

Isolation and Structure of a Homoleptic Yttrium Trimethylsilylmethyl Complex [☆]

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Abstract

YCl_3 reacts with 2 equivalents of $LiCH_2SiMe_3$ and 2 equivalents of $LiOCMe_3$ to form $\{(Me_3SiCH_2)_x(Me_3CO)_{1-x}Y(\mu-OCMe_3)_4[Li(THF)]_4(\mu_4-Cl)\}^+[Y(CH_2SiMe_3)_4]^-$, **1**. The anion in **1** has a tetrahedral arrangement of terminal alkyl groups around yttrium. The cation is a heterometallic Li_4Y mixed ligand species containing six anionic groups: a bridging Cl, four bridging $OCMe_3$ units, and a terminal ligand which is a disordered mixture of $OCMe_3$ and CH_2SiMe_3 . In the cation, a square plane of four $OCMe_3$ groups is oriented on top of a square plane of four $Li(THF)$ groups to form overall a square antiprism which is capped below with a chloride and above with an yttrium attached to the disordered $CHSiMe_3/OCMe_3$ group. **1** crystallizes from toluene in the space group $P\bar{1}$ with $a = 11.383$ (2) Å, $b = 17.057$ (3) Å, $c = 20.036$ (4) Å, $\alpha = 95.684$ (14)°, $\beta = 94.028$ (13)°, $\gamma = 90.031$ (12)°, $V = 3861.5$ (11) Å³ and $D_{Calc.} = 1.112$ Mg m⁻³ for $Z = 2$. Least squares refinement of the model based on 6562 reflections ($|F_o| > 4.0\sigma(|F_o|)$) converged to a final $R_F = 7.1\%$.

Keywords: Yttrium; Alkyl; Alkoxide; Heterobimetallica; Lithium; Silicon

1. Introduction

The organometallic chemistry of yttrium and the lanthanide metals involving metal–carbon single bonds is dominated by complexes containing cyclopentadienyl groups as ancillary stabilizing ligands [1–5]. Homoleptic lanthanide alkyl complexes are not common [1–5], and only three types of compounds have been structurally characterized: $LnMe_6Li_3$ ($Ln = La$, [6] Er, [7] Ho, [8] Lu [9]), $Ln[CH(SiMe_3)_2]_3$, ($Ln = La, Sm$) [10] and $Lu(CMe_3)_4Li$ [11].

Among the alkyl ligands in yttrium and lanthanide chemistry, trimethylsilyl-substituted alkyls are used extensively owing to the absence of β -hydrogens [12]. Numerous structures of complexes containing the bis(trimethylsilyl)methyl ligand, $-CH(SiMe_3)_2$, have been reported [10,13–19] but relatively few examples of complexes of the less sterically bulky (trimethylsilyl)methyl ligand, $-CH_2SiMe_3$, have been structurally characterized [15,20–22].

We report here the structure of a rare example of a homoleptic tetraalkyl yttrium complex containing the CH_2SiMe_3 ligand, $[Y(CH_2SiMe_3)_4]^-$. This anion is isolated as the salt $\{(Me_3SiCH_2)_x(Me_3CO)_{1-x}Y(\mu-OCMe_3)_4[Li(THF)]_4(\mu_4-Cl)\}^+[Y(CH_2SiMe_3)_4]^-$, **1**. **1** represents an unusual segregation of ligands in the formation of a complicated ion pair complex.

2. Experimental section

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 were freshly distilled and dried as previously described [23]. Yttrium trichloride (Rhône-Poulenc) was dried as previously described [24]. $LiOCMe_3$ was prepared from freshly sublimed $LiCMe_3$ and $HOCMe_3$ (distilled from CaH_2 onto K and distilled) in hexanes. Trimethylsilylmethyl lithium (Aldrich, 1.0 M in pentanes) was dried in vacuo to remove pentanes and purified by sublimation. ¹H and ¹³C NMR spectra were recorded on a General Electric GN500 spectrometer. ¹H NMR chemical shifts were assigned

[☆] This paper is dedicated to Prof. H Schumann on the occasion of his 60th birthday.

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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 (t) and in THF- d_8 at δ 67.4 (p). Infrared spectra were obtained on a Perkin Elmer 1600 FT-IR spectrometer.

