Synthetic and Structural Studies of the Cyclopentadienyl-Free Yttrium Alkyl Alkoxide and Aryloxide Complexes $[(Me_3Si)_2CH]_2Y(\mu\text{-}OCMe_3)_2Li(THF)$ and $[Me_3SiCH_2]_2Y(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2$

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YCl_3 reacts with 2 equiv of $LiCH(SiMe_3)_2$ and 2 equiv of $LiOCMe_3$ in THF to form the dialkyl dialkoxide complex $[(Me_3Si)_2CH]_2Y(\mu\text{-}OCMe_3)_2Li(THF)$, **1**. The yttrium in **1** is surrounded by a distorted tetrahedral arrangement of two terminal alkyl groups and two bridging alkoxide groups, and the coordination around lithium is trigonal planar. The reaction of YCl_3 with 2 equiv of $LiCH_2SiMe_3$ and 1 equiv of $LiOC_6H_3{}^tBu_2$-2,6 in THF forms the neutral dialkyl aryloxide complex $(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2$, **2**. The coordination geometry around yttrium in **2** is a distorted trigonal bipyramid with the THF groups in the apical positions.

Introduction

Although historically the organometallic chemistry of yttrium and the lanthanide metals has been dominated by cyclopentadienyl ligands, in recent years there has been considerable interest in developing alternative auxiliary ligands to solubilize and stabilize reactive complexes of these metals.[1−13] Alkoxide and aryloxide ligands are attractive for this purpose since they form strong bonds to these oxophilic metals and may allow a wider range of reactions to be realized. Since these ligands can be conveniently obtained in great variety from alcohols, considerable variation in steric and electronic features is possible.

Previous studies in this area necessarily focused on the basic chemistry of homoleptic alkoxide systems,[11,12,14−22] but recently some reports of mixed-ligand alkyl alkoxide complexes have appeared.[22−26] Some of these complexes appear to have high reactivity, but further development in this area depends on convenient syntheses of a greater variety of mixed-ligand alkyl alkoxide species.

To date the most straightforward syntheses of yttrium alkyl alkoxides have involved cyclopentadienyl-containing systems, eq 1.[5,27] Formation of cyclopentadienyl-free yttrium alkyl alkoxides has been more complicated as indicated in eqs 2[24] and 3.[28] In a samarium system, a dilithium species has been reported as shown in eq 4.[25]

$$(C_5Me_5)Ln(OAr)_2 + LiCH(SiMe_3)_2 \xrightarrow{\text{hexanes}} (C_5Me_5)(OAr)Ln(CH(SiMe_3)_2) + LiOAr \quad (1)$$

$$Ln = Y, Ce;\ OAr = OC_6H_3{}^tBu_2\text{-}2,6$$

Reported here are two straightforward syntheses of cyclopentadienyl-free alkyl yttrium alkoxide and aryloxide complexes which show that by using the right combinations of metal, alkyl, and alkoxide or aryloxide, such complexes can be made directly from halide

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$$[(C_9H_7)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2 + 4LiCH_2SiMe_3 \xrightarrow[\text{2. THF}]{\text{1. hexanes}} 2(Me_3SiCH_2)Y[(\mu\text{-}CH_2)_2SiMe_2][(\mu\text{-}OCMe_3)Li(THF)_2]_2 + 2LiC_9H_7 \quad (2)$$

$$YCl_3 + 2LiCH_2SiMe_3 + 2LiOCMe_3 \xrightarrow{\text{THF}} \{(Me_3SiCH_2)_x(Me_3CO)_{1-x}Y(\mu\text{-}OCMe_3)_4[Li(THF)]_4\text{-}(\mu_4\text{-}Cl)\}^+[Y(CH_2SiMe_3)_4]^- \quad (3)$$

$$Sm(OAr)_3(THF)_2 + 3LiCH_2R \xrightarrow{\text{THF}} [Li(THF)]_2[Sm(OAr)_3(CH_2R)_2] + LiCH_2R \quad (4)$$

$$OAr = OC_6H_3{}^{i}Pr_2\text{-}2,6;\ R = SiMe_3$$

precursors. In the alkoxide case, the *tert*-butoxide ligand is used since this group has been shown to have an extensive chemistry with yttrium.[2,15,18,23,24,28–30] For the aryloxide case, the common 2,6-di-*tert*-butylphenoxide ligand is used.[5,6,21,31,32]

