Synthesis of Yttrium and Lanthanide Silyloxy Complexes from Anhydrous Nitrate and Oxo Alkoxide Precursors and the X-ray Crystal Structure of [Ce(OSiPh3)3(THF)3](THF)

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The anhydrous trivalent nitrates $(NH_4)_xLn(NO_3)_{3+x}$ (Ln = Y, Ce, Nd, Pr), prepared by heating $Ln(NO_3)_3(H_2O)_y$, in the presence of NH_4NO_3, react with 3 + x equiv of $NaOSiPh_3$ in THF to form $[Ln(OSiPh_3)_3(THF)_3](THF)$ complexes. The cerium complex crystallizes from THF at -30 °C in the monoclinic space group $P2_1$ with unit cell dimensions a = 14.679 (2) Å, b = 16.432 (3) Å, c = 15.021 (3) Å, β = 115.86 (1.2)°, and Z = 2. Least-squares refinement of the model based on 6685 reflections (F^2 > $3.0\sigma(F^2)$) converged to a final R_F = 0.033. The six oxygen-bound ligands describe a *fac*-octahedral geometry around cerium with average Ce–O(OSiPh3) and Ce–O(THF) distances of 2.222 (4) and 2.591 (4) Å, respectively. Crystals of the Ln = Pr and Y complexes have very similar unit cell dimensions. The anhydrous tetravalent nitrate $(NH_4)_2Ce(NO_3)_6$ reacts with 6 equiv of (a) $NaOSiPh_3$ in DME to form $Ce(OSiPh_3)_4(DME)$ and (b) $NaOSiEt_3$ in CH_3CN to form $Ce(OSiEt_3)_4$. $(NH_4)_3Y(NO_3)_6$ reacts with NaO^iPr in 2-propanol to form $Y_5(O^iPr)_{13}O$, which reacts with Ph_3SiOH to form $[Y(OSiPh_3)_3(THF)_3](THF)$.

Introduction

The alkoxide group is an important ligand in inorganic chemistry because it can provide a strong metal–oxygen bond along with a flexible organic moiety with which to vary solubility as well as steric and electronic factors.[2] Aryloxide and silyloxide ligands further extend the range of possibilities for the "OR" ligand. Recently, there has been increased interest in utilizing these ligands in the chemistry of yttrium and the lanthanide metals.[3-17] Alkoxide complexes of these metals provide chemically more robust alternatives to the more common cyclopentadienide complexes in organometallic and catalytic applications. Moreover, the alkoxides may be useful as precursors to unusual materials such as superconducting oxides via hydrolytic sol–gel processes.

Although recent reports on alkoxides and aryloxides of yttrium and the lanthanides have appeared, little is known about silyloxide derivatives. An early report on Me3SiO complexes of trivalent erbium and gadolinium is in the literature,[18] but neither these products nor their "Ln(O^iPr)_3" precursors were fully defined by X-ray crystallography. Indeed, the composition of the yttrium analogue[19] of "Er(O^iPr)_3" has been shown to be $Y_5(O^iPr)_{13}O$.[12,15]

More information is known about silyloxy complexes of tetravalent cerium, however. The synthesis of the compounds $Ce(OSiR_3)_4$ (R = Ph, Me, Et) has been reported[17] as well as the X-ray crystal structure of $Ce(OSiPh_3)_4(MeOCH_2CH_2OMe)$.[16]

In this report, we describe the synthesis of a series of silyloxy complexes of the trivalent lanthanides, namely the triphenylsilyloxy complexes $[Ln(OSiPh_3)_3(THF)_3](THF)$ including the X-ray crystal structure of the Ln = Ce derivative. Two synthetic routes are described. One route employs anhydrous lanthanide nitrates as starting materials and demonstrates that these nitrates can be used as a new class of precursor to homoleptic silyloxy complexes. In contrast, previous synthesis of alkoxides of these metals using the elemental metals or metal trihalides as starting materials have been shown to form alkoxide complexes that incorporate oxide[12,15] and halide[9,10,20] ligands in some cases. A second route to these silyloxy complexes is based upon an oxo alkoxide starting material derived from a nitrate and demonstrates that alcoholysis of an oxide-containing precursor can generate an oxide-free product.

Experimental Section

All manipulations were carried out with the exclusion of oxygen and moisture by using either a nitrogen-filled, recirculating glovebox or Schlenk techniques with argon as an inert gas. The nitrates Ce(NO3)3(H2O)6, Pr(NO3)3(H2O)6, Nd(NO3)3(H2O)6, and Y(NO3)3(H2O)5 were obtained from Rhone-Poulenc and dehydrated by using a modification of the literature procedure[21] as described below.[22] Anhydrous (NH4)2Ce(NO3)6 (CAN) was obtained from Rhone-Poulenc and stored under nitrogen until used. Ph3SiOH and Et3SiOH were purchased from Huls (Petrarch Systems), and anhydrous THF, DME, CH3CN, and iPrOH were purchased from Aldrich. NH4NO3 (puriss. p.a. grade) was obtained from Fluka Chemicals. NaOSiPh3 and NaOSiEt3 were prepared by reacting the silanols with sodium in THF. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX 90Q FT NMR spectrometer at 27 °C, and the IR spectra, on a Perkin-Elmer 283B IR spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, or by Dornis and Kolbe, Mulheim, FRG. Crystals suitable for X-ray structure analysis were obtained by recrystallizing the compounds twice from a saturated THF solution at -30 °C.

Dehydration of Lanthanide Nitrates with NH4NO3.[21] Ln(NO3)3·(H2O)_x (0.01 mol) was mixed with NH4NO3 (0.02 mol for Ln = Ce, Pr, Nd; 0.02–0.04 mol for Ln = Y), and deionized water was added until

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a clear solution had been formed. Most of the water was then removed on a hot plate at temperatures around 80–100 °C. The remaining solid was transferred to a mortar and ground to a fine powder. The material was then kept in a vacuum oven overnight at 100–110 °C and 25 Torr. Karl Fischer analysis showed no water in the product. $(NH_4)_2Ln(NO_3)_5$ (Ln = Ce, Pr, Nd) was obtained in quantitative yield. Anal. Calcd: Ce, 28.82; Pr, 28.93; Nd, 29.42. Found: Ce, 28.77; Pr, 28.94; Nd, 29.58. The yttrium complex could be obtained as $(NH_4)_4Y(NO_3)_7$ (Anal. Calcd: Y, 14.94. Found: Y, 15.05), $(NH_4)_3Y(NO_3)_6$ (Anal. Calcd: Y, 17.27. Found: Y, 17.91), or $(NH_4)_2Y(NO_3)_5$ (Anal. Calcd: Y, 20.44. Found: Y, 20.27) depending on how much NH_4NO_3 was added in the dehydration step. The anhydrous lanthanide nitrates are hygroscopic and should be stored under anhydrous conditions.

