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A New Method of Synthesis of Monomeric Aryloxide Complexes of Manganese(II): Structures of Manganese Phenoxides

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Abstract. Monomeric manganese(II) complexes of bulky alkyl/aryl-substituted phenoxides, $[\mathrm{Mn}\{\mathrm{C_6H}_n R_m\mathrm{O}\}_2(\mathrm{DME})]$ [**1**: $R = \mathrm{C_6H_5}$, $n = 3$, $m = 2$ (2,6); **2**: $R = \mathrm{Me_3C}$, $n = 3$, $m = 2$ (2,6); **3**: $R = \mathrm{Me_3C}$, $n = 2$, $m = 3$ (2,4,6)] were prepared in yields of 37, 44 and 72 %, respectively, from the reaction of manganese powder, $\mathrm{Hg(C_6F_5)_2}$ and the corresponding phenol in the presence of a little mercury in dimethoxyethane (DME). The compounds were characterized spectroscopically and by magnetic measurements. The single crystal structures of **1** and **3** and also of the mixed phenoxide complex $[\mathrm{Mn}\{(\mathrm{C_6H_3(C_6H_5)_2}\text{-2,6-O}\}\{\mathrm{C_6H_3(Me_3C)_2}\text{-2,6-O}\}(\mathrm{DME})]$ **4** are reported.

Introduction

Metal alkoxides have enjoyed almost a century of interest [1], initially intermittent, beginning with the first report of aluminium alkoxides in 1899 by *Tishchenko* [2], and then of bimetallic alkoxides by *Meerwein* and co-workers in the 1920s [3]. The further development of the modern chemistry of metal alkoxides began in the laboratory of *Bradley* in the 1950s [4], and has burgeoned therefrom. In the 1980s, interest in soluble monomeric transition metal alkoxides and aryloxides was advanced by their observed intermediary role in processes such as the carboxylation of olefins [5] and the hydrogenation of aldehydes and ketones [6]. In the same period the onset of sol-gel technology and the development of the MOCVD process for the deposition of metal oxides paved the way for the extensive use of these compounds as precursors for metal oxides in the manufacture of electronic, ceramics and other high-tech materials [4d, 7], spurring a search for new efficient methods of synthesis and isolation, which are often impeded by their extreme sensitivity to air and moisture, as well as their proclivity to polymerization. The latter tendency has been somewhat obviated by using sterically bulky aryloxide ligands, first developed by *Horvath* [8]. To date, synthetic approaches for organo-oxo derivatives of the transition metals mainly involve the reaction of alcohols, phenols or phenoxides with the following classes of compounds: (i) arylalkyl metal complexes, e.g. $[\mathrm{Mn(CH_2CMe_2Ph)_2}]_2$ [9] and $\mathrm{Zr(CH_2Ph)_4}$ or $\mathrm{Zr(CH_2C_6H_4F)_4}$ [10]; (ii) metal halides, e.g. $[\mathrm{MnCl_2(MeCN)}]$ or $[\mathrm{CrCl_3(THF)_3}]$ [11]; (iii) metal amides $[M\{\mathrm{N(SiMe_3)_2}\}_2]_2$ (M = Mn, Fe), giving homoleptic aryloxides $[M\{\mathrm{OAr}\}_2]_n$ (n = 1 [8], n = 2 [12]. Other specific methods involve the reaction of Group 4–6 metal halides with 2,6-dimethylphenoxy(trimethyl)silane [13], and the unusual utilization of simple binary carbonyls, e.g. $[M_2(\mathrm{CO})_{10}]$ (M = Mn, Re) in the presence of 1,2-bis(diphenylphosphanyl)ethane (dppe) to yield *fac*-$[(\mathrm{CO})_3(\mathrm{dppe})\mathrm{MO}R]$ (R = Me, Et, Ph) [14]. However, despite these various methods, soluble monomeric alkoxides or phenoxides of the d-block elements remain scarce, though slightly more numerous for manganese [1, 4d], for which a higher interest has arisen because of the conversion of acylmanganese complexes to alkoxy carbonyl derivatives upon treatment with *syn*-gas [15]. Alternative methods are therefore highly desirable.

