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Synthesis and structure of alkali metal ‘ate’ complexes in the yttrium/2,6-dimethylphenoxide system

William J. Evans [a,*], Mohammad A. Ansari [a], Joseph W. Ziller [a], Saeed I. Khan [b]

[a] Department of Chemistry, University of California, Irvine, CA 92697-2025, USA
[b] Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095, USA

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Abstract

The neutral complex $Y(OAr)_3(THF)_3$, **1**, ($Ar = C_6H_3Me_2$-2,6) prepared from $Y[N(SiMe_3)_2]_3$ and HOAr, can be converted to the ionic ‘ate’ salts $[(DME)Li]_2[(\mu\text{-}OAr)_4Y(OAr)]$, **2**, $[(THF)_3K][(\mu\text{-}OAr)_2Y(OAr)_2(THF)_2]$, **3**, and $[Na(THF)_6][(C_5Me_5)Y(OAr)_3]$, **4**, with the alkali metal reagents LiOAr, KOAr, and NaC_5Me_5 (DME = dimethoxyethane). The yttrium center in complex **2** is square pyramidal with the terminal aryloxide ligand in the apical position and no agostic interactions. The octahedral coordination environment around yttrium in **3** is formed by two bridging aryloxides, two terminal aryloxides and two THF molecules. This complex has close K–C(*ipso*) contacts of 3.288(9) and 3.400(10) Å. Complex **4** contains an isolated hexasolvated cation and a formally 6-coordinate yttrium atom in which the three aryloxide oxygen atoms and the η^5-C_5Me_5 ring centroid describe a distorted tetrahedron. © 1998 Elsevier Science S.A.

Keywords: Yttrium; Alkoxide; ‘Ate’ complex; Pentamethylcyclopentadienide; Alkali metal

1. Introduction

Recent developments in materials science [1–4] and organometallic chemistry [5–8] have spurred interest in alkoxide complexes of yttrium and the lanthanide metals. Alkoxides may be useful in assembling molecular precursors for materials applications and may function as solubilizing, stabilizing ligands alternative to the common cyclopentadienyl groups. Although alkoxide compounds of these metals have been known for many years [9–11], the extensive variation in structure and composition possible with this class is only now being revealed [12,13].[1] Products of varying structure and composition are observed depending on the metal/ligand combination and the particular starting materials used. Many of the variations observed are due to the incorporation of alkali metals, halides, and oxides.

Our studies of the 2,6-dimethylphenoxide ligand, $OC_6H_3Me_2$-2,6 (OAr in this paper), have shown that in combination with yttrium this group has the favorable property of making not one, but two neutral complexes free of alkali metals, oxides and halides, as shown in Eqs. (1) and (2) [31].

$$YCl_3(THF)_3 + 3NaOAr \rightarrow \underset{\mathbf{1}}{Y(OAr)_3(THF)_3} + 3NaCl \qquad (1)$$

$$2Y(OAr)_3(THF)_3 \rightleftharpoons \underset{1a}{[Y(\mu\text{-}OAr)(OAr)_2(THF)]_2} + 4THF \qquad (2)$$

This is unusual since formation of anionic ‘ate’ salts by incorporation of alkali metals with halide, alkoxide, or oxide units is a very common result [18,29].

The conversion of the trisolvated monomer, $Y(OAr)_3(THF)_3$, **1**, to the monosolvated dimer, $[Y(\mu\text{-}OAr)(OAr)_2(THF)]_2$, **1a**, suggests that this yttrium/2,6-dimethylphenoxide system provides access to a reactive, coordinatively unsaturated intermediate with less than three THF ligands per yttrium which can add THF but should add other ligands as well. We have examined the possibility of making organometallic derivatives of this Y/OAr system by adding anionic alkyl and cyclopentadienyl reagents to $[Y(\mu\text{-}OAr)(OAr)_2(THF)]_2$ in toluene. However, these reac-

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[*] Corresponding author.

[1] Only some reviews and leading Ref. [14–31] are given here.

tions repeatedly led to the formation of alkali metal 'ate' salt products. To learn more about such compounds and this crucial aspect of the synthetic chemistry, we have studied the deliberate synthesis and structural characterization of representative 'ate' salts for this metal/ligand combination.

2. Experimental section

All the complexes described in Sections 2.1, 2.2, 2.3, 2.4, 2.5, 2.6 and 2.7 were handled with rigorous exclusion of air and moisture using standard Schlenk, vacuum line, and glove box techniques. Solvents were dried and physical measurements obtained as previously described [32]. YCl_3 [33] and $Y[N(SiMe_3)_2]_3$ [34] were prepared according to the literature. 2,6-Dimethylphenol (Aldrich) was sublimed before use. NMR spectra were recorded using a General Electric QE-300 spectrometer at 20°C.

2.1. *Improved synthesis of $Y(OAr)_3(THF)_3$, **1** [31]*

HOAr (366 mg, 3 mmol) was added to $Y[N(SiMe_3)_2]_3$ (570 mg, 1.0 mmol) in 20 ml of THF. The clear colorless solution was stirred for 24 h and centrifuged. The solution was evaporated to dryness and the resulting solid was recrystallized from THF/hexanes at room temperature to form **1** as colorless crystals (610 mg, 90%). The ^{1}H NMR spectrum was identical to that reported earlier [31].