2.1. $\{Y(CH_2SiMe_3)_x(OCMe_3)_{5-x}[Li(THF)]_4Cl\}^+ [Y(CH_2SiMe_3)_4]^-$, **1**

In a glovebox, YCl_3 (200 mg, 1.02 mmol) was slurried in THF (ca. 10 ml) and stirred for 5 min. $LiCH_2SiMe_3$ (193 mg, 2.04 mmol) was added, to form a clear colorless solution. After stirring for 5 min, $LiOCMe_3$ (163 mg, 2.04 mmol) was added, and the reaction mixture was stirred for 18 h, to produce a clear pale yellow solution. THF was removed by rotary evaporation, and the resulting oily solid was extracted with toluene and hexanes. The toluene-soluble fraction was dried by rotary evaporation to give a pale yellow solid (424 mg, 67% based on Y). Crystals suitable for X-ray diffraction were grown from a concentrated toluene solution of **1** at $-35^\circ C$. 1H NMR: (C_6D_6) δ 3.54 (s, THF); 1.45, 1.42, 1.31 (three overlapping broad singlets, $OCMe_3$, THF); 0.53, 0.47 (overlapping broad singlets, $\Delta\nu_{1/2} = 60$ Hz, $CH_2Si(CH_3)_3$); -0.43 , -0.52 (overlapping broad singlets, $CH_2Si(CH_3)_3$). 1H NMR: (THF- d_8) 1.33 (s, $\mu-OCMe_3$), 1.29 (s, $\mu-OCMe_3$), 0.07 (s, $CH_2Si(CH_3)_3$), -0.03 (br s, $CH_2Si(CH_3)_3$), -0.82 (br s, $CH_2Si(CH_3)_3$), -1.04 (s, $CH_2Si(CH_3)_3$). ^{13}C NMR: (C_6D_6) 68.4 (THF), 35.9 ($OC(CH_3)_3$), 34.6 ($OC(CH_3)_3$), 34.3 ($OC(CH_3)_3$), 25.1 (THF), 4.6 ($SiCH_3$). ^{13}C NMR: (THF- d_8) 35.5 ($OC(CH_3)_3$), 34.8 ($OC(CH_3)_3$), 32.5 ($OC(CH_3)_3$), 5.1 ($Si(CH_3)_3$), 0.00 ($Si(CH_3)_3$). IR: (KBr) 2960 s, 2882 m, 1626 w, 1462 w, 1359 m, 1231 s, 1190 s, 1036 m, 1005 m, 933 s, 851 br s, 749 m, 667 w. Anal. Calc. for $Y_2C_{52}ClH_{121}Li_4O_9Si_4$, Y, 14.29. Found: Y, 14.1.

2.2. General Aspects of X-ray Data Collection, Structure Determination, and Refinement

A colorless crystal of approximate dimensions $0.42 \times 0.43 \times 0.50$ mm was immersed in Paratone-D oil under nitrogen, then manipulated in air onto a glass fiber and transferred to the nitrogen stream of a Syntex P2₁ diffractometer (Siemens R3m/V System) 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 using standard techniques similar to those of Churchill [25]. Details are given in Table 1.

All 10774 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. Any reflection with $I(\text{net}) < 0$ was assigned the value $|F_o| = 0$. There were no systematic extinctions nor any diffraction symmetry

Table 1

Experimental data for the X-ray diffraction study of $\{(Me_3SiCH_2)_x(Me_3CO)_{1-x}Y(\mu-OCMe_3)_4[Li(THF)]_4(\mu_4-Cl)\}^+[Y-(CH_2SiMe_3)_4]^-$, **1**