We have developed a simple and useful route for the synthesis of phenoxides of the lanthanoid(II) and (III) elements [4d, 16] through redox transmetallation/ligand exchange, which involves the direct reaction of the metal, bis(pentafluorophenyl)mercury (and other diaryl mercurials) and phenol HOAr [Equation (1)].

$$M + \mathrm{Hg(C_6F_5)_2} + 2\mathrm{HOAr} \rightarrow M(\mathrm{OAr})_2 + 2\mathrm{C_6F_5H} + \mathrm{Hg} \qquad (1a)$$

$$2Ln + 3\mathrm{Hg(C_6F_5)_2} + 6\mathrm{HOAr} \rightarrow 2Ln(\mathrm{OAr})_3 + 6\mathrm{C_6F_5H} + 3\mathrm{Hg} \qquad (1b)$$

Having successfully carried out the redox transmetallation reaction between $\mathrm{Hg(C_6F_5)_2}$ and Mn powder [Equation (2)] [17], even though manganese is much less electropositive than the lanthanoid elements, the application of the more generally

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useful one-pot reaction (1a) to manganese appears possible. This paper describes the results of the investigation, including the structures of three bulky aryloxides of manganese(II). Four related reported structures are those of dinuclear manganese 2,4,6-tri-*tert*-butylphenoxide [12], the monomeric acetonitrile complex [11], $[Mn(C_6H_2(CF_3)_3\text{-}2,4,6)_2(THF)_3]$ [18], and $[Mn(OCPh_3)_2(py)_2]$ [12].

$$Mn + Hg(C_6F_5)_2 \rightarrow Mn(C_6F_5)_2 + Hg \qquad (2)$$

Experimental Section

General Procedures and Physical Measurements

Manipulations were carried out using Schlenk techniques or in a drybox under an argon atmosphere, as all the compounds were extremely sensitive to oxygen/water. Tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), and hexane were distilled from sodium/benzophenone prior to use. Manganese powder was obtained from Merck, and dried at 140 °C before use. 2,6-diphenylphenol (Aldrich) were used as supplied while 2,6-di-*tert*-butylphenol (Merck) and 2,4,6-tri-*tert*-butylphenol (Aldrich) were recrystallised from ethanol and evacuated dry before use. Bis(pentafluorophenyl)mercury(II) was prepared according to reported methods [19]. Elemental analyses (of evacuated samples) were carried out by microanalytical laboratories at the University of Otago, New Zealand, University Sains Malaysia, Malaysia or the Research School of Chemistry, Australian National University, Canberra. IR spectra were recorded as Nujol mulls on a Perkin–Elmer 1600 Series FTIR spectrometer. Mass spectra were recorded on a VG Micromass 7070F mass spectrometer, using a sample holder which could be loaded in the drybox. Magnetic moments were determined using a Johnson–Matthey magnetic susceptibility balance calibrated with $Ni(en)_3S_2O_3$.

Syntheses

$[Mn\{C_6H_3(C_6H_5)_2\text{-}2,6\text{-}O\}_2(DME)]$ (1): A suspension of manganese powder (0.50 g, 9.1 mmol) and mercury (3 drops) in a DME solution (25 mL) of bis(pentafluorophenyl)mercury(II) (1.09 g, 2.04 mmol) and 2,6-diphenylphenol (0.50 g, 2.03 mmol) in a stoppered flask, was ultrasonicated at 50–60 °C. The reaction, monitored by IR spectra of sample aliquots, took 4 days for completion. The resultant mixture was filtered through a disk of Celite. The filtrate was concentrated to saturation point and left to crystallise at –30 °C. Three successive crops of colourless needles of **1** were collected (total 0.24 g, 0.38 mmol, 37 % yield). Found: C, 72.79, 72.92, 81.53; H, 6.20, 6.11, 6.28; Mn, 9.06, 10.27. $C_{40}H_{36}MnO_4$ (635.6) requires C, 75.58; H, 5.71; Mn, 8.64 %. {With loss of DME, $C_{36}H_{26}MnO_2$ (545.5) requires C, 79.26; H, 4.80; Mn, 10.07 %.} **IR** (Nujol): $\tilde{\nu}$ = 2855vs, 1590m, 1583m, 1560w, 1411s, 1318wsh, 1293s, 1249m, 1169w, 1104w, 1086vw, 1062m, 1026w, 871wsh, 856m, 804w, 768msh, 754s, 748s, 723wsh, 713m, 693m, 605m, 588m, 478w cm^{-1}. **MS** (*m*/*z*) : 545 ($[Mn\{C_6H_3(C_6H_5)_2O\}_2]^+$), 300 ($[Mn\{C_6H_3(C_6H_5)_2O\}]^+$), 246 ($[C_6H_3(C_6H_5)_2OH]^+$), together with lower intensity molecular mass fragments: 845 ($[Mn_2\{C_6H_3(C_6H_5)_2O\}_3]^+$) and 599 ($[(Mn_2\{C_6H_3(C_6H_5)_2O\}_2) - H]^+$). μ_{eff} = 5.82 B.M.

