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New coordination environments for yttrium formed *in situ* by heterometallic bridging: crystal structures of $(C_5H_4SiMe_3)Y[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]_2$ and $(Me_3SiCH_2)Y[(\mu\text{-}CH_2)_2SiMe_2][(\mu\text{-}OR)Li(THF)_2]_2$ *

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Abstract

The bimetallic yttrium complexes $[(C_5R_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$ react with aluminum and lithium organometallic reagents to give complexes containing new combinations of ligands held together by heterometallic bridging atoms. $[(C_5H_4SiMe_3)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, **1**, reacts with $AlMe_3$ to form the mixed-metal mixed-ligand complex $(C_5H_4SiMe_3)Y[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]_2$, **2**, which contains a formally seven-coordinate yttrium linked to two four-coordinate aluminum atoms by bridging methyl and tert-butoxide ligands. Complex **2** contains two four-membered Y–O–Al–Me rings. $[(C_9H_7)Y(\mu\text{-}OR)(OR)]_2$, **3**, reacts with $LiCH_2SiMe_3$ to give a mixture of products from which $(Me_3SiCH_2)Y[(\mu\text{-}CH_2)_2SiMe_2][(\mu\text{-}OR)Li(THF)_2]_2$, **4**, can be isolated by crystallization from hexane/THF. Complex **4** contains a pentacoordinate yttrium atom ligated by a terminal CH_2SiMe_3 group, two bridging tert-butoxide ligands, and the two bridging methylene moieties of a $(\mu\text{-}CH_2)_2SiMe_2$ group. Each lithium atom is coordinated to two molecules of THF and the alkoxide and methylene bridges. The bridging groups combine to make three fused four-membered metallacyclic rings, two Y–O–Li–C rings and one Y–C–Si–C ring. The structures of **2** and **4** were determined by single crystal X-ray diffraction studies.

1. Introduction

Much of the organometallic chemistry of yttrium and the lanthanide metals involves complexes containing two cyclopentadienyl ligands [1]. Although these complexes have an extensive chemistry, a more diverse selection of stabilizing ligand environments would provide greater opportunities for developing the reaction chemistry of these metals. The same is true for the other early transition metals and the actinides.

Recently, alternative coordination environments for yttrium and the lanthanides have been explored by use of the tert-butoxide ligand [2–7]. Preliminary studies showed that trimetallic complexes of general formula, $Ln_3(OR)_3(\mu\text{-}OR)_3(\mu_3\text{-}OR)(\mu_3\text{-}Z)Z(L)_2$ (Ln = Y or a lanthanide; R = CMe_3; Z = OR, O, or halide; L = THF, ROH) [2–5], are commonly formed whenever yttrium or the lanthanides are ligated with two or more tert-butoxide ligands. Recently, it has been shown that the trimetallic structure in these complexes can be disrupted by organometallic reagents such as alkali metal cyclopentadienides [6] and trimethylaluminum [7]. These studies have revealed the existence of two new structural classes, namely, the bimetallic complexes $[(C_5R_5)Y(\mu\text{-}OR)(OR)]_2$ [6], which contain one cyclopentadienyl ring per yttrium, and the cyclopentadienyl-free monoyttrium complexes $Y[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]_3$ and $(Me_3CO)(THF)Y[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]_2$ [7].

We describe here studies of the reactivity of the dimeric $[(C_5R_5)Y(\mu\text{-}OR)(OR)]_2$ complexes, which show that even more diverse coordination environments can be assembled by using other metals to bridge small ligands together. Hence, the complexes

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* Dedicated to Prof. M.F. Lappert, an outstanding contributor to many areas of organometallic chemistry, on the occasion of his 65th birthday.

reported here demonstrate how a set of ligands too small to saturate and stabilize yttrium sterically can be connected through heterometallic bridging to yield isolable complexes. Specifically, we have investigated the reactions of $[(C_5R_5)Y(\mu\text{-}OR)(OR)]_2$ with $AlMe_3$ [8] and $LiCH_2SiMe_3$ [9] to determine if hybrid coordination environments containing alkyl, alkoxy, and cyclopentadienyl ligands can be synthesized in a direct manner. Fully characterized mixed-ligand mixed-metal complexes containing such components are rare, and are of interest with respect to lanthanide-based diene polymerization systems [10].

2. Experimental details

All compounds described below were handled with rigorous exclusion of air and water by use of Schlenk, vacuum line, and glove box techniques. Physical measurements were obtained and solvents were dried as previously described [11]. $[(C_5H_4SiMe_3)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$ and $[(C_9H_7)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$ were prepared from YCl_3, $NaOCMe_3$, and $KC_5H_4SiMe_3$ and KC_9H_7 respectively, as previously described [6].