Formula	$[C_{36}H_{77}ClLi_4O_{8.75}YSi_{0.25}] \cdot [C_{16}H_{44}Si_4Y] \cdot 1/2(C_7H_8)$
FW	1293.0
Temp (K)	163
Crystal System	Triclinic
Space Group	$P\bar{1}$
a (Å)	11.383 (2)
b (Å)	17.057 (3)
c (Å)	20.036 (4)
α (deg)	95.684 (14)
β (deg)	94.028 (13)
γ (deg)	90.031(12)
Volume (Å ³)	3861.5 (11)
Z	2
D_{calcd} (Mg m ⁻³)	1.112
Diffractometer	Syntex P2 ₁ (Siemens R3m/V System)
Radiation	Mo K α ($\lambda = 0.710730$ Å)
Monochromator	highly oriented graphite
Data Collected	$+h, \pm k, \pm l$
Scan Type	$\theta-2\theta$
Scan Range (deg)	1.2 plus K α -separation
Scan Speed, deg min ⁻¹ (in ω)	3.0
2θ Range (deg)	4.0 to 45.0
μ (Mo K α), mm ⁻¹	1.637
Absorption Correction	semi-empirical (ψ -scan method)
Reflections Collected	10774
w^{-1}	$\sigma^2(F_o) + 0.00030(F_o)^2$
Reflections with ($ F_o > 4\sigma(F_o)$)	6562
No. of Variables	584
R_F	7.1%
R_{wF}	7.7%
Goodness of Fit	1.78

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.

All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package [26] or the SHELXTL PLUS program set [27]. The analytical scattering factors for neutral atoms were used throughout the analysis [28]; 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 $\sigma^2(|F_o|) + 0.0007(|F_o|)^2$.

The structure was solved by direct methods (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 $U(\text{iso}) = 0.082$ Å². There is a half a toluene solvent molecule present per

formula unit and it is disordered. The cation contains a disordered ligand which is a mixture of OCMe_3 and CH_2SiMe_3 (approximately 75% OCMe_3 ; 25% CH_2SiMe_3). The site-occupancy factors for the disordered atoms were fixed accordingly. Si(5B) is a composite Si/C atom and was refined as a silicon atom with occupancy = 0.57143 to account for the 75:25% disorder. Hydrogen atoms on the disordered ligands and the toluene molecule were not included in the refinement. Refinement of the model led to a convergence with $R_F = 7.1\%$, $R_{wF} = 7.7\%$ and $\text{GOF} = 1.78$ for 584 variables refined against those 6562 data with $|F_o| > 4.0\sigma(|F_o|)$. A final difference-Fourier map yielded $\rho(\text{max}) = 0.84 \text{ e}\text{\AA}^{-3}$.

3. Results

3.1. Synthesis

Recent studies of mixed ligand alkyl alkoxide complexes of yttrium and the lanthanides have shown interesting reactivity patterns [22,29–31]. In an attempt to make a mixed alkyl alkoxide directly from simple starting materials, the reaction of YCl_3 with two equivalents of $\text{LiCH}_2\text{SiMe}_3$ followed by two equivalents of LiOCMe_3 in THF was examined to determine if a complex such as $[\text{Y}(\text{OCMe}_3)_2(\text{CH}_2\text{SiMe}_3)_2]^-$ would form (cf. $[\text{Ln}(\text{CMe}_3)_4]^-$, (Lu , $^{11}\text{Y}^{32}$). The main product isolated from this reaction was the toluene soluble species, **1**, which had a ^1H NMR spectrum which contained resonances attributable to CH_2SiMe_3 and OCMe_3 . Since the specific arrangement of the ligands could not be deduced from this information, X-ray crystallography was used to reveal that **1** was $\{\text{Y}(\text{CH}_2\text{SiMe}_3)_x(\text{OCMe}_3)_{5-x}[\text{Li}(\text{THF})_4\text{Cl}]\}^+[\text{Y}(\text{CH}_2\text{SiMe}_3)_4]^-$, Figs. 1 and 2. Hence, the direct reaction of these reagents shows a nearly complete segregation of

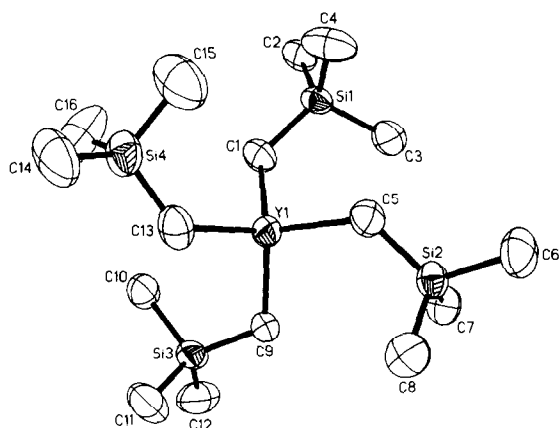


Fig. 1. Thermal ellipsoid plot of $[\text{Y}(\text{CH}_2\text{SiMe}_3)_4]^-$ with thermal ellipsoids drawn at the 50% level.