2.2. *Synthesis of $[(MeOCH_2CH_2OMe)Li]_2[(\mu\text{-}OAr)_4Y(OAr)]$, **2***

LiOAr (128 mg, 1.0 mmol) was added to a solution of **1** (334 mg, 0.5 mmol) in 10 ml of THF. The reaction mixture was stirred for 24 h at ambient temperature and centrifuged. The solution was dried on a rotary evaporator to yield a white powder. X-ray quality crystals (340 mg, 76%) were grown by layering $MeOCH_2CH_2OMe$ (DME) and hexanes on a THF solution at −38°C. Anal. Calcd. for $C_{48}H_{65}O_9Li_2Y$: C, 64.86; H, 7.37; Y, 10.0. Found: C, 65.41, H, 8.69, Y, 11.2. ^{1}H NMR (crude product before addition of DME, THF-d_8) δ 6.81 (d, 10H, $C_6H_3Me_2$), 6.34 (t, 5H, $C_6H_3Me_2$), 2.39 (s, 30H, $C_6H_3Me_2$). ^{1}H NMR (crystalline **2**, THF-d_8) 6.77 (d, 10H, $C_6H_3Me_2$), 6.15 (t, 5H, $C_6H_3Me_2$), 3.50 (s, 8H, $CH_3OCH_2CH_2OCH_3$), 3.33 (s, 12H, $CH_3OCH_2CH_2OCH_3$), 2.19 (s, 30H, $C_6H_3Me_2$). ^{13}C NMR (THF-d_8) 166.6, 128.2, 125.2, 111.6 ($C_6H_3Me_2$), 72.7 ($CH_3OCH_2CH_2OCH_3$), 58.9 ($CH_3OCH_2CH_2OCH_3$), 18.5 ($C_6H_3Me_2$). IR (Nujol) 1461 s, 1376 m, 1270 s, 1231 m, 1193 w, 1117 w, 1086 w, 1072 m, 1022 w, 872 w, 848 m, 758 w, 746 m, 691 m cm^{-1}.

2.3. *$[(THF)_3K][(\mu\text{-}OAr)_2Y(OAr)_2(THF)_2]$, **3***

KOAr (80 mg, 0.5 mmol) was added to a solution of **1** (337, 0.5 mmol) in 10 ml of THF. The reaction was stirred for 10 h and centrifuged. A small amount of solid was obtained and discarded. The volume of the solution was reduced to half and the solution was layered with a few drops of hexanes and cooled to −38°C. Large block-shaped colorless crystals (320 mg, 66%) formed in 24 h. Anal. Calcd. for $C_{52}H_{76}O_9KY$: C, 64.18; H, 7.87; K, 4.02; Y, 9.14. Found: C, 63.86; H, 7.63; K, 4.15; Y, 9.40. ^{1}H NMR (THF-d_8) 6.67 (d, 8H, $C_6H_3Me_2$), 6.17 (t, 4H, $C_6H_3Me_2$), 2.18 (s, 24H, $C_6H_3Me_2$). ^{13}C NMR (benzene-d_6) 162.5, 127.3, 125.3, 113.5 ($C_6H_3Me_2$), 67.4 (THF), 31.7 ($C_6H_3Me_2$), 25.5 (THF), 17.9 ($C_6H_3Me_2$), 13.6 ($C_6H_3Me_2$). IR (Nujol) 1588 s, 1461 s, 1377 s, 1287 m, 1236 m, 1089 w, 1073 w, 914 w, 746 w, 726 w, 697 w cm^{-1}.

2.4. *$[(C_5Me_5)Y(OAr)_3][Na(THF)_6]$, **4***

A 5 ml THF solution of NaC_5Me_5 (158 mg, 1.0 mmol) was added to a 10 ml THF solution of **1** (667 mg, 1.0 mmol). The reaction was stirred for 16 h and was centrifuged. The volume of the solution was reduced to half, the solution was layered with a few drops of hexanes, and the solution was cooled to −38°C to produce colorless crystals (750 mg, 72%). Anal. Calcd. for $C_{58}H_{90}O_9NaY$: C, 66.78; H, 8.7; Na, 2.20; Y, 8.52. Found: C, 68.78; H, 6.03; Na, 2.38; Y, 9.06. ^{1}H NMR (benzene-d_6) 7.06 (d, 6H, $C_6H_3Me_2$), 6.74 (t, 3H, $C_6H_3Me_2$), 3.32 (m, 24H, THF), 2.35 (s, 18H, $C_6H_3Me_2$), 2.11 (s, 15H, C_5Me_5), 1.27 (m, 24H, THF). ^{13}C NMR (benzene-d_6) 161.0, 128.4, 125.0, 116.4 ($C_6H_3Me_2$), 116.8 (C_5Me_5), 67.5 (THF), 25.2 (THF), 17.9 ($C_6H_3Me_2$), 10.5 (C_5Me_5). IR (Nujol) 1590 m, 1462 s, 1377 m, 1295 m, 1241 w, 1088 m, 1047 m, 913 w, 864 m, 782 w, 755 w, 710 w cm^{-1}.