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 glovebox techniques. Solvents were dried and distilled,[33] and yttrium trichloride (Rhône-Poulenc) was dried as described previously.[34] $LiOCMe_3$ was prepared from $LiCMe_3$ (freshly sublimed) and $HOCMe_3$ (distilled from K) in hexanes and was purified by sublimation before use.[28] Bis(trimethylsilyl)chloromethane (Aldrich) was dried over P_2O_5 and reacted with lithium powder (Aldrich, −325 mesh) to produce (bis(trimethylsilyl)methyl)lithium,[35] which was purified by sublimation. ((Trimethylsilyl)methyl)lithium (Aldrich, 1.0 M in pentanes) and *tert*-butyllithium (Aldrich, 1.0 M in hexanes) were dried in vacuo to remove solvent and purified by sublimation. Freshly sublimed 2,6-di-*tert*-butylphenol (Aldrich) was reacted with the $LiCMe_3$ in hexanes to form $LiOC_6H_3{}^tBu_2$-2,6, which was filtered off, dried, and purified by sublimation. ^1H and ^{13}C NMR spectra were recorded on General Electric GN500 and Omega 500 spectrometers. ^1H NMR chemical shifts were assigned relative to residual protons in C_6D_6 at δ 7.15 and in THF-d_8 at δ 1.79. ^{13}C NMR chemical shifts were assigned relative to carbons in C_6D_6 at δ 128.0 and in THF-d_8 at δ 67.4. Infrared spectra were obtained on a Perkin-Elmer 1600 FTIR. Elemental analyses were done by Analytische Laboratorien, D-51547 Gummersbach, Germany.

$[(Me_3Si)_2CH]_2Y(\mu\text{-}OCMe_3)_2Li(THF)$, 1. In a glovebox, YCl_3 (120 mg, 0.62 mmol) was slurried in THF (*ca.* 10 mL) and stirred. After 5 min, $LiCH(SiMe_3)_2$ (205 mg 1.23 mmol) was added to form a clear pale yellow solution. Five minutes later, $LiOCMe_3$ (98.7 mg, 1.23 mmol) was added and the mixture was stirred for 18 h. THF was removed from the clear pale yellow solution by rotary evaporation, and the resulting oily solid was extracted with hexanes. Upon centrifugation, a colorless hexane soluble layer was separated from an oily brown hexane insoluble layer and a white powder (presumably LiCl). The hexane-soluble fraction was dried by rotary evaporation to give **1** as a colorless solid (209 mg, 54%). Crystals suitable for X-ray diffraction were grown from a concentrated toluene solution at −35 °C. ^1H NMR (C_6D_6): δ 3.32 (s, 4H, THF), 1.32 (s, 9H, $OC(CH_3)_3$), 1.22 (s, 4H, THF), 0.48 (s, 18H, $(Si(CH_3)_3)_2$), −0.90 (d, 1H, $CH(SiMe_3)_2$, J_{Y-H} = 2.6 Hz). ^{13}C NMR (C_6D_6): δ 71.4 ($OCMe_3$), 68.4 (THF), 34.3 ($OC(CH_3)_3$), 25.1 (THF), 5.9 ($Si(CH_3)_3$), 1.4 ($CHSiMe_3$). IR (KBr): 2965 s, 2888 m, 1460 w, 1361 m, 1245 s, 1204 m, 1016 s, 957 s, 846 s, 763 m, 664 m cm^{-1}. Anal. Calcd for $C_{26}H_{64}LiO_3Si_4Y$: C, 49.34; H, 10.19; Li, 1.10; Y, 14.05. Found: C, 48.73; H, 10.21; Li, 1.39; Y, 14.35. Molecular weight (isopiestic, toluene): calcd, 633; found, 670. Thermal decomposition of **1** begins to be evident at about 60 °C.

