A Comparative Synthetic and Structural Study of Triphenylmethoxide and Triphenylsiloxide Complexes of the Early Lanthanides, Including X-ray Crystal Structures of La₂(OCPh₃)₆ and Ce₂(OSiPh₃)₆

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La[N(SiMe₃)₂]₃ reacts with 3 equiv of triphenylmethanol in toluene to form the dimer [La(OCPh₃)₂(μ-OCPh₃)]₂ (**1**) in 90% yield. **1** crystallizes in the triclinic space group $P\bar{1}$ with a = 12.019 (3) Å, b = 14.287 (2) Å, c = 16.375 (3) Å, α = 73.99 (1)°, β = 85.39 (2)°, γ = 76.07 (2)°, V = 2622.8 (8) Å³, and D_{calcd} = 1.34 Mg/m³ for Z = 1. Least-squares refinement on the basis of 10 950 observed reflections led to a final R_F = 3.7%. Each lanthanum atom in **1** is surrounded by two terminal and two unsymmetrically bridging alkoxide ligands such that the four oxygen donor atoms nearly describe a tetrahedron. The bridging La–O distances are 2.389 (2) and 2.483 (2) Å, and the terminal La–O distances average 2.180 (5) Å. The cerium analogue [Ce(OCPh₃)₂(μ-OCPh₃)]₂ (**2**) can be prepared similarly, and a single-crystal analysis shows it to be isomorphous with **1**. Triphenylsilanol reacts with Ln[N(SiMe₃)₂]₃ (Ln = La, Ce) in toluene to form the analogous Ph₃SiO complexes [Ln(OSiPh₃)₂(μ-OSiPh₃)]₂ (Ln = La (**3**), Ce (**4**)). Complex **4** crystallizes from toluene in the triclinic space group $P\bar{1}$ with a = 13.766 (2) Å, b = 14.376 (1) Å, c = 14.603 (2) Å, α = 73.34 (1)°, β = 70.45 (1)°, γ = 75.87 (1)°, V = 2573.4 (5) Å³, and D_{calcd} = 1.37 Mg/m³ for Z = 1. Least-squares refinement on the basis of 5599 observed reflections led to a final R_F = 6.3%. The structure of **4** is similar to that of **1** except that the four oxygen atoms surrounding each metal center approximate a square-pyramidal geometry which has a carbon atom of one of the arene rings in one basal position. By single-crystal analysis, complex **3** is isomorphous with **4**. Complexes **3** and **4** dissolve in THF to form the previously characterized Ln(OSiPh₃)₃(THF)₃ complexes. Compounds **1** and **2** are less soluble than **3** and **4** but dissolve in hot THF to form the more soluble THF adducts, Ln(OCPh₃)₃(THF)ₓ.

Introduction

Recent studies of yttrium and lanthanide alkoxide chemistry have shown that a wide variety of structural types are available for these complexes.[1-14] The formulas such as Y(OR)₃ or Ln-(OR)₃, which have been traditionally used to describe alkoxides of these elements,[15,16] have been more precisely defined by X-ray diffraction studies which have revealed compositions as diverse as M₆(OR)₁₇Cl,[1] M₅(OR)₁₃O,[2,3] M₃(OR)₈ClL₂,[4,5] M₂(OR)₆L₂,[6] M₂(OR)₆L,[7] M₂(OR)₆,[8] and M(OR)₃L₃[6,7,9,10] in addition to M(OR)₃[17] (M = yttrium or lanthanide, L = THF or ROH). There is clearly a wide variation in the degree of oligomerization and variety of heteroligands which can be incorporated into yttrium and lanthanide alkoxide compounds, and this appears to be highly dependent upon which R group is present in the alkoxide ligand.

To fully utilize the chemical opportunities available through alkoxide-ligated yttrium and lanthanide systems, a detailed understanding of the dependence of these structures and compositions on the alkoxide ligand is needed. In the course of studying this area, a confluence of our interests in (a) dimer to solvated-mo-nomer interconversions which may be potentially useful in synthesis[6] and (b) the utility of siloxides versus alkoxides[9] has led us to study complexes of the triphenylmethoxide ligand, OCPh₃, and the triphenylsiloxide ligand, OSiPh₃.

Previously, it had been shown that triphenylsiloxide complexes of formula Ln(OSiPh₃)₃(THF)₃ (Ln = Ce, Pr, Nd, Y) could be conveniently obtained from the readily accessible lanthanide and yttrium nitrates.[9] These complexes had a *fac*-octahedral structure analogous to the structure of the aryloxide complex Y-(OC₆H₃Me₂-2,6)₃(THF)₃.[6] The latter complex readily interconverted between this monomeric trisolvated form and a dimeric form containing just one molecule of THF per metal atom, i.e., [Y(OC₆H₃Me₂-2,6)₂(μ-OC₆H₃Me₂-2,6)(THF)]₂.[6] It was of interest to learn if the siloxides had an analogous dimeric form and how this related to an unsolvated triphenylsiloxide of formula [Y(OSiPh₃)₃]ₙ, identified as an intermediate in the preparation of Y(OSiPh₃)₃(THF)₃ by the general route[18] of reacting an alcohol with an amide, in this case Y[N(SiMe₃)₂]₃.[7,10] We were also interested in determining if silicon-free analogues of the triphenylsiloxide ligand could be prepared with the triphenylmethoxide ligand. We present here a comparative study of these ligands attached to lanthanum and cerium in which both unsolvated dimeric and solvated monomeric forms are accessible.

Experimental Section

All manipulations were performed under dry nitrogen using Schlenk, vacuum-line, and glovebox techniques. CDCl₃ and CD₂Cl₂ were dried over 3A molecular sieves and all other solvents were distilled from sodium benzophenone ketyl. The Ln[N(SiMe₃)₂]₃ complexes were prepared according to a modified literature procedure[19] (see below) using KN-(SiMe₃)₂ (Aldrich) and lanthanide trichlorides (Research Chemicals), dehydrated by following established procedures.[20] Triphenylmethanol and triphenylsilanol (Aldrich) were degassed (10⁻⁴ Torr) prior to use. NMR spectra were obtained on GE 300-MHz and GN 500-MHz instruments. IR spectra were obtained on a Nicolet 5DXB FTIR spectrometer. Elemental analyses were obtained from the Analytische Laboratorien, Engelskirchen, Germany. Complexometric metal analyses were performed as previously described.[21]

Ln[N(SiMe₃)₂]₃. In the glovebox, KN(SiMe₃)₂ in toluene (60 mL of 0.5 M, 30 mmol) was added to a stirred suspension of LaCl₃ (2.453 g, 10.0 mmol) in THF. After the mixture was stirred for 16 h, the solvent

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Table I. Crystallographic Data for [La(OC(C$_6$H$_5$)$_3$)$_3$]$_2$·3C$_7$H$_8$ (1)

La$_2$C$_{135}$H$_{114}$O$_6$	fw = 2202.33
a = 12.019 (3) Å	space group = $P\bar{1}$ (C_i^1; No. 2)
b = 14.287 (2) Å	T = 183 K
c = 16.375 (3) Å	λ(Mo Kα) = 0.710 73 Å
α = 73.99 (1)°	ρ_{calcd} = 1.34 g cm^{-3}
β = 85.39 (2)°	μ = 0.862 cm^{-1}
γ = 76.07 (2)°	transm coeff = 0.7348–0.8133
V = 2614.6 (8) Å^3	R_F = 3.7%
Z = 1	R_{wF} = 4.9%