Diffraction-quality colourless crystals were deposited from DME solution after standing several days at ambient temperature.

$[Mn\{C_6H_3(Me_3C)_2\text{-}2,6\text{-}O\}_2(DME)]$ (2): A suspension of manganese powder (1.0 g, 18.2 mmol) and mercury (3 drops) in a solution of 2,6-di-*tert*-butylphenol (0.84 g, 4.08 mmol) and bis(pentafluorophenyl)-mercury(II) (2.18 g, 4.08 mmol) in DME (25 mL) was ultrasonicated in a stoppered flask at 50–60 °C. The reaction, monitored by the IR spectra of sample aliquots, took 4 days to reach completion. The resultant mixture was filtered through Celite, and the pale yellow filtrate concentrated to ca. 5 mL, mixed with a little *n*-hexane and left to crystallise overnight at –28 °C. Three crops of fine colourless crystals of **2** were collected (total weight 0.49 g, 0.89 mmol, 44 % yield). Found: C, 72.29; H, 9.05; Mn, 11.92. $C_{32}H_{52}MnO_4$ (555.7) requires C, 69.16; H, 9.43; Mn, 9.89 %. {With loss of DME, $C_{28}H_{42}MnO_2$ (465.6) requires C, 72.23; H, 9.09; Mn, 11.80 %.} **IR** (Nujol): $\tilde{\nu}$ = 2855vs, 1581m, 1409vs, 1291ssh, 1277s, 1198m, 1150vw, 1100m, 1048s, 1025m, 863s, 869s, 822m, 751s, 738s, 657m, 547w cm^{-1}. **MS** (*m*/*z*): 464 ($[(Mn\{C_6H_3(Me_3C)_2O\}_2) - H]^+$), 410 ($[(Mn\{C_6H_3(Me_3C)O\}_2] - C_4H_7]^+$, 408 ($[(Mn\{C_6H_3(Me_3C)O\}_2) - C_4H_9]^+$, 351 $[(Mn\{C_6H_3(Me_3C)O\}_2) - 2(C_4H_9)]^+$, 206 ($[Mn\{C_6H_3(Me_3C)O\} + 3H]^+$), 191($[Mn\{C_6H_3(Me_2C)O) + 3H]^+$), 175 ($[Mn\{C_6H_3(MeC)O\} + 2H]^+$). μ_{eff} = 5.90 B.M.

Single crystals of **2** could be obtained from DME/hexane at –28 °C but these rapidly lost solvent of crystallisation, even when submerged in oil, precluding a structure determination.

On exposure to a trace amount of air, a solution of **2** turned orange-brown. Subjection of the solid residue to sublimation at ca. 80 °C/10^{-6} Torr, gave some orange crystals, the crystal structure of which confirmed the quinonoid compound **5** [8a].

