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Synthesis, structure, and reactivity of cyclopentadienyl-free trimethylsilylmethyl yttrium di-tert-butylphenoxide complexes[1]

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Abstract

The chemistry of yttrium with the trimethylsilylmethyl/2,6-di-tert-butyl-phenoxide ligand combination has been examined. The anionic dialkyl–diaryloxide complexes, $\{(Me_3SiCH_2)_2Ln(OC_6H_3{}^tBu_2\text{-}2,6)_2\}^-$ (Ln = Y, Lu), were prepared and their reactivity and that of the neutral dialkyl–aryloxide complex $(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2$, **1**, has been studied and compared with cyclopentadienyl-containing organolanthanide complexes. $\{(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)_2\}\{[(THF)_3Li]_2Cl\}$, **2**, was prepared from the reaction of YCl_3 with two equivalents of $LiCH_2SiMe_3$ and two equivalents of $LiOC_6H_3{}^tBu_2\text{-}2,6$ and crystallized with an unusual cation which can be viewed as a LiCl adduct of $[Li(THF)_x]^+$. $[(Me_3SiCH_2)_2Lu(OC_6H_3{}^tBu_2\text{-}2,6)_2][Li(THF)_4](THF)_2$, **3**, was prepared analogously and crystallized with a conventional cation. Both **2** and **3** have distorted tetrahedral coordination geometries around the metals. Ring-opening polymerization of ε-caprolactone was observed for **1**–**3**, but only complex **1** was found to polymerize ethylene. NMR and mass spectroscopic analyses show that the more reactive complex **1** also exhibits metallation reactivity with pyridine, toluene, phenylacetylene, CH_3CN, Me_2CHCN, PhCN, and $PhCH_2CN$ and insertion chemistry with Me_3CNC, CO, CO_2, PhNCO, and PhNCS. However, isolation of the organometallic products has been difficult due to the complexity of the reaction mixtures. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cyclopentadienyl-free; Trimethylsilylmethyl; Yttrium; Di-tert-butylphenoxide; Polymerization; Metallation

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1. Introduction

Currently, there is considerable interest [1,2] in developing the chemistry of organometallic yttrium and lanthanide alkyl and hydride complexes involving solubilizing and stabilizing ancillary ligands other than the commonly used cyclopentadienyl ligands [3–6]. Many types of alternative ancillary ligand systems have been studied, including alkoxides and aryloxides [7–14], cyclooctatetraenides [15], carboranes [16–18], polypyrazolylborates [19–23], amides [24,25], phosphides [26,27], porphyrins [28], aza-crowns [29], benzamidinates [30,31], and alkoxyamides [32,33]. Although alkoxide and aryloxide ligands are attractive because they offer strong metal oxygen bonds which can stabilize complexes of these electropositive metals, relatively few alkyl complexes are known in which the only supporting co-ligands are OR or OAr groups [34–38]. We are aware of only six examples in this class which have been characterized by X-ray crystallography: $\{(Me_3SiCH_2)_x(Me_3CO)_{1-x}Y(\mu\text{-}OCMe_3)_4[Li(THF)]_4(\mu_4\text{-}Cl)\}[Y(CH_2SiMe_3)_4]$ [34], $(Me_3SiCH_2)Y[(\mu\text{-}CH_2)_2SiMe_2][(\mu\text{-}OCMe_3)Li(THF)_2]_2$ [35], $[(Me_3SiCH_2)_2\text{-}Sm(OC_6H_3^iPr_2\text{-}2,6)_3][Li(THF)]_2$ [36], $[(Me_3Si)_2CH]La[\mu\text{-}(OC_6H_2^tBu_2\text{-}4,6)_2]$ [37], $\{[(Me_3Si)_2CH]_2Y(\mu OCMe_3)_2\}\{Li(THF)\}$ [38], and $(Me_3SiCH_2)_2Y(OC_6\text{-}H_3{}^tBu_2\text{-}2,6)(THF)_2$ [38]. Since $(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2$, **1**, can be synthesized by a straightforward reagent-efficient route [38] (Eq. (1)), we have chosen to examine its reactivity which includes polymerization, metallation, and insertion reactions.

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[1] Dedicated to Professor Akira Nakamura, whose broad contributions to organometallic chemistry have greatly enriched the field.

