(2)	1.733(10)
Y(1)−N(1)	2.611(9)	N(3)−Si(3)	1.679(10)
Y(1)−N(3)	2.237(9)	N(4)−Si(4)	1.705(11)
Y(1)−N(4)	2.221(9)	N(4)−Si(5)	1.744(12)
O(1)−Si(1)	1.606(7)		
	Angles		
Y(1)−O(1)−Si(1)	141.2(4)	O(1)−Y(1)−N(1)	82.7(3)
Y(1)−N(1)−C(7)	114.9(7)	O(1)−Y(1)−N(3)	106.7(3)
Y(1)−N(3)−Si(2)	119.7(5)	O(1)−Y(1)−N(4)	117.2(3)
Y(1)−N(3)−Si(3)	117.0(5)	O(1)−Si(1)−C(1)	106.4(5)
Y(1)−N(4)−Si(4)	114.9(6)	O(1)−Si(1)−C(10)	107.9(5)
Y(1)−N(4)−Si(5)	126.6(5)	O(1)−Si(1)−C(19)	108.1(5)
N(1)−Y(1)−N(3)	136.8(3)	Si(1)−C(1)−C(2)	121.7(9)
N(1)−Y(1)−N(4)	98.2(3)	C(1)−C(2)−C(7)	119.0(11)
N(3)−Y(1)−N(4)	112.9(3)	C(2)−C(7)−N(1)	114.1(9)

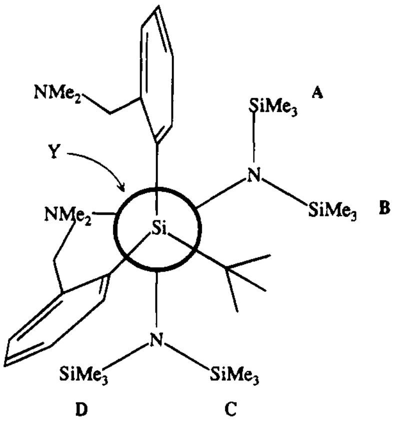
[a] Estimated standard deviation in parentheses.

distorted from the ideal tetrahedral configuration due to the narrow siloxide angle (N(1)-Y(1)-O(1) 82.7(3)°) and the larger size of the silylamide ligands. A close nonbonded contact between Si(4) and Y(1) of 3.322(4) Å is observed. However, none of the three methyl carbons on Si(4) approach within 3.5 Å of Y(1) and this close approach is therefore probably necessitated by unfavorable steric interactions between the two silylamide ligands, rather than a reflection of any agostic interaction with the metal center. Indeed, observation of hindered silylamide rotation supports this explanation (*vide infra*).

The Y(1)−O(1) distance of 2.093(7) Å is long in comparison to structurally characterized lanthanide triphenylsiloxides (OR = $OSiPh_3$; $[Ce(OR)_2(\mu\text{-}OR)]_2$,[13a] $[Ln(OR)_3(THF)_3]\cdot THF$, Ln = La,[13b] Ce,[13c] Y;[13b,13d] $Ce(OR)_4(DME)\cdot$toluene;[13e] $Y(OR)_3(O{=}PBu_3)_2$;[13b] $[Y(OR)_4(DME)]^-[K(DME)_4]^+$ [13b]). After correction for differences in ionic radii due to coordination number and oxidation state,[14] these compounds predict a Y−O bond length range of 1.95−2.08 Å. Restricting the comparison to Y (2.00−2.08 Å) or four-coordinate (2.03−2.08 Å) complexes leads to the same conclusion. Similarly, the complexes $[Y(OR)_2(HOR)(\mu\text{-}OR)_2]Y(OR)_2$ (OR = OSi^tBuMe_2)[13b] and $Y[OSi^tBu_2(CH_2)_3NMe_2]_3$[10] predict Y−O bond lengths in the range 2.01−2.06 Å. The latter complex, which is trigonal bipyramidal with two axially coordinated NMe_2 groups, also predicts a Y−N distance of 2.57(1) Å. The observed Y(1)−N(1) distance of 2.611(9) Å provides further support for the high degree of steric crowding in **2**. Only $Yb[OSi^tBu_2(CH_2)_3NMe_2]_3[OSi^tBu_2(CH_2)_3NMe_2H]$, which we have previously shown to be very crowded,[10] has Ln−O bonds of comparable length (predicts 2.09−2.12 Å). The Y(1)−O(1)−Si(1) angle of 141.2(4)° is considerably more bent than those found in other lanthanide siloxides (157.8−179.7°),[13] perhaps reflecting a requirement for chelation.