Table II. Crystallographic Data for [Ce(OSi(C$_6$H$_5$)$_3$)$_3$]$_2$·2C$_7$H$_8$ (4)

Ce$_2$C$_{122}$H$_{106}$O$_6$Si$_6$	fw = 2116.93
a = 13.766 (2) Å	space group = $P\bar{1}$ (C_i^1, No. 2)
b = 14.376 (1) Å	T = 183 K
c = 14.603 (2) Å	λ(Mo Kα) = 0.710 73 Å
α = 74.34 (1)°	ρ_{calcd} = 1.37 g cm^{-3}
β = 70.45 (1)°	μ = 0.944 cm^{-1}
γ = 75.87 (1)°	transm coeff = 0.8070–0.9347
V = 2573.9 (5) Å^3	R_F = 6.3%
Z = 1	R_{wF} = 7.0%

was removed by rotary evaporation. The resulting solid was extracted with pentane, undissolved solids were separated from the mixture by centrifugation, and the pentane was removed from the solution by rotary evaporation. The resulting solid was sublimed under a dynamic vacuum (110 °C, 10^{-4} Torr) to yield La[N(SiMe$_3$)$_2$]$_3$ (3.230 g, 5.2 mmol, 52%) as a white solid, pure by NMR spectroscopy. Yellow Ce[N(SiMe$_3$)$_2$]$_3$ was prepared similarly.

[La(OCPh$_3$)$_2$(μ-OCPh$_3$)]$_2$ (1). In the glovebox, triphenylmethanol (403 mg, 1.55 mmol) dissolved in toluene (8 mL) was added to a solution of La[N(SiMe$_3$)$_2$]$_3$ (386 mg, 0.62 mmol) in toluene (8 mL), and the solution was mixed. The product precipitated as colorless crystals upon standing overnight. When the crystals were washed with hexane, they turned into a powder (possibly due to the loss of lattice toluene (see below)). The powder was dried by rotary evaporation to give 1 (447 mg, 0.24 mmol, 94%). Anal. Calcd for La$_2$C$_{114}$H$_{90}$O$_6$: La, 15.15; C, 74.67; H, 4.95. Found: La, 15.30; C, 74.38; H, 5.10. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.19 (d, J = 7.2 Hz, 2 H), 7.11 (t, J = 7.3 Hz, 2 H), 6.95 (t, J = 7.8 Hz, 4 H), 6.74 (d, J = 7.2 Hz, 4 H), 6.62 (t, J = 7.3 Hz, 1 H), 6.55 (t, J = 7.5 Hz, 2 H). ^{13}C NMR (CD$_2$Cl$_2$): δ 151.2 (ipso), 147.8 (μ ipso), 130.3 (p), 129.5 (μ p), 128.9 (o), 128.2 (μ o), 127.6 (m), 126.2 (μ m). X-ray-quality crystals could be recovered prior to washing with hexane. Anal. Calcd for the tris(toluene) solvate, La$_2$C$_{135}$H$_{114}$O$_6$: La, 13.17. Found: La, 13.0. IR (Nujol): 1950 br w, 1875 br w, 1595 m, 1485 m, 1145 s, 1090 s, 1050 s, 1025 s, 1000 s, 940 m, 925 m, 895 m, 780 s, 765 m, 750 s, 700 s, 640 s cm^{-1}.

X-ray Data Collection and Structure Determination and Refinement for [La(OCPh$_3$)$_2$(μ-OCPh$_3$)]$_2$ (1). A clear crystal of approximate dimensions 0.33 × 0.37 × 0.40 mm was oil-mounted on a glass fiber and transferred to the Syntex P2$_1$ automated four-circle diffractometer which is equipped with a modified LT-1 low-temperature system. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described methods similar to those of Churchill.[22] Intensity data were collected at 183 K using a θ–2θ scan technique with Mo Kα radiation under the conditions described in Table I. All 12 713 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric space group $P\bar{1}$ (C_i^1; No. 2) was tried first and later confirmed to be correct by successful refinement of the model.

All crystallographic calculations were carried out using either a locally modified version of the UCLA Crystallographic Computing Package[23] or the SHELXTL PLUS program set.[24] The analytical scattering factors for neutral atoms were used throughout the analysis;[25a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[25b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0003(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. The molecule is a dimer which is located about an inversion center at ($^1/_2$, 0, $^1/_2$). There are three toluene solvent molecules per dimer. One of the toluene solvent molecules is ordered and is in a general position. It is related to itself by the inversion center at ($^1/_2$, 0, $^1/_2$). There is a disordered toluene which lies about an inversion center at (1, $^1/_2$, 0). (See the supplementary material for a description of the disordered toluene.) Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. (The eight hydrogen atoms of the disordered toluene were not included.) Refinement of positional and thermal parameters led to convergence with R_F = 3.7%, R_{wF} = 4.9%, and GOF = 1.92 for 667 variables refined against those 10 950 data with $|F_o|$ > 3.0σ($|F_o|$) (R_F = 3.4% and

R_{wF} = 4.8% for those 10 280 data with $|F_o|$ > 6.0σ($|F_o|$)). A final difference-Fourier synthesis showed no significant features, ρ(max) = 0.70 e Å^{-3}.

[Ce(OCPh$_3$)$_2$(μ-OCPh$_3$)]$_2$ (2). In the glovebox, a solution of triphenylmethanol (397 mg, 1.52 mmol) in toluene (8 mL) was added to Ce[N(SiMe$_3$)$_2$]$_3$ (386 mg, 0.62 mmol) in toluene (8 mL) and the solution was mixed. The product precipitated as crystals upon standing overnight. The crystals turned to powder upon washing with hexane. Drying by rotary evaporation yielded 2 as a pale yellow powder (421 mg, 0.23 mmol, 90%). Anal. Calcd for Ce$_2$C$_{114}$H$_{90}$O$_6$: Ce, 15.26. Found: Ce, 15.0. ^{1}H NMR (CD$_2$Cl$_2$): δ 6.82 (br t, J = 6.6 Hz, 1 H), 6.49 (br d, J = 6.2 Hz, 2 H), 4.77 (br, 2 H). ^{13}C NMR (CD$_2$Cl$_2$): δ 156.4, 127.2, 125.5, 125.2. X-ray-quality crystals could be recovered prior to washing with hexane. Anal. Calcd for crystals, Ce$_2$C$_{142}$H$_{122}$O$_6$: Ce, 13.27. Found: Ce, 12.7. IR (Nujol): 1950 br w, 1875 br w, 1815 br w, 1595 m, 1490 m, 1445 m, 1145 s, 1090 m, 1045 s, 1025 s, 1000 s, 935 m, 920 m, 900 m, 775 s, 755 s, 735 s, 700 s, 640 s cm^{-1}.