$[Ce(OSiPh_3)_3(THF)_3](THF)$ (1). $(NH_4)_2Ce(NO_3)_5$ (3 g, 6.17 mmol) and $NaOSiPh_3(THF)$ (11.42 g, 30.8 mmol) were placed in a Schlenk flask with 40 mL of THF. Immediately upon stirring, NH_3 gas evolution was observed. After being stirred overnight, the reaction mixture was filtered with a Schlenk frit and the white precipitate (1.70 g; 1.75 g expected for 5 equiv of $NaNO_3$) was washed with 20 mL of THF. The combined clear filtrates were concentrated under vacuum to a volume of ca. 40 mL and stored overnight at −30 °C to give transparent crystals of $[Ce(OSiPh_3)_3(THF)_3](THF)$ (1), which were isolated by filtration and dried under vacuum (5 g, 65%). Mp: 145–146 °C. Anal. Calcd for $CeSi_3O_7C_{70}H_{77}$: C, 67.02; H, 6.14. Found: C, 67.96; H, 5.99. ^1H NMR (0.27 M in $CDCl_3$): δ 0.51 ($\Delta\nu_{1/2}$ = 14 Hz, THF, 32), 7.16 ($\Delta\nu_{1/2}$ = 13 Hz, Ph, 27), 8.19 ($\Delta\nu_{1/2}$ = 22 Hz, Ph, 18). ^{13}C NMR ($CDCl_3$): δ 23.69 (THF), 60.96 (THF); 127.59; 128.68; 136.05; 144.72. ^1H NMR (0.20 M in CD_3CN) δ 1.55 ($\Delta\nu_{1/2}$ = 10 Hz, THF, 16), 1.79 (CD_3CN), 2.99 ($\Delta\nu_{1/2}$ = 19 Hz, THF, 16), 7.32 ($\Delta\nu_{1/2}$ = 9 Hz, Ph, 27), 8.60 ($\Delta\nu_{1/2}$ = 22 Hz, Ph, 18). ^{13}C NMR (CD_3CN): 25.79 (THF), 66.69 (THF), 128.56, 129.48, 136.84, 146.49. IR (KBr): 3040 m, 2960 m, 2870 m, 1965 w, 1900 w, 1830 w, 1760 w, 1590 w, 1480 w, 1425 s, 1260 m, 1180 w, 1105 s, 1060 w, 1025 m, 1010 m, 990 w, 950 s, 870 (Ce–O–Si),[23] 790 w, 735 m, 690 s cm^{-1}.

$[Pr(OSiPh_3)_3(THF)_3](THF)$ (2). Reaction of $(NH_4)_2Pr(NO_3)_5$ (2.00 g, 4.11 mmol) with $NaOSiPh_3(THF)$ (3.32 g, 20.5 mmol) as described above for **1** formed a white precipitate (1.73 g; 1.74 g expected for $NaNO_3$) and **2** as light green crystals (3.5 g, 68%). Mp: 130–132 °C. Anal. Calcd for $PrSi_3O_7C_{70}H_{77}$: C, 66.98; H, 6.14. Found: C, 67.20; H, 6.24. ^1H NMR (0.28 M in $CDCl_3$): δ −16.70 ($\Delta\nu_{1/2}$ = 49 Hz, THF, 16), −8.28 ($\Delta\nu_{1/2}$ = 24 Hz, THF, 16), 8.36 (Ph, 9), 8.76 ($\Delta\nu_{1/2}$ = 17 Hz, Ph, 18), 16.85 ($\Delta\nu_{1/2}$ = 31 Hz, Ph, 18). ^{13}C NMR ($CDCl_3$): δ 10.80 (THF), 28.03 (THF), 130.52, 143.63, 161.84. IR (KBr): 865 cm^{-1} (Pr–O–Si).

$[Nd(OSiPh_3)_3(THF)_3](THF)$ (3). Reaction of $(NH_4)_2Nd(NO_3)_5$ (1.8 g, 3.67 mmol) with $NaOSiPh_3(THF)$ (6.8 g, 18.3 mmol) as described above for **1** formed a white precipitate (1.51 g; 1.56 g expected for 5 equiv of $NaNO_3$) and **3** as blue crystals (3 g, 65%). Mp: 140–142 °C. Anal. Calcd for $NdSi_3O_7C_{70}H_{77}$: C, 66.80; H, 6.12. Found: C, 66.61; H, 6.15. ^1H NMR (0.17 M in $CDCl_3$): δ −7.18 ($\Delta\nu_{1/2}$ = 56 Hz, THF, 16), −3.22 ($\Delta\nu_{1/2}$ = 16 Hz, THF, 16), 7.85 ($\Delta\nu_{1/2}$ = 18 Hz, Ph, 27), 12.00 ($\Delta\nu_{1/2}$ = 44 Hz, Ph, 18). ^{13}C NMR ($CDCl_3$): δ 19.03, 44.61, 128.89, 129.44, 138.98, 152.62. IR (KBr): 867 cm^{-1} (Nd–O–Si).