$[Me_3SiCH_2]_2Y(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2$, 2. As described for **1**, YCl_3 (0.920 g, 4.71 mmol) was treated with $LiCH_2SiMe_3$ (0.887 g, 9.42 mmol) and $LiOC_6H_3{}^tBu_2$-2,6 (1.00 g, 4.71 mmol) in THF and the clear yellow-brown solution was stirred for 18 h. THF was removed by rotary evaporation, and the resulting off white solid was extracted with toluene. Removal of toluene by rotary evaporation gave **2** as an off white solid (2.69 g, 93%). After drying, **2** has only limited solublity in toluene but is highly soluble in THF. Crystals suitable for X-ray diffraction were grown from a concentrated toluene/THF solution at −35 °C. ^1H NMR (THF-d_8): δ 6.97 (d, 2H, phenoxide meta-H, J_{H-H} = 7.7 Hz), 6.34 (t, 1H, phenoxide para-H, J_{H-H} = 7.7 Hz), 1.51 (s, 18H, $OC_6H_3(Me_3)_2$), −0.03 (s, 18H, CH_2SiMe_3), −0.52 (d, 4H, CH_2SiMe_3, J_{Y-H} = 3.6 Hz). ^{13}C NMR (THF-d_8): δ 138.2, 124.5, 114.7 (phenoxide), 68.2 (THF), 35.7 ($OC_6H_3(CMe_3)_2$), 32.1 (CH_2SiMe_3), 26.4 (THF), 4.9 (CH_2SiMe_3). IR (KBr): 2954 s, 2892 s, 1580 m, 1456 m, 1410 s, 1380 m, 1262 s, 1195 m, 1097 m, 1041 s, 862 s, 744 s, 651 m cm^{-1}. Anal. Calcd for $C_{30}H_{59}O_3Si_2Y$: Y, 14.51. Found: Y, 13.5. Molecular weight (isopiestic, THF): calcd for $C_{30}H_{59}O_3Si_2Y$, 613; found, 1100. Thermal decomposition of **2** begins to be evident at about 60 °C.

X-ray Data Collection, Structure Determination, and Refinement for $[(Me_3Si)_2CH]_2Y(\mu\text{-}OCMe_3)_2Li(THF)$, 1. A colorless crystal of approximate dimensions 0.17 × 0.33 × 0.42 mm was immersed in Paratone-D oil under nitrogen and then manipulated in air onto a glass fiber and transferred to the nitrogen stream of a Syntex P4 diffractometer.[36] Determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out according to standard procedures.[37] Low-temperature (163 K) intensity data were collected via a $2\theta-\omega$ scan technique with Mo Kα radiation.

All 2612 data were corrected for Lorentz and polarization effects and placed on an approximately absolute scale. The Laue symmetry is $2/m$, and the lattice type is C-centered (hkl; $h + k = 2n$). The systematic extinction observed is $h0l$ for $l = 2n + 1$. The two possible monoclinic space groups are Cc and $C2/c$.

All crystallographic calculations were carried out using the UCI-modified version of the UCLA Crystallographic Computing Package[38] and the SHELXTL[39] program. The analytical scattering factors[40] for neutral atoms were used throughout the analysis. The structure was solved and refined (SHELXTL) in both of the above space groups but neither initially proved satisfactory. The molecular C_2 symmetry does not

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appear to be crystallographic. This may in part account for the unsatisfactory refinement in the centrosymmetric space group. It was necessary to refine four different models to determine the most reasonable structure. Details of these refinements follow.

Model A (Space Group *C*2/*c*). In this model, yttrium, O(2), and Li(1) are located on a 2-fold rotation axis and were assigned site occupancy factors of 0.5. Thermal parameters are higher than expected, and several light atoms cannot be refined anisotropically. The metric parameters (distances and angles) are not consistent with a well-resolved structure. The tetrahydrofuran ring was disordered. Residual electron density was observed near all of the carbon atoms. The value of w*R*2 was 0.3350 for this refinement (Y and Si atoms anisotropic, hydrogens included except on the THF ligand), and *R*1 was 0.1382.

Model B (Space Group *C*2/*c*). This model was refined with two separate components for each of the carbon atoms labeled C(1) to C(11). Site occupancy factors were allowed to refine and resulted in each carbon atom having a SOF of 0.50. *U*(iso) values for the carbon atoms ranged from 0.05 to 0.09 Å^2, and it was again necessary to refine the light atoms isotropically. The *U*(eq) values for the silicon atoms were slightly higher than expected at 0.06 and 0.07 Å^2. The five atoms of the THF ligand were include with SOF = 0.5 for each. Bond distances and angles were improved over the model A refinement but were still deemed not acceptable. The value of w*R*2 was 0.2558 (*R*1 = 0.1041).