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$$YCl_3 + 2LiCH_2SiMe_3 + LiOC_6H_3{}^tBu_2\text{-}2,6 \xrightarrow{THF} (Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2 \quad (1)$$

Since this $(Me_3SiCH_2)/(OC_6H_3{}^tBu_2\text{-}2,6)$ ligand combination provides a reactive complex, we have also expanded on the synthetic chemistry of this ligand set. The preparation of an anionic 'ate' complex was examined since this type of species is common in this area of chemistry ([11]c, [34–36,38]) and such species could be accessible from **1**. Accordingly, the dialkyldiaryloxide yttrium complex $\{(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)_2\}^-$ was synthesized. We also examined the lutetium analog, $[(Me_3SiCH_2)_2Lu(OC_6H_3{}^tBu_2\text{-}2,6)_2]^-$, to verify the usual assumption that yttrium and the late lanthanides are similar and to determine if this heavier metal would be advantageous in the characterization of reaction products [39]. The reaction chemistry of these 'ate' complexes has also been examined and is compared with that of **1**.

2. Experimental section

All of the chemistry described below was performed under nitrogen with rigorous exclusion of air and water using standard Schlenk, vacuum line and glove box techniques. Solvents, including C_6D_6 and THF-d_8 (Cambridge Isotopes), were dried and distilled [40] and YCl_3 and $LuCl_3$ (Rhône-Poulenc) were dried [41] as described previously. $(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2$, **1**, was prepared as previously described [38]. Ethylene, carbon monoxide, and hydrogen (research grade, Matheson) were used as purchased. Carbon dioxide (99.999%, Matheson) was subjected to three freeze–pump–thaw cycles before use. Pyridine (Acros) was dried and distiled from CaH_2 before use. Toluene-d_8 (Cambridge Isotopes), phenylacetylene, acetonitrile, iso-propylnitrile, benzonitrile, phenylacetonitrile, tert-butyl-iso-nitrile, phenyl iso-cyanate, and phenyl iso-thiocyanate (Acros) were dried over 4Å molecular sieves and vacuum distiled before use. ^1H- and ^{13}C-NMR spectra were recorded on General Electric GN500, Omega 500, and Bruker DRX-400 spectrometers. Infrared spectra were obtained on Perkin Elmer 1600 FTIR and MIDAC Prospect FTIR spectrophotometers. GC-MS data were obtained on a Micromass Autospec instrument running in the EI mode. Carbon and hydrogen analytical data were obtained on a Carlo Erba EA1108 and metal analysis was obtained by complexometric titration [42].

*2.1. Synthesis of $\{(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)_2\}$ $\{[(THF)_3Li]_2Cl\}$, **2***

In a glove box, YCl_3 (0.156 g, 0.797 mmol) was added to THF (15 ml) and stirred. After 5 min, $LiCH_2SiMe_3$ (0.150 g 1.593 mmol) was added to form a slightly cloudy, pale yellow solution. After another 5 min, $LiOC_6H_3{}^tBu_2\text{-}2,6$ (0.338 g, 1.593 mmol) was added and the mixture was stirred for 12 h. THF was removed from the slightly cloudy, pale yellow solution by rotary evaporation and the resulting oily solid was extracted with toluene (10 ml). The toluene soluble fraction was separated by centrifugation from an off-white powder and was dried to a white solid (0.010 g) which was discarded. The off-white powder was extracted with THF (10 ml) producing a pale yellow solution and a white powder. The pale yellow solution was dried by rotary evaporation to an off-white powder (0.703 g, 85%), which analyzed for $\{(Me_3SiCH_2)_2Y\text{-}(OC_6H_3{}^tBu_2\text{-}2,6)_2\}\{[(THF)_2Li]_2Cl\}(LiCl)$, i.e. the partially desolvated LiCl adduct of **2**, see below. Anal Calc. for $C_{52}H_{96}YO_6Si_2Li_3Cl_2$: C, 58.08; H, 9.00; Y, 8.27. Found: C, 58.6; H, 9.0; Y, 8.5. Colorless crystals of $\{(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)_2\}\{[(THF)_3Li]_2Cl\}$, **2**, suitable for X-ray diffraction were grown from a concentrated THF solution at −38°C over a period of several weeks. ^1H-NMR (THF-d_8) δ 6.94 (d, 4H, m-$OC_6H'_3$ Bu_2-2,6), 6.29 (t, 2H, p-$OC_6H_3{}^tBu_2$-2,6), 1.46 (s, 36H, $OC_6H_3{}^tBu_2$-2,6), −0.09 (s, 18H, $CH_2Si(CH_3)_3$), −0.57 (d, 4H, CH_2SiMe_3, $J_{Y-C-H} = 3.7$ Hz). ^{13}C-NMR (THF-d_8) δ 164.2, 138.2, 124.5, 114.7 (phenoxide), 68.2 (THP), 35.6 ($OC_6H_3{}^tBu_2$-2,6), 32.1 ($CH_2Si(CH_3)_3$), 26.3 (THF), 4.9 ($CH_2Si(CH_3)_3$). IR (KBr): 3072 w, 3053 w, 2952 s, 2886 m, 1582 w, 1459 w, 1410 s, 1384 m, 1355 w, 1263 s, 1235 w, 1199 w, 1104 w, 1044 s, 887 m, 861 s, 820 m, 749 m, 655 w cm^{-1}.