[La(OSiPh$_3$)$_2$(μ-OSiPh$_3$)]$_2$ (3). In the glovebox, triphenylsilanol (398 mg, 1.44 mmol) dissolved in toluene (8 mL) was added to La[N(SiMe$_3$)$_2$]$_3$ (355 mg, 0.57 mmol) in toluene (8 mL). When the solution was allowed to stand overnight, colorless crystals precipitated. 3 remained crystalline after washing with hexane and drying by rotary evaporation (393 mg, 0.19 mmol, 77%). Anal. Calcd for the crystals, La$_2$C$_{122}$H$_{106}$Si$_6$O$_6$: La, 13.14. Found: La, 12.9. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.37 (d, J = 6.7 Hz, 2 H), δ 7.16 (t, J = 7.4 Hz, 1 H), 6.96 (t, J = 7.5 Hz, 2 H). ^{13}C NMR (CD$_2$Cl$_2$): δ 138.2 (ipso), 135.2 (o), 129.9 (p), 128.5 (m). ^{29}Si NMR (CDCl$_3$): δ −25.3. IR (Nujol): 1965 br w, 1895 br w, 1830 br w, 1775 br w, 1580 m, 1425 s, 1115 s, 1030 w, 1000 w, 970 s, 920 s, 880 s, 745 m, 735 m, 710 sh, 700 s cm^{-1}. MW (isopiestic in CH$_2$Cl$_2$): calcd for La(OSiPh$_3$)$_3$, 965; found, 1010 ± 60.

[Ce(OSiPh$_3$)$_2$(μ-OSiPh$_3$)]$_2$ (4). In the glovebox, triphenylsilanol (403 mg, 1.47 mmol) in toluene (8 mL) was added to Ce[N(SiMe$_3$)$_2$]$_3$ (365 mg, 0.59 mmol) in toluene (8 mL). When the solution was allowed to stand overnight, pale yellow crystals of 4 formed, which were washed with hexanes and dried by rotary evaporation (425 mg, 0.20 mmol, 83%). Anal. Calcd for the crystals, Ce$_2$C$_{122}$H$_{106}$Si$_6$O$_6$: Ce, 13.4. Found: Ce, 13.24. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.49 (br, 2 H), 6.77 (br, 3 H). ^{13}C NMR (CD$_2$Cl$_2$): δ 129.7, 127.2, 127.1. IR (Nujol): 1955 br w, 1895 br w, 1825 br w, 1775 br w, 1600 m, 1425 s, 1115 s, 1035 w, 1000 w, 970 s, 920 s, 875 s, 745 m, 735 m, 710 sh, 700 s cm^{-1}.

X-ray Data Collection and Structure Determination and Refinement for [Ce(OSiPh$_3$)$_2$(μ-OSiPh$_3$)]$_2$ (4). A clear plate of approximate dimensions 0.10 × 0.23 × 0.33 mm was oil-mounted on a glass fiber and handled as described above for 1. Intensity data were collected at 183 K using a θ–2θ scan technique with Mo Kα radiation under the conditions described in Table II. All 7097 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric space group $P\bar{1}$ (C_i^1; No. 2) was tried first and later confirmed to be correct by successful refinement of the model. All crystallographic calculations were carried out as described above for 1. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0005(|F_o|)^2$.

The structure was solved by an automatic Patterson routine (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.05 Å^2. The molecule is a dimer which is located about an inversion center at (0, 1, $^1/_2$). There are two toluene solvent molecules per dimer. Refinement of positional and thermal parameters led to convergence with R_F = 6.3%, R_{wF} = 7.0%, and GOF = 2.22 for 614 variables refined against those 5999 data with $|F_o|$ > 3.0σ($|F_o|$) (R_F = 5.3% and R_{wF} = 6.9% for those 4993 data with $|F_o|$ > 6.0σ($|F_o|$)). A final difference-Fourier synthesis showed no significant features, ρ(max) = 0.56 e Å^{-3}.

La(OCPh$_3$)$_3$(THF)$_x$ (5). In the glovebox, La$_2$(OCPh$_3$)$_6$ (200 mg, 0.11 mmol) was placed in THF (8 mL) and the slurry was heated until the solvent began to boil. Removal of THF by rotary evaporation gave 5 as a white microcrystalline powder in quantitative yield by NMR spec-

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troscopy. Anal. Calcd for LaC$_{65}$H$_{61}$O$_5$: La, 13.09; C, 73.58; H, 5.79. Found: La, 13.35; C, 73.44; H, 5.92. Crystals were grown from THF at −30 °C. Anal. Calcd for the crystals, LaC$_{73}$H$_{76}$O$_7$: La, 11.52. Found: La, 11.5. ^{1}H NMR (C$_6$D$_6$): 7.57 (d, J = 8.2 Hz, 18 H), 7.2–7.0 (multiplet), 3.41 (m, THF, 16 H), 1.22 (m, THF, 16 H). ^{1}H NMR (THF-d_8): δ 7.48 (d, J = 7.2 Hz, 2 H), 6.95 (t, J = 7.1 Hz, 1 H), 6.88 (t, J = 7.3 Hz, 2 H), 3.60 (br, THF), 1.74 (br, THF). ^{13}C NMR (THF-d_8): δ 153.7 (ipso), 129.6 (o), 127.6 (m), 125.7 (p). IR (Nujol): 1955 br w, 1885 br w, 1815 br w, 1595 m, 1485 s, 1445 s, 1300 w, 1195 w, 1145 s, 1090 s, 1060 s, 1035 s, 940 m, 915 m, 895 m, 880 m, 780 s, 760 s, 700 s, 640 s cm^{-1}.

Ce(OCPh$_3$)$_3$(THF)$_x$ (6). In the glovebox, Ce$_2$(OCPh$_3$)$_6$ (200 mg, 0.11 mmol) was placed in THF (8 mL) and the slurry was heated to near boiling. Removal of THF by rotary evaporation gave **6** as a pale yellow microcrystalline powder in quantitative yield. Anal. Calcd for CeC$_{65}$H$_{61}$O$_5$: Ce, 13.19. Found: Ce, 12.8. Crystals were grown from THF at −30 °C. Anal. Calcd for the crystals, CeC$_{73}$H$_{76}$O$_7$: Ce, 11.61. Found: Ce, 11.6. ^{1}H NMR (THF-d_8): δ 7.15–7.30 (br, 3 H), 6.9 (br d, J = 6.6 Hz, 2 H), 3.59 (br, coord THF), 1.75 (br, coord THF). ^{13}C NMR (THF-d_8): δ 162.2 (ipso), 130.3 (o), 128.1 (m), 126.1 (p). IR (Nujol): 1955 br w, 1885 br w, 1815 br w, 1595 m, 1485 s, 1445 s, 1300 w, 1195 w, 1145 s, 1090 s, 1060 s, 1035 s, 940 m, 915 m, 895 m, 880 m, 780 s, 760 s, 700 s, 640 s cm^{-1}.
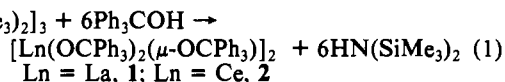
La(OSiPh$_3$)$_3$(THF)$_3$ (7). In the glovebox, La$_2$(OSiPh$_3$)$_6$ (200 mg, 0.09 mmol) was placed in THF (8 mL) and the solution was heated to near boiling while stirring. THF was removed by rotary evaporation, yielding a white microcrystalline powder in quantitative yield by NMR spectroscopy. X-ray-quality crystals were obtained from THF at −30 °C. Anal. Calcd for LaC$_{70}$H$_{77}$Si$_3$O$_7$: La, 11.08. Found: La, 11.0. ^{1}H NMR (C$_6$D$_6$): δ 7.94 (d, J = 6.1 Hz, 18 H, o), 7.19–7.11 (multiplet), 3.55 (multiplet, THF, 16 H), 1.18 (multiplet, THF, 16 H). ^{1}H NMR (THF-d_8): δ 7.66 (d, J = 6.7 Hz, 2 H), 7.19 (t, J = 7.4 Hz, 1 H), 7.07 (t, J = 7.3 Hz, 2 H), 3.60 (br, THF), 1.74 (br, THF). ^{13}C NMR (THF-d_8): δ 142.5 (ipso), 136.0 (o), 128.8 (p), 127.8 (m). ^{29}Si NMR (CDCl$_3$): δ −30.9. IR (Nujol): 1965 br w, 1890 br w, 1830 br w, 1775 br w, 1600 m, 1585 m, 1450 s, 1185 m, 1110 s, 1070 s, 1030 s, 1015 s, 1000 s, 965 br s, 875 br s, 740 s, 705 s cm^{-1}.