2.5. *X-ray data collection and structure refinement for $[(DME)Li]_2[(\mu\text{-}OAr)_4Y(OAr)]$, **2***

A crystal of dimensions 0.20 × 0.25 × 0.30 mm mounted in a Lindeman capillary under dinitrogen in a dry box was placed in the cold nitrogen stream of a Picker diffractometer modified at UCLA which was operating at a temperature of 156(2) K. Intensity data were collected with graphite monochromated Mo Ka radiation up to maximum 2θ of 50°. Of the 2241 total reflections collected only 970 were observable above $I > 2\sigma(I)$. Other details of data collection are given in Table 1.

The structure was solved by heavy atom methods using SHELX86 [35]. The complex crystallizes in the orthorhombic space group $P22_12_1$. The structure was refined using SHELX76 [36]. All of the hydrogen atoms

Table 1
Crystallographic data for [(DME)Li]$_2$[(μ-OC$_6$H$_3$Me$_2$-2,6)$_4$Y(OC$_6$H$_3$Me$_2$-2,6)], **2**, [(THF)$_3$K][(μ-OC$_6$H$_3$Me$_2$-2,6)$_2$Y(OC$_6$H$_3$Me$_2$-2,6)$_2$(THF)$_2$], **3**, and [Na(THF)$_6$][((C$_5$Me$_5$)Y(OC$_6$H$_3$Me$_2$-2,6)$_3$], **4**

Compound	**2**	**3**	**4**
Formula	$C_{48}H_{65}O_9Li_2Y$	$C_{52}H_{76}O_9KY$	$C_{58}H_{90}O_9NaY$
Formula weight	888.79	973.1	1043.24
Space group	$P22_12_1$	$P2_1/n$	$P2_1/n$
a, Å	12.537(2)	14.301(6)	14.610(2)
b, Å	12.947(2)	19.623(6)	20.846(3)
c, Å	14.609(2)	18.599(8)	19.451(2)
β, °		97.99(3)	92.67(1)
Z	2	4	4
V, Å^3	2371.4(7)	5169(4)	5917(1)
D, calculated, g cm^{-3}	1.24	1.25	1.17
Radiation, λ	0.7107	0.71073	0.7107
Abs. coefficient, μ, mm^{-1}	1.285	1.26	1.045
R_F	0.063	0.089	0.079
$R_{(w)F}$	0.062	0.097	0.081
$(\lvert Fo\rvert > \times\sigma$ $(\lvert Fo\rvert))$, x =	4	3	3
GOF	1.58	1.46	2.853

were calculated and attached to appropriate carbon atoms at a fixed distance with a fixed isotropic *U*. Aryloxide groups were refined as rigid groups.

2.6. X-ray data collection and structure refinement for [(THF)$_3$K][(μ-OAr)$_2$Y(OAr)$_2$(THF)$_2$], **3**

A colorless crystal of approximate dimensions 0.40 × 0.80 × 0.83 mm was mounted on a Siemens P4 diffractometer operating at a temperature of 156(2) K. Intensity data were collected with graphite monochromated Mo Kα radiation up to a maximum 2θ of 45°. Of the 5902 total reflections collected only 4651 were observable above 3σ. Details of data collection are given in Table 1.

All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package (C. Strouse, University of California, Los Angeles, CA, 1981, personal communication) or the SHELXTL PLUS program set [37]. The analytical scattering factors for neutral atoms were used throughout the analysis [38]; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion [38] were included. The quantity minimized during least-squares analysis was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.002(|F_o|)^2$.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and $U(iso)$ = 0.08 Å^2. The diffraction symmetry was $2/m$ with systematic absences $0k0$ for $k = 2n + 1$, and $h0l$ for $h + l = 2n + 1$. The centrosymmetric space group $P2_1/n$ is therefore uniquely defined. Refinement of positional and thermal parameters led to convergence with $R_F = 8.9\%$, $R_{wF} = 9.7\%$ and GOF = 1.46 for 569 variables refined against those 4651 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map was devoid of significant features, $\rho(\max) = 1.20$ e Å^{-3}

2.7. X-ray data collection and structure refinement for [Na(THF)$_6$][(C$_5$Me$_5$)Y(OAr)$_3$], **4**

A crystal of dimensions 0.1 × 0.2 × 0.2 mm was handled as described for **2** in Section 2.5. Intensity data were collected up to a maximum 2θ of 55°. Of the 4477 total reflections collected only 2664 were observable above 3σ. Details of data collection are given in Table 1.