2.1. *$(C_5H_4SiMe_3)Y[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]_2$, 2*

In a glove box, $AlMe_3$ (0.31 ml, 3.2 mmol) was syringed into a solution of $[(C_5H_4SiMe_3)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$ (0.60 g, 0.81 mmol) in hexanes. Within 30 min, the reaction mixture became cloudy. After 8 h the solvent was removed *in vacuo* and **2** was extracted with hexanes. A saturated solution of **2** in toluene was kept at -34°C for 12 h to give crystals suitable for an X-ray study (0.75 g, 90%). Anal. Found: C, 53.77; H, 9.92; Al, 10.80; Y, 18.45. $C_{22}H_{49}O_2Al_2SiY$ calc.: C, 54.09; H, 10.11; Al, 11.05; Y, 18.19%. ^1H NMR (C_6D_6): δ 6.46 (m, $C_5H_4SiMe_3$); 1.27 (s, $OCMe_3$); 0.24 (s, $C_5H_4SiMe_3$); -0.28, -0.29 ($AlMe_3$). (THF-d_8): δ 6.42 (m, $J = ca.$ 2 Hz, $C_5H_4SiMe_3$); 6.16 (m, $J = ca.$ 2 Hz, $C_5H_4SiMe_3$); 1.25 (s, $OCMe_3$); 1.19 (s, $OCMe_3$); 0.32 (s, $C_5H_4SiMe_3$); -0.77 (s, $AlMe_3$); -0.90 (s, $AlMe_3$). ^{13}C NMR (THF-d_8): δ 120 ($C_5H_4SiMe_3$); 113 ($C_5H_4SiMe_3$); 35 ($OCMe_3$); 33 (s,

TABLE 1. Summary of X-ray data for $[(C_5H_4SiMe_3)Y[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]_2$, **2**, and $(Me_3SiCH_2)Y[(\mu\text{-}CH_2)_2SiMe_2][(\mu\text{-}OCMe_3)Li(THF)_2]_2$, **4**.

	2	4
Formula	$C_{22}H_{49}O_2Al_2SiY$	$C_{32}H_{71}Li_2O_6Si_2Y$
Fw	516.6	710.9
Temperature (K)	168	168
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ [C_{2h}^5; no. 14]	$P2_1$ [C_2^2; no. 4]
a (Å)	10.972(4)	10.5407(16)
b (Å)	31.677(5)	18.931(3)
c (Å)	8.498(3)	11.3892(12)
β (deg)	99.48(2)	111.984(10)
V(Å^3)	2913.3(14)	2107.4(5)
Z	4	2
D_{calc} (Mg m^{-3})	1.178	1.120
Diffractometer	Siemens P3 (R3m/V System)	Siemens R3m/V
Radiation	Mo-Kα (λ = 0.710730 Å)	λ = 0.710730
Monochromator	Highly oriented graphite	Highly oriented graphite
Data collected	$+h, +k, \pm l$	$+h, +k, \pm l$
Scan type	θ–2θ	θ–2θ
Scan width	1.20 deg. plus Kα-separation	1.20 deg. plus Kα-separation
Scan speed (in ω)	3.00	3.00
2θ range	4.0 to 45.0°	4.0 to 50.0°
μ (Mo-Kα) mm^{-1}	2.126	1.479
Absorption correction	Semi-empirical (ψ-scan method)	Semi-empirical (ψ-scan method)
Reflections collected	4156	4086
Unique reflections with ($\mid F_o \mid > 0$)	3549	3708
Reflections with ($\mid F_o \mid > X\sigma(\mid F_o \mid)$)	3091 $X = 3.0$	3424 $X = 3.0$
No. of variables	277	388
R_F(%)	5.2	4.5
R_{wF}(%)	5.3	4.6
Goodness of fit	1.51	1.29

$OC\mathit{Me}_3$); 0.8 (s, $C_5H_4Si\mathit{Me}_3$); −9.1 ($AlMe_3$); −9.3 ($AlMe_3$). IR: (KBr) 2975s, 2931s, 2893m, 2825w, 1475w, 1394w, 1369m, 1250s, 1175s, 1044m, 925m, 900m, 887m, 837m, 788m, 763m, 687m cm^{-1}.

2.1.1. X-ray data collection, structure determination, and refinement for $(C_5H_4SiMe_3)Y[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]_2$, 2

Under nitrogen, a colorless crystal of approximate dimensions 0.17 mm × 0.46 mm × 0.56 mm was immersed in Paratone-D oil [12*]. The oil-coated crystal was then attached in air to a glass fiber which was placed in the nitrogen stream of a Siemens P3 diffractometer (R3m/V System) equipped with a modified LT-2 low-temperature system. Subsequent set-up operations (determination of accurate unit cell dimensions and orientation matrix) and collection of low-temperature (173 K) intensity data were carried out by standard techniques similar to those described by Churchill *et al.* [13]. Details appear in Table 1.

All 4156 data were corrected for absorption, and for Lorentz and polarization effects, and were placed on an approximately absolute scale. Diffraction symmetry was $2/m$ with systematic absences for $0k0$ where $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The centrosymmetric space group $P2_1/c$ [C_{2h}^5; No. 14] is therefore uniquely defined.