Ce(OSiPh$_3$)$_3$(THF)$_3$ (8). In the glovebox, Ce$_2$(OSiPh$_3$)$_6$ (200 mg, 0.09 mmol) was placed in THF (8 mL) and the solution was heated to near boiling while stirring. The THF was then removed by rotary evaporation, yielding a very pale yellow microcrystalline powder in quantitative yield. Anal. Calcd for CeC$_{70}$H$_{77}$Si$_3$O$_7$: Ce, 11.17. Found: Ce, 11.2. The ^{1}H NMR spectrum matched that previously reported.[9] ^{29}Si NMR (CDCl$_3$): δ +15.3.

Results and Discussion

Synthesis. Triphenylmethanol readily reacts in toluene with the amides Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = La, Ce) to form unsolvated dimeric triphenylmethoxide complexes of formula [Ln-(OCPh$_3$)$_2$(μ-OCPh$_3$)]$_2$ (eq 1). When a deficiency of tri-

$$2Ln[N(SiMe_3)_2]_3 + 6Ph_3COH \rightarrow$$
$$[Ln(OCPh_3)_2(\mu\text{-}OCPh_3)]_2 + 6HN(SiMe_3)_2 \quad (1)$$
$$Ln = La, 1; Ln = Ce, 2$$

phenylmethanol is used, the products are readily obtained as crystalline materials in high yield. Neither of these complexes is very soluble in toluene, CH$_2$Cl$_2$, or THF, even in the presence of triphenylmethanol.

An X-ray diffraction study of **1** (see below) showed that the complex crystallized with three toluene molecules of solvation in the lattice. This is consistent with the fact that washing the crystals with hexane converts them into a powder which, by elemental analysis, contains a higher percentage of metal. Complex **2** is isomorphous with **1** (Table I)[26] and is presumed to be isostructural.

Triphenylsiloxide analogues of **1** and **2** were obtained by an analogous synthetic route as shown in eq 2. X-ray diffraction

$$2Ln[N(SiMe_3)_2]_3 + 6Ph_3SiOH \rightarrow$$
$$[Ln(OSiPh_3)_2(\mu\text{-}OSiPh_3)]_2 + 6HN(SiMe_3)_2 \quad (2)$$
$$Ln = La, 3; Ln = Ce, 4$$

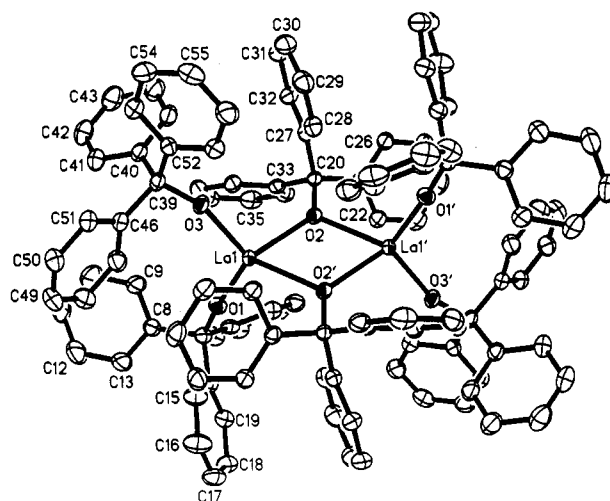studies showed that **3** and **4** were also isomorphous (Table II).[27]

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(26) Complex **2** crystallizes in space group $P\bar{1}$ with a = 12.095 (3) Å, b = 14.198 (4) Å, c = 16.370 (4) Å, α = 74.31 (2)°, β = 85.05 (2)°, γ = 75.27 (2)°, V = 2626 (1) Å^3, and D_{calcd} = 1.34 g cm^{-3} for Z = 1.

(27) Complex **3** crystallizes in space group $P\bar{1}$ with a = 13.786 (5) Å, b = 14.372 (4) Å, c = 14.641 (5) Å, α = 73.56 (3)°, β = 70.50 (3)°, γ = 75.87 (3)°, V = 2686 (2) Å^3, and D_{calcd} = 1.36 g cm^{-3} for Z = 1.

Figure 1. ORTEP diagram of [La(OC(C$_6$H$_5$)$_3$)$_3$]$_2$ (**1**) with the probability ellipsoids drawn at the 40% level. The hydrogen atoms have been omitted for clarity.
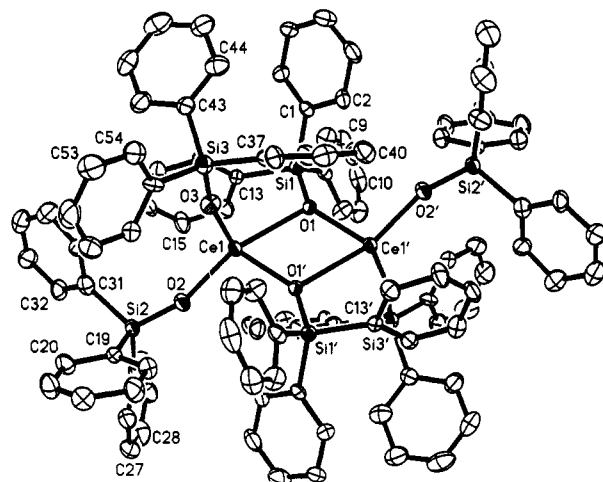

Figure 2. ORTEP diagram of [Ce(OSi(C$_6$H$_5$)$_3$)$_3$]$_2$ (**4**) with the probability ellipsoids drawn at the 40% level. The hydrogen atoms have been omitted for clarity.

The complete X-ray analysis of **4** showed that it contained two toluene molecules of solvation in the lattice. Complexes **3** and **4** are also not very soluble in toluene. However, in contrast to **1** and **2**, they are much more soluble in CH$_2$Cl$_2$ and THF. This contrast in solubility is one significant difference between complexes of OCPh$_3$ ligands and those of OSiPh$_3$ ligands.