The structure was solved by heavy atom methods using SHELX86 [35]. The complex crystallizes with one [Y(C$_5$Me$_5$)(OAr)$_3$]$^-$[Na(THF)$_6$]$^+$ ion pair per asymmetric unit in monoclinic space group $P2_1/n$. The structure was refined using SHELX76 [36]. All of the hydrogen atoms were calculated and attached to appropriate carbon atoms with a fixed isotropic *U*. The phenoxide group involving O(3) was found to be disordered and was refined at two different orientations. The large thermal parameters associated with many atoms of the THF groups showed partial disorder. Three of these disordered THF groups, those involving O(40), O(45), and O(55), were refined at more than one orientation with constrained bond lengths and fixed temperature factors. In the final cycle of least-squares refinement, all of the THF and disordered aryloxide atoms were kept isotropic and the remaining atoms were refined with anisotropic temperature factors.

3. Results and discussion

3.1. Reaction with lithium 2,6-dimethylphenyloxide

$Y(OC_6H_3Me_2\text{-}2,6)_3(THF)_3$, **1**, reacts with 1 equivalent of $LiOC_6H_3Me_2\text{-}2,6$ in THF to give a colorless powder which does not crystallize readily from THF. Addition of DME gave crystals of $[(DME)Li]_2[(\mu\text{-}OAr)_4Y(OAr)]$, **2**. The reaction was repeated with the stoichiometry appropriate for **2** and a yield of > 70% was obtained according to Eq.(3).

$$\underset{\mathbf{1}}{Y(OAr)_3(THF)_3} + 2LiOAr \xrightarrow{\text{THF/DME}} \underset{\mathbf{2}}{[(DME)Li]_2[(\mu\text{-}OAr)_4Y(OAr)]} \qquad (3)$$

^{1}H NMR spectroscopy shows that all of the aryloxide groups in **2** are equivalent on the NMR time scale at down to −60°C. Since the data were not structurally definitive, an X-ray diffraction study was carried out. Complex **2** crystallizes as the trimetallic species, $[(DME)Li]_2[(\mu\text{-}OAr)_4Y(OAr)]$, **2**, which contains both bridging and terminal aryloxide ligands, Fig. 1.

3.2. Structure of $[(DME)Li]_2[(\mu\text{-}OAr)_4Y(OAr)]$, 2

Bond distances and angles in **2** are given in Table 2. Complex **2** contains a C_2 axis which is coincident with the Y–O(3)–C(17) vector. The five aryloxide ligands are arranged in a square pyramidal geometry around yttrium with 145.32(5) and 145.80(5)° O–Y–O angles between the basal aryloxides and 107.10(2) and 107.34(2)° Y–O–Y angles between the axial aryloxide and the basal positions. The two unique bridging aryloxide Y–O distances, 2.179(8) and 2.221(8) Å, are longer than the 2.098(1) Å Y–O distance for the unique terminal aryloxide as expected. In comparison, $[Y(\mu\text{-}OAr)(OAr)_2(THF)]_2$, **1a**, has 2.275(6) and 2.277(5) Å bridging Y–O bond lengths and 2.049(6) and 2.075(6) Å terminal distances [31].

The Li atoms are located in a distorted tetrahedral coordination environment formed by the two bridging aryloxide ligands and a bidentate DME ligand. No Li · · · C agostic interactions were observed within 4 Å of Li. The 1.927(3) Å average Li–OAr distance is in the 1.811(17)–1.995(12) Å range found in the literature [39–43]. The 76.71(1)° O(DME)–Li–O(DME) angle is