*2.2. Synthesis of $[(Me_3SiCH_2)_2Lu(OC_6H_3{}^tBu_2\text{-}2,6)_2][Li(THF)_4](THF)_2$, **3***

In a glove box, $LuCl_3$ (0.149 g, 0.531 mmol) was added to THF (15 ml) and stirred. After 5 min, $LiCH_2SiMe_3$ (0.100 g, 1.062 mmol) was added to form a slightly cloudy, pale yellow solution. After another 5 min, $LiOC_6H_3{}^tBu_2\text{-}2,6$ (0.225, 1.062 mmol) was added and the mixture was stirred for 12 h. THF was removed from the slightly cloudy, pale yellow solution by rotary evaporation, and the resulting oily solid was extracted with toluene (10 ml). The toluene soluble fraction was separated by centrifugation from an off-white powder and was dried to a white solid (0.278 g, 50%), which analyzed for $[(Me_3SiCH_2)_2Lu(OC_6H_3{}^tBu_2\text{-}2,6)_2][Li(THF)_4](LiCl)$, the partially desolvated LiCl adduct of **3**, see below. Anal. Calc. for $C_{52}H_{96}LuO_6Si_2Li_2Cl$: C, 56.89; H, 8.81; Lu, 15.94. Found: C, 56.9; H, 8.4; Lu, 16.5. Colorless crystals of $[(Me_3SiCH_2)_2Lu(OC_6H_3{}^tBu_2\text{-}2,6)_2][Li(THF)_4](THF)_2$, **3**, suitable for X-ray diffraction were grown from a concentrated toluene–THF solution at −38°C over a period of several weeks. ^1H-NMR (THF-d_8) δ 6.93 (d, 4H, m-$OC_6H_3{}^tBu_2$-2,6), 6.28 (t, 2H, p-$OC_6H_3{}^tBu_2$-2,6), 1.45 (s, 36H,

$OC_6H_3{}^tBu_2$-2,6), −0.09 (s, 18H, $CH_2Si(CH_3)_3$), −0.73 (s, 4H, CH_2SiMe_3). ^{13}C-NMR (THF-d_8) δ 138.4, 124.5, 114.7 (phenoxide), 68.2 (THF), 39.2, 35.6 ($OC_6H_3{}^tBu_2$-2,6), 32.1 ($CH_2Si(CH_3)_3$), 26.4 (THF), 5.1 ($CH_2Si(CH_3)_3$). IR (KBr): 3073 w, 3053 w, 2950 s, 2886 m, 1583 w, 1459 w, 1410 s, 1384 m, 1356 w, 1265 s, 1235 w, 1200 w, 1104 w, 1042 s, 867 s, 820 m, 749 m, 657 w cm^{-1}.

2.3. Reactions with ε-caprolactone

In three separate reactions, ε-caprolactone (ca. 2 ml, 18 mmol) was added to solutions of 0.025 g of **1** (0.041 mmol) in toluene (1 ml), **2** (0.022 mmol) in THF (1 ml), and **3** (0.021 mmol) in toluene (1 ml). The solutions were mixed, and rapidly (1–5 min) produced gelatinous solids which hardened over 1 h to yellow poly(ε-caprolactone).

2.4. Reaction of 1 with ethylene

Complex **1** (0.100 g, 0.163 mmol) was stirred under ethylene (70 psi) in toluene (10 ml). After 18 h, brown–white solids were present in the reaction vessel. Methanol (15 ml) was added to the reaction mixture followed by H_2O (25 ml). Filtration and drying of the off-white solids yielded 0.130 g of material insoluble in hot toluene.

2.5. NMR tube reactions

For reactions with liquid substrates, **1** (0.015–0.110 mmol) was dissolved in a mixture of THF-d_8 (ten drops) and C_6D_6 (1 ml) in an NMR tube, and two equivalents of substrate were added via a microsyringe. The NMR tubes were evacuated to the vapor pressure of the solvent and sealed. The ^{1}H-NMR spectra were taken after 30 min and were monitored for several weeks.

For reactions with gaseous substrates, **1** (0.05 mmol) was dissolved in a mixture of THF-d_8 (ten drops) and C_6D_6 (1 ml) in an NMR tube modified with a gas-inlet; greaseless stopcock valve. The NMR tubes were attached to a vacuum line, degassed by three freeze–pump–thaw cycles, and the substrate was admitted to a pressure of 1 atm. The tubes were sealed and the ^{1}H-NMR spectra were taken after 30 min and were monitored for several weeks.