All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package [14] or the SHELXTL PLUS program set [15]. The analytical scattering factors for neutral atoms were used throughout the analysis [16a]; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion [16b] were included. The quantity minimized during least-squares analysis was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0005(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares techniques. The hydrogen atoms on C(7) and C(14) were located from a difference-Fourier map and refined (x, y, z and U_{iso}). The remaining hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and $U_{iso} = 0.08$ Å^2. Refinement of positional and thermal parameters (isotropic for carbon atoms) led to convergence with $R_F = 5.2\%$, $R_{wF} = 5.3\%$ and GOF = 1.51 for 277 variables refined against those 3091 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier synthesis showed no significant features, $\rho(\max) = 0.72$ eÅ^{-3}. Bond distances and angles are given in Table 2, and atomic coordinates are listed in Table 3.

TABLE 2. Selected bond distances (Å) and angles (deg) for $(C_5H_4SiMe_3)Y[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]_2$, 2

Y(1)–Al(1)	3.094(2)	Y(1)–Al(2)	3.160(2)
Y(1)–O(2)	2.280(4)	Al(2)–O(2)	1.841(4)
Y(1)–C(7)	2.577(7)	Al(1)–C(7)	2.054(7)
Y(1)–C(14)	2.562(6)	Al(2)–C(14)	2.025(7)
Y(1)–H(7B)	2.44(7)	Al(1)–C(5)	1.965(6)
Y(1)–H(14C)	2.51(6)	Al(1)–C(6)	1.959(6)
Y(1)–Cn [a]	2.356	Al(2)–C(13)	1.968(7)
Y(1)–C) ($C_5H_4SiMe_3$)avg	2.64(3)	Al(2)–C(14)	2.025(7)
Y(1)–O(1)–Al(1)	97.1(2)	Y(1)–C(7)–Al(1)	83.0(2)
Y(1)–O(2)–Al(2)	99.6(2)	Y(1)–C(14)–Al(2)	86.2(2)
Cn–Y(1)–O(2)	108.5	O(1)–Al(1)–C(7)	96.2(2)
Cn–Y(1)–O(1)	118.9	O(2)–Al(2)–C(14)	98.1(2)
Cn–Y(1)–C(7)	112.9	O(1)–Al(1)–C(5)	108.9(2)
Cn–Y(1)–C(14)	110.3	O(1)–Al(1)–C(6)	117.9(2)
O(1)–Y(1)–C(7)	73.8(2)	O(2)–Al(2)–C(12)	112.9(2)
O(2)–Y(1)–C(14)	74.0(2)	O(2)–Al(2)–C(13)	112.5(2)
O(1)–Y(1)–C(14)	86.7(2)	C(5)–Al(1)–C(6)	116.6(3)
O(2)–Y(1)–C(7)	91.2(2)	C(5)–Al(1)–C(7)	109.1(3)
O(1)–Y(1)–C(14)	86.7(2)	C(6)–Al(1)–C(7)	105.8(3)
O(2)–Y(1)–C(7)	91.2(2)	C(12)–Al(2)–C(13)	117.6(3)
O(1)–Y(1)–O(2)	132.5(1)	C(12)–Al(2)–C(14)	109.0(3)
C(7)–Y(1)–C(14)	136.8(2)	C(13)–Al(2)–C(14)	104.4(3)

[a] Cn = Cyclopentadienyl ring centroid.

2.2. $(Me_3SiCH_2)Y[(\mu\text{-}CH_2)_2SiMe_2][(\mu\text{-}OCMe_3)Li(THF)_2]_2$, 4

In a glove box, a solution of $LiCH_2SiMe_3$ (2.84 ml, 2.84 mmol) in hexanes was added by syringe to $[(C_9H_7)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$ (0.50 g, 0.71 mmol) dissolved in hexanes. A white precipitate formed immediately. After stirring for 8 h, the solvent was removed by rotary evaporation. The hexane soluble fraction was concentrated and cooled to −34°C. When this failed to produce crystals, several drops of THF were added and the mixture was again cooled to −34°C. After a prolonged period, a mixture of crystals had been formed, and from these, colorless **4** was separated and identified by X-ray crystallography.

2.2.1. X-ray data collection, structure determination, and refinement for $(Me_3SiCH_2)Y[(\mu\text{-}CH_2)_2SiMe_2][(\mu\text{-}OCMe_3)Li(THF)_2]_2$, 4

A colorless crystal of approximate dimensions 0.33 mm × 0.33 mm × 0.40 mm was handled, as described for **2** and examined on a Syntex P2$_1$ automated four-circle diffractometer, which was equipped with a modified LT-1 low-temperature system. Details appear in Table 1. The 4086 data were handled as described for **1**. The diffraction symmetry was $2/m$ with systematic absences $0k0$ for $k = 2n + 1$. The two possible mono-

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* Reference number with asterisk indicates a note in the list of references.