Model C (Space Group *Cc*). The refinement of this model was carried out with site occupancy factors = 1.0 for all atoms. There are no atoms related by symmetry. This model refined better than either A or B. Distances, angles, and thermal parameters were more consistent, and all non-hydrogen atoms were refined anisotropically. The value of w*R*2 was 0.1248 (*R*1 = 0.0481). The refinement program (SHELXTL) flagged this refinement indicating that a racemic twin was possible.

Model D (Space Group *Cc*). This refinement was identical to that for model C but included the TWIN and BASF parameters in the SHELXTL program. Distances, angles, and thermal parameters were again consistent and within acceptable ranges. The value of w*R*2 decreased to 0.1136 for the anisotropic refinement (*R*1 = 0.0445). The BASF value converged to 0.55 indicating a nearly equal racemic twin.

It was decided on the basis of the metrical data that the refinements based on either of the two noncentrosymmetric models were preferable to those based on the centrosymmetric models. The structure reported here is that refined according to model D which is based on refinement of a racemic twin. Hydrogen atoms were included using a riding model.

X-ray Data Collection, Structure Determination, and Refinement for $(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2$, 2. A colorless crystal of approximate dimensions 0.20 × 0.23 × 0.30 mm was handled as described for **1**. Although the intensity data were weak, it was decided to proceed with data collection ($2\theta_{max} = 40.0°$). Low-temperature (163 K) intensity data were collected via a $\theta-2\theta$ scan technique with Mo Kα radiation under the conditions given in Table 1.

All 6718 data were corrected for absorption[38] and for Lorentz and polarization effects and were placed on an approximately absolute scale. Any reflection with I(net) < 0 was assigned the value $|F_o| = 0$. There were no systematic extinctions nor any diffraction symmetry other than the Friedel condition. The two possible triclinic space groups are the noncentrosymmetric $P1$ [C_1^1; No. 1] or the centrosymmetric $P\bar{1}$ [C_1^1; No. 2]. Refinement of the model using the centrosymmetric space group proved it to be the correct choice.

Crystallographic calculations were carried out with the same programs used for **1**. The analytical scattering factors[41] for neutral atoms were used throughout the analysis; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included. The quantity minimized during least-squares analysis was $\sum w(F_o - F_c)^2$, where w^{-1} was defined as $\sigma^2(|F_o|) + 0.0004(|F_o|)^2$.

Table 1. Experimental Data for the X-ray Diffraction Studies of $[(Me_3Si)_2CH]_2Y(\mu\text{-}OCMe_3)_2Li(THF)$, 1 and $(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2$, 2[a]

	1	2
formula	$C_{26}H_{54}LiO_3Si_4Y$	$C_{30}H_{59}O_3Si_2Y$
fw	632.98	612.9
temp (K)	163(2)	163(2)
cryst system	monoclinic	triclinic
space group	*Cc*	$P\bar{1}$
a (Å)	18.321(2)	13.053(3)
b (Å)	14.406(3)	15.910(3)
c (Å)	15.055(2)	19.579(3)
α (deg)	90	67.184(13)
β (deg)	104.603(9)	71.377(14)
γ (deg)	90	89.68(2)
V (Å^3)	3845.2(10)	3519.1(11)
Z	4	4
D_{calcd} (Mg/m^3)	1.093	1.157
diffractometer	Siemens P4	Siemens P4
data collcd	$+h,+k,\pm l$	$+h,\pm k,\pm l$
scan type	$\theta-\theta$	$\theta-2\theta$
scan range (deg)	1.2	1.12
scan speed (deg min^{-1}) (in ω)	3.0	3.0
2θ range (deg)	4.0−45.0	4.0−40.0
μ(Mo Kα) mm^{-1})	1.662	1.75
reflcns collcd	2612	6718
reflections with ($|F_o| > 4.0\sigma(|F_o|)$	2290	3305
no. of variables	317	319
refinement[b]	*R*1, 5.69%; w*R*2,11.36%	R_F, 6.3%; R_{wF}, 6.7%
goodness of fit	1.110	1.67
abs corr	none	semi-empirical (φ-scan method)

[a] Radiation: Mo Kα ($\bar{\lambda}$ = 0.710 730 Å). Monochromator: highly oriented graphite. [b] $R1 = R_F = [\sum||F_o| - |F_c||/\sum|F_o|]$; $R_{wF} = [\sum w(||F_o| - |F_c||)/\sum w|F_o|]$; $wR2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$.