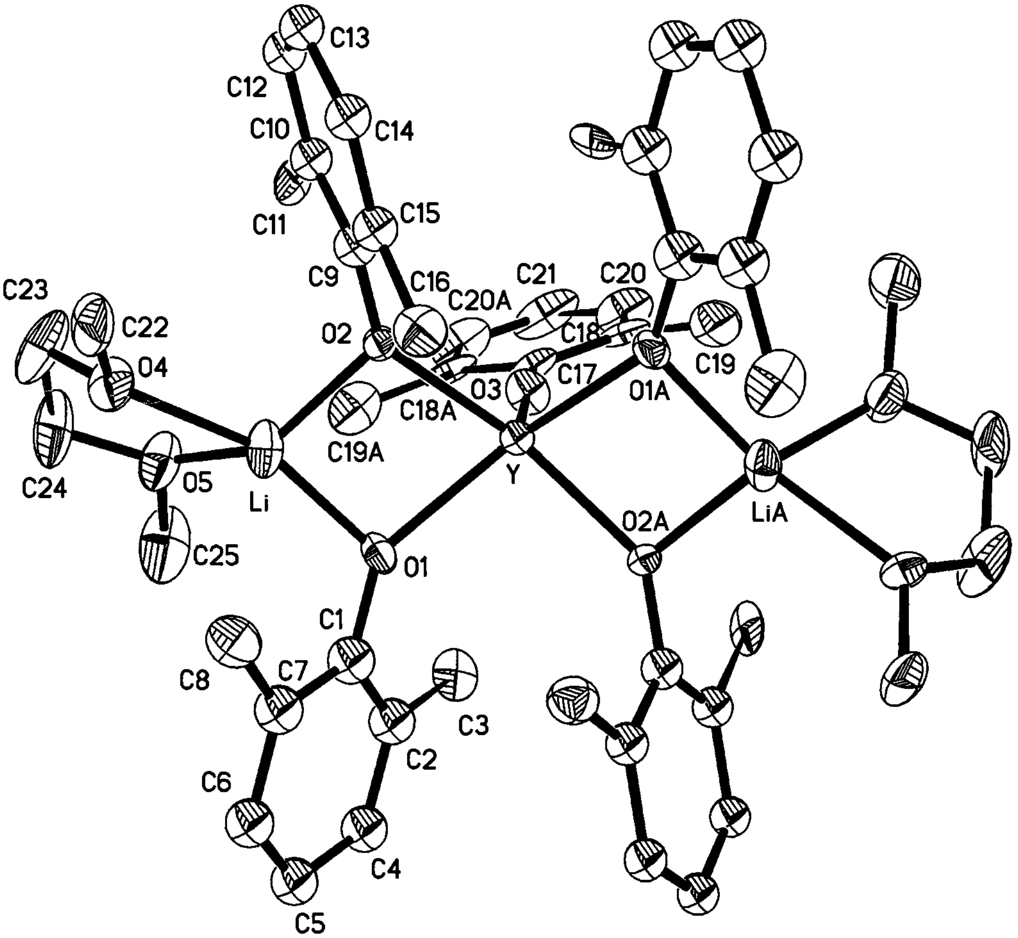

Fig. 1. Structure of $[(DME)Li]_2[(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_4Y(OC_6H_3Me_2\text{-}2,6)]$, **2**, with thermal ellipsoids drawn at the 50% probability level.

Table 2
Important angles (deg) and distances (Å) for $[(DME)Li]_2[(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_4Y(OC_6H_3Me_2\text{-}2,6)]$, **2**, $[(THF)_3K][(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_2Y(OC_6H_3Me_2\text{-}2,6)_2(THF)_2]$, **3**, and $[Y(\mu\text{-}OC_6H_3Me_2\text{-}2,6)(OC_6H_3Me_2\text{-}2,6)_2(THF)]_2$, **5**

2		**3**		**5**	
bridging Y-O(1)	2.221(8)	bridging Y(1)-O(1)	2.197(6)	bridging Y-O	2.277(5)
bridging Y-O(2)	2.179(8)	bridging Y(1)-O(2)	2.213(6)		2.275(6)
terminal Y-O(3)	2.098(1)	terminal Y(1)-O(3)	2.153(6)	terminal Y-O	2.075(5)
		terminal Y(1)-O(4)	2.122(6)		2.046(6)
		Y(1)-O(5) (THF)	2.453(6)		
		Y(1)-O(6) (THF)	2.484(6)		
Li-O(1)	1.928(3)	K(1)-O(1)	2.661(6)		
Li-O(2)	1.925(3)	K(1)-O(2)	2.668(6)		
Li-O(4) (DME)	2.025(3)	K(1)-O(7) (THF)	2.744(9)		
Li-O(5) (DME)	2.015(3)	K(1)-O(8) (THF)	2.693(10)		
		K(1)-O(9) (THF)	2.756(9)		
		K(1)-C(1)	3.288(9)		
		K(1)-C(9)	3.400(10)		
Y-O(1)-Li	97.35(1)	O(1)-Y(1)-O(2)	81.1(2)		
Y-O(2)-Li	98.84(1)	O(1)-Y(1)-O(3)	104.0(2)		
O(4)-Li-O(5)	76.71(1)	O(1)-Y(1)-O(4)	105.9(2)		
O(1)-Y-O(2)	74.45(4)	O(1)-Y(1)-O(5)	79.1(2)		
O(1)-Y-O(1)A	145.32(5)	O(1)-Y(1)-O(6)	161.6(2)		
O(1)-Y-O(2)A	95.32(4)	O(2)-Y(1)-O(3)	108.5(2)		
O(1)-Y-O(3)	107.34(2)	O(2)-Y(1)-O(4)	103.1(2)		
O(2)-Y-O(3)	107.10(2)	O(2)-Y(1)-O(5)	159.8(2)		
		O(2)-Y(1)-O(6)	80.7(2)		
		O(3)-Y(1)-O(4)	39.2(2)		
		O(3)-Y(1)-O(5)	80.1(2)		
		O(3)-Y(1)-O(6)	79.5(2)		
		O(4)-Y(1)-O(5)	79.0(2)		
		O(4)-Y(1)-O(6)	80.7(2)		
		O(5)-Y(1)-O(6)	119.2(2)		
		O(1)-K(1)-O(2)	65.1(2)		
		Y(1)-O(1)-C(1)	145.5(5)		
		Y(1)-O(2)-C(9)	141.3(5)		

smaller than the 87.41(1)° O(OAr)–Li–O(OAr) angle due to the chelation of the DME ligand.

3.3. Reaction with potassium 2,6-dimethylphenyloxide

In contrast to the system above, the reaction of **1** with one equivalent of KOAr produces $[(THF)_3K][(\mu\text{-}OAr)_2Y(OAr)_2(THF)_2]$, **3**, which crystallizes easily from THF/hexanes in $>60\%$ yield according to Eq. (4).

$$\underset{\mathbf{1}}{Y(OAr)_3(THF)_3} + KOAr \xrightarrow{THF} \underset{\mathbf{3}}{[(THF)_3K][(\mu\text{-}OAr)_2Y(OAr)_2(THF)_2]} \qquad (4)$$

Since the NMR spectra of **3** were similar to those of **2** and not structurally definitive, **3** was also characterized by X-ray diffraction (Fig. 2).