TABLE 3. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2 ×10^4) for **2**

Atom	x	y	z	U_{eq} [a]
Y(1)	3757(1)	3673(1)	2738(1)	203(2)
Al(1)	3125(2)	4573(1)	1435(2)	294(6)
Al(2)	6298(2)	3592(1)	5084(2)	346(6)
Si(1)	936(2)	3168(1)	−607(2)	290(5)
O(1)	2551(3)	4241(1)	2956(4)	252(12)
O(2)	5841(3)	3597(1)	2900(4)	272(13)
C(1)	1654(5)	4393(2)	3926(6)	289(19)
C(2)	391(6)	4395(3)	2912(8)	795(35)
C(3)	1598(7)	4106(2)	5293(8)	712(33)
C(4)	2023(8)	4823(2)	4554(9)	854(38)
C(5)	4625(6)	4869(2)	2445(7)	480(24)
C(6)	1916(6)	4905(2)	−9(7)	516(26)
C(7)	3618(7)	4082(2)	93(8)	325(22)
C(8)	6743(6)	3556(2)	1820(8)	386(22)
C(9)	6212(6)	3282(2)	404(7)	505(26)
C(10)	7919(6)	3340(2)	2700(8)	544(27)
C(11)	7046(6)	3999(2)	1302(8)	574(28)
C(12)	6648(6)	3018(2)	5954(7)	474(24)
C(13)	7490(6)	4041(2)	5848(8)	640(28)
C(14)	4683(6)	3796(2)	5671(7)	345(23)
C(15)	1700(6)	3104(2)	−2404(6)	410(22)
C(16)	−203(5)	2732(2)	−564(7)	428(22)
C(17)	112(6)	3685(2)	−693(7)	433(22)
C(18)	2125(5)	3115(2)	1223(6)	239(18)
C(19)	1931(5)	3133(2)	2836(6)	281(19)
C(20)	2968(6)	2966(2)	3823(7)	353(21)
C(21)	3829(5)	2847(2)	2877(7)	328(20)
C(22)	3326(5)	2939(2)	1291(6)	250(19)

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

clinic space groups are the non-centrosymmetric $P2_1$ [C_2^2; no. 4] or the centrosymmetric $P2_1/m$ [C_{2h}^2; no. 11]. It was later determined that the non-centrosymmetric space group was correct. Refinement of positional and thermal parameters led to convergence with $R_F = 4.5\%$, $R_{wF} = 4.6\%$ and GOF = 1.29 for 388 variables refined against those 3424 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier synthesis showed no significant features, $\rho(\max) = 0.41$ eÅ^{-3}. Bond distances and angles are listed in Table 4, and atomic coordinates are listed in Table 5. Tables of thermal parameters and hydrogen atom coordinates for both **2** and **4** have been deposited with the Cambridge Crystallographic Data Centre.

TABLE 4. Bond distances (Å) and angles (deg) for $(Me_3SiCH_2)Y[(\mu\text{-}CH_2)_2SiMe_2][(\mu\text{-}OCMe_3)Li(THF)_2]_2$ **4**

Y(1)–O(1)	2.192(4)	Y(1)–C(5)	2.450(8)
Y(1)–O(2)	2.174(4)	Y(1)–Si(1)	3.147(2)
Li(1)–O(1)	1.913(12)	Y(1)–C(1)	2.507(5)
Li(2)–O(2)	1.953(12)	Y(1)–C(2)	2.572(6)
Li(1)–O(3)	1.990(13)	Li(1)–C(1)	2.310(13)
Li(1)–O(4)	2.001(13)	Li(2)–C(2)	2.251(12)
Li(2)–O(5)	1.997(14)	Si(1)–C(1)	1.855(7)
Li(2)–O(6)	1.998(13)	Si(1)–C(1)	1.843(7)
Y(1)···Li(1)	3.044(13)		
Y(1)···Li(2)	3.008(12)		
O(1)–Y(1)–O(2)	104.8(1)	Y(1)–C(1)–Si(1)	91.1(3)
C(1)–Y(1)–C(2)	71.3(2)	Y(1)–C(2)–Si(1)	89.3(3)
C(1)–Y(1)–O(1)	84.5(2)	Li(1)–C(1)–Si(1)	148.2(5)
C(2)–Y(1)–O(2)	85.9(2)	Li(2)–C(2)–Si(1)	133.6(5)
O(1)–Li–C(1)	96.8(6)	C(5)–Y(1)–O(1)	103.8(2)
O(1)–Li–C(1)	100.9(6)	C(5)–Y(1)–O(2)	111.4(2)
Y(1)–O(1)–Li(1)	95.5(4)	C(5)–Y(1)–C(1)	115.2(2)
Y(1)–O(2)–Li(2)	93.4(3)	C(5)–Y(1)–C(2)	92.8(2)
Y(1)–C(1)–Li(1)	78.2(3)		
Y(1)–C(2)–Li(2)	76.8(3)		