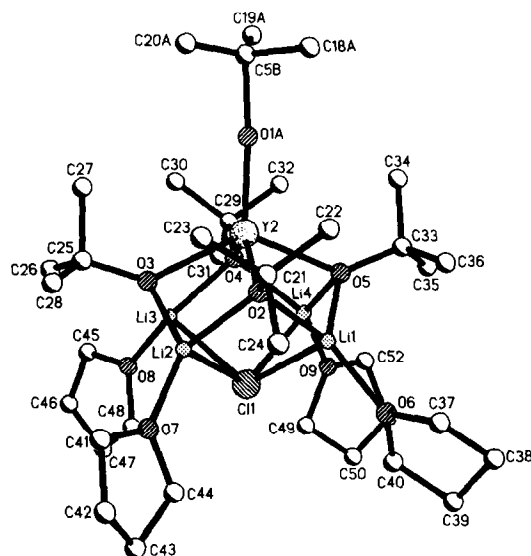
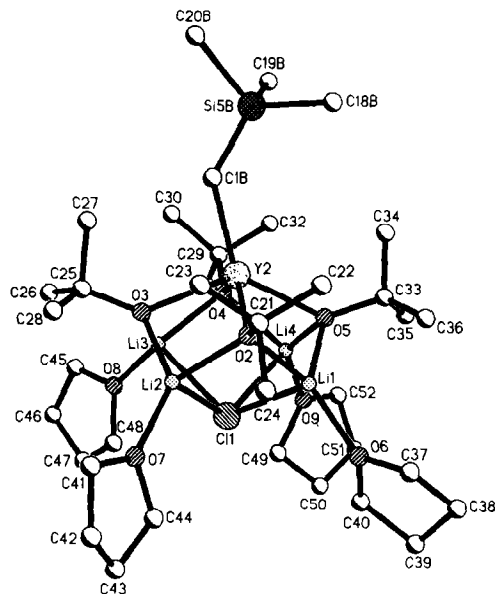


Fig. 2. (a) Ball and stick model of the Me_3SiCH_2 -containing component of the disordered $\{(\text{Me}_3\text{SiCH}_2)_x(\text{Me}_3\text{CO})_{1-x}\text{Y}(\mu\text{-OCMe}_3)_4[\text{Li}(\text{THF})_4(\mu_4\text{-Cl})]\}^+$. (b) Ball and stick model of the Me_3CO -containing component of the disordered $\{(\text{Me}_3\text{SiCH}_2)_x(\text{Me}_3\text{CO})_{1-x}\text{Y}(\mu\text{-OCMe}_3)_4[\text{Li}(\text{THF})_4(\mu_4\text{-Cl})]\}^+$.

the alkyl and alkoxide reagents into the anionic and cationic components, respectively.

3.2. Structure of the anion

The $[\text{Y}(\text{CH}_2\text{SiMe}_3)_4]^-$ anion is only the second example of a structurally characterized homoleptic tetrakis(trimethylsilylmethyl) complex in the literature. The only other example is the main-group complex $[\text{In}(\text{CH}_2\text{SiMe}_3)_4]^-$ [33]. The geometry about Y(1) in the anion describes a tetrahedron, with C–Y–C angles ranging from 105.9 (3) to 113.2 (3)°. This tetrahedral ar-

rangement is also seen in $[\text{In}(\text{CH}_2\text{SiMe}_3)_4]^-$ [33] and $[\text{Y}(\text{CMe}_3)_4]^-$ [11]. The Y(1)–C bond distances in the four coordinate anion (2.382 (8) to 2.420 (9) Å range and 2.41 (2) Å average) are surprisingly similar to the average 2.42 (2) Å Y–C bond distance in formally eight coordinate $[(\text{C}_5\text{H}_5)_2\text{Y}(\text{CH}_2\text{SiMe}_3)_2]^-$ [21]. Although indium is 0.1 Å smaller than yttrium [34], the average In–C(CH₂SiMe₃) distance in $[\text{In}(\text{CH}_2\text{SiMe}_3)_4]^-$ is 2.239 (8) Å [33].