3.4. Structure of $[(THF)_3K][(\mu\text{-}OAr)_2Y(OAr)_2(THF)_2]$, 3

The coordination environment of **3** has some similarities to that of **2** in that the aryloxide groups bound through O(1) and O(3) are bridging to an alkali metal and the aryloxide bound through O(4) is terminal. However, instead of completing the coordination sphere with two more bridging groups as in **2**, the remaining ligands on yttrium are two THF molecules and a terminal aryloxide. Hence, a six coordinate complex is found rather than a five coordinate compound.

The geometry is quite distorted from octahedral with O–Y–O angles ranging from 79.1(2) to 108.5(2)° between *cis* ligand donor atoms and from 139.2(2) to 161.6(2)° between *trans* ligands. Complex **3** has 2.197(6) and 2.213(6) Å bridging Y–O bond lengths and 2.122(6) and 2.153(6) Å terminal Y–O distances which fall in the normal ranges compared to **2** and **1a**. The 2.493(6) and 2.484(6) Å Y–O(THF) distances are longer than the 2.417(12) Å analogs in $Y_3(OCMe_3)_8Cl(THF)_2$ [27], the 2.36(2)–2.45(2) Å distances in $Y_3(OCMe_3)_7Cl_2(THF)_2$ [28], and the 2.33(4)–2.37(3) Å distances in $Y_{14}(OCMe_3)_{24}Cl_{10}O_2(THF)_4$ [28], all of which contain six coordinate yttrium.

The potassium in **3** is ligated by seven donor atoms, three oxygen atoms from THF molecules, two oxygen atoms of the bridging aryloxides, and the *ipso* carbon

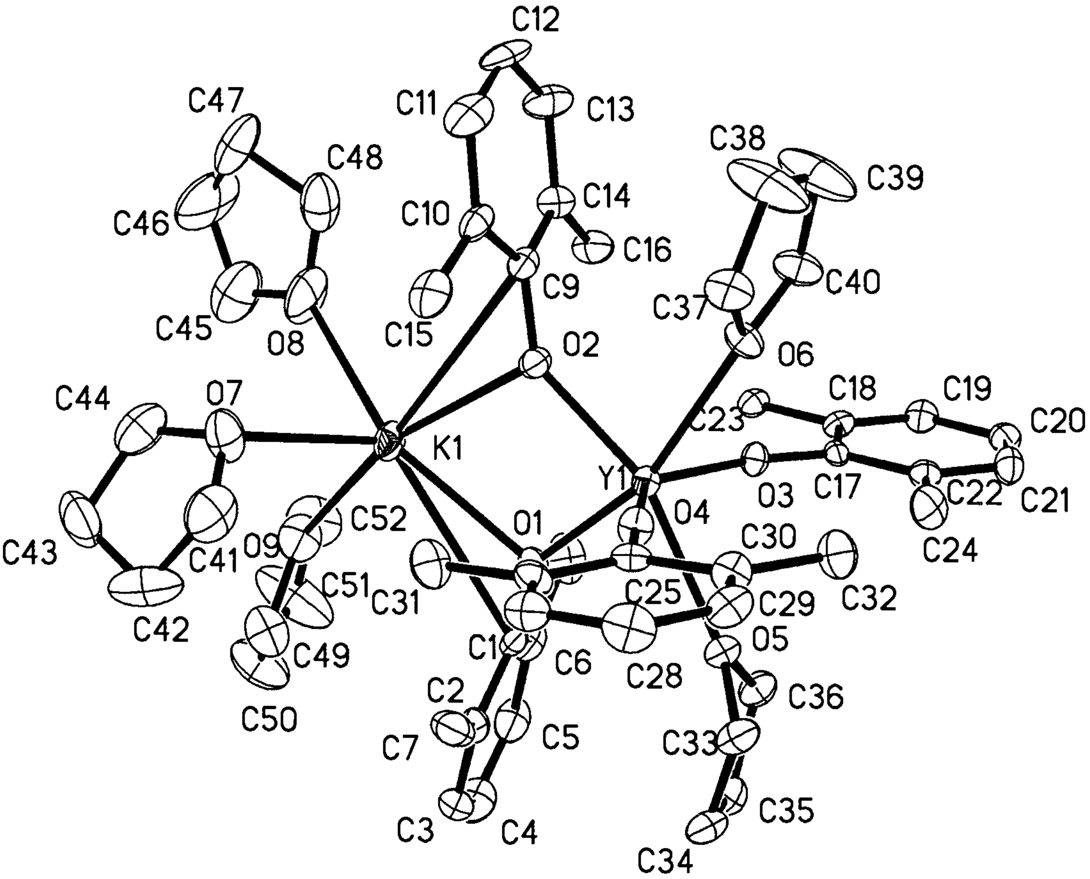

Fig. 2. Structure of $[(THF)_3K][(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_2Y(OC_6H_3Me_2\text{-}2,6)_2(THF)_2]$, **3**, with thermal ellipsoids drawn at the 30% probability level.