Fluxional Behavior of 2 and 3. The variable temperature ^1H NMR behavior of **2** is shown in Figure 2 for the temperature range −40 to +110 °C. At −40 °C four silylamide $SiMe_3$ groups are clearly visible (δ −0.40 to +0.65 ppm). The siloxide 2−(*N*,*N*-dimethylaminomethyl)phenyl arms are also inequivalent. The NMe_2 groups of the coordinated arm are inequivalent from each other (1.79 and 2.16 ppm) while those of the noncoordinated arm are equivalent (1.73 ppm). The low temperature spectrum is consistent with the solid state structure (Figure 1; shown schematically in **II**[15]). The silicon center is chiral rendering the CH_2 groups of both chelate arms diastereotopic. Upon warming from −10 to +50 °C, the $SiMe_3$

II



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[13] (a) Evans, W. J.; Golden, R. E.; Ziller, J. W. *Inorg. Chem.* **1991**, *30*, 4963. (b) McGeary, M. J.; Coan, P. S.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 1723. (c) Gradeff, P. S.; Yunlu, K.; Deming, T. J.; Olofson, J. M.; Doedens, R. J.; Evans, W. J. *Inorg. Chem.* **1990**, *29*, 420. (d) McGeary, M. J.; Coan, P. S.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 3283. (e) Gradeff, P. S.; Yunlu, K.; Gleizes, A.; Galy, J. *Polyhedron* **1989**, *8*, 1001.

[14] Shannon, R. D. *Acta Cryst. A* **1976**, *A32*, 751.

[15] Viewed down the Y- - -Si vector. The siloxide oxygen has been omitted.

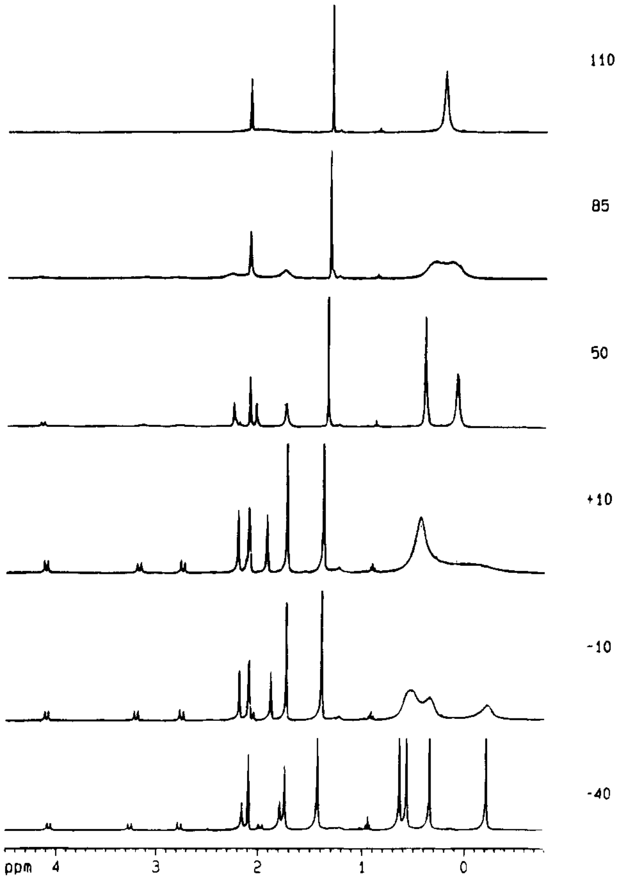

Figure 2. Variable temperature ^{1}H NMR spectra of **2**.