3.3. Structure of the cation

The overall geometry of the core of the cation can be described as a distorted bicapped square antiprism, with

Table 2

Selected bond distances (Å) and angles (°) for $\{(\text{Me}_3\text{-SiCH}_2)_x(\text{Me}_3\text{CO})_{1-x}\text{Y}(\mu\text{-OCMe}_3)_4[\text{Li}(\text{THF})_4(\mu_4\text{-Cl})]^+[\text{Y}(\text{CH}_2\text{-SiMe}_3)_4]^-$, **1**

Y(1)–C(1)	2.416(8)	Y(1)–C(9)	2.403(8)
Y(1)–C(5)	2.420(9)	Y(1)–C(13)	2.382(8)
Y(2)–Cl(1)	3.263(2)	Y(2)–O(2)	2.261(5)
Y(2)–Li(1)	2.970(13)	Y(2)–O(3)	2.270(5)
Y(2)–Li(2)	2.994(15)	Y(2)–O(4)	2.271(5)
Y(2)–Li(3)	2.978(16)	Y(2)–O(5)	2.276(5)
Y(2)–Li(4)	3.006(13)		
Cl(1)–Li(1)	2.470(15)	Li(2)–O(3)	2.025(14)
Cl(1)–Li(2)	2.438(13)	Li(2)–O(7)	1.932(16)
Cl(1)–Li(3)	2.485(14)	Li(3)–O(3)	1.985(17)
Cl(1)–Li(4)	2.482(14)	Li(3)–O(4)	1.990(16)
Li(1)–O(2)	1.984(13)	Li(3)–O(8)	1.946(17)
Li(1)–O(5)	1.982(15)	Li(4)–O(4)	1.993(13)
Li(1)–O(6)	1.918(14)	Li(4)–O(5)	2.005(15)
Li(2)–O(2)	2.001(16)	Li(4)–O(9)	1.925(14)
Y(1)–C(1)–Si(1)	123.3(5)	C(1)–Y(1)–C(5)	111.3(3)
Y(1)–C(5)–Si(2)	123.1(4)	C(1)–Y(1)–C(9)	105.9(3)
Y(1)–C(9)–Si(3)	118.5(4)	C(5)–Y(1)–C(9)	111.4(3)
Y(1)–C(13)–Si(4)	124.7(4)	C(1)–Y(1)–C(13)	113.2(3)
C(9)–Y(1)–C(13)	109.1(3)	C(5)–Y(1)–C(13)	106.2(3)
O(2)–Y(2)–O(3)	81.5(2)	Cl(1)–Li(3)–O(3)	87.0(5)
O(2)–Y(2)–O(4)	134.5(2)	Cl(1)–Li(3)–O(4)	89.9(5)
O(3)–Y(2)–O(4)	81.1(2)	O(3)–Li(3)–O(4)	95.9(7)
O(2)–Y(2)–O(5)	80.7(2)	Cl(1)–Li(3)–O(8)	107.3(7)
O(3)–Y(2)–O(5)	131.5(2)	O(3)–Li(3)–O(8)	133.7(8)
O(4)–Y(2)–O(5)	80.1(2)	O(4)–Li(3)–O(8)	127.0(8)
Li(1)–Cl(1)–Li(2)	75.4(5)	Cl(1)–Li(4)–O(4)	89.9(5)
Li(1)–Cl(1)–Li(3)	121.2(5)	Cl(1)–Li(4)–O(5)	88.0(5)
Li(2)–Cl(1)–Li(3)	78.7(5)	O(4)–Li(4)–O(5)	94.1(6)
Li(1)–Cl(1)–Li(4)	76.6(5)	Cl(1)–Li(4)–O(9)	100.8(6)
Li(2)–Cl(1)–Li(4)	122.7(5)	O(4)–Li(4)–O(9)	126.5(7)
Li(3)–Cl(1)–Li(4)	74.8(4)	O(5)–Li(4)–O(9)	138.0(7)
Cl(1)–Li(1)–O(2)	89.8(5)	Y(2)–O(2)–Li(1)	88.6(4)
Cl(1)–Li(1)–O(5)	88.9(5)	Y(2)–O(2)–Li(2)	89.0(4)
O(2)–Li(1)–O(5)	95.6(6)	Li(1)–O(2)–Li(2)	97.8(6)
Cl(1)–Li(1)–O(6)	106.4(7)	Y(2)–O(3)–Li(2)	88.2(5)
O(2)–Li(1)–O(6)	133.1(8)	Y(2)–O(3)–Li(3)	88.6(5)
O(5)–Li(1)–O(6)	127.6(7)	Li(2)–O(3)–Li(3)	102.2(6)
Cl(1)–Li(2)–O(2)	90.3(5)	Y(2)–O(4)–Li(3)	88.4(5)
Cl(1)–Li(2)–O(3)	87.4(5)	Y(2)–O(4)–Li(4)	89.4(4)
O(2)–Li(2)–O(3)	94.6(7)	Li(3)–O(4)–Li(4)	98.5(6)
Cl(1)–Li(2)–O(7)	107.3(6)	Y(2)–O(5)–Li(1)	88.2(4)
O(2)–Li(2)–O(7)	125.8(7)	Y(2)–O(5)–Li(4)	89.0(4)
O(3)–Li(2)–O(7)	135.8(8)	Li(1)–O(5)–Li(4)	100.7(6)