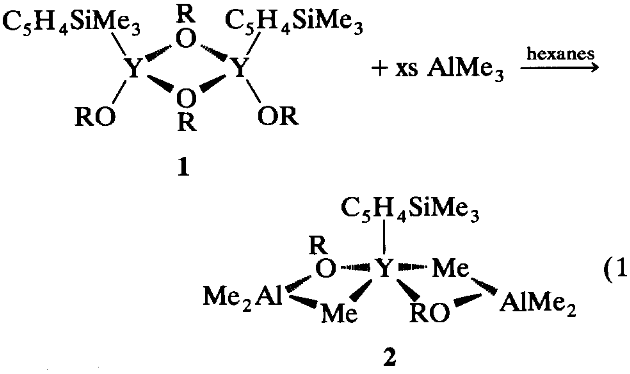
TABLE 5. Atomic coordinates (×10^4) for **4**

Atom	x	y	z
Y(1)	8161(1)	2970	2501(1)
Si(1)	5954(2)	3552(1)	−28(2)
Si(2)	6192(2)	1321(1)	2632(2)
Li(1)	9648(11)	2691(6)	714(9)
Li(2)	7060(11)	4277(6)	3286(10)
O(1)	10013(4)	2468(2)	2449(4)
O(2)	8893(4)	3885(2)	3721(3)
O(3)	9778(6)	2083(3)	−662(5)
O(4)	10637(4)	3520(3)	373(4)
O(5)	6432(4)	4000(3)	4672(4)
O(6)	6318(5)	5261(3)	3024(4)
C(1)	7336(5)	2908(4)	133(5)
C(2)	5875(6)	3637(4)	1556(6)
C(3)	4229(6)	3331(5)	−1315(6)
C(4)	6496(9)	4418(4)	−482(7)
C(5)	7203(7)	2076(4)	3491(6)
C(6)	7130(8)	763(4)	1882(7)
C(7)	4600(7)	1618(4)	1328(7)
C(8)	5642(10)	703(5)	3655(8)
C(9)	11089(6)	1991(3)	3146(6)
C(10)	10943(10)	1805(5)	4390(8)
C(11)	10985(9)	1320(4)	2401(8)
C(12)	12452(7)	2348(4)	3383(8)
C(13)	10102(6)	4274(3)	4338(6)
C(14)	10991(8)	3893(5)	5543(7)
C(15)	9732(8)	5010(4)	4660(8)
C(16)	10873(8)	4340(5)	3452(9)
C(17)	8765(10)	1561(5)	−1331(9)
C(18)	8973(12)	1413(7)	−2493(10)
C(19)	10229(14)	1747(10)	−2388(13)
C(20)	10803(10)	2096(7)	−1189(10)
C(21)	9968(10)	3957(7)	−680(10)
C(22)	10754(11)	4547(7)	−639(14)
C(23)	12073(8)	4500(4)	460(8)
C(24)	12045(7)	3754(4)	921(7)
C(25)	5073(7)	3739(5)	4438(7)
C(26)	5112(11)	3470(8)	5643(8)
C(27)	6515(11)	3271(6)	6340(8)
C(28)	7326(8)	3771(6)	5912(7)
C(29)	5735(9)	5576(4)	3810(9)
C(30)	5140(11)	6270(5)	3211(8)
C(31)	5192(17)	6252(7)	2028(12)
C(32)	5976(11)	5678(5)	1895(8)

3. Results and discussion

3.1. A trimethylaluminum monocyclopentadienyl yttrium tert-butoxide complex, $(C_5H_4SiMe_3)Y[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]_2$, 2

The dimeric structure of $[(C_5H_4SiMe_3)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, **1** [6], was cleaved by $AlMe_3$ in hexane during 8 h at ambient temperature to give $(C_5H_4SiMe_3)Y[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]_2$, **2**, in 90% yield (eqn. (1)). Complex **2** was isolated by removal of solvent, and extraction with hexane. Crystals obtained at −34°C had the structure shown in Fig. 1. Thus the Lewis acidity of $AlMe_3$ is sufficient to bring about cleavage of the bridging $(RO)Y(\mu\text{-}OR)_2Y(OR)$ core in **1**, providing a clean route to the mixed ligand complex. Monocyclopentadienyl tert-butoxide alkyl complexes of yttrium have not been accessible in the past [17*,18].



(1)

Since yttrium tert-butoxide complexes are typically six coordinate [2–5] and yttrium cyclopentadienyl complexes are typically eight coordinate [1,19], the seven-coordinate yttrium in the mixed ligand complex **2** represents a compromise. Comparison of **2** with its monocyclopentadienyl precursor, **1**, which contains six-coordinate yttrium [6], shows that the chelating unit $[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]$ is less bulky than the chelating $(\mu\text{-}OCMe_3)_2Y(OCMe_3)(C_5H_4SiMe_3)$ unit in **1**.