$[Y(OSiPh_3)_3(THF)_3](THF)$ (4). Reaction of $(NH_4)_4Y(NO_3)_7$ (1.5 g, 2.52 mmol) with $NaOSiPh_3(THF)$ (6.55 g, 17.7 mmol) as described above for **1** formed a white precipitate (1.51 g; 1.50 g expected for 7 equiv of $NaNO_3$) and **4** as colorless crystals (2 g, 66%). Mp: 135–136 °C. Anal. Calcd for $YSi_3O_7C_{70}H_{77}$: C, 69.87; H, 6.41. Found: C, 69.98; H, 6.48. ^1H NMR ($CDCl_3$): δ 1.56 (s, THF, 16), 3.65 (s, THF, 16), 7.14 (Ph, 9), 7.22 (Ph, 18), 7.57 (Ph, 18). ^{13}C NMR ($CDCl_3$): δ 25.21, 69.04, 127.33, 128.68, 135.02, 139.63. IR (KBr): 865 cm^{-1} (Y–O–Si).

$Ce(OSiPh_3)_4(DME)$ (5). $(NH_4)_2Ce(NO_3)_6$ (2.00 g, 3.64 mmol) and $NaOSiPh_3(THF)$ (8.11 g, 21.8 mmol) were dissolved in 40 mL of DME. Immediately upon stirring, NH_3 gas was evolved. After the mixture was stirred overnight, a white precipitate was isolated by filtration and washed with 10 mL of DME (1.80 g; 1.85 g expected for 6 equiv of $NaNO_3$). The pale orange filtrate was reduced to a volume of ca. 25 mL and stored overnight at −30 °C to form **5** as a white/gray precipitate. The upper liquid layer was decanted and the remaining solid suspended in 20 mL of DME. After the mixture was stirred for ca. 1 h, most of the impurities were extracted into the solvent. Subsequent filtration and washing with 10 mL of DME gave **5** as a light yellow powder (3.5 g, 72%). Anal. Calcd for $CeSi_4O_6C_{76}H_{70}$: C, 68.54; H, 5.26. Found: C, 68.58; H, 5.61. The NMR and IR spectra and melting point were identical with those

of samples of the crystallographically characterized product obtained by ligand exchange from $Ce(O^iPr)_4$.[16]

Preparation of $Ce(OSiEt_3)_4$ (6). $(NH_4)_2Ce(NO_3)_6$ (2.00 g, 3.64 mmol) and $NaOSiEt_3$ (3.6 g, 22.0 mmol) were dissolved in 40 mL of CH_3CN. Immediately upon stirring, NH_3 gas was evolved and most of the CAN had reacted after 30 min. After the mixture was stirred overnight, the white precipitate was filtered out and washed with 10 mL of CH_3CN to give a white precipitate (1.82 g; 1.87 g expected for 6 equiv of $NaNO_3$). The orange/yellow filtrate was evaporated to dryness and dried at 40 °C under vacuum to give **6** as a yellow/brown powder (2.0 g, 83%). Anal. Calcd for $CeSi_4O_4C_{24}H_{60}$: C, 43.34; H, 9.03. Found: C, 42.80; H, 8.96. The NMR and IR spectra and melting point were identical with those of the product obtained from $Ce(O^iPr)_4$.[17]

Synthesis of $Y_5(O^iPr)_{13}O$ (7) from $(NH_4)_3Y(NO_3)_6$. In a Schlenk flask, sodium (5.3 g, 230.4 mmol) was reacted with 50 mL of ^iPrOH under reflux until a clear solution was obtained. After the mixture was cooled to room temperature, 40 mL of ^iPrOH and 60 mL of toluene were added. Under gentle heating (ca. 30 °C) and stirring NaO^iPr went into solution and $(NH_4)_3Y(NO_3)_6$ (19.62 g, 38.1 mmol) was added as a solid. The mixture was stirred for 6 h at room temperature and 11 h at 75 °C. After filtration at room temperature the white precipitate was washed on the Schlenk frit with two 20-mL portions of *n*-pentane to yield $NaNO_3$ (19 g; 19.58 g expected for 6 equiv of $NaNO_3$). The clear and colorless filtrate was evaporated to dryness under vacuum to yield **7** as a white powder (9 g, 95%). Crystals suitable for X-ray structure determination and NMR, IR, and elemental analyses were grown as follows. The white powder (1 g) was extracted with 20 mL of ^iPrOH and 3 mL of toluene and the solution filtered. The clear filtrate was kept at −5 to −10 °C for ca. 1 week to form colorless transparent crystals (0.5 g). Another crop of crystals (0.15 g) was obtained by keeping the mother liquor at −30 °C for 5 days. Anal. Calcd for $Y_5O_{14}C_{39}H_{91}$: C, 38.12; H, 7.41; N, 0.0; Y, 36.21. Found: C, 37.64; H, 7.38; N, 0.0; Y, 36.75. The ^1H NMR spectrum of **7** in $CDCl_3$ is identical with the literature spectrum.[15] The IR spectrum (KBr) is nearly identical with the Nujol spectrum reported for "$Y(O^iPr)_3$".[24] ^{13}C NMR ($CDCl_3$): δ 27.49, 28.16, 28.53 (CH_3), 66.59, 66.88, 67.16 (CH). Single crystals of **7** from two different preparations were found to be isostructural with $Y_5(O^iPr)_{13}O$.[12,15]

Synthesis of 4 from 7. A clear solution of Ph_3SiOH (3.38 g, 12.2 mmol) in 5 mL of THF was added to a solution of $Y_5(O^iPr)_{13}O$ (1 g, 0.815 mmol; prepared as described above) in 5 mL of THF. A white precipitate formed immediately. After the mixture was stirred 30 min, 25 mL of THF was added and the reaction was heated to 75 °C. The precipitate disappeared. After stirring (30 min), the solution was cooled to −30 °C. Colorless transparent crystals of **4** (2.2 g, 48%) formed overnight. Another crop of crystals (0.2 g, 15%) was obtained after 2 weeks. Anal. Calcd for $YSi_3O_7C_{70}H_{77}$: C, 69.87; H, 6.41. Found: C, 69.57; H, 6.27. The NMR and IR spectra and melting point were identical with those of **4** obtained directly from $(NH_4)_4Y(NO_3)_7$.