2.6. Preparative scale reactions

For reactions with liquid substrates, **1** (0.163–0.366 mmol) was dissolved in a mixture of toluene (10 ml) and THF (1 ml). Two equivalents of substrate were added via a microsyringe and the reactions were stirred for up to 12 h. Volatiles were removed by rotary evaporation. The reaction products were extracted with toluene and THF and analyzed by NMR and IR spectroscopy. Since the spectroscopic data indicated mixtures of products, elemental analysis on single pure products was not obtainable.

For reactions with gaseous substrates, **1** (0.330–0.489 mmol) was dissolved in a mixture of toluene (10 ml) and THF (1 ml) in a 50 ml round bottom flask equipped with an adapter with a greaseless stopcock. The flask was attached to a vacuum line, degassed, and the substrate was admitted to a pressure of 1 atm. After the solution was stirred for up to 12 h, the flask was returned to the glove box and the solution was worked up as described above.

2.7. X-ray data collection, structure determination, and refinement for $\{(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)_2\}\{[(THF)_3Li]_2Cl\}$, 2

A colorless crystal of approximate dimensions 0.13 × 0.37 × 0.58 mm was mounted on a glass fiber and transferred to a Siemens P4 diffractometer. The determination of Laue symmetry, crystal class, unit cell parameters and the crystal's orientation matrix were carried out according to standard procedures [43]. Intensity data were collected at 163 K using a 2θ-ω scan technique with Mo–K_α radiation. The raw data were processed with a local version of CARESS [44] which employs a modified version of the Lehman–Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles. Subsequent calculations were carried out using the SHELXTL program [45]. All 9394 data were corrected for absorption [46] and for Lorentz and polarization effects and placed on an approximately absolute scale. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. Experimental details appear in Table 1.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis [47]. Hydrogen atoms were included using a riding model. Unfortunately, the limited quality of the crystal prevented a better refinement from being achieved. At convergence, $wR_2 = 0.2036$ and GOF = 1.053 for 668 variables refined against all 8866 unique data. (As a comparison for refinement on F, $R_1 = 0.0758$ for those 5199 data with $I > 2.0\sigma I$.)

2.8. X-ray data collection, structure determination, and refinement for $[(Me_3SiCH_2)_2Lu(OC_6H_3{}^tBu_2\text{-}2,6)_2][Li(THF)_4](THF)_2$, 3

A colorless crystal of approximate dimensions 0.20

× 0.23 × 0.30 mm was handled as described for **2**. All 6025 data were corrected for Lorentz and polarization effects, and were placed on an approximately absolute scale. The diffraction symmetry was *mmm* with the systematic and the systematic absences are consistent with either space group $Pna2_1$ or *Pnma*. It was later determined that the non-centrosymmetric space group $Pna2_1$ was correct. At convergence, $wR_2 = 0.1781$ and GOF = 1.013 for 314 variables refined against 6023 unique data. (As a comparison for refinement on F, $R_1 = 0.0638$ for those 3854 data with $I > 2.0\sigma I$.) The high R value is indicative of poor crystal quality.

3. Results and discussion

3.1. Synthesis

Previous studies of yttrium alkyl alkoxide and aryloxide complexes showed that the neutral complex $(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2$, **1**, readily formed with this 'small alkyl–large aryloxide' ligand combination according to Eq. (1) [38]. In contrast, the combination of the larger alkyl, $(Me_3Si)_2CH$, and the alkoxide, $OCMe_3$, preferentially formed the anionic, tetra-ligand 'ate' complex $[(Me_3Si)_2CH]_2Y(\mu\text{-}OCMe_3)_2Li(THF)$, as shown in Eq. (2) [38].

Table 1
Experimental data for the X-ray diffraction studies of $\{(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)_2\}\{[(THF)_3Li]_2Cl\}$, **2**, and $(Me_3SiCH_2)_2Lu(OC_6H_3{}^tBu_2\text{-}2,6)_2\}[Li(THF)_4](THF)_2$, **3**

Compound	**2**	**3**
Formula	$C_{60}H_{112}ClLi_2O_8Si_2Y$	$C_{60}H_{112}LiO_8Si_2Lu$
Formula weight	1155.92	1199.59
Temperature (K)	163	158
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Pna2_1$
a (Å)	11.543(10)	20.760(4)
b (Å)	16.335(12)	16.557(8)
c (Å)	18.99(2)	19.327(6)
α (°)	94.42(6)	90
β (°)	97.19(3)	90
γ (°)	106.07(5)	90
V (Å^3)	3390(5)	6644(4)
Z	2	4
$D_{calc.}$ (g cm^{-3})	1.132	1.199
θ Range (°)	2.00–22.50	2.11–25.0
μ(Mo–K$_\alpha$) (mm^{-1})	0.981	1.568
Reflections collected	9394	6025
Independent reflections	8866 ($R_{int} = 0.0495$)	6025 ($R_{int} = 0.000$)
Observed reflections ($I > 2\sigma I$)	5199	6023
Data/restraints/parameters	8866/0/668	6023/1/314
Goodness-of-fit	1.053	1.013
Final R indices ($I > 2\sigma I$)^a	$R_1 = 0.0758$, $wR_2 = 0.1695$	$R_1 = 0.0638$, $wR_2 = 0.0477$
R indices (all data)	$R_1 = 0.1465$, $wR_2 = 0.2036$	$R_1 = 0.1151$, $wR_2 = 0.0781$
Absorption correction	Semi-empirical from ψ-scans	None