$[Mn\{C_6H_2(Me_3C)_3\text{-}2,4,6\text{-}O\}_2\ (DME)]$ (3): A suspension of manganese powder (1.0 g, 18.2 mmol) and mercury (3 drops) in a solution 2,4,6-tri-*tert*-butylphenol (0.66 g, 2.51 mmol) and bis(pentafluorophenyl)mercury(II) (1.34 g, 2.50 mmol) in DME (25 mL) was ultrasonicated at 50–60 °C. The reaction monitored by the IR spectra of sample aliquots, took 6 days for completion. The resultant mixture was filtered through Kieselguhr (5 × 1.2 cm), giving a pale brown solution, which was concentrated in vacuo to ca. 2 mL. Addition of *n*-hexane (ca. 2 mL), followed by cooling for several h at –28 °C, gave fine colourless crystals of **3** (0.60 g, 0.90 mmol, 72 % yield). Found: C, 73.28, 76.31; H, 11.17, 10.96; Mn, 9.23. $C_{40}H_{68}MnO_4$ (667.9) requires C, 71.93; H, 10.26; Mn, 8.23 %. {With loss of DME, $C_{36}H_{58}MnO_2$ (577.8) requires C, 74.84; H, 10.12; Mn, 9.51 %.} **IR** (Nujol): $\tilde{\nu}$ = 2855vs, 1424vs, 1359m, 1296s, 1273vs, 1244m, 1218w, 1194m, 1156vw, 1120w, 1096w, 1051s, 1019w, 974w, 920w, 890wsh, 878m, 862m, 839s, 820wsh, 785m, 746m, 723wsh, 668vw, 644w, 546m, 469m cm^{-1}. **MS** (*m*/*z*): 998 $[Mn_2(C_6H_2(Me_3C)_3O)_3(C_6H_2(Me)O) - H]^+$, 262 ($[(C_6H_2(Me_3C)_3OH)]^+$), 248 ($[(C_6H_2(Me_3C)_3OH) - CH_2]^+$), 247 $[(C_6H_2(Me_3C)_3OH) - Me]^+$ and 245 $[(C_6H_2(Me_3C)_3OH) - Me - 2H]^+$. μ_{eff} = 6.03 B.M.

Diffraction-quality single crystals were deposited from DME/hexane solution after prolonged standing at –28 °C.

$[Mn\{C_6H_3(C_6H_5)_2\text{-}2,6\text{-}O\}\{C_6H_3(Me_3C)_2\text{-}2,6\text{-}O\}(DME)]$ (4): The compound was fortuitously similarly deposited from DME/hexane in low yield. Found: C, 72.89; H, 10.11. $C_{36}H_{44}MnO_4$ (595.7) requires C 72.59, H, 7.45 %. {With loss of DME, $C_{32}H_{34}MnO_2$ (505.6) requires C, 76.03; H, 6.78 %.}

Structure Determinations

For **1** and **4**, unique data sets were measured using a single counter instrument at ca. 295 K (monochromatic Mo-K_α radiation, λ = 0.71073 Å; $2\theta/\theta$ scan mode) Gaussian absorption corrections were applied. For **3**, a full sphere of CCD area detector diffractometer data was measured at ca. 130 K (ω-scans), an "empirical"/multiscan absorption correction being applied. In all structures, all unique data were used in the full-matrix least-squares refinements on F^2, refining anisotropic displacement parameters for the non-hydrogen atoms, hydrogen atom treatment following a riding model (reflection weights: $(\sigma^2(F_o)^2 + (aP)^2 (+ bP))^{-1}$ $(P = (F_o^2 + 2F_c^2)/3)$). N_o reflections with $F > 4\sigma(F)$ were considered "observed". Neutral atom complex scattering factors were employed within the SHELXL 97 program [20]. Pertinent results are given below and in the Tables and Figures the latter showing non-hydrogen atoms with 50 % displacement amplitude envelopes, hydrogen atoms having arbitrary radii of 0.1 Å. Full.cif depositions (excluding structure factor amplitudes) reside with the Cambridge Crystallographic Data Centre, CCDC-733616, -733617, -733618. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Crystal/Refinement Data

1. [Mn{$C_6H_3(C_6H_5)_2$-2,6-O}$_2$(DME)] ≡ $C_{40}H_{36}MnO_4$, M = 635.6. Monoclinic, space group $C2/c$ (C_{2h}^6, No.15), a = 11.050(13), b = 12.455(14), c = 23.992(8) Å, β = 99.02(6)°, V = 3261 Å^3. D_c (Z = 4) = 1.295 g·cm^{-3}. μ_{Mo} = 0.45 mm^{-1}; specimen: = 0.32 × 0.25 × 0.12 mm; $T_{min/max}$ = 0.97. $2\theta_{max}$ = 50°; N = 2849, N_o = 905; $R1$ = 0.060, $wR2$ = 0.21 (a = 0.087), S = 1.13. $|\Delta\rho_{max}|$ = 0.54 e·Å^{-3}.