Crystal Structure of 1. All crystallographic data were collected at −60 °C on a Nicolet $P2_1$ diffractometer from a crystal fragment of dimensions 0.65 × 0.55 × 0.35 mm that had been cut from a larger hexagonal plate. General procedures used in the structure analysis have been described.[25,26] Crystallographic data are given in Table I; further details are included with the supplementary material. Refined unit cell parameters were based upon the setting angles of 30 reflections with $30° \leq 2\theta \leq 35°$. A total of 8083 intensity data with $2\theta \leq 55°$ were collected; of these, 6685 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the structure refinement. Intensity statistics were consistent with expectations for a noncentrosymmetric structure. Solution of the structure was accomplished by a combination of direct and heavy-atom methods. Final least-squares refinement included anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms in fixed, idealized positions. Refinement of the alternative enantiomorph yielded higher R factors (R = 0.036, R_w = 0.046). Computer programs utilized included a local version of the

Table I. Crystallographic Data for $[Ce(OSiPh_3)_3(THF)_3](THF)$

$CeC_{70}H_{77}O_7Si_3$	fw = 1254.75
space group $P2_1$	T = −60 °C
a = 14.679 (2) Å	ρ_{calcd} = 1.278 g cm^{-3}
b = 16.432 (3) Å	λ(Mo Kα) = 0.710 73 Å
c = 15.021 (3) Å	μ = 8.11 cm^{-1}
β = 115.86 (1.2)°	$R(F_o)$ = 0.033
V = 3260.3 (9) Å^3	$R_w(F_o)$ = 0.042
Z = 2	

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Table II. Final Fractional Coordinates for [Ce(OSiPh₃)₃(THF)₃](THF)

atom	x	y	z	U(eq),^{a} Å^2	atom	x	y	z	U(eq),^{a} Å^2
Ce	0.7915 (0.2)	0.0000	0.6816 (0.2)	338 (1)	C(31)	1.0680 (4)	−0.1854 (4)	0.7479 (4)	504 (42)
Si(1)	0.7374 (1.1)	−0.1529 (1.0)	0.8431 (1.0)	413 (10)	C(32)	0.9930 (5)	−0.2288 (5)	0.7614 (5)	689 (57)
Si(2)	1.0511 (1.0)	−0.0743 (1.0)	0.7165 (1.0)	422 (10)	C(33)	1.0014 (7)	−0.3111 (6)	0.7821 (6)	911 (77)
Si(3)	0.6381 (1.1)	−0.0957 (1.0)	0.4281 (1.0)	421 (10)	C(34)	1.0863 (8)	−0.3532 (5)	0.7898 (6)	868 (86)
O(1)	0.7604 (3)	−0.0860 (3)	0.7779 (3)	555 (34)	C(35)	1.1617 (8)	−0.3107 (6)	0.7769 (7)	900 (89)
O(2)	0.9444 (3)	−0.0420 (3)	0.7051 (3)	538 (31)	C(36)	1.1527 (6)	−0.2285 (5)	0.7577 (6)	701 (65)
O(3)	0.6959 (3)	−0.0472 (2)	0.5296 (3)	496 (29)	C(37)	0.7068 (4)	−0.1922 (3)	0.4289 (4)	475 (43)
O(4)	0.6346 (3)	0.0806 (3)	0.6674 (4)	637 (37)	C(38)	0.8052 (5)	−0.2054 (4)	0.5012 (5)	515 (47)
O(5)	0.8776 (3)	0.1010 (3)	0.8263 (4)	760 (41)	C(39)	0.8595 (6)	−0.2743 (5)	0.5006 (5)	713 (65)
O(6)	0.8218 (3)	0.1286 (3)	0.5965 (3)	678 (39)	C(40)	0.8152 (7)	−0.3324 (5)	0.4283 (6)	818 (84)
O(7)	0.5107 (6)	−0.8202 (5)	0.9360 (7)	1381 (102)	C(41)	0.7183 (7)	−0.3216 (5)	0.3579 (6)	804 (79)
C(1)	0.7361 (4)	−0.2573 (4)	0.7910 (4)	452 (39)	C(42)	0.6645 (6)	−0.2524 (4)	0.3574 (5)	656 (58)
C(2)	0.7326 (4)	−0.2652 (5)	0.6967 (4)	536 (46)	C(43)	0.5054 (4)	−0.1203 (3)	0.4076 (4)	460 (40)
C(3)	0.7308 (6)	−0.3401 (5)	0.6569 (6)	688 (67)	C(44)	0.4873 (6)	−0.1405 (5)	0.4897 (6)	647 (62)
C(4)	0.7317 (6)	−0.4107 (5)	0.7075 (6)	752 (71)	C(45)	0.3878 (7)	−0.1549 (6)	0.4791 (6)	827 (80)
C(5)	0.7349 (7)	−0.4044 (5)	0.7990 (6)	784 (77)	C(46)	0.3081 (7)	−0.1526 (6)	0.3848 (8)	899 (98)
C(6)	0.7383 (6)	−0.3288 (4)	0.8422 (5)	644 (58)	C(47)	0.3237 (5)	−0.1339 (5)	0.3040 (6)	716 (60)
C(7)	0.6100 (4)	−0.1344 (4)	0.8405 (4)	459 (39)	C(48)	0.4227 (5)	−0.1190 (4)	0.3150 (5)	585 (49)
C(8)	0.5252 (4)	−0.1768 (5)	0.7800 (5)	605 (51)	C(49)	0.6262 (4)	−0.0346 (4)	0.3176 (4)	484 (41)
C(9)	0.4297 (5)	−0.1570 (7)	0.7724 (6)	866 (70)	C(50)	0.6801 (5)	−0.0548 (5)	0.2641 (5)	675 (59)
C(10)	0.4188 (5)	−0.0927 (7)	0.8268 (6)	862 (73)	C(51)	0.6675 (6)	−0.0086 (8)	0.1814 (6)	869 (78)
C(11)	0.5033 (6)	−0.0474 (6)	0.8865 (6)	796 (71)	C(52)	0.6072 (9)	0.0576 (7)	0.1543 (6)	1059 (92)
C(12)	0.5975 (5)	−0.0687 (5)	0.8945 (5)	617 (53)	C(53)	0.5533 (7)	0.0797 (5)	0.2083 (6)	882 (73)
C(13)	0.8341 (5)	−0.1478 (4)	0.9758 (5)	637 (50)	C(54)	0.5641 (6)	0.0335 (4)	0.2867 (5)	673 (54)
C(14)	0.8134 (7)	−0.1775 (7)	1.0536 (5)	945 (78)	C(55)	0.5397 (8)	0.0372 (6)	0.6592 (7)	971 (90)
C(15)	0.8880 (12)	−0.1675 (11)	1.1499 (7)	1583 (144)	C(56)	0.4597 (6)	0.0678 (5)	0.5606 (7)	883 (74)
C(16)	0.9746 (15)	−0.1355 (11)	1.1735 (9)	1768 (170)	C(57)	0.5131 (13)	0.1355 (11)	0.5429 (10)	1675 (183)
C(17)	0.9950 (10)	−0.1048 (7)	1.1015 (12)	1840 (156)	C(58)	0.5985 (9)	0.1564 (7)	0.6271 (10)	1198 (129)
C(18)	0.9266 (7)	−0.1108 (6)	0.9992 (7)	1057 (87)	C(59)	0.9820 (6)	0.0980 (6)	0.8988 (6)	899 (74)
C(19)	1.0648 (4)	−0.0557 (3)	0.5986 (4)	460 (41)	C(60)	0.9893 (9)	0.1459 (12)	0.9779 (9)	1711 (149)
C(20)	1.1576 (5)	−0.0582 (4)	0.5942 (5)	570 (50)	C(61)	0.8911 (10)	0.1903 (10)	0.9508 (9)	1478 (146)
C(21)	1.1665 (6)	−0.0410 (4)	0.5065 (6)	648 (62)	C(62)	0.8300 (8)	0.1532 (11)	0.8681 (10)	1991 (162)
C(22)	1.0821 (7)	−0.0214 (5)	0.4229 (5)	782 (77)	C(63)	0.7720 (8)	0.1425 (6)	0.4913 (6)	955 (87)
C(23)	0.9884 (6)	−0.0187 (5)	0.4245 (5)	772 (68)	C(64)	0.8423 (19)	0.1994 (10)	0.4740 (12)	1992 (255)
C(24)	0.9796 (5)	−0.0349 (4)	0.5117 (4)	585 (48)	C(65)	0.9188 (10)	0.2275 (9)	0.5648 (15)	1562 (193)
C(25)	1.1573 (4)	−0.0183 (3)	0.8180 (4)	485 (45)	C(66)	0.9124 (7)	0.1761 (6)	0.6402 (8)	1033 (94)
C(26)	1.2091 (5)	−0.0497 (5)	0.9134 (4)	693 (56)	C(67)	0.5963 (9)	−0.8172 (7)	0.9252 (9)	1109 (123)
C(27)	1.2866 (6)	−0.0039 (10)	0.9863 (5)	972 (71)	C(68)	0.6313 (10)	−0.7345 (8)	0.9348 (12)	1410 (166)
C(28)	1.3132 (6)	0.0713 (8)	0.9652 (7)	999 (87)	C(69)	0.5468 (9)	−0.6818 (6)	0.9327 (8)	1029 (110)
C(29)	1.2657 (7)	0.1004 (6)	0.8759 (7)	953 (91)	C(70)	0.4788 (8)	−0.7405 (7)	0.9477 (8)	1062 (105)
C(30)	1.1870 (5)	0.0579 (6)	0.7995 (5)	674 (59)					