resonances pass through coalescence and reappear as two sharp singlets of equal intensity while the chelate arms of the siloxide ligand *remain* inequivalent. This process can therefore only be due to free rotation about the Y−N(SiMe$_3$)$_2$ bonds rendering the A/B and C/D SiMe$_3$ pairs equivalent. The free energy of activation for Y−N(silylamide) rotation was estimated from the coalescence temperatures as $\Delta G^*_{\text{rotation}} = 53 \pm 1$ kJ/mol.[16,17] Continued heating from +85 to 110 °C results in further collapse of the two SiMe$_3$ signals to a single resonance. This process also results in collapse of the inequivalent 2-(*N,N*-dimethylaminomethyl)phenyl arms to a single set of resonances and is consistent with exchange of free and coordinated NMe$_2$ groups (an "arm on−arm off" process). The free energy of activation for this process is $\Delta G^*_{\text{arm exchange}} = 72 \pm 1$ kJ/mol.

The high value of $\Delta G^*_{\text{rotation}}$ is not surprising given the evidence presented earlier for steric crowding in the solid-state structure. On the other hand, the remarkably high value of $\Delta G^*_{\text{arm exchange}}$ requires further comment. In the relatively uncrowded complex, Y[OSi^{t}Bu$_2$(CH$_2$)$_3$NMe$_2$]$_3$, exchange of free and coordinated *N,N*-dimethylaminopropyl arms is extremely facile, occurring rapidly on the NMR time scale even at −80 °C.[10] This is consistent with the well-known lability of lanthanide−Lewis base adducts.[18] Thus, it seems likely to us that the large value of $\Delta G^*_{\text{arm exchange}}$ derives from a large energy barrier to reorientation of the siloxide ligand such that the free 2-(*N,N*-dimethylaminomethyl)phenyl arm can coordinate. This explanation is reasonable given the steric congestion at yttrium noted earlier.

Complex **3** exhibits very similar NMR behavior to **2**. This is not surprising given the similarity in solid-state structure (*vide supra*). Values of $\Delta G^*_{\text{rotation}} = 57 \pm 1$ kJ/mol for the phenoxide rotation processes and $\Delta G^*_{\text{arm exchange}} = 75 \pm 1$ kJ/mol for the NMe$_2$ exchange process were derived from variable temperature ^{1}H NMR. The similarity between the $\Delta G^*_{\text{rotation}}$ and $\Delta G^*_{\text{arm exchange}}$ values observed for **3**, compared with those observed for **2**, is reasonable given the similar steric bulk of the N(SiMe$_3$)$_2$ and OC$_6$H$_3$^{t}Bu$_2$-2,6 ligands.[19,20]

The ^{29}Si variable temperature NMR of **2** is consistent with the ^{1}H NMR behavior. Four silylamide resonances are observed at low temperature but no silylamide signals were observed at temperatures above +30 °C. The ^{29}Si resonance of the siloxide ligands in **2** and **3** appear ca. 8 ppm upfield of the signal in **1** and show coupling to ^{89}Y of 5 Hz. Very similar values were obtained for Y[OSi^{t}Bu$_2$(CH$_2$)$_3$NMe$_2$]$_3$ (10 ppm upfield; $^2J(^{29}\text{Si}-^{89}\text{Y}) = 6$ Hz).[10]

Yttrium Alkyl Preparation. Reaction of **3** with 2 equiv of LiCH$_2$SiMe$_3$ proceeds smoothly in toluene with elimination of LiOC$_6$H$_3$^{t}Bu$_2$-2,6 to yield colorless crystals of **4**, as shown in the equation below. Elemental analysis confirmed that only 1 equiv of LiOC$_6$H$_3$^{t}Bu$_2$-2,6 was eliminated. Complex **4**, while crystalline, loses hexane very readily and a crystal structure could not be obtained. The high toluene solubility and steric bulk of the ligands suggest that a monomeric structure is likely. Attempts to prepare neutral Y[OSi^{t}BuAr$_2$][OC$_6$H$_3$^{t}Bu$_2$-2,6][CH$_2$SiMe$_3$] by reaction of 1 equiv of LiCH$_2$SiMe$_3$ with **3** produced complex mixtures of products containing **4** as a major component.