Diffractometer, Siemens P4; radiation, Mo–K$_\alpha$ ($\lambda = 0.710730$ Å).
Monochomator, highly oriented graphite.
Scan type, 2θ-ω; scan width, 1.2°; scan speed, 3.0° min^{-1}.
[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$.
$wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma\{w(F_o^2)^2\}]^{1/2}$.

$$YCl_3 + 2\ LiCH(SiMe_3)_2 + 2\ LiOCMe_3 \xrightarrow{THF} [(Me_3Si)_2CH]_2Y(\mu\text{-}OCMe_3)_2Li(THF) \tag{2}$$

To determine if an anionic complex analogous to that in Eq. (2) could be made with the (Me_3SiCH_2)–$(OC_6H_3{}^tBu_2\text{-}2,6)$ ligand combination, the reaction of YCl_3 with two equivalents of $LiCH_2SiMe_3$ and two equivalents of $LiOC_6H_3{}^tBu_2\text{-}2,6$ in THF was conducted. The ^{1}H- and ^{13}C-NMR data on the THF soluble reaction product were consistent with the presence of the anticipated dialkyl–diaryloxide complex, $\{(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)_2\}^-$: the alkyl and aryloxide ligands were present in a 1:1 ratio and the methylene resonance due to the CH_2SiMe_3 groups was a doublet which displayed characteristic yttrium coupling with $J_{Y-C-H} = 3.7$ Hz [35,38,48–50]. Although the anionic organometallic portion of **2** was easily characterized by NMR, little information could be obtained about the cation in solution. Moreover, elemental analysis of the crude product indicated the presence of LiCl as a contaminant. Since the complex was only soluble in THF, complete separation of the LiCl was difficult. However, recrystallization of this material led to the isolation of the desired complex which formed with the unusual cation $\{[(THF)_3Li]_2Cl\}^+$ (Eq. (3)).

$$YCl_3 + 2\ LiCH_2SiMe_3 + 2\ LiOC_6H_3{}^tBu_2\text{-}2,6 \xrightarrow{THF} \{(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)_2\}^-\{[(THF)_3Li]_2Cl\}^+\ \mathbf{2} \tag{3}$$

A reaction analogous to Eq. (3) was examined with lutetium to determine if the chemistry paralleled that of yttrium. This is usually the case [39], but detailed comparisons had not been made in an alkyl alkoxide or aryloxide system. Since these systems proved to be challenging (see below), we sought to determine if lutetium would offer any advantages. The reaction of $LuCl_3$ with two equivalents of $LiCH_2SiMe_3$ and two equivalents of $LiOC_6H_3{}^tBu_2\text{-}2,6$ in THF formed a product whose NMR spectra were consistent with the presence of the analogous anionic dialkyl–diaryloxide complex, $\{[Me_3SiCH_2]_2Lu(OC_6H_3{}^tBu_2\text{-}2,6)_2\}^-$. The ^{1}H-NMR spectrum of the lutetium product is very similar to that of **2** except that the methylene resonance is shifted slightly upfield and displays no metal-to-alkyl coupling as expected for lutetium in comparison to

Table 2
Selected bond distances (Å) and angles (°) for $\{(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)_2\}\{[(THF)_3Li]_2Cl\}$, **2**, and $\{(Me_3SiCH_2)_2Lu(OC_6H_3{}^tBu_2\text{-}2,6)_2\}[Li(THF)_4](THF)_2$, **3**