^{a} U(eq) = one-third of the trace of the orthogonalized U matrix.

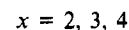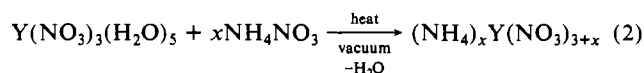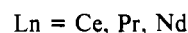**Table III.** Selected Bond Distances (Å) and Angles (deg) for [Ce(OSiPh₃)₃(THF)₃](THF) (**1**)

Distances			
Ce(1)–O(1)	2.208 (4)	Ce(1)–O(4)	2.584 (4)
Ce(1)–O(2)	2.224 (4)	Ce(1)–O(5)	2.584 (4)
Ce(1)–O(3)	2.234 (4)	Ce(1)–O(6)	2.606 (4)

Angles			
O(1)–Ce–O(2)	100.4 (1.5)	O(3)–Ce–O(4)	87.3 (1.4)
O(1)–Ce–O(3)	103.3 (1.6)	O(3)–Ce–O(5)	160.3 (1.6)
O(1)–Ce–O(4)	87.2 (1.5)	O(3)–Ce–O(6)	86.9 (1.4)
O(1)–Ce–O(5)	91.4 (1.8)	O(4)–Ce–O(5)	80.3 (1.5)
O(1)–Ce–O(6)	165.6 (1.6)	O(4)–Ce–O(6)	83.1 (1.5)
O(2)–Ce–O(3)	101.3 (1.5)	O(5)–Ce–O(6)	76.5 (1.7)
O(2)–Ce–O(4)	166.8 (1.5)	Ce–O(1)–Si(1)	176.4 (3)
O(2)–Ce–O(5)	88.6 (1.5)	Ce–O(2)–Si(2)	177.0 (3)
O(2)–Ce–O(6)	87.3 (1.6)	Ce–O(3)–Si(3)	169.9 (2)

UCLA Crystallographic Computing Package,[27] MITHRIL,[28] and the graphics portions of the SHELXTL package.[29]

Final atomic parameters for the non-hydrogen atoms are listed in Table II, and selected bond distances and angles are tabulated in Table III. Full tables of all other crystallographic results are included with the supplementary material.

Unit Cell Parameters for 2 and 4. Crystals of **2** and **4** handled as described above for **1** were found to have essentially the same unit cell dimensions as **1**. Unit cell parameters for [Pr(OSiPh₃)₃(THF)₃](THF):
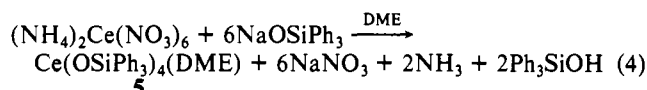
(27) Strouse, C. E. Personal communication.
(28) Gilmore, C. J. *MITHRIL: A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data*; University of Glasgow: Glasgow, U.K., 1983.
(29) *SHELXTL Plus*; Nicolet Instrument Corp.: Madison, WI, 1988.