The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model. There are two independent molecules of the formula unit present.

Results

The $(Me_3Si)_2CH/OCMe_3$ Ligand Combination. The reaction of YCl_3 with 2 equiv of $LiCH(SiMe_3)_2$ followed by 2 equiv of $LiOCMe_3$ in THF forms $[(Me_3Si)_2CH]_2Y(\mu\text{-}OCMe_3)_2Li(THF)$, **1** (Figure 1), in moderate yield, ca. 50%, eq 5. The reaction is analogous to the reaction of

$$YCl_3 + 2LiCH(SiMe_3)_2 + 2LiOCMe_3 \xrightarrow{THF} [(Me_3Si)_2CH]_2Y(\mu\text{-}OCMe_3)_2Li(THF) \quad (5)$$

YCl_3 with 2 equiv of $LiCH_2SiMe_3$ and 2 equiv of $LiOCMe_3$ (eq 3),[28] but in this case the stoichiometrically expected product is obtained instead of $\{(Me_3SiCH_2)_x(Me_3CO)_{1-x}Y(\mu\text{-}OCMe_3)_4[Li(THF)]_4(\mu_4\text{-}Cl)\}^+[Y(CH_2SiMe_3)_4]^-$, **3**. The simplicity of this reaction is therefore likely to be due to the large steric bulk of the $(Me_3Si)_2CH$ ligand. In many cases, this ligand has proven to be the best choice for obtaining stable alkyl complexes.[25−28,42−50] Indeed, one might consider the alkyl, $CH(SiMe_3)_2$, to be

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[41] SHELXTL Empirical Absorption Correction program (see ref 39).

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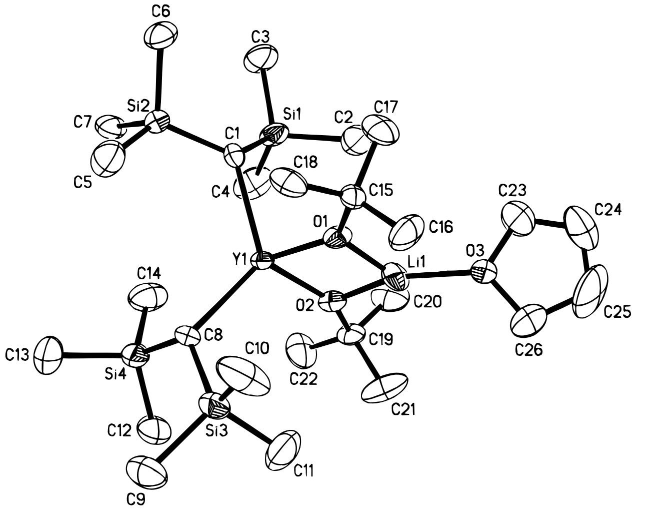

Figure 1. Thermal ellipsoid plot of $[(Me_3Si)_2CH]_2Y(\mu\text{-}OCMe_3)_2Li(THF)$, **1**, drawn at the 50% probability level.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $\{[(Me_3Si)_2CH]_2Y(\mu\text{-}OCMe_3)_2Li(THF)\}$, 1