Complexes **3** and **4** readily dissolve in THF to form the solvated species Ln(OSiPh$_3$)$_3$(THF)$_3$ (eq 3). These complexes can be

$$[Ln(OSiPh_3)_2(\mu\text{-}OSiPh_3)]_2 \xrightarrow{THF} 2Ln(OSiPh_3)_3(THF)_3 \quad (3)$$
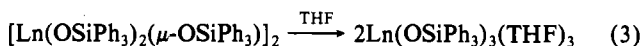
isolated as crystalline materials with one molecule of THF in the lattice, as previously determined by X-ray diffraction studies.[7,9,10] The THF-solvated triphenylmethoxide complexes cannot be obtained analogously due to the insolubility of **1** and **2**. However, when a slurry of **1** or **2** in THF is heated to the boiling point, solvated species do form as shown in eq 4. Elemental analyses

$$[Ln(OCPh_3)_2(\mu\text{-}OCPh_3)]_2 \xrightarrow[\Delta]{THF} 2Ln(OCPh_3)_3(THF)_x \quad (4)$$
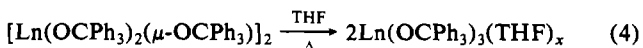
of crystals of these products are consistent with x = 4; i.e., the compounds are analogous to the [Ln(OSiPh$_3$)$_3$(THF)$_3$](THF) species which contain one molecule of THF in the lattice.[7,9,10] Powders containing less THF are obtained when the samples are dried and washed with hexane before elemental analysis. Crystals suitable for X-ray analysis have not yet been obtainable.

Structural Studies. The structures of [La(OCPh$_3$)$_2$(μ-OCPh$_3$)]$_2$ (**1**) and [Ce(OSiPh$_3$)$_2$(μ-OSiPh$_3$)]$_2$ (**4**), determined by X-ray

Table III. Selected Bond Distances (Å) and Angles (deg) for [La(OCPh$_3$)$_2$(μ-OCPh$_3$)]$_2$ (1)

Distances			
La(1)–O(1)	2.175 (2)	La(1)–O(2)	2.389 (2)
La(1)–O(3)	2.184 (3)	La(1)–O(2′)	2.483 (2)
La(1)–C(22′)	3.106 (3)	O(1)–C(1)	1.409 (4)
O(2)–C(20)	1.431 (4)	O(3)–C(39)	1.411 (4)

Angles			
O(1)–La(1)–O(2)	116.1 (1)	O(1)–La(1)–O(3)	116.2 (1)
O(1)–La(1)–O(2′)	111.3 (1)	O(1)–La(1)–C(22′)	116.3 (1)
O(2)–La(1)–O(3)	105.2 (1)	O(2)–La(1)–O(2′)	70.8 (1)
O(2)–La(1)–C(22′)	116.9 (1)	O(3)–La(1)–O(2′)	127.6 (1)
O(3)–La(1)–C(22′)	80.4 (1)	O(2′)–La(1)–C(22′)	59.2 (1)
La(1)–O(2)–La(1′)	109.2 (1)	La(1)–O(1)–C(1)	174.1 (2)
La(1)–O(2)–C(20)	120.9 (1)	La(1)–O(3)–C(39)	160.8 (2)

Table IV. Selected Bond Distances (Å) and Angles (deg) for [Ce(OSiPh$_3$)$_2$(μ-OSiPh$_3$)]$_2$ (4)

Distances			
Ce(1)–O(1)	2.583 (5)	Ce(1)–O(2)	2.185 (6)
Ce(1)–O(3)	2.141 (7)	Ce(1)–O(1′)	2.345 (6)
Ce(1)–C(13)	2.982 (9)	O(1)–Si(1)	1.625 (7)
O(2)–Si(2)	1.618 (6)	O(3)–Si(3)	1.628 (7)

Angles			
O(1)–Ce(1)–O(2)	157.5 (2)	O(1)–Ce(1)–O(3)	100.2 (2)
O(1)–Ce(1)–O(1′)	74.3 (2)	O(1)–Ce(1)–C(13)	58.4 (2)
O(2)–Ce(1)–O(3)	102.2 (2)	O(2)–Ce(1)–O(1′)	135.8 (2)
O(2)–Ce(1)–C(13)	120.5 (2)	O(3)–Ce(1)–O(1′)	98.7 (2)
O(3)–Ce(1)–C(13)	95.1 (2)	O(1′)–Ce(1)–C(13)	132.4 (2)
Ce(1)–O(1)–Ce(1′)	105.7 (2)	Ce(1)–O(1)–Si(1)	109.8 (3)
Ce(1)–O(2)–Si(2)	161.4 (5)	Ce(1)–O(3)–Si(3)	166.5 (4)
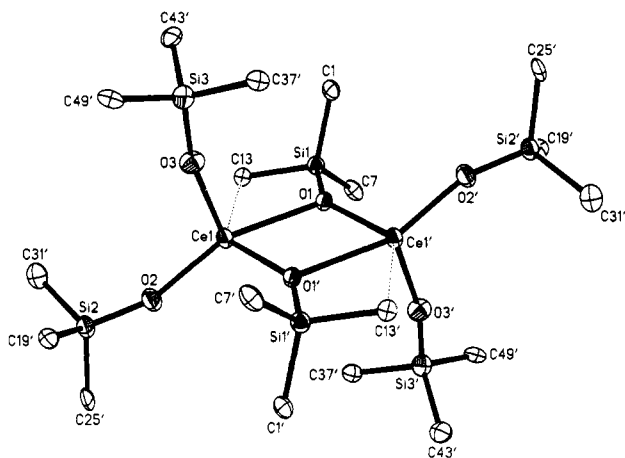
Figure 3. ORTEP diagram of [Ce(OSi(C$_6$H$_5$)$_3$)$_3$]$_2$ (4) with the probability ellipsoids drawn at the 40% level. All hydrogen and arene carbons except the ipso carbons have been omitted for clarity.

diffraction studies, are shown in Figures 1 and 2, respectively. Selected bond distances and angles are given in Tables III and IV. Each of the lanthanide centers in each structure is coordinated by four OEPh$_3$ ligands (E = C, Si), two of which are terminal and two of which are bridging.

In 1, the four oxygen atoms form a distorted tetrahedron about the lanthanum centers. The angle between the plane containing La(1), O(1), and O(3) and the plane containing La(1), O(2), and O(2′) is 75.4° compared to the 90° angle of an undistorted tetrahedron. The overall structure is similar to that of {Ce[OCH-(CMe$_3$)$_2$]$_2$[μ-OCH(CMe$_3$)$_2$]}$_2$ (9),[8] which has an analogous dihedral angle of 84.1°.