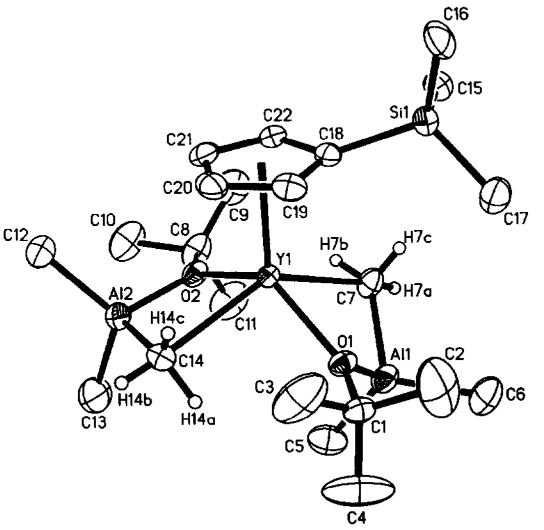


Fig. 1. ORTEP diagram of $(C_5H_4SiMe_3)Y[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]_2$, **2**, with probability ellipsoids drawn at the 50% level.

Since few monocyclopentadienyl yttrium complexes are known [6,17,20] and most mixed-metal lanthanide and yttrium aluminum complexes involve $(C_5R_5)_2Ln$ moieties [21], direct comparison of the structural parameters of **2** cannot be made. However, the 2.64 (3) Å $Y{-}C(C_5H_4SiMe_3)$ average distance is comparable to the 2.69 (3) Å distance in **1** [6] and the distances in $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OCH_3)]_2$ (2.63 (1) Å) [22], $[(C_5H_4SiMe_3)_2Y(\mu\text{-}Cl)]_2$, (2.67 (1) Å) [22], and $(C_5H_4SiMe_3)_2Y(\mu\text{-}OCMe_3)_2Li(THF)_2$ (2.74 (4) Å) [6]. The 2.579 (8) Å $Y{-}C(\mu\text{-}C)$ bond in **2** appears to be shorter than the analogous bonds in $Y[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]_3$, **5** (2.688 (28) Å) [7] and $(Me_3CO)(THF)Y[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]_2$, **6** (2.712 (24) Å) [7], but it is equal to the 2.57 (2)–2.60 (2) Å distances in $(C_5H_5)_2Y(\mu\text{-}Me)_2AlMe_2$ [8,23]. The average $Y{-}O(\mu\text{-}O)$ distance of 2.269 (11) Å is similar to the distances observed in **5** and **6** [2.209 (14) Å and 2.254 (2) Å] and is in the normal range for bridging yttrium tert-butoxide ligands [2–5]. The hydrogen atoms on C(7) and C(14) were located and refined, and reveal a distorted trigonal bipyramidal geometry around these five-coordinate carbon atoms with yttrium and H(7a) and H(14a) in the axial positions. The Y–C–H(axial) angles are 165 (4)° and 168 (5)°, the angles between equatorial ligands average 119° and range from 103 (6)° to 136 (4)°, and the angles between axial and equatorial ligands average 90° and range from 71 (5)° to 101 (5)°. This arrangement puts H(7B) and H(14C) within 2.44 (7) Å and 2.51 (6) Å of the yttrium respectively. A variety of geometries are known for bridging methyl groups [21a,b,24].

3.2. An alkyl yttrium tert-butoxide complex containing the $(\mu\text{-}CH_2)_2SiMe_2$ ligand, $(Me_3SiCH_2)Y[(\mu\text{-}CH_2)_2SiMe_2][(\mu\text{-}OCMe_3)Li(THF)_2]_2$, 4

The indenyl derivative $[(C_9H_7)Y(\mu\text{-}OR)(OR)]_2$, **3** [6], reacts with $LiCH_2SiMe_3$ to form hexane-soluble products, which had ^1H NMR spectra that lacked indenyl resonances and contained resonances for $OCMe_3$ and CH_2SiMe_3 ligands. The alkyl resonances displayed couplings of 3 Hz, consistent with $^2J_{YH}$ splitting [25,26] and products of general formula "$Y(OCMe_3)_{3-x}(CH_2SiMe_3)_x$" were indicated. Similar reactivity had been observed in reactions of $LiCH_2SiMe_3$ with other $[(C_5R_5)Y(\mu\text{-}OR)(OR)]_2$ complexes [6,27] and these reactions apparently generate a