Complex **2**		Complex **3**	
Y(1)–O(1)	2.091(5)	Lu(1)–O(1)	2.079(8)
Y(1)–O(2)	2.097(5)	Lu(1)–O(2)	2.075(9)
Y(1)–C(29)	2.404(8)	Lu(1)–C(29)	2.42(3)
Y(1)–C(33)	2.420(8)	Lu(1)–C(33)	2.29(2)
Si(1)–C(29)	1.843(9)	Si(1)–C(29)	1.83(2)
Si(2)–C(33)	1.835(8)	Si(2)–C(33)	1.85(2)
O(1)–Y(1)–O(2)	110.9(2)	O(1)–Lu(1)–O(2)	110.4(3)
O(1)–Y(1)–C(29)	111.4(2)	O(1)–Lu(1)–C(29)	112.6(7)
O(1)–Y(1)–C(33)	108.0(2)	O(1)–Lu(1)–C(33)	109.3(7)
O(2)–Y(1)–C(29)	107.8(2)	O(2)–Lu(1)–C(29)	105.8(8)
O(2)–Y(1)–C(33)	114.0(2)	O(2)–Lu(1)–C(33)	115.1(7)
C(29)–Y(1)–C(33)	104.5(3)	C(29)–Lu(1)–C(33)	103.5(5)
Li(1)–Cl(1)	2.263(13)		
Li(2)–Cl(1)	2.27(2)		
Li(1)–O(3)	1.90(2)	Li(1)–O(3)	1.93(4)
Li(1)–O(4)	1.98(2)	Li(1)–O(4)	1.83(4)
Li(1)–O(5)	1.92(2)	Li(1)–O(5)	2.04(4)
Li(2)–O(6)	1.94(2)	Li(1)–O(6)	1.74(4)
Li(2)–O(7)	1.93(2)		
Li(2)–O(8)	1.98(2)		
Li(1)–Cl(1)–Li(2)	151.9(6)		

yttrium. As in the yttrium synthesis, the crude product had analytical data which indicated contamination with LiCl. However, since this lutetium product was soluble in toluene, recrystallization gave a LiCl-free product with a conventional $[Li(THF)_4]^+$ counter-cation as shown in Eq. (4).

$$LuCl_3 + 2\ LiCH_2SiMe_3 + 2\ LiOC_6H_3{}^tBu_2\text{-}2,6 \xrightarrow{THF} [(Me_3SiCH_2)_2Lu(OC_6H_3{}^tBu_2\text{-}2,6)_2]^-[Li(THF)_4]^+(THF)_2 \quad (4)$$

3.2. Structure

Complexes **2** and **3** crystallize with nearly identical four coordinate, distorted tetrahedral geometries around yttrium and lutetium, respectively. The respective yttrium and lutetium O(1)–Ln–O(2) angles of 110.9(2) and 110.4(3)° and the C(29)–Ln–C(33) angles of 104.5(3) and 103.5(5)° in complexes **2** and **3** are within experimental error (Table 2).

The 2.404(4) and 2.420(8) Å $Y–C(CH_2SiMe_3)$ bond lengths in **2** (Fig. 1) are within the error limits of the analogous distances in five coordinate $(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2$, **1** (2.411(13) and 2.427(16) Å) [38], and are similar to those in four coordinate $[Y(CH_2SiMe_3)_4]^-$ (2.382(8)–2.420(9) Å), eight coordinate $[(CsH_5)_2Y(CH_2SiMe_3)_2]^-$ (2.42(2) Å average) ([48]a), and seven coordinate (4,13-diaza-18-crown-6)$Y(CH_2SiMe_3)$ (2.45(2) Å) ([29]a). The average 2.094(3) Å $Y–O(OC_6H_3{}^tBu_2\text{-}2,6)$ distance in **2** is also equivalent within error limits to the analogous Y–O lengths in structures of other coordination numbers: **1** (2.084(11) Å) [38], $Y(OC_6H_3{}^tBu_2\text{-}2,6)_3$ (2.00(2) Å) ([13]b), and $(C_5Me_5)Y(OC_6H_3{}^tBu_2\text{-}2,6)_2$ (2.096(4) and 2.059(3) Å) ([14]a).

The lutetium aryloxide and alkyl bond distances in **3** (Fig. 2) are similar to those in **2** when differences in ionic radii are taken into consideration [51]. The average $Lu–C(CH_2SiMe_3)$ bond distance of 2.36(7) Å in **3** is consistent with the analogous distances in $(C_5H_5)_2Lu(CH_2SiMe_3)(THF)$ (2.376(17) Å) [52], and the 2.329(15) Å average distance for the two independent molecules of $\{(C_5Me_5)Lu(CH_2SiMe_3)[CH(SiMe_3)_2]Cl\}\{Li(THF)_2\}$ [53].

Although the structures of the organometallic anions of **2** and **3** are similar, different cations are found in the crystals isolated for X-ray crystallography. The $[Li(THF)_4]^+$ cation in **3** is conventional and consists of a lithium atom tetrahedrally coordinated by four THF ligands with normal Li–O bond distances. However, in complex **2** a $\{[(THF)_3Li]_2Cl\}^+$ cation is isolated. This species is effectively a LiCl adduct of the $[Li(THF)_4]^+$ cation in **3**. It consists of two lithium atoms tetrahedrally coordinated by three THF ligands and linked by a bridging chloride atom with a Li–Cl–Li angle of 151.9(6)° and an average Li–Cl distance of 2.267(4) Å. This cation has been previously observed in $\{[(C_5H_5)_2Zr(PPh)]_2\}\{[(THF)_3Li]_2Cl\}$ [54], but in this case the cation has a 180° Li–Cl–Li angle and equivalent Li–Cl distances of 2.246(17) Å.