$a = 14.65$ (1) Å, $b = 16.34$ (2) Å, $c = 14.92$ (2) Å, $\beta = 115.9$ (1)°, $V = 3213$ (7) Å^3. Unit cell parameters for [Y(OSiPh₃)₃(THF)₃](THF): $a = 14.55$ (1) Å, $b = 16.38$ (1) Å, $c = 14.83$ (1) Å, $\beta = 115.66$ (5)°, $V = 3188$ (3) Å^3.

Results

Synthesis. Commercially available lanthanide and yttrium nitrates can be conveniently dehydrated in the presence of ammonium nitrate, as shown in eq 1 and 2.[21,22] The reactions are quantitative.

$$Ln(NO_3)_3(H_2O)_x + 2NH_4NO_3 \xrightarrow[\substack{\text{vacuum} \\ -H_2O}]{\text{heat}} (NH_4)_2Ln(NO_3)_5 \quad (1)$$

$$Ln = Ce, Pr, Nd$$

$$Y(NO_3)_3(H_2O)_5 + xNH_4NO_3 \xrightarrow[\substack{\text{vacuum} \\ -H_2O}]{\text{heat}} (NH_4)_xY(NO_3)_{3+x} \quad (2)$$

$$x = 2, 3, 4$$
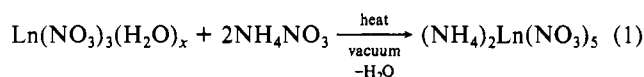
These anhydrous trivalent nitrates reacted readily with NaOSiPh₃(THF) in THF to form the complexes [Ln(OSiPh₃)₃(THF)₃](THF) according to eq 3. In all cases, gas evolution

$$(NH_4)_xLn(NO_3)_{3+x} + (3 + x)NaOSiPh_3(THF) \rightarrow$$
$$[Ln(OSiPh_3)_3(THF)_3](THF) + (3 + x)NaNO_3 +$$
$$Ln = Ce\ (\mathbf{1}), Nd\ (\mathbf{2}),$$
$$Pr\ (\mathbf{3}), Y\ (\mathbf{4}),$$
$$xPh_3SiOH + xNH_3 \quad (3)$$
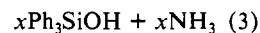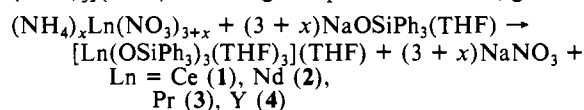
started immediately upon combining the reagents. This is typical of reactions of ammonium nitrate metal complexes with anionic

reagents of this type and has been observed previously in reactions of $(NH_4)_2Ce(NO_3)_6$ (CAN) with NaC_5H_5[30] and with sodium alkoxides.[4,5,31] The amount of white precipitate recovered in each of the four reactions represented in eq 3 was close to that expected for the quantitative formation of $NaNO_3$. This byproduct is also generated in the reactions of CAN with alkoxide reagents.[4,5,31] After the precipitate was separated by filtration, the products were isolated by crystallization at low temperature, which left the Ph_3SiOH byproduct in solution. The yields were typically 65%.

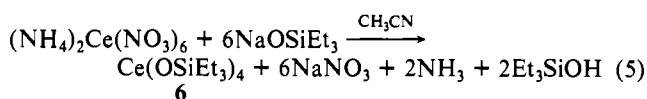Complexes 1–4 were characterized by NMR and IR spectroscopy and by elemental analysis. $[Ce(OSiPh_3)_3(THF)_3](THF)$ was structurally characterized by X-ray crystallography (see below), and the praseodymium and yttrium complexes were found to have essentially the same unit cell parameters. The silyloxide complexes are soluble in chloroform, toluene, and THF. 1 dissolves in CD_3CN to give a spectrum containing free THF; i.e., displacement of THF by acetonitrile solvent apparently occurs. Except for the cerium derivative, these complexes are only moderately air-sensitive. $[Ce(OSiPh_3)_3(THF)_3](THF)$ (1) showed high air sensitivity as a solid as well as in solution. A clear, colorless NMR sample of 1 in $CDCl_3$ turned yellow immediately on exposure to air. However, subsequent NMR examination of the sample showed that approximately 5 h were required for complete oxidation. At this point, the sample exhibited THF signals characteristic of a diamagnetic system and tested positive for Ce(IV) by using the barium 4-(phenylamino)benzenesulfonate indicator.[32] The THF molecule of crystallization contained in crystals of these molecules can be removed relatively easily. The length and temperature of drying affects how much of this fourth THF is retained.

The reactivity of $NaOSiPh_3$ was also investigated with the tetravalent nitrate precursor CAN according to eq 4. The reaction

$$(NH_4)_2Ce(NO_3)_6 + 6NaOSiPh_3 \xrightarrow{DME}$$
$$Ce(OSiPh_3)_4(DME) + 6NaNO_3 + 2NH_3 + 2Ph_3SiOH \quad (4)$$
$$\mathbf{5}$$

proceeded in much the same manner as the reactions discussed above; i.e., gas evolved, a white precipitate formed, and the product was isolated in about 70% yield. Reaction 4 was carried out in DME to facilitate isolation of the product as the DME adduct, $Ce(OSiPh_3)_4(DME)$,[16] and the product was identical with the crystallographically characterized product isolated by reaction of Ph_3SiOH with $Ce(O^iPr)_4$.[16]

The preparation of the ethyl analogue 6 from a nitrate precursor was also investigated according to eq 5. In this case, the reaction

$$(NH_4)_2Ce(NO_3)_6 + 6NaOSiEt_3 \xrightarrow{CH_3CN}$$
$$Ce(OSiEt_3)_4 + 6NaNO_3 + 2NH_3 + 2Et_3SiOH \quad (5)$$
$$\mathbf{6}$$

was conducted in acetonitrile, because it was previously determined that this was a favorable solvent for the isolation of $Ce(OSiEt_3)_4$ from the reaction of Et_3SiOH with $Ce(O^iPr)_4$.[17] Complex 6 was isolated in over 80% yield by this synthetic route. Reactions 4 and 5 taken together demonstrate that the nitrate/alkoxide reaction can be successfully run in solvents other than THF. It is interesting to note that, in both reactions 4 and 5, there is no indication for a partial reduction of CAN by the NH_3 formed during the reaction, although recent research has shown that CAN can be easily reduced by NH_3 gas.[33]

The reaction of $(NH_4)_3Y(NO_3)_6$ with NaO^iPr was investigated to determine if the nitrate precursor route would give a product of the "$Y(O^iPr)_3$" type previously mentioned in the literature[24,34]

(30) Gradeff, P. S.; Yunlu, K.; Deming, T. J.; Olofson, J. M.; Ziller, J. W.; Evans, W. J. *Inorg. Chem.* **1989**, *28*, 2600–2604.