The coordination environment around cerium in 4 is not nearly so regular. The disparate angles O(1)–Ce–O(2), 157.5 (2)°, and O(1)–Ce–O(1′), 74.3 (2)°, eliminate regular four-coordinate geometries. As shown in Figure 3, the geometry defined by the four oxygen atoms may be more easily viewed as a distorted square pyramid with O(3) in the axial position and a basal position missing. Interestingly, the ipso carbon of one of the phenyl rings,

Table V. Final Fractional Coordinates for [La(OC(C$_6$H$_5$)$_3$)$_3$]$_2$·3C$_7$H$_8$ (1)

	x	y	z	U(eq),[a] Å^2
La(1)	4970 (1)	786 (1)	3791 (1)	241 (1)
O(1)	4632 (2)	2409 (2)	3487 (1)	325 (8)
O(2)	3839 (2)	2 (2)	4921 (1)	274 (7)
O(3)	4839 (2)	149 (2)	2743 (1)	324 (8)
C(1)	4374 (3)	3451 (2)	3377 (2)	300 (10)
C(2)	3370 (3)	3737 (2)	3967 (2)	324 (11)
C(3)	3166 (3)	3064 (3)	4718 (2)	386 (12)
C(4)	2263 (3)	3308 (3)	5261 (2)	449 (14)
C(5)	1542 (3)	4235 (3)	5064 (3)	481 (15)
C(6)	1738 (3)	4932 (3)	4329 (3)	516 (15)
C(7)	2635 (3)	4686 (3)	3786 (3)	462 (14)
C(8)	4061 (3)	3980 (2)	2438 (2)	352 (11)
C(9)	3392 (3)	3599 (3)	2028 (2)	496 (15)
C(10)	3104 (4)	4040 (4)	1181 (3)	670 (20)
C(11)	3467 (4)	4872 (4)	739 (3)	699 (20)
C(12)	4116 (5)	5272 (4)	1132 (3)	793 (23)
C(13)	4419 (4)	4825 (3)	1983 (3)	622 (18)
C(14)	5456 (3)	3745 (2)	3573 (2)	312 (10)
C(15)	6494 (3)	3314 (3)	3256 (3)	424 (13)
C(16)	7497 (3)	3577 (3)	3374 (3)	533 (16)
C(17)	7460 (3)	4275 (3)	3813 (3)	462 (14)
C(18)	6434 (3)	4711 (3)	4137 (2)	415 (13)
C(19)	5432 (3)	4443 (2)	4014 (2)	354 (11)
C(20)	2672 (3)	−74 (2)	4927 (2)	268 (10)
C(21)	2230 (3)	−251 (2)	5855 (2)	283 (10)
C(22)	2490 (3)	325 (3)	6347 (2)	333 (11)
C(23)	2120 (3)	209 (3)	7185 (2)	408 (13)
C(24)	1469 (3)	−478 (3)	7541 (2)	461 (14)
C(25)	1186 (3)	−1045 (3)	7062 (2)	433 (13)
C(26)	1580 (3)	−943 (3)	6223 (2)	358 (12)
C(27)	2596 (3)	−931 (2)	4546 (2)	299 (10)
C(28)	3537 (3)	−1706 (2)	4520 (2)	364 (12)
C(29)	3477 (4)	−2459 (3)	4155 (2)	468 (14)
C(30)	2452 (4)	−2458 (3)	3822 (3)	514 (16)
C(31)	1510 (3)	−1704 (3)	3851 (2)	466 (15)
C(32)	1568 (3)	−943 (3)	4215 (2)	377 (12)
C(33)	1965 (3)	915 (2)	4369 (2)	291 (10)
C(34)	1097 (3)	1568 (3)	4681 (2)	372 (12)
C(35)	487 (3)	2446 (3)	4130 (3)	475 (14)
C(36)	737 (3)	2658 (3)	3271 (3)	514 (15)
C(37)	1588 (3)	2003 (3)	2955 (2)	447 (13)
C(38)	2202 (3)	1143 (3)	3499 (2)	361 (12)
C(39)	4881 (3)	25 (2)	1915 (2)	302 (10)
C(40)	3649 (3)	372 (3)	1573 (2)	334 (11)
C(41)	3308 (3)	1163 (3)	868 (2)	410 (12)
C(42)	2171 (3)	1434 (3)	602 (2)	497 (15)
C(43)	1375 (3)	938 (3)	1038 (3)	558 (17)
C(44)	1710 (3)	139 (3)	1749 (3)	519 (16)
C(45)	2833 (3)	−141 (3)	2005 (2)	417 (13)
C(46)	5673 (3)	664 (2)	1370 (2)	325 (11)
C(47)	5559 (3)	1628 (3)	1457 (2)	428 (13)
C(48)	6242 (4)	2243 (3)	992 (3)	522 (16)
C(49)	7055 (4)	1918 (3)	428 (2)	540 (16)
C(50)	7179 (3)	960 (3)	336 (2)	470 (14)
C(51)	6492 (3)	347 (3)	797 (2)	366 (12)
C(52)	5309 (3)	−1089 (2)	1941 (2)	309 (11)
C(53)	5152 (3)	−1441 (3)	1256 (2)	414 (13)
C(54)	5515 (4)	−2450 (3)	1287 (3)	506 (16)
C(55)	6036 (4)	−3125 (3)	2004 (3)	503 (15)
C(56)	6191 (4)	−2788 (3)	2685 (3)	497 (15)
C(57)	5826 (3)	−1777 (3)	2657 (2)	396 (12)
C(58)	90 (8)	6457 (6)	2012 (4)	1074 (37)
C(59)	1139 (5)	6729 (5)	1852 (4)	913 (29)
C(60)	1200 (6)	7683 (7)	1539 (4)	1022 (36)
C(61)	281 (9)	8379 (6)	1297 (5)	1286 (46)
C(62)	−711 (8)	8206 (7)	1382 (5)	1180 (43)
C(63)	−891 (6)	7286 (8)	1774 (5)	1163 (45)
C(64)	−94 (12)	5504 (9)	2357 (7)	3097 (133)
C(65)	9483 (16)	3458 (11)	596 (15)	1268 (98)
C(66)	8574 (12)	3684 (9)	1111 (9)	992 (62)
C(67)	8168 (13)	4617 (10)	1193 (8)	973 (61)
C(68)	8668 (13)	5392 (9)	721 (7)	902 (57)
C(69)	9615 (11)	5202 (12)	210 (9)	878 (63)
C(70)	9913 (8)	4093 (8)	214 (7)	1324 (54)

[a] Equivalent isotropic U defined as one-third of the trace of the or-

Table VI. Final Fractional Coordinates for [Ce(OSi(C₆H₅)₃)₃]₂·2C₇H₈ (4)