3.3. Reactivity

The reactivity of complexes **1–3** was examined with a variety of substrates whose reaction chemistry with cyclopentadienyl-containing alkyl complexes is well characterized [4–6]. Each of the complexes **1–3** was observed to polymerize ε-caprolactone. This is not unusual reactivity considering that both alkyl and alkoxide complexes of electropositive metals ring open polymerize this substrate [55]. Reactivity with ethylene, a substrate also readily polymerized by cyclopentadienyl-containing lanthanide alkyls [56], was more limited. Only the neutral complex $(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2$, **1**, was observed to initiate the polymerization of ethylene. Complex **1** did not initiate the polymerization of butadiene at 15 psi or propylene at 60 psi at room temperature.

Further reactivity studies with this alkyl/aryloxide ligand combination were confined to **1** since it was found to be the most reactive and since it was found that the lithium aryloxide complex $[(THF)Li(OC_6H_3{}^tBu_2\text{-}2,6)]_2$ [57], readily forms in these systems. Since

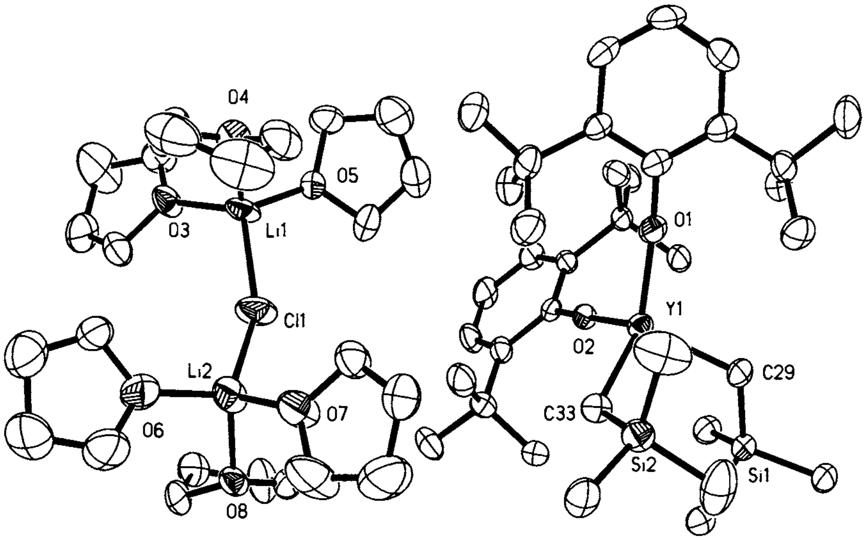

Fig. 1. Thermal ellipsoid plot of $\{(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)_2\}\{[(THF)_3Li]_2Cl\}$, **2**, drawn at the 50% probability level.

this lithium complex often is the first product to crystallize from solution, the lithium-containing anions **2** and **3** were less desirable for reactivity studies. This also made it necessary to prepare **1** with exact reagent stoichiometries.

Complex **1** exhibits metallation reactivity with phenylacetylene and pyridine as determined by the formation of Me_4Si in the ^{1}H-NMR spectra of reaction mixtures and by the loss of Y–C–H coupling in the CH_2SiMe_3 resonance. The product mixture obtained from the phenylacetylene reaction exhibited an infrared absorption at 2047 cm^{-1}, which is consistent with the presence of a $(C{\equiv}CPh)^-$ ligand. Unfortunately, the ^{1}H-NMR spectra of these products contained several resonances in the aromatic region and a single metallated product could not be isolated from either reaction. Even at lowered temperatures complicated product mixtures were observed. Control reactions showed no evidence for metallation of the toluene solvent (or benzene or THF) at room temperature. Complex **1** also forms $SiMe_4$ when it is treated with nitriles, RCN (R = Me, Me_2CH, Ph, $PhCH_2$). However, these reactions appeared to be even more complicated than the other metallations.

When **1** was treated with ^{t}BuNC, CO, and CO_2, the ^{1}H-NMR spectra revealed rapid loss of the yttrium-alkyl coupling and a downfield shift of the methylene resonances in each case. The alkyl and aryloxide resonances were broad in these spectra suggesting the presence of many products and single organometallic products were not isolated. Evidence for insertion of each of these substrates into the $Y{-}CH_2SiMe_3$ bond of **1** was obtained from the mass spectra of deuterolyzed reaction mixtures. Signals for $Me_3SiCH_2C(H){=}NCMe_3$, $Me_3SiCH_2CO]_2$, and $Me_3SiCH_2CO_2H$ were observed. The fact that these insertion coupled products have no deuterium indicates that the ligands formed by insertion react with hydrogen sources in the system and are lost from the metal before deuterolysis. This is consistent with the complexity observed in ^{1}H-NMR spectra of these reaction products.