$$\underset{\mathbf{3}}{\text{Y[OSi}^t\text{BuAr}_2\text{][OC}_6\text{H}_3{}^t\text{Bu}_2\text{-2,6]}_2} + 2\text{LiCH}_2\text{SiMe}_3 \rightarrow$$

$$\underset{\mathbf{4}}{\{\text{Y[OSi}^t\text{BuAr}_2\text{][OC}_6\text{H}_3{}^t\text{Bu}_2\text{-2,6][CH}_2\text{SiMe}_3]_2\}^-\text{Li}^+}$$

Complex **4** shows very complicated ^{1}H NMR behavior (Figure 3). It is clear that at +40 °C the complex is undergoing a rapid fluxional process (or processes) which renders both 2-(*N,N*-dimethylaminomethyl)phenyl arms of the siloxide and both CH$_2$SiMe$_3$ groups equivalent.[21] Cooling to −20 °C results in several significant spectral changes. The CH$_2$SiMe$_3$ ligand environments become inequivalent as evidenced by the observation of two SiMe$_3$ resonances (δ 0.45 and 0.30 ppm). Further,

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(16) The free energy of activation was calculated from the coalescence temperature (T_c) using the equal population, two-site exchange equation: $\Delta G^* = (1.912 \times 10^{-2})(T_c)[9.972 + \log(T_c/\delta\nu)]$ in kJ/mol where $\delta\nu$ is the separation of the resonances in Hz and T_c is in K (Sandstrom, J. *Dynamic NMR Spectroscopy*; Pergamon: London, 1982; pp 77−91). The error in ΔG^* of ± 1 kJ/mol was estimated assuming a liberal error of ±5 °C in estimation of T_c.

(17) In principle, since the two silylamide groups in **2** remain inequivalent even with rapid rotation about the Y−N bonds, $\Delta G^*_{\text{rotation}}$ need not be identical for both silylamide groups. In practice however, $\Delta G^*_{\text{rotation}}$ is virtually identical for both silylamide groups and this is the value reported here. The same arguments apply to $\Delta G^*_{\text{rotation}}$ for the phenoxide groups in **3**.

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

(19) A particularly good illustration of this is provided by comparison of the U−O bond distances in U[OC$_6$H$_3$^{t}Bu$_2$-2,6]$_4$ (2.135(4) Å) and U[OC$_6$H$_3$^{t}Bu$_2$-2,6]$_3$[N(SiMe$_3$)$_2$]$_3$ (2.145(8) Å). Replacement of three phenoxides by silylamides has little effect on the U−O bond length indicating the steric congestion in both compounds is similar (Berg, J. M.; Clark, D. L.; Huffman, J. C.; Morris, D. E.; Sattelberger, A. P.; Streib, W. E.; Van der Sluys, W. G.; Watkin, J. G. *J. Am. Chem. Soc.* **1992**, *114*, 10811).

(20) Both Ln[OC$_6$H$_3$^{t}Bu$_2$-2,6]$_3$ and Ln[N(SiMe$_3$)$_2$]$_3$ have been reported to form adducts, although no directly comparable compounds are available in the literature. Ln[N(SiMe$_3$)$_2$]$_3$[Ph$_3$P=O] (Ln = La, Eu, Lu): (a) Bradley, D. C.; Ghotra, J. S.; Hart, F. A.; Hursthouse, M. B.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1166. (b) Aspinall, H. C.; Moore, S. R.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1992**, 153. Ln[N(SiMe$_3$)$_2$]$_3$[Ph$_2$C=O] (Ln = La, Eu, Tb, Yb, Y): (c) Allen, M.; Aspinall,H. C.;Moore, S. R.; Hursthouse, M. B.; Karvalov, A. I. *Polyhedron* **1992**, *11*, 409. Ce[OC$_6$H$_3$^{t}Bu$_2$-2,6]$_3$[^{t}BuNC]$_2$: (d) Stecher, H. A.; Sen, A.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 1130.