the Y and Cl atoms in the capping positions, four Li atoms in one square face of the antiprism and four O(OCMe₃) atoms in the other square face (Fig. 2). The coordination geometry of five coordinate Y(2) is best described as a square pyramid, with four μ_3 -OCMe₃ in the base of the pyramid, each bridging to two Li atoms. This is a low coordination number for yttrium complexes with tert-butoxide ligands, which are typically at least six coordinate [35–39]. The only other similar five coordinate yttrium tert-butoxide complex is $(\text{Me}_3\text{-SiCH}_2)_2\text{Y}[(\mu\text{-CH}_2)_2\text{SiMe}_2][(\mu\text{-OCMe}_3)_4\text{Li}(\text{THF})_2]_2$, [22] which also contains bridging lithium ions. Each Li atom in the cation in **1** is also coordinated to one THF and the μ_4 -Cl. The geometry of the cation in **1** is fairly regular. For example, the O–Y(2)–O angles for adjacent oxygens have a range of only 80.1 (2) to 81.5 (2)°.

The bond distances in the cation in **1** (Table 2) are not unusual. The 2.270 (5) Å average Y–O(μ_3 -OCMe₃) distance is on the short side of the 2.306 (8)–2.556 (13) Å range of Y–O(μ_3 -OCMe₃) distances found in $\text{Y}_3(\mu_3\text{-OCMe}_3)(\mu_3\text{-Cl})(\mu\text{-OCMe}_3)_3(\text{OCMe}_3)_4(\text{THF})_2$, $\text{Y}_3(\mu_3\text{-OCMe}_3)(\mu_3\text{-Cl})(\mu\text{-OCMe}_3)_3(\text{OCMe}_3)_3(\text{Cl})(\text{THF})_2$, $[\text{Y}_4(\mu_3\text{-OCMe}_3)_2(\mu\text{-OCMe}_3)_4(\text{OCMe}_3)_4(\mu_4\text{-O})(\mu\text{-Cl})_2\text{Li}_4(\mu\text{-OCMe}_3)_2]_2$, and $\text{Y}_{14}(\text{OCMe}_3)_{28}\text{Cl}_{10}\text{O}_2(\text{THF})_4$ [32,36]. The Y(2)···Cl(1) distance of 3.263 (2) Å is too long to be considered a bonding interaction. For example, Y–Cl(μ_3 -Cl) distances in the yttrium alkoxides just listed do not exceed 2.897 (6) Å [36]. The 2.00 (3) average Li–O(μ_3 -OCMe₃) is statistically similar to the 1.87 (3) Å Li–O(μ_3 -OCMe₃) average distance in $[\text{nBuLi} \cdot \text{LiOCMe}_3]_4$ [40].

4. Conclusion

The reaction of YCl₃ with 2 equivalents of LiOCMe₃ and LiCH₂SiMe₃ does not yield a simple mixed alkyl alkoxide. Instead the ion pair $\{(\text{Me}_3\text{SiCH}_2)_x(\text{Me}_3\text{CO})_{1-x}\text{Y}(\mu\text{-OCMe}_3)_4[\text{Li}(\text{THF})_4(\mu_4\text{-Cl})]^+[\text{Y}(\text{CH}_2\text{SiMe}_3)_4]^-$, is formed which contains an unusual example of a homoleptic tetrakis(trimethylsilylmethyl)complex ion in a salt in which ligand segregation has occurred.

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