Y(1)−O(1)	2.117(7)	Y(1)−O(2)	2.125(8)
Y(1)−C(8)	2.440(9)	Y(1)−C(1)	2.462(9)
Y(1)−Li(1)	2.896(14)	Si(1)−C(1)	1.843(9)
Si(2)−C(1)	1.827(8)	Si(3)−C(8)	1.858(9)
Si(4)−C(8)	1.824(10)	Li(1)−O(1)	1.92(2)
Li(1)−O(2)	1.92(2)	Li(1)−O(3)	1.900(14)
O(1)−C(15)	1.409(12)	O(2)−C(19)	1.435(12)
O(1)−Y(1)−O(2)	83.1(2)	O(1)−Y(1)−C(8)	110.3(3)
O(2)−Y(1)−C(8)	114.7(3)	O(1)−Y(1)−C(1)	97.7(3)
O(2)−Y(1)−C(1)	116.6(3)	C(8)−Y(1)−C(1)	123.5(3)
Li(1)−O(2)−Y(1)	91.4(7)	Li(1)−O(1)−Y(1)	91.4(6)
O(2)−Li(1)−O(1)	94.1(6)		
O(3)−Li(1)−O(2)	137(2)	O(3)−Li(1)−O(1)	127.5(12)
Si(1)−C(1)−Y(1)	112.6(4)	Si(2)−C(1)−Y(1)	123.1(4)
Si(3)−C(8)−Y(1)	121.9(4)	Si(4)−C(8)−Y(1)	105.6(4)
C(15)−O(1)−Y(1)	140.8(6)	C(15)−O(1)−Li(1)	126.9(8)
C(19)−O(2)−Y(1)	151.6(7)	C(19)−O(2)−Li(1)	116.9(9)

an “R*” ligand analogous to Cp*, C_5Me_5, in cyclopentadienyl chemistry.

Complex **1** was initially characterized by ^1H NMR spectroscopy which indicated the presence of alkoxide ligands and alkyl ligands in a 1:1 ratio. The alkyl resonance was a doublet which displayed characteristic yttrium coupling with $J_{Y-H} = 2.6$ Hz.[24,43,51−54] Definitive characterization of **1** was obtained by an X-ray diffraction study.

The complex has the expected geometric arrangement of ligands for the formally four-coordinate yttrium and the three-coordinate lithium, namely tetrahedral and trigonal planar, respectively. The tetrahedron of ligands around yttrium is distorted as expected for a heteroleptic system with some bridging and some very bulky terminal ligands. Hence, the 123.5(3)° C(1)−Y(1)−C(8) angle between the R* groups is larger and the 83.1(2)° O(1)−Y(1)−O(2) angle between the bridging alkoxides is smaller than the normal tetrahedral angle. The four-membered YO_2Li metallacycle is only slightly distorted from a square arrangement with angles of 83.1(2), 91.4(6), 94.1(6), and 91.4(7)°.

The Y(1)−O(1) and Y(1)−O(2) distances of 2.117(7) and 2.125(8) Å for the bridging alkoxides in **1** are slightly shorter than the 2.192(4) and 2.174(4) Å Y−O distances in five-coordinate $(Me_3SiCH_2)Y[(\mu\text{-}CH_2)_2SiMe_2]\text{-}[(\mu\text{-}OCMe_3)Li(THF)_2]_2$[24] and much shorter than the average distance of 2.270(5) Å in **3** which also contains a five coordinate yttrium.[28] The 1.92(2) Å Li(1)−O(1) and Li(1)−O(2) distances in **1** are equivalent within the error limits to the 1.912(13) and 1.953(12) Å Li−(μ-O) lengths in $(Me_3SiCH_2)Y[(\mu\text{-}CH_2)_2SiMe_2][(\mu\text{-}OCMe_3)Li(THF)_2]_2$[24] and the 1.996(13) Å average distance Li−(μ-O) distance in **3**,[28] both of which have four-coordinate lithium.

The 2.462(9) Å Y(1)−C(1) and 2.440(9) Å Y(1)−C(8) distances are comparable to the 2.468(7) Å Y−C[CH$(SiMe_3)_2$] distance in $Cp^*_2YCH(SiMe_3)_2$,[43] which is formally seven coordinate excluding agostic interactions which are common for this ligand.[25,27,43−45,47,48] $Cp^*_2YCH(SiMe_3)_2$ has distorted Y−C−Si angles ranging from 97.1(3) to 138.6(4)° due to the agostic interactions, but in **1** the analogous angles span a narrower range: 105.6(4)−123.1(4)°. Within the limit of the crystallographic data, no comments can be made about agostic interactions in **1**.