(31) Evans, W. J.; Deming, T. J.; Olofson, J. M.; Ziller, J. W. *Inorg. Chem.* **1989**, *28*, 4027–4034.

(32) Scott, W. W. *Standard Methods of Chemical Analysis*, 5th ed.; van Nostrand: Princeton, NJ, 1939; Vol. 1, p 1206.

(33) Bourleaux, G.; Colombet, P.; Rouxel, J.; Gradeff, P. S.; Mauermann, H. *C. R. Acad. Sci., Ser. 2* **1988**, *307*, 2021.

(34) Mazdiyasni, K. S.; Lynch, C. T.; Smith, J. S. *Inorg. Chem.* **1966**, *5*, 342–346.

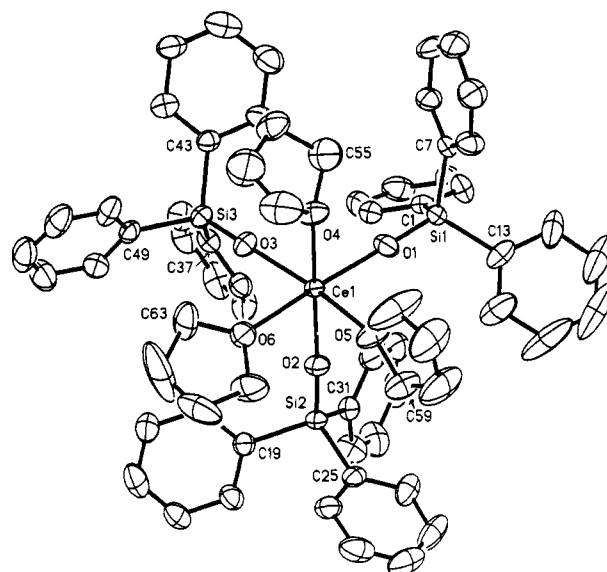**Figure 1.** Molecular structure of $Ce(OSiPh_3)_3(THF)_3$ viewed down the pseudo-3-fold axis.

or if the recently discovered oxo alkoxide $Y_5(O^iPr)_{13}O$[12,15] would be formed. Equation 6 shows that the latter product is obtained. The 95% yield suggests that this product is apparently a favored product in the yttrium isopropoxide system.[35]

$$(NH_4)_3Y(NO_3)_6 + xNaO^iPr \xrightarrow{^iPrOH}$$
$$Y_5(O^iPr)_{13}O + 6NaNO_3 + 3NH_3 \quad (6)$$
$$\mathbf{7}$$
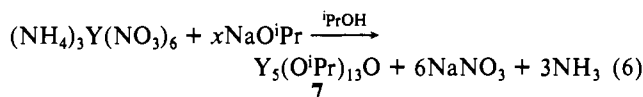
Interestingly, compound 7 reacted with Ph_3SiOH to form $[Y(OSiPh_3)_3(THF)_3](THF)$ (eq 7) rather than an oxo derivative.

$$Y_5(O^iPr)_{13}O + \text{excess } Ph_3SiOH \rightarrow$$
$$[Y(OSiPh_3)_3(THF)_3](THF) + {}^iPrOH \quad (7)$$
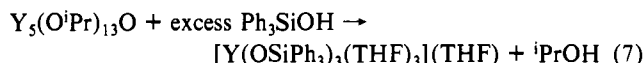
Other products are formed, as indicated by the 63% yield, but this reaction does demonstrate that alcoholysis reactions on oxo alkoxides can form oxo-free products. Unit cell constants were obtained on crystals of both the starting material and the product in this reaction to confirm this result. $[Pr(OSiPh_3)_3(THF)_3](THF)$ (3) can also be prepared in this way via an intermediate alkoxide although the identity of the intermediate is less well-known. Hence, Ph_3SiOH reacts with the product of the reaction of $(NH_4)_2Pr(NO_3)_5$ with NaO^nPr to form 3.

Crystallography. The structure of the $Ce(OSiPh_3)_3(THF)_3$ part of 1 is shown in Figure 1, and selected bond distances and angles are given in Table III. The fourth THF in 1 is not coordinated. The six oxygen-bound ligands roughly define an octahedron with the two sets of ligands oriented in a facial arrangement. The 89.5° average of the 12 O–Ce–O angles involving pairs of cis ligands is consistent with an octahedral geometry, but the angles involving pairs of THF ligands are significantly less than 90° and the angles involving pairs of $OSiPh_3$ ligands are significantly more than 90°. The overall structure is similar to that of $Y(OC_6H_3Me_2-2,6)_3(THF)_3$ (8).[39]

The 2.222 (4) Å average $Ce–O(OSiPh_3)$ distance can be compared with the 2.12 (2) Å average $Ce–O(OSiPh_3)$ length in tetravalent, six-coordinate $Ce(OSiPh_3)_4(DME)$.[16] The 0.10-Å difference is close to the 0.14-Å difference in radii of six-coordinate Ce^{3+} and Ce^{4+} cited by Shannon.[36] The 174.4° average value for the Ce–O–Si angles is also similar to the 174° average in those of $Ce(OSiPh_3)_4(DME)$. Large angles of this type are often explained in terms of multiple bonding. For example, in $ZrCl_2(OSiPh_3)_2(DME)$,[37] the 171° Zr–O–Si angle was correlated with

(35) Note that this $M_5L_{13}O$ unit has been observed to be a favorable product in other systems.[6]
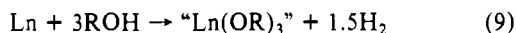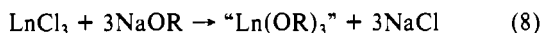
(36) Shannon, R. D. *Acta Crystallogr., Sect A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751–767.