3. [Mn{$C_6H_2(Me_3C)_3$-2,4,6-O}$_2$(DME)] ≡ $C_{40}H_{68}MnO_4$, M = 667.9. Monoclinic, space group $P2_1/c$ (C_{2h}^5, No.14), a = 14.828(3), b = 14.505(2), c = 36.988(5) Å, β = 95.34(2)°, V = 7921 Å^3. D_c (Z = 8) = 1.120 g·cm^{-3}. μ_{Mo} = 0.37 mm^{-1}; specimen: not recorded; $T_{min/max}$ = 0.95. $2\theta_{max}$ = 45°; N = 9817, N_o = 4946; $R1$ = 0.12, $wR2$ = 0.31 (a = 0.13, b = 43), S = 1.05. $|\Delta\rho_{max}|$ = 0.87 e·Å^{-3}.

Variata. The data were weak and limited in scope and would support meaningful anisotropic displacement parameter refinement for Mn only.

4. [Mn{$C_6H_3(C_6H_5)_2$-2,6-O}{$C_6H_3(Me_3C)_2$-2,6-O}(DME)] ≡ $C_{36}H_{44}MnO_4$, M = 595.7. Monoclinic, space group $P2_1/c$, a = 13.125(3), b = 15.682(10)), c = 17.15(2) Å, β = 111.41(7)°, V = 3286 Å^3. D_c (Z = 4) = 1.204 g·cm^{-3}. μ_{Mo} = 0.44 mm^{-1}; specimen: = 0.50 × 0.42 × 0.28 mm; $T_{min/max}$ = 0.93. $2\theta_{max}$ = 50°; N = 5308, N_o = 3118; $R1$ = 0.049, $wR2$ = 0.13 (a = 0.038, b = 3.9), S = 1.08. $|\Delta\rho_{max}|$ = 0.28 e·Å^{-3}.

Results and Discussion

Synthesis of Manganese Phenoxides

The reaction between manganese powder, bis(pentafluorophenyl)mercury, $Hg(C_6F_5)_2$ and substituted phenols, HOAr, in the presence of a little mercury, has been investigated. A typical reaction was carried out by ultrasonication at 50–60 °C, of a suspension of four equivalents of manganese to one equivalent of $Hg(C_6F_5)_2$ and HOAr, together with a few drops of mercury, in 1,2-dimethoxyethane (DME). The reactions with 2,6-diphenylphenol and 2,6-di-*tert*-butylphenol took four days to reach completion, while that with 2,4,6-tri-*tert*-butylphenol required six days. From the product solutions, colourless crystals of DME solvates of bis(phenoxo)manganese (**1**–**3**) were obtained in yields of 37, 44 and 72 %, respectively.

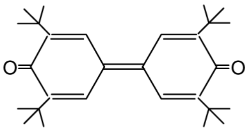
Previous work [17] has demonstrated that redox transmetallation occurs between $Hg(C_6F_5)_2$ and manganese [Equation (2)]. It is therefore likely that the compounds **1**–**3** are formed by a subsequent protolytic ligand exchange [Equation (3)], as has been established for Ln^{II} and Ln^{III} compounds [22].

$$Mn(C_6F_5)_2 + 2HOAr \rightarrow Mn(OAr)_2 + 2C_6F_5H \qquad (3)$$

This methodology lends itself to a convenient one-pot synthesis, with attractive mild reaction conditions for metal alkoxides or aryloxides, which are often thermally unstable.

These compounds are extremely air- and moisture-sensitive; this feature together with facile loss of lattice solvent led to generally unsatisfactory microanalytical data. Compound **1** at different stages after isolation gave manganese analyses corresponding to either retention or loss of DME, whilst those for **2** and **3** indicated loss of DME. The C, H analysis of **2** was consistent with loss of DME, as was the average of two carbon analyses for **3**, whilst the C analysis of **4** was consistent with DME retention, but both this and **3** gave high % H values. Easy loss of THF from [Mn($C_6H_2(Me_3C)_3$-2,4,6-O]$_2$(THF)$_2$] has been reported [8a]. Electron impact mass spectra of **1**–**3** showed no evidence for DME, indicative of easy loss. **1** and **3** gave Mn_2-containing ions, as would be expected for unsolvated species, since the structure of [Mn($C_6H_2(Me_3C)_3$-2,4,6-O)$_2$]$_2$] is an aryloxo-bridged dimer [12]. Additionally intense mononuclear manganese-containing ions were observed for **1** and **2**, but not **3**, and **2**, for which an X-ray structure could not be obtained, gave no dinuclear ions. Their pale yellow solutions rapidly turned orange-brown to brown, in the presence of traces of air. The IR spectroscopic data indicate the absence of free phenol from adventitious hydrolysis. Their magnetic moments (5.82–6.03 B.M.) correspond to five unpaired electrons, consistent with the presence of high-spin Mn^{II} compounds.