(21) Complex **4** decomposes rapidly in solution at temperatures above 40 °C.

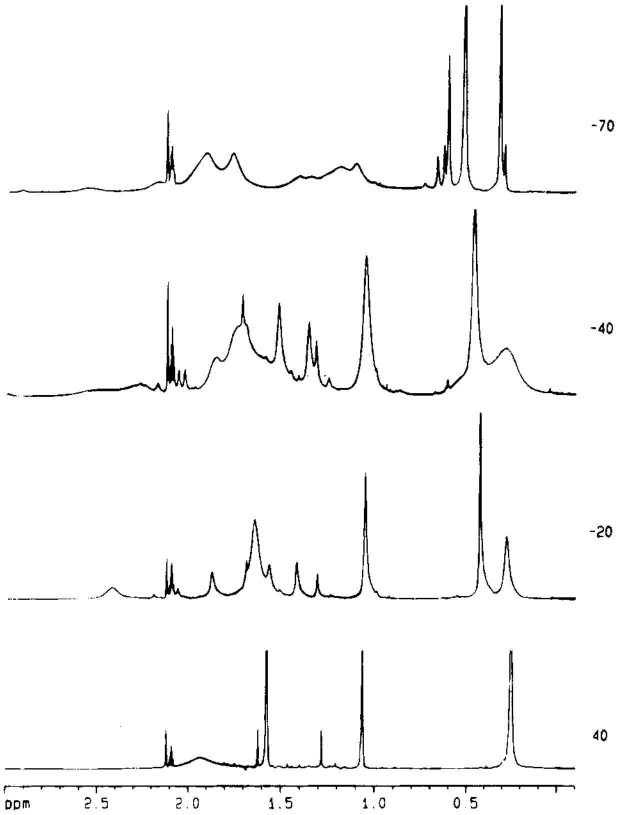

Figure 3. Variable temperature ^1H NMR spectra of **4**.

all methyl groups of the NMe_2 donors become inequivalent (δ 2.42, 1.90, 1.55, and 1.40 ppm). The observation of 4 methyl resonances of equal intensity in both the ^1H and ^{13}C NMR spectrum is consistent with coordination of both NMe_2 arms, in contrast to the 1:1:2 pattern observed in the limiting low temperature spectra of **2** and **3**. This data alone does not allow us to determine which metal center, yttrium or lithium, is involved in this interaction.

As the temperature is lowered further to −70 °C, the ^1H NMR spectrum becomes more complex. At this temperature, the phenoxide *tert*-butyl (ca. δ 1.8 to 2.0 ppm) and siloxide *tert*-butyl (δ 1.15 ppm) resonances become extremely broad. However, the two major $SiMe_3$ resonances sharpen once more and several new resonances appear in this region.[22] The CH_2SiMe_3 resonances sharpen into two distinct sets of doublets (Figure 4). Coupling to ^{89}Y is not observed, but this is not surprising since $^2J_{YH}$ is generally 2−3 Hz and the line widths observed here are about 5 Hz.[5,23] We were able to locate two doublets in the ^{13}C NMR spectrum corresponding to the 4 major CH_2SiMe_3 signals by using a $^{13}C-^1H$ COSY experiment at −60 °C. The chemical shifts and coupling constants (δ 36.1 ,$^1J_{YC}$ = 40 Hz and δ 24.5, $^1J_{YC}$ = 36 Hz) for these carbons are very similar to those observed for other yttrium alkyls.[5,24] The origin of the minor set of CH_2SiMe_3 resonances is not immediately obvious.[25]

Schaverien has recently reported replacement of only one phenoxide during reaction of $Cp^*Y(OC_6H_3{}^tBu_2\text{-}2,6)_2$ with $KCH(SiMe_3)_2$ although MeLi reportedly leads to replacement of both