a short Zr–O bond distance and attributed to d_π–p_π bonding. On the other hand, the 170.7 (2) and 161.3 (2)° Co–O–Si angles in $[Co(OSiPh_3)_2(THF)]_2$[38] were discussed in terms of steric crowding. Too little structural information is available on $OSiPh_3$ complexes to determine if the Ce–O bonds in **1** involve multiple bonding. Comparison with the tetravalent, nominally six-coordinate complex $Ce(OCMe_3)_2(NO_3)_2(HOCMe_3)_2$ (**9**)[31] reinforces this idea. The Ce–O–C angles in **9** are also large, 168.9 (6) and 170.2 (7)°, but the Ce–O(OCMe₃) distances of 2.026 (5) and 2.023 (5) Å are shorter than those in $Ce(OSiPh_3)_4(DME)$.

Discussion

Equation 3 provides the first crystallographically characterized silyloxy complexes of the trivalent lanthanides. Since complexes can be obtained for both early lanthanide metals and for the late lanthanide mimic, yttrium,[19] it appears that Ph_3SiO is a good general ligand with which to make OR derivatives of all of the metals in this series. The Ph_3SiO ligand also appears to offer some favorable steric features. The isolation of tris THF adducts for cerium, praseodymium, and yttrium places the Ph_3SiO ligand in an intermediate position with respect to the size of other monodentate OR ligands used with yttrium and the lanthanides. The $OSiPh_3$ ligand is not as large as the 2,6-di-*tert*-butylphenoxide ligand, which forms $Ln(OR)_3$ compounds,[3,7,13] and it is not as small as the *tert*-butoxide and isopropoxide ligands, which form polymetallic bridged complexes.[9,10,12,14] The similarity of the structures of **1** and $Y(OC_6H_3Me_2\text{-}2,6)_3(THF)_3$ (**8**)[39] suggests that $OSiPh_3$ and $OC_6H_3Me_2$-2,6 may be interchangeable in terms of size and would provide useful comparisons of aryloxy and silyloxy ligation. As in **8**, the THF ligands in **1** are sites of potential further reactivity via THF dissociation.

Equation 3 also demonstrates that anhydrous nitrates are useful precursors to OR complexes of yttrium and the lanthanides. In the past, the synthesis of trivalent alkoxide complexes of these metals has been accomplished primarily by the three methods shown in eq 8–10. For tetravalent cerium complexes, an alternative route via anhydrous CAN is available.[4,5] Now an alternative pathway to trivalent alkoxides is also available through the trivalent anhydrous nitrates. One experimental advantage to using the nitrate route is that the $NaNO_3$ byproduct tends to form a relatively coarse precipitate that can be filtered more easily than the NaCl byproduct formed in eq 8. In addition, no anions from the

$$LnCl_3 + 3NaOR \rightarrow \text{``}Ln(OR)_3\text{''} + 3NaCl \qquad (8)$$

$$Ln + 3ROH \rightarrow \text{``}Ln(OR)_3\text{''} + 1.5H_2 \qquad (9)$$

$$\text{``}Ln(OR)_3\text{''} + 3R'OH \rightarrow \text{``}Ln(OR')_3\text{''} + 3ROH \qquad (10)$$

lanthanide starting material are incorporated into the structure as can happen in eq 8.[9,10]

Examination of the reactivity of the yttrium nitrate precursor with NaO^iPr showed that this route did not prevent formation of the oxide-containing product $Y_5(O^iPr)_{13}O$.[12,15] Nevertheless, this oxo alkoxide complex can be used to form an oxide-free silyloxide complex, as shown in eq 7. To our knowledge, this is the first example of the conversion of a known oxo alkoxide of this type via alcoholysis to an oxo-free product. Previous attempts to form silyloxy complexes in this way led to oxo silyloxy products.[40] In most cases, the direct reaction of $NaOSiR_3$ with the metal nitrate will be the preferred synthetic route to a silyloxy complex. However, if it was preferable to use a silanol instead of a sodium siloxide precursor, eq 6 and 7 could be coupled to provide a nitrate-based route to silyloxy complexes.

The oxo alkoxide to silyloxide conversion in eq 7 raises interesting questions regarding the alcoholysis reactions in the literature.[2] It is possible that even though precursors labeled "Ln(O^iPr)_3" were actually oxo alkoxides, their alcoholysis reactions could give oxide-free products. This, of course, would be highly dependent on the nature of the alcohol used.

Conclusion

Silyloxy derivatives of trivalent lanthanides and yttrium have been synthesized and fully characterized by X-ray crystallography. The $OSiPh_3$ group appears to be a useful ligand for the synthesis of OR complexes of all of the metals in this series, and the synthetic chemistry appears to be successful in several different solvents. Anhydrous trivalent metal nitrate compounds have been shown to be good alternative precursors to these silyloxides and to oxo alkoxides as well. The conversion of an oxo alkoxide complex to an oxide-free silyloxide species demonstrates yet another synthetic route to OR complexes of these metals.

Note Added in Proof. A communication on the structure of $[Y(OSiPh_3)_3(THF)_3](THF)$ has recently appeared: McGeary, M. J.; Coan, P. S.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 3283–3284.

Supplementary Material Available: Tables of crystallographic experimental details, bond distances and angles, hydrogen atom positional parameters, and thermal parameters (13 pages); a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

(37) Babian, E. A.; Hrncir, D. C.; Bott, S. G.; Atwood, J. L. *Inorg. Chem.* **1986**, *25*, 4818–4821.

(38) Sigel, G. A.; Bartlett, R. A.; Decker, D.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1987**, *26*, 1773–1780.

(39) Evans, W. J.; Olofson, J. M.; Ziller, J. W. *Inorg. Chem.*, in press.

(40) Compare: Poncelet, O.; Hubert-Pfalzgraf, L. G.; El Khokh, N.; Daran, J.-C. *Abstracts of Papers*, 196th National Meeting of the American Chemical Society, Los Angeles, CA; American Chemical Society: Washington, DC, 1988; INOR 231.