Attempts to prepare neutral alkyl alkoxide species with these ligands did not lead to a single, readily isolable complex. Hence, neither the reaction of YCl_3 with 2 equiv of $LiCH(SiMe_3)_2$ and 1 equiv of $LiOCMe_3$ nor the reaction with 1 equiv of the alkyl and 2 equiv of the alkoxide produced a neutral complex in good yield. Instead, in both cases, mixtures of complexes were observed by NMR which included some **1** formed by ligand redistribution.

The isolation of anionic $[LnZ_4]^-$ “ate” salts (Z = monoanionic ligand) such as **1** is not uncommon in lanthanide chemistry. Numerous examples have been reported and constitute a convenient way to increase coordination number for these large metals.[25,48,49,55−60] The fact that this mode of increasing the coordination number involves bridging ligands which tend to be less reactive than terminal ligands in these complexes[5,6,52] probably adds to the stabilization obtained. The fact that the alkyls in **1** are terminal and the alkoxides are bridging is consistent with the relative sizes of the ligands.

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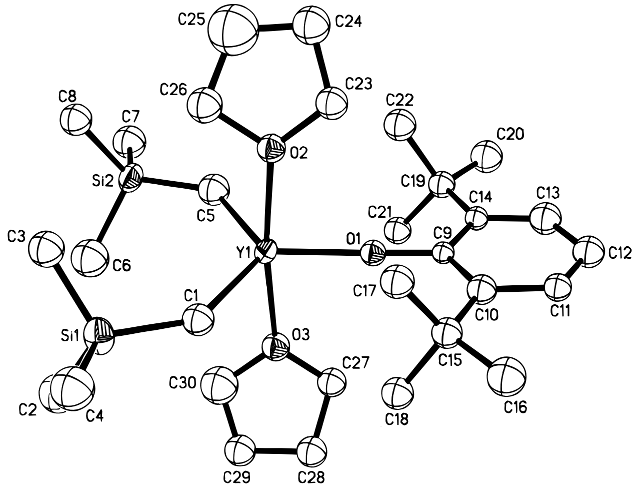

Figure 2. Thermal ellipsoid plot of $(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2$, **2**. drawn at the 50% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[(CH_3)_3SiCH_2]_2Y(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2$, 2

Y(1)−O(1)	2.084(11)	Y(1)−O(2)	2.343(9)
Y(1)−O(3)	2.343(9)	Y(1)−C(1)	2.427(16)
Y(1)−C(5)	2.411(13)	Si(1)−C(1)	1.822(17)
Si(2)−C(5)	1.837(15)	O(1)−C(9)	1.334(21)
O(1)−Y(1)−O(2)	85.7(4)	O(1)−Y(1)−O(3)	86.9(4)
O(2)−Y(1)−O(3)	172.6(4)	O(1)−Y(1)−C(1)	116.6(4)
O(2)−Y(1)−C(1)	92.4(4)	O(3)−Y(1)−C(1)	91.0(4)
O(1)−Y(1)−C(5)	119.7(5)	O(2)−Y(1)−C(5)	91.1(4)
O(3)−Y(1)−C(5)	92.5(4)	C(1)−Y(1)−C(5)	123.7(5)
Y(1)−O(1)−C(9)	178.8(10)	Y(1)−C(1)−Si(1)	136.6(6)
Y(1)−C(5)−Si(2)	135.5(9)		

The $Me_3SiCH_2/OC_6H_3{}^tBu_2$-2,6 Ligand Combination. This combination of ligands, in contrast to that described above, readily forms a neutral complex. Reaction of YCl_3 with 2 equiv of $LiCH_2SiMe_3$ followed by 1 equiv of $LiOC_6H_3{}^tBu_2$-2,6 in THF forms $(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)(THF)_2$, **2** (Figure 2), in >90% yield, eq 6. The ^1H NMR spectrum of **2** indicated the

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

presence of alkyl ligands and aryloxide ligands in a 2:1 ratio, and the alkyl resonance appeared as a characteristic doublet due to $J_{Y-H} = 3.5$ Hz.[24,43,51,53,54] Again, for definitive characterization of **2** an X-ray diffraction study was necessary.

The two independent molecules in the crystal structure of **2** are essentially the same. The following discussion is based on data on the molecule of **2** labeled 1. Complex **2** crystallizes as a slightly distorted trigonal bipyramid with a 172.6° O(THF)−Y−O(THF) angle between the axial ligands. The largest ligands are in the equatorial positions as expected. The 85.7(4), 91.1(4), and 92.4(4)° axial ligand−Y−equatorial ligand angles are close to the expected 90°.