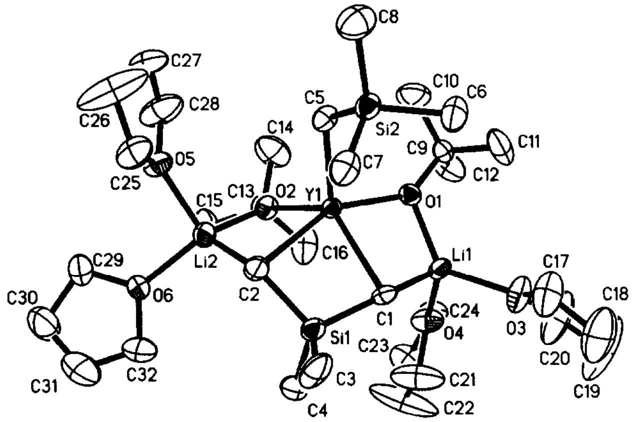


Fig. 2. ORTEP diagram of $(Me_3SiCH_2)Y[(\mu\text{-}CH_2)_2SiMe_2][(\mu\text{-}OCMe_3)Li(THF)_2]_2$, **4**, with probability ellipsoids drawn at the 50% level.

highly reactive system, because all of these reactions appear to be quite sensitive to specific reaction conditions including the choice of cyclopentadienyl complex used as the precursor.

When the product mixture formed from the reaction of **3** with $LiCH_2SiMe_3$ was set aside for a prolonged period to crystallize, crystals of the alkyl alkoxide complex, $(Me_3SiCH_2)Y[(\mu\text{-}CH_2)_2SiMe_2][(\mu\text{-}OCMe_3)Li(THF)_2]_2$, **4** (Fig. 2) were obtained. Although this reaction is too complicated to be synthetically useful at present, isolation of this complex enabled determination of the first crystallographic data for a cyclopentadienyl-free alkyl alkoxide complex of yttrium [17]. As in the case of **2**, bridging by another metal allows this combination of ligands to form an isolable complex. In addition, complex **4** reveals the formation of an unexpected ligand, the dialkyl species $(\mu\text{-}CH_2)_2SiMe_2$, formally derived by metallation of a methyl group of a CH_2SiMe_3 ligand.

Complex **4** contains a five-coordinate yttrium center ligated by two bridging tert-butoxide ligands, a terminal CH_2SiMe_3 group, and the two bridging methylene groups of a $(\mu\text{-}CH_2)_2SiMe_2$ moiety. This is a surprisingly low coordination number for yttrium in view of the size of the ligands. Although coordination numbers as low as three are known for yttrium aryloxide complexes of the bulky $OC_6H_3{}^tBu_2$-2,6 ligand [28] and four- and five-coordinate complexes of yttrium are known with the sterically encumbered $OSiPh_3$ and $OSiMe_2{}^tBu$ ligands [29], yttrium complexes with tert-butoxide [2–7] and small alkyl ligands [30] are generally at least six coordinate.

The three carbon and two oxygen donor atoms which surround yttrium in **4** have an irregular square pyramidal geometry in which C(5) is the axial position. The irregularity arises in part because the 71.3(2)° C(2)–Y(1)–C(1) angle resulting from the chelating nature of the $(\mu\text{-}CH_2)_2SiMe_2$ ligand is much smaller than the 104.8(1)° O(1)–Y(1)–O(2) angle which would normally be equivalent in a regular square pyramid. The 128.5(2)° C(1)–Y(1)–O(2) and 154.9(2)° C(2)–Y(1)–O(1) angles between the *trans* basal ligands are also quite different, but neither is close enough to 180° to qualify as the C_3 axis of a trigonal bipyramid.

The $(\mu\text{-}CH_2)_2SiMe_2$ ligand, the first to be structurally identified in an yttrium or lanthanide complex [31*], generates a metallacyclobutane ring which has a fold angle (*i.e.* the dihedral angle between the C(2)–Y(1)–C(1) plane and the C(2)–Si(1)–C(1) plane) of 15.0°. This is large compared to fold angles in other comparable early transition metal and actinide complexes: 5.8° in $(C_5Me_5)_2Th(CH_2SiMe_2CH_2)$ [32], 7.7° in $(C_5H_5)_2Ti(CH_2SiMe_2CH_2)$ [33], and 4.7° in $(C_5H_5)_2Zr(CH_2SiMe_2CH_2)$ [34]. However, it is similar to the fold angles in $(C_5H_5)_2Nb(CH_2SiMe_2CH_2)$ [34], 10.4° and $(C_5H_5)_2Mo(CH_2SiMe_2CH_2)$ [34], 14.3°.

The metallacyclobutane ring in **4** differs from those in other systems in that it is fused on each side to two other four-membered rings comprised of Y, C, O, and Li atoms. This three-ring fused structure is unprecedented in $(\mu\text{-}CH_2)_2SiMe_2$ chemistry. The extended steric protection which is generated by this fused ring system may explain why a stable five-coordinate complex of yttrium can be isolated with small alkyl and tert-butoxide ligands.