atoms of the aryl rings in the bridging aryloxides. The 2.693(10)–2.756(9) Å K–O(THF) distances are in the normal range [44,45], but the 2.661(6) and 2.668(6) Å K–O(OAr) distances are shorter than the analogous distances in $K[Nd(OC_6H_3Pr^i_2\text{-}2,6)_4]$ (2.760(8) Å) [46] and $[KSm(OC_6H_3{}^tBu_2\text{-}2,6)_3]_n$ (2.778(6) and 2.967(9) Å) [47]. The 3.288(9) and 3.400(10) Å K–C(*ipso*) distances in **3** are similar to the analogous K–C(*ipso*) distances in $K[Nd(OC_6H_3Pr^i_2)_4]$ (3.256(9) Å) [46], and $[KSm(OC_6H_3{}^tBu_2)_3]_n$ (3.310(10) and 3.534(13) Å) [47]. In comparison, in the extended structure of $KBPh_4$, the K–C distances average 3.191(5) Å [48] and the average K–C(C_5H_5) distances in $\{K[(\mu\text{-}C_5H_5)_2Nd(\mu\text{-}O\text{-}C_6H_3Me_2\text{-}2,6)_2]\}_n$ [49], $K[C_5H_4(SiMe_3)]$ [50], and $K[C_5(CH_2C_6H_5)_5]\cdot 3THF$ [51] are 3.17(13), 3.00(2), and 3.04(4) Å, respectively.

3.5. Reaction with sodium pentamethylcyclopentadienide

NaC_5Me_5 reacts with **1** in THF to form a toluene soluble product which has a simple ^1H NMR spectrum containing two singlets attributable to the methyl groups in C_5Me_5 and $OC_6H_3Me_2$. X-ray crystallography was carried out to determine that the solid state structure of this product was the ion pair $[Na(THF)_6][(C_5Me_5)Y(OAr)_3]$, **4**. As shown in Eq. (5), the C_5Me_5 ligand effectively replaces three THF molecules in **1**.

$$NaC_5Me_5 + \underset{\mathbf{1}}{Y(OAr)_3(THF)_3} \xrightarrow{THF} \underset{\mathbf{4}}{[Na(THF)_6][(C_5Me_5)Y(OAr)_3]} \quad (5)$$

The $[(C_5Me_5)Y(OAr)_3]^-$ anion is rare in that most anionic alkoxide and aryloxide complexes of yttrium and the lanthanides are homoleptic not heteroleptic and the anions are connected to the cations by bridging

Table 3
Important angles (deg) and distances (Å) for the $[(C_5Me_5)Y(OC_6H_3Me_2\text{-}2,6)_3]^-$ ion in **4**

Y(1)-O(1)	2.092(10)	O(1)-Y(1)-O(2)	106.4(2)
Y(1)-O(2)	2.087(11)	O(1)-Y(1)-O(3)	106.3(2)
Y(1)-O(3)	2.103(10)	O(2)-Y(1)-O(3)	103.4(2)
Y(1)-C(1)	2.65(2)	O(1)-Y(1)-cent	112.1
Y(1)-C(3)	2.64(2)	O(2)-Y(1)-cent	111.4
Y(1)-C(5)	2.65(2)	O(3)-Y(1)-cent	116.3
Y(1)-C(7)	2.62(2)	Y(1)-O(1)-C(11)	161.9(2)
Y(1)-C(9)	2.68(2)	Y(1)-O(2)-C(19)	168.8(2)
Y(1)-cent[a]	2.369	Y(1)-O(3)-C(27)	144.1(2)

[a] Cent is the C_5Me_5 ring centroid.