	x	y	z	$U(\text{eq})$,^{a} Å^2
Ce(1)	-193 (1)	8643 (1)	5713 (1)	241 (2)
Si(1)	789 (2)	9168 (2)	3121 (2)	250 (11)
Si(2)	-227 (2)	6821 (2)	8145 (2)	288 (11)
Si(3)	-2929 (2)	8891 (2)	5615 (2)	324 (12)
O(1)	411 (4)	9792 (4)	3983 (4)	231 (25)
O(2)	-91 (5)	7711 (4)	7162 (4)	337 (29)
O(3)	-1768 (5)	8649 (5)	5770 (5)	348 (29)
C(1)	-95 (7)	9492 (7)	2298 (6)	291 (42)
C(2)	-597 (7)	10442 (7)	2057 (7)	339 (44)
C(3)	-1206 (9)	10693 (9)	1382 (8)	505 (55)
C(4)	-1304 (9)	9990 (9)	978 (8)	549 (61)
C(5)	-775 (9)	9029 (8)	1207 (7)	457 (54)
C(6)	-187 (8)	8790 (8)	1855 (7)	392 (48)
C(7)	2140 (7)	9236 (7)	2315 (7)	318 (43)
C(8)	2480 (8)	8972 (8)	1399 (7)	429 (50)
C(9)	3525 (9)	8946 (8)	808 (8)	495 (53)
C(10)	4220 (9)	9223 (8)	1118 (9)	541 (55)
C(11)	3926 (8)	9513 (8)	1978 (9)	504 (56)
C(12)	2879 (8)	9542 (8)	2594 (8)	416 (49)
C(13)	777 (7)	7862 (6)	3869 (6)	203 (37)
C(14)	1639 (8)	7370 (7)	4225 (7)	388 (47)
C(15)	1611 (9)	6459 (7)	4917 (8)	448 (51)
C(16)	728 (9)	6056 (8)	5278 (7)	443 (51)
C(17)	-166 (8)	6522 (7)	4909 (7)	394 (48)
C(18)	-108 (8)	7409 (7)	4226 (7)	324 (44)
C(19)	-1389 (7)	7174 (7)	9197 (7)	293 (43)
C(20)	-1887 (8)	6467 (8)	9955 (7)	404 (48)
C(21)	-2701 (8)	6703 (8)	10718 (8)	501 (55)
C(22)	-3102 (8)	7656 (8)	10761 (8)	428 (50)
C(23)	-2633 (9)	8390 (8)	10026 (8)	483 (54)
C(24)	-1763 (7)	8128 (7)	9259 (7)	345 (45)
C(25)	999 (8)	6483 (7)	8580 (7)	337 (45)
C(26)	998 (9)	6557 (7)	9476 (8)	432 (51)
C(27)	1944 (10)	6302 (8)	9736 (9)	549 (61)
C(28)	2847 (10)	6002 (9)	9069 (11)	632 (67)
C(29)	2871 (9)	5920 (9)	8170 (9)	557 (59)
C(30)	1953 (8)	6141 (8)	7915 (8)	433 (50)
C(31)	-473 (8)	5711 (7)	7862 (7)	352 (45)
C(32)	159 (9)	4781 (7)	7976 (7)	411 (49)
C(33)	-91 (9)	4024 (8)	7762 (8)	448 (53)
C(34)	-887 (9)	4125 (8)	7407 (8)	495 (55)
C(35)	-1539 (9)	5062 (8)	7255 (8)	513 (57)
C(36)	-1327 (8)	5823 (8)	7533 (8)	395 (49)
C(37)	-3225 (7)	10256 (7)	5130 (7)	315 (44)
C(38)	-4176 (8)	10850 (7)	5508 (7)	376 (47)
C(39)	-4290 (8)	11856 (8)	5150 (8)	421 (51)
C(40)	-3519 (8)	12297 (8)	4397 (8)	426 (50)
C(41)	-2580 (8)	11716 (8)	4040 (8)	435 (52)
C(42)	-2457 (8)	10728 (7)	4377 (7)	362 (46)
C(43)	-2960 (7)	8245 (8)	4693 (7)	342 (45)
C(44)	-2974 (8)	8706 (9)	3701 (8)	473 (54)
C(45)	-2927 (9)	8182 (10)	3025 (9)	542 (60)
C(46)	-2838 (9)	7172 (11)	3306 (10)	639 (69)
C(47)	-2772 (9)	6683 (9)	4268 (10)	536 (60)
C(48)	-2831 (8)	7209 (8)	4933 (9)	477 (55)
C(49)	-3908 (8)	8455 (7)	6822 (9)	319 (45)
C(50)	-3634 (9)	8094 (7)	7707 (9)	413 (50)
C(51)	-4330 (11)	7736 (9)	8590 (8)	624 (67)
C(52)	-5346 (11)	7741 (9)	8585 (9)	663 (68)
C(53)	-5640 (9)	8101 (10)	7759 (9)	606 (63)
C(54)	-4915 (9)	8462 (8)	6863 (8)	507 (56)
C(55)	4286 (11)	5474 (19)	2121 (14)	1079 (109)
C(56)	4347 (10)	4696 (13)	2845 (15)	948 (84)
C(57)	4548 (13)	4744 (17)	3668 (17)	1222 (118)
C(58)	4633 (17)	5713 (22)	3734 (15)	1276 (147)
C(59)	4557 (15)	6395 (18)	3048 (22)	1377 (151)
C(60)	4329 (13)	6364 (14)	2156 (18)	1046 (109)
C(61)	4130 (14)	5436 (20)	1212 (12)	2133 (213)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

C(13), is in the position of the missing basal ligand in this square-pyramidal perspective.

The significance of the location of the ipso carbon with respect to cerium can be evaluated by examining metal carbon distances

in other lanthanide and actinide arene complexes. The M–C-(arene) average distances in $(\eta^6\text{-}C_6Me_6)Sm(\eta^2\text{-}AlCl_4)_3$,[28] $(\eta^6\text{-}C_6H_4Me_2)Sm(\eta^2\text{-}AlCl_4)_3$,[29] $(\eta^6\text{-}C_6H_6)Sm(\eta^2\text{-}AlCl_4)_3$,[30] and $(\eta^6\text{-}C_6H_6)Nd(\eta^2\text{-}AlCl_4)_3$[30] are 2.89 (5), 2.89 (4), 2.91 (6), and 2.93 (3) Å, respectively. Considering the differences in metallic radii,[31] the 2.982 (9) Å Ce–C(13) distance is within 0.04 Å of these M–C(arene) distances. The Ce–C(13) distance is also within the 2.82 (1)–3.02 (1) Å range of U(III)–C(arene) distances in [U(OC₆H₃ᵢPr₂-2,6)₃]₂,[32] a complex which is dimeric due to metal–arene interactions (Ce(III) is only 0.015 Å smaller than U(III)).[31] These metrical data suggest that the Ce–C(13) distance is appropriate for an interaction between cerium and the aryl rings of the OSiPh₃ ligand. In contrast, an analogously short metal–ring distance is not found in **1**. The closest La–C(arene) distance in **1** involves the ortho carbon C(22) (Figure 1). The observed 3.106 (3) Å La–C distance is equivalent to a 3.084 Å Ce–C distance,[31] which is beyond the range of previously observed lanthanide–arene carbon distances.

The La–O distances in **1** involving terminal alkoxide ligands, 2.175 (2) and 2.184 (3) Å, are shorter than the two La–O distances involving bridging alkoxides, 2.389 (2) and 2.483 (2) Å, as is typical for yttrium and lanthanide alkoxides. These distances are similar to those in **4**, which has 2.141 (7) and 2.185 (6) Å terminal distances and 2.345 (6) and 2.583 (5) Å bridging distances, except that the asymmetry in the bridging distances in **4** is greater. For comparison, in **9** the bridging alkoxide distances are 2.363 (3) and 2.422 (2) Å and the terminal bond lengths are 2.142 (2) and 2.152 (3) Å. The long 2.583 (5) Å Ce(1)–O(1) distance in **4** is the longest M–O bond length among the three structures and is located at the site where the close cerium–arene distance is found.

All three complexes have remarkably similar O–M–O and M–O–M angles within the bridging unit: the O–M–O angles are 70.8 (1), 74.3 (2), and 74.3 (1)° and the M–O–M angles are 109.2 (1), 105.7 (2), and 105.7 (1)° for **1**, **4**, and **9**, respectively. The M–O–E angles of the terminal ligands are all within the 160–169° range except for the 174.1 (2)° angle of La–O(1)–C(1). A final point of structural comparison involves the O–Si versus O–C distances in the ligands. The O–Si distances in **4** average 1.62 Å compared to the 1.42 Å average C–O distances in **1**. This difference may provide added flexibility to the ligand set, which allows the metal–arene ring interaction to occur in **4**.