As a result of the ring fusions, the C(1) and C(2) atoms of the methylene groups are five coordinate. Since these five-coordinate carbon atoms involve methylene rather than methyl groups, three of the five substituents on the carbon atoms can be reliably located by X-ray crystallography and evaluated in terms of the geometry around these carbons. Although the hydrogen atoms were located in the crystallographic analysis, they could not be refined and their angular parameters cannot be discussed. The other angles around C(1) and C(2) are interesting in terms of the *differences* between these chemically equivalent positions in the same molecule. Similarity is observed between the two Y–C–Li angles, 78.2(3)° and 76.8(3)°, and between the two Y–C–Si angles, 91.1(3)° and 89.3(3)°, but the Li–C–Si angles are quite different, 148.2(5)° and 133.6(5)°. Hence, the (substituent)–carbon–(substituent) angles in such five-coordinate carbon structures may vary considerably despite chemical equivalence.

The 2.192(4) Å and 2.174(4) Å Y–O(μ-$OCMe_3$) distances in **4** are at the low end of the 2.19(2)–2.358(10) Å range previously observed [2,3,5–7]. The 2.450(8) Å Y(1)–C(5) bond length can be compared to the analogous distances in the eight-coordinate

$[(C_5H_5)_2Y(CH_2SiMe_3)_2]^-$ (2.402(6) Å and 2.445(6) Å) [35] and $(C_5H_5)_2Lu(CH_2SiMe_3)(THF)$ (2.376(17) Å) [36]. The latter complexes should have longer distances owing to their higher formal coordination number. The Y–C(5) distance is comparable to the 2.46(1) Å and 2.51(1) Å Th–C distances in $(C_5Me_5)_2Th(CH_2SiMe_3)_3$ [37], which involves a metal with a radius at least 0.15 Å larger [38]. Hence, the Y–C(5) bond is longer than expected. The 2.507(5) Å and 2.572(6) Å Y–C (bridging methylene) bonds are longer than the terminal bond, as expected, and these bonds also seem long in comparison to the bridging alkyl ligands in eight-coordinate $[(C_5H_5)_2Y(\mu\text{-}CH_3)]_2$, which has 2.545(11) Å Y–C(bridging) distances [25]. The Li–O(μ-OCMe$_3$) and Li–O(THF) bond distances are not unusual. The 2.310(13) Å and 2.251(12) Å Li–C distances are comparable to the Y–C distances when the difference in the radii of these metals is considered, but they are at the long end of the 2.15(2)–2.29(1) Å range of Li–C distances in $(LiCH_2SiMe_3)_6$ [39].

Metallation of silylmethyl moieties has been observed in highly reactive early transition metal, lanthanide, and actinide complexes of the type $(C_5Me_5)_2ScMe(THF)$ [40], $(C_5Me_5)_2MeLu(\mu\text{-}Me)Lu(C_5Me_5)_2$ [41], $(C_5Me_5)_2SmMe(THF)$ [11], and $(C_5Me_5)_2Th(CH_2SiMe_3)_2$ [37]. The most relevant of these examples is the thorium complex, which reacts at 80°C during 48 h to make the metallacyclic compound $(C_5Me_5)_2\overline{Th(CH_2SiMe_2CH_2)}$ [32]. The complexity of the reaction leading to **4** does not allow a discussion of the reaction pathway, but we note that the apparent formation of the $(\mu\text{-}CH_2)_2SiMe_2$ ligand from the CH_2SiMe_3 ligands in this system is the first time such an early-metal-based metallation has been accomplished in the absence of pentamethylcyclopentadienyl ligands.

4. Conclusion

Both **2** and **4** contain combinations of ligands previously unattainable in yttrium chemistry. In both cases the ligands that coordinate to the yttrium would not be expected to form stable complexes in the absence of the heterometal. The structural data for **2** show that the $[(\mu\text{-}OCMe_3)(\mu\text{-}Me)AlMe_2]$ unit constitutes a sterically bulky chelating ligand that can stabilize monocyclopentadienyl yttrium complexes without any unusual bonding interactions. The synthetic data show that this type of $[(\mu\text{-}OR)(\mu\text{-}Me)AlMe_2]$ ligand can be readily assembled from alkoxide complexes. It seems likely that reactions of alkylaluminum reagents with alkoxide complexes would provide a general route to a variety of stabilized mixed ligand complexes and that stabilizing coordination environments other than the common bis(cyclopentadienyl) cases can be produced for yttrium and related metals by assembling chelating ligands *in situ* with heterometallic reagents.

Complex **4** demonstrates another example of the utility of heterometallic reagents to assemble coordination environments not normally accessible. In this case, bridging lithium ions stabilize an unusually low coordination number for yttrium considering the size of the ligands surrounding it. Moreover, although metallacyclobutane rings involving $(\mu\text{-}CH_2)_2SiMe_2$ ligands are known in early transition metal and actinide complexes [31–34] no examples have previously been reported in which this four-membered ring is fused to two other four-membered rings. This extended fused ring system may be the crucial factor that allows the isolation of a five-coordinate structure with the small individual ligands. Hence, this complex can be considered to contain a macrocyclic O_2C_2 tetradentate ligand, namely $[(Me_3CO)(THF)_2LiCH_2SiMe_2CH_2Li\text{-}(THF)_2\text{-}(OCMe_3)]^{4-}$.

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