Insertion chemistry also occurs with **1** and PhNCO and PhNCS. ^{1}H-NMR analysis shows that these reactions are rapid and inserted products $PhN(H)C({=}O)\text{-}CH_2SiMe_3$ and $PhN(H)C({=}S)CH_2SiMe_3$ were found in the mass spectra of the deuterolyzed products. Ligand fragmentation resulting in loss of $SiMe_3$ was also found in these systems, since $PhN(H)C({=}O)CH_3$ and $PhN(H)C({=}S)CH_3$ were identified among the reaction products. Both the lack of deuterium incorporation into the inserted products and the ligand fragmentation are consistent with the high degree of reactivity in these systems and with the fact that inserted organometallic products were not isolated for analysis by X-ray crystallography.

Complex **1** was found to have reactivity comparable with that of the most reactive of cyclopentadienyl lanthanide and yttrium alkyl complexes. Although metallation of $PhC{\equiv}CH$ is quite facile with a variety of cyclopentadienyl-containing lanthanide alkyl complexes [58–61], metallation of pyridine ([61]a, [62–64]) and acetonitrile [65,66] has been observed only for the more reactive C_5Me_5-supported alkyls, $(C_5Me_5)_2LnR(THF)_x$ ($x = 0$,1). The insertion of ^{t}BuNC [66–68], Co [64,69], and CO_2 [68,70–72] in Ln–R bonds has also been previously observed in cyclopentadienyl-containing lanthanide alkyl complexes, but these reactions often are less complicated and give better yields of a single

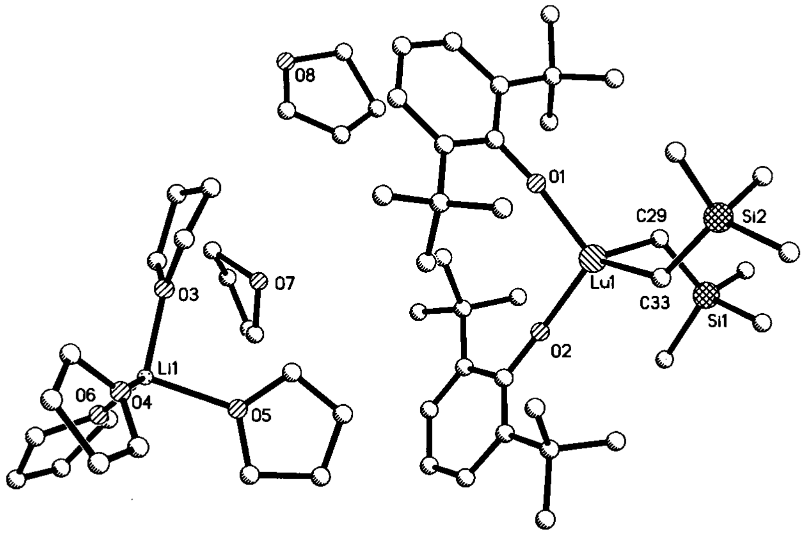

Fig. 2. Ball and stick plot of $\{(Me_3SiCH_2)_2Lu(OC_6H_3{}^tBu_2\text{-}2,6)_2\}[Li(THF)_4](THF)_2$, **3**.

product. Insertion of PhNCO in Ln–R bonds has only been observed in the more highly reactive cyclopentadienide-containing lanthanide systems ([67]c, [73]). However, unlike the reaction of many cyclopentadienide-containing lanthanide alkyls [4–6], no reaction was observed between **1** and H_2 in either toluene or THF at ambient temperatures. Reduced reactivity of alkyls to hydrogen in alkoxide-substituted complexes has been observed previously ([9]b, [14]a).

4. Conclusion

The neutral complex $(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2$, **1**, reacts with substrates traditionally reactive with cyclopentadienyl-containing lanthanide alkyl complexes and has higher reactivity than the anionic analogs, $[(Me_3SiCH_2)_2Ln(OC_6H_3{}^tBu_2\text{-}2,6)_2]^-$ (Ln = Y, Ln). Polymerization, metallation, and insertion reactions are observed for **1**, but complicated mixtures of products are formed which do not readily yield single isolable products in contrast to reactions of cyclopentadienyl yttrium alkyl complexes. Although the reactivity of the alkyl-aryloxide complexes is comparable to the most reactive of the cyclopentadienyl-substituted complexes, the cyclopentadienyl ligands are clearly superior to aryloxides as ancillary ligands in providing single completely identifiable reaction products.

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