From an air-contaminated solution of **2**, orange crystals were isolated, the crystal structure of which confirmed the quinoxide compound **5**, previously obtained in high yield from the oxidation of unsolvated [Mn{$C_6H_3(Me_3C)_2$-2,6-O}$_2$] (**2-DME**) with excess O_2 [8a], and in low yield by the oxidation of 2,6-di-^{t}butylphenol with Co^{II} complexes of Schiff bases [21].



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Molecular Structures

The results of the single-crystal X-ray studies in all three cases are consistent with the presence of mononuclear [Mn($C_6H_nR_mO$)$_2$(DME)] species, the manganese atom being coordinated by a pair of *O*-phenoxide donors and an *O*,*O*'-DME chelate. In **4**, one molecule, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure, in

3, two, and in **1**, one half of a molecule, the manganese atom being disposed on a crystallographic twofold axis, which relates the two phenoxide ligands and passes through the centre of the (disordered) central C–C bond of the DME ligand. Throughout the array Mn–O(DME) (ca. 2.2 Å) are appreciably longer than Mn–O(phenoxide) (ca. 1.9 Å), consistent with the loss of DME; O(DME)–Mn–O(DME) angles are similar (ca. 74°). The chelate array conforms to (*quasi*-) twofold symmetry with C–O–C–C torsions *trans* and O–C–C–O ca. 53° (Table 1) (Exception: the ligand of molecule 2 of compound **3**, where one of the C–O–C–C torsions is 83(1)°.) Mn–O distances are rather erratic [e.g. in **4**: 2.171(3), 2.225(3) Å], presumably a consequence of hindrances consequent on the sprawling of the bulky phenoxide substituents (Figure 1).

Table 1. Manganese atom environments for compounds **1**, **3** and **4**.

	1	**3** (mols. 1,2)	**4**
Distances /Å			
Mn–O(Ph)	1.958(4)	1.905(7), 1.916(7)	1.895(2)
		1.931(7), 1.932(7)	1.906(2)
Mn–O(DME)	2.221(5)	2.189(7), 2.178(8)	2.171(3)
		2.218(8), 2.255(8)	2.225(3)
Angles/degrees			
O(Ph)–Mn–O(Ph)	109.2(2)	137.4(3), 141.0(3)	125.6(1)
O(Ph_1)–Mn–O(DME)	91.6(2)	98.8(3), 98.3(3)	94.3(1)
	155.1(2)	104.0(3), 117.4(3)	122.3(1)
		117.4(3), 108.6(3)	124.0(1)
		107.3(3), 97.0(3)	105.5(1)
O(DME)–Mn–O(DME)	72.3(2)	73.3(3), 74.6(3)	74.9(1)
Mn–O(Ph)–C(Ph)	133.4(4)	127.9(6), 135.5(6)	149.9(2)
		177.3(7), 143.2(7)	172.0(3)
Mn–O(DME)–C(DME)	115.3(8)	106.2(7), 108.9(7)	109.3(2)
	117.8(6)	116.9(6), 113.4(7)	114.3(2)
Mn–O(DME)–C(Me)	126.9(5)	127.8(8), 119.4(7)	121.4(2)
		125.7(6), 133.0(7)	124.3(2)
DME torsion angles/degrees			
C–O–C–C	159(1)	–157(1), 83(1)	–175.0(4)
	–160(1)	–177(1), 166(1)	–176.0(4)
O–C–C–O	50(2)	–55(1), 53(1)	–53.7(6)
Mn–O–C–C	25(2)	58(1), –54(1)	48.2(4)
	–39(2)	26(1), –26(1)	33.0(5)