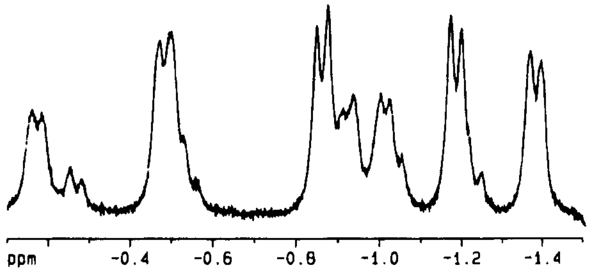

Figure 4. ^1H NMR spectrum (−70 °C) showing the CH_2SiMe_3 region of **4**.

phenoxide ligands.[5] In the present case, reaction of **4** with 1 or 2 equiv of MeLi failed to produce clean products. It is possible that the dangling NMe_2 arm *promotes* formation of an anionic "ate" complex by stabilizing the Li^+ counterion. Originally, we had envisioned this group coordinating to yttrium and stabilizing the newly formed dialkyl complex as the bulky phenoxides were replaced by less bulky alkyls. Since this does not appear to be the case, we are also investigating the analogous OSi^tBu_2Ar ligand system, complexes of which are not expected to possess dangling donor functions.

Conclusions

The new chelating arylsiloxide **I** allows formation of stable mono(siloxide) complexes which show no tendency to undergo ligand redistribution. The phenoxide derivative **3**, an important precursor to alkyl complexes, is readily accessible from silylamide **2**. Further, metathesis with LiR eliminates $LiOC_6H_3{}^tBu_2\text{-}2,6$ *without* loss of siloxide ligation or ligand redistribution. These results bode well for the use of chelating siloxides as ancillary ligands in organoyttrium and -lanthanide chemistry. Further application of this, and related, siloxide ligands to lanthanide chemistry is being actively pursued.

Acknowledgment. We wish to thank Mrs. Kathy Beveridge and Dr. Becky Chak for help with the X-ray crystallographic studies, Mrs. Chris Greenwood for assistance with ^{89}Y NMR, and Mr. David McGillivray and Mr. Les Shallig for running the mass spectra. D.J.B. thanks the NSERC (Canada) and the University of Victoria for financial support.

Supplementary Material Available: Full tables of distances (Table S1), angles (Table S2), and anisotropic thermal parameters (Table S3) for **2** (3 pages) are available. Ordering information is given on any current masthead page.

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(22) The low temperature spectrum shown here is reproducible. Repeated recrystallizations and preparation of fresh samples does not alter the appearance or relative intensity of the resonances observed.

(23) The doublet patterns in Figure 4 are due to geminal coupling between the CH_2SiMe_3 protons ($^2J_{HH}$ = 8 to 12 Hz).

(24) Examples from previous work in our group: $Y[DAC][CH_2SiMe_3]$ (δ = 21.0, $^1J_{YC}$ = 39 Hz) and $Y[DAC][CH(SiMe_3)_2]$ (δ = 24.5, $^1J_{YC}$ = 34 Hz). (DAC = deprotonated 4,13-diaza-18-crown-6): Lee, L.; Berg, D. J.; Bushnell, G. W. *Organometallics*, in press.

(25) The presence of two sets of resonances of unequal intensity for the CH_2SiMe_3 protons is consistent with observation of both components of an equilibrium between two yttrium alkyls (assuming the fourth CH_2 resonance of the minor set is obscured by the −0.48 ppm CH_2 resonance of the major set). Some support for this proposal comes from the ^{89}Y NMR spectra which reveal 2 resonances in ca. 2:1 ratio at −70 °C (δ 765 and 755 ppm) and a single resonance (δ 758 ppm) at room temperature. Such an equilibrium could possibly involve dissociation of **4** to form $LiOC_6H_3{}^tBu_2$ and a neutral yttrium alkyl $Y[OSi^tBuAr_2][CH_2SiMe_3]_2$ as the second yttrium-containing component. On the other hand, under closer inspection Figure 4 appears to show at least one other CH_2SiMe_3 resonance (δ −0.27 ppm) which may represent an impurity or another species in an even more complex system of equilibria. Obviously, the data in hand do not allow a definitive explanation for the observed low temperature behavior of this complex.