Differences between OCPh₃ and OSiPh₃ metal complexes have been noticed previously with cobalt.[33] Hence, the reaction of {Co[N(SiMe₃)₂]₂}₂ with HOCPh₃ in THF formed a monomer, Co(OCPh₃)₂(THF)₂, whereas HOSiPh₃ formed a THF-solvated dimer, [Co(OSiPh₃)₂(THF)]₂. The OCPh₃ complex could be converted to a dimer in toluene, but in this case, an unsolvated dimer was isolated, [Co(OCPh₃)₂]₂. In these complexes, the O–Si bonds were again approximately 0.2 Å larger than the O–C bonds, and this may provide the flexibility to incorporate THF into the dimeric OSiPh₃ complex.

Differences between the unsolvated OCPh₃ and OSiPh₃ complexes can also be observed in solution. ¹H, ¹³C, and ²⁹Si NMR spectroscopy and an isopiestic molecular weight determination of **3** are consistent with the presence of a monomer in CD₂Cl₂ solution. However, the ¹H and ¹³C NMR spectra of **1** show two types of phenyl resonances, consistent with terminal and bridging groups in a dimer.

Conclusion

The results of this study show that the OCPh₃ and OSiPh₃ ligands can form analogous solvated and unsolvated lanthanide complexes. Comparison of the unsolvated dimers with **9** shows that these ligands are comparable in size to OCH(CMe₃)₂. The

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differences between OCPh₃ and OSiPh₃ may arise primarily from the differing O–C and O–Si distances. With La and Ce, the longer distance in the OSiPh₃ complexes provides flexibility to the ligand set, which may allow metal–(arene ring) interactions to occur. Since this less congested ligand set may also allow solvents to displace the metal–arene interaction and form solvated complexes, the enhanced solubility of **3** and **4** over **1** and **2** may also result from the longer O–Si distance. Hence, OCPh₃ ligands may be advantageous when reduced solubility is required and vice versa for OSiPh₃.

Note Added in Proof. A note on the structure of the yttrium analogue of **3** and **4** has recently appeared: Coan, P. S.; McGeary, M. J.; Lobkovsky, E. B.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 3570–3572.

Chemistry of (Octaethylporphyrinato)lutetium and -yttrium Complexes: Synthesis and Reactivity of (OEP)MX Derivatives and the Selective Activation of O₂ by (OEP)Y(μ-Me)₂AlMe₂

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Reaction of ML₃ (M = Lu, Y; L = CH(SiMe₃)₂, O-2,6-C₆H₃ᵗBu₂) with octaethylporphyrin (OEPH₂) affords (OEP)ML complexes [M = Lu (**1a**), Y (**1b**), L = CH(SiMe₃)₂; M = Lu (**2a**), Y (**2b**), L = O-2,6-C₆H₃ᵗBu₂]. The crystal structure of (OEP)LuCH(SiMe₃)₂ (**1a**) shows a highly dished porphyrin skeleton with the square-pyramidal, five-coordinate lutetium atom 0.918 Å out of the N₄ plane of the porphyrin ligand. Crystal data: monoclinic, *P*2₁/*c*, *a* = 14.879 (6) Å, *b* = 20.644 (10) Å, *c* = 14.161 (5) Å, *β* = 96.38 (3)°, *Z* = 4, *T* = 200 K, and *R* = 0.045 (4098 reflections with *I* ≥ 2*σ*(*I*)). Alkyl species **1** undergo facile protonolysis with HO-2,6-C₆H₃ᵗBu₂, HCCᵗBu, or H₂O to give monomeric alkoxide, dimeric alkynyl, and dimeric hydroxide species [(OEP)MX]ₙ (*n* = 1, 2) [M = Lu, Y; X = O-2,6-C₆H₃ᵗBu₂ (**2a,b**), CCᵗBu (**3a,b**), OH (**4a,b**)], respectively. Titration of (OEP)M(μ-OH)₂M(OEP) (**4**) with H₂O affords water adducts (OEP)M(μ-OH)₂(H₂O)ₓM(OEP). A synthetically more convenient route to **1** is via reaction of **2** with LiCH(SiMe₃)₂. In marked contrast to the facile hydrogenation of Ln(C₅Me₅)₂CH(SiMe₃)₂, alkyl species **1** do not undergo σ-bond metathesis with H₂ (20 atm, 25 °C, C₆D₁₂). Reaction of (OEP)YOC₆H₃ᵗBu₂ (**2b**) with MeLi (2 equiv) in ether affords ether-insoluble (OEP)Y(μ-Me)₂Li(OEt₂) (**5**). Treatment with AlMe₃ (2 equiv) in hexane yields monomeric, highly fluxional (OEP)Y(μ-Me)₂AlMe₂ (**6**), which selectively activates O₂ to afford (OEP)Y(μ-OMe)₂AlMe₂ (**7**). Comparison of the reactivity of these species, particularly **1** and **6**, with their C₅H₅ and C₅Me₅ counterparts is described. ¹⁷O NMR data on labeled **4a**, **4b**, and **7** are presented and discussed.

Introduction

Porphyrin complexes of the late transition metals have attracted considerable attention as models for cytochrome P450 and as olefin oxidation catalysts.¹ In contrast, the chemistry of aluminum,² early transition metal,³ lanthanide,⁴ or actinide⁵ species supported by a porphyrin ligand has been less well studied. Despite the range of metals for which porphyrin complexes are known, there are no examples which possess a lanthanide–carbon σ bond. Previous preparations of porphyrin complexes have frequently employed synthetic methods seemingly incompatible with the preparation of very hydrolytically sensitive species, involving heating the components in an imidazole melt or refluxing in 1,2,4-trichlorobenzene, followed by chromatography on alumina.

As part of our investigation of different ligand types capable of supporting lanthanide *alkyl* complexes, we rationalized that a porphyrin ligand would provide an alternative and acceptable coordination environment in organolanthanide chemistry and that the pendant porphyrin alkyl groups would provide sufficient steric protection and hydrocarbon solubility. The constraint of other attendant ligands to a mutually trans geometry by the porphyrin

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Table I. Crystal Data and Data Collection Parameters for **1a**ᵃ

chem formula	C₄₃H₆₃LuN₄Si₂
mol wt	867.12
space group	*P*2₁/*c* (No. 14)
a, Å	14.879 (6)
b, Å	20.644 (10)
c, Å	14.161 (5)
β, deg	96.38 (3)
V, Å³	4323 (3)
Z	4
*D*calcd, g cm⁻³	1.33
μ(Mo K*α*) cm⁻¹	23.7
λ, Å	0.71069
T, K	200
no. of obsd refcns, *I* > 2*σ*(*I*)	4098
R	0.045 (0.071 using all 5675 unique data)
*R*w	0.043 (0.051 using all 5675 unique data)
goodness of fit; no. of params	1.154; 464

ᵃ $R = \sum|\Delta|/\sum|F_o|$; $R_w = [\sum w\Delta^2/\sum wF_o^2]^{1/2}$; $S = [\sum w\Delta^2/(NO - NV)]^{1/2}$; $\Delta = F_o - F_c$.

framework and the corresponding inhibition of cis coordination necessary⁶ for β-hydride elimination and olefin insertion reactions⁷