The 2.411(13) and 2.427(16) Å $Y-C(CH_2SiMe_3)$ bond distances in **2** are similar to the analogous distances in the four-coordinate $[Y(CH_2SiMe_3)_4]^-$ (2.382(8)−2.420(9) Å),[28] eight-coordinate $[(C_5H_5)_2Y(CH_2SiMe_3)_2]^-$ (2.42(2) Å average),[51] and seven-coordinate (4,13-diaza-18-crown-6)$Y(CH_2SiMe_3)$ (2.45(2) Å).[8] The 2.084(11) Å $Y-O(OC_6H_3{}^tBu_2\text{-}2,6)$ distance in **2** is within error limits of the analogous Y−O lengths in $Y(OC_6H_3{}^tBu_2\text{-}2,6)_3$ (2.00(2) Å)[21] and $[(C_5Me_5)Y(OC_6H_3{}^tBu_2\text{-}2,6)_2$ (2.096(4) and 2.059(3) Å).[5]

Attempts to make the $[(Me_3SiCH_2)_2Y(OC_6H_3{}^tBu_2\text{-}2,6)_2]^-$ "ate" salt analogous to **1** with this ligand combination were unsuccessful. Reaction of YCl_3 with 2 equiv of $LiCH_2SiMe_3$ followed by 2 equiv of $LiOC_6H_3{}^tBu_2$-2,6 yielded a solution which by NMR spectroscopy contained **2** as the main product. Crystallizations of these solutions yielded $[(THF)LiOC_6H_3{}^tBu_2\text{-}2,6]_2$,[61] rather than the yttrium "ate" salt. Attempts to make the neutral monoalkyl dialkoxide, $(Me_3SiCH_2)Y(OC_6H_3{}^tBu_2\text{-}2,6)_2(THF)_x$, were also unsuccessful. The reaction of YCl_3 with 1 equiv of $LiCH_2SiMe_3$ and 2 equiv of $LiOC_6H_3{}^tBu_2$-2,6 produced complicated NMR spectra which included resonances for **2** formed by ligand redistribution.

Discussion

Three direct YCl_3/LiR/(LiOR or LiOAr) reactions have now been reported in the literature to give fully characterized products as shown in eqs 3, 5, and 6. The basis for the preference to form these three different types of products is not clear. The fact that complexes **1** and **2** could be isolated when many other ligand combinations do not give crystallographically characterizable alkyl alkoxide or aryloxide species is not easily rationalized. Since **1** has large alkyl ligands and small alkoxides and **2** has small alkyls and a large alkoxide, there appears to be some balance in steric bulk in each complex. However, the steric saturation needed to isolate a stable complex can obviously be obtained by other means—formation of an "ate" salt or THF adduct formation. The segregation of ligands in $\{Y(CH_2SiMe_3)_x(OCMe_3)_{5-x}[Li(THF)]_4Cl\}^+[Y(CH_2SiMe_3)_4]^-$,[28] eq 3, suggests that formation of mixed-ligand complexes involving ligands of similar size may be disfavored compared to the formation of homoleptic species. If these initial results are general, then mixed alkyl alkoxide or aryloxide complexes will be most readily obtained using ligands of disparate sizes.

Conclusion

Formation of mixed-ligand alkyl alkoxide and aryloxide complexes of yttrium can occur in a straightforward manner if the appropriate combination of ligands is used. Too little data on this subject are available to attribute to steric or electronic factors the propensity of the $(Me_3Si)_2CH/OCMe_3$ combination to form the "ate" salt, **1,** and the $Me_3SiCH_2/OC_6H_3{}^tBu_2$-2,6 combination to form the neutral complex, **2**, but clearly the particular mixture of ligands is critical. This is encouraging with respect to the reactivity of these yttrium alkyl alkoxide and aryloxide complexes, since these preferences, once understood, may be useful in controlling reaction pathways.

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Supporting Information Available: Text describing X-ray procedures, figures showing the complexes, and tables of crystal data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters (36 pages). Ordering information is given on any current masthead page.

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