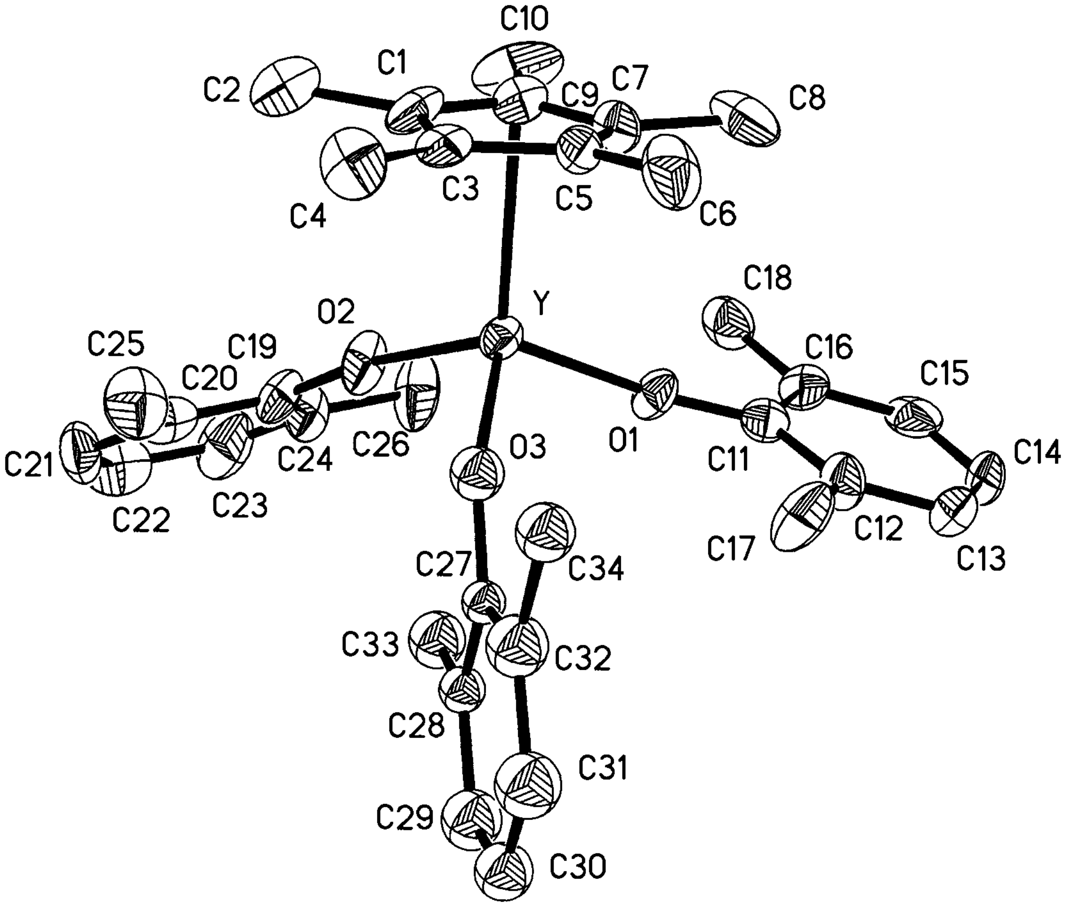

Fig. 3. Structure of the $[(C_5Me_5)(OC_6H_3Me_2\text{-}2,6)_3]^-$ ion in **4** with thermal ellipsoids drawn at the 30% probability level.

ligands. Previously reported heteroleptic alkoxide anions are limited to the bridged species $[K(\mu\text{-}Cp)_2Nd(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_2]_n$ [49], $(C_5H_4SiMe_3)_2Y(\mu\text{-}OCMe_3)_2Li(THF)_2$ [52], $[(Me_3Si)_2CH]_2Y(\mu\text{-}OCMe_3)_2Li(THF)$ [53], $(Me_3SiCH_2)Y[(\mu\text{-}CH_2)_2SiMe_2][(\mu\text{-}OCMe_3)Li(THF)_2]_2$ [54], and $[(Me_3C)_3CO]_3Nd(\mu\text{-}Cl)Li(THF)_3$ [26].

3.6. Structure of $[Na(THF)_6][(C_5Me_5)Y(OAr)_3]$, 4

The two ions comprising complex **4** are sufficiently separated in the solid state that they are non-interacting. Bond distances and angles are given in Table 3 and the anion is shown in Fig. 3. The centroid of the C_5Me_5 ring and the three oxygen atoms of the $OC_6H_3Me_2$ ligands form a distorted tetrahedron around yttrium with angles ranging from 103.4(4) to 116.3(4)°. The bonding parameters in **4** are not exceptional: the 2.087(11) to 2.103(10) Å Y–O distances are in the range typical of terminal yttrium 2,6-dimethylphenoxides and the 2.62(2) to 2.68(2) Å Y-C(C_5Me_5) distances are normal [55]. Although complexes of general formula $[(C_5R_5)Y(OR)_3]^-$ are very reasonable for yttrium and the lanthanides, the closest examples in the literature are the neutral compounds $(C_5Me_5)Ce(OC_6H_3^tBu_2)_2$ [56], $[(C_5R_5)Y(\mu\text{-}OCMe_3)(OCMe_3)_2]_2$, ($C_5R_5 = C_5Me_5$, C_9R_7, $C_5H_4SiMe_3$) [52], $[(C_5H_5)_2Y(\mu\text{-}OCMe_3)_2Y(C_5H_5)(OCMe_3)]$ [52], and $(C_5H_4SiMe_3)_2Y(\mu\text{-}OCMe_3)_2Li(THF)_2$ [52].

4. Conclusion

The 2,6-dimethylphenoxide ligand can make a variety of complexes with yttrium. Although neutral alkali metal free complexes can be readily made, as shown in Eqs. (1) and (2), in the presence of the appropriate alkali metal reagents, addition reactions to form anionic ‘ate’ salts can also readily occur, Eqs. (3)–(5). The 2,6-dimethylphenoxide ligand can support five and six coordination at yttrium in both terminal and bridging modes. It is clear from the differences in complexes **2** and **3**, that variations in preferred structures can be influenced quite easily by factors beyond the immediate coordination sphere of yttrium. Choice of alkali metal and recrystallization solvent can have critical influences on the structures obtained.

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