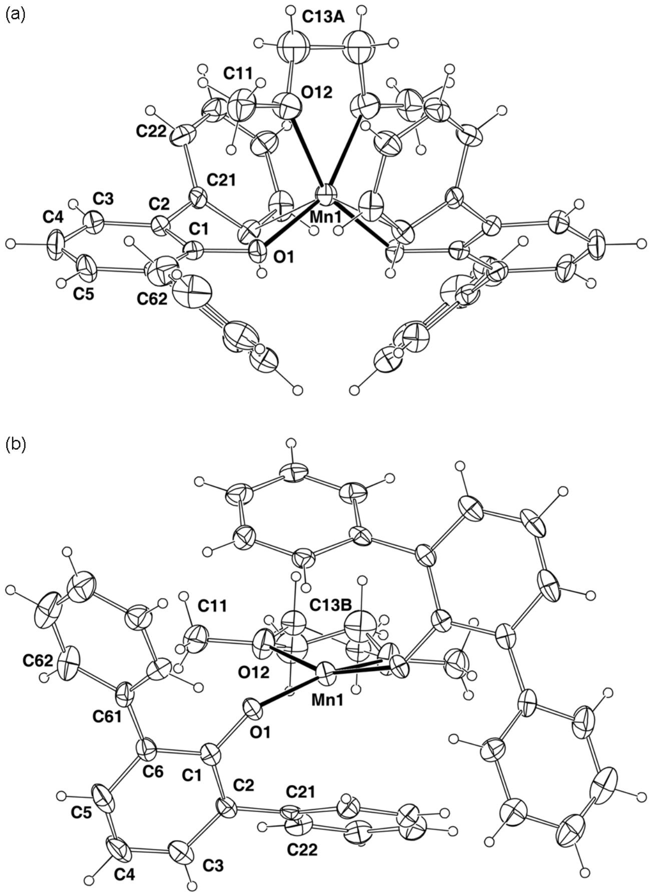

Figure 1. Molecular projections of [Mn{$C_6H_3(C_6H_5)_2$-2,6-O}$_2$(DME)] (**1**). (The $(CH_2)_2$ bridge of the DME is disordered (see text)) (a) down and (b) normal to the twofold axis.

Similarly erratic are parameters associated with the bonding of the phenoxide ligands. Again, within **4**, where the Mn–O distances are essentially identical [1.895(2), 1.906(2) Å], associated Mn–O–C angles differ by 20° (Table 1), and across all compounds the range of Mn–O–C is 127.9(6)–177.3(7)° (both within the one compound, **3**, Figure 2). The O–Mn–O angles between the phenoxide donors also vary widely from 109.2(2) (**1**) through 125.6(1) (**4**) to 137.4(3)/141.0(3)° in **3**. The coordination environments in **3** and **4** may be viewed as highly distorted four-coordinate tetrahedral, with O(DME)–Mn–O(Ph) ranging between 94.3(1)–124.0(1)° (both extremes in **4**). More remarkable is the environment found in **1**. Here the phenyl substituents on the ligand have a role to play; the dihedral angles between their C_6 planes (χ^2 3.9, 8.0) and the central C_6 ring plane (χ^2 9.5) are 49.6(2), 43.6(3)°, with one of the rings (and its twofold image) approaching the manganese atom in a *quasi*(-offset)-η^6 mode. The distance between the manganese atom and one of the *ortho* carbon atoms of the ring is 2.838(6) Å; the C–Mn–C angle is 149.4(2)°. Distances between the manganese atom and adjacent pendant and *meta*-ring atoms are 3.080(7) and 3.464(7) Å. Despite their long distances, the pair of Mn–C(*ortho*) interactions may be regarded as incipient occupants of a pair of *trans* sites in a six-coordinate array – the Mn(*O*-DME)$_2$(*O*-OPh)$_2$ array is remarkably 'flat' and *quasi*-planar four-coordinate. In **4**, the phenyl substituents are similarly twisted with respect to the central ring (interplanar C_6/C_6 dihedral angles: 41.6(2), 51.6(2)°), but the closest approach to the manganese atom of any ring atom here is 3.412(5) Å (again from an *ortho* atom) (Figure 3).

The existence of metal alkoxides or aryloxides in the monomeric state requires the presence of bulky ligands to hinder or prevent intermolecular association. For manganese(II), few examples have been structurally characterized [11, 12, 18], to the best of our knowledge, viz. the four-coordinate complexes [Mn{$C_6H_2(Me_3C)_3$-2,4,6-O}$_2$(MeCN)$_2$].2MeCN [11], (Mn–O 1.910(6) Å, O–Mn–O 121.2(3)°, Mn–O–C 179.1(5)°) and [Mn($OCPh_3$)$_2$(py)$_2$] [12], (Mn–O 1.956(4) Å (×2), O–Mn–O 140.4(2), Mn–O–C 131.2(4), 131.3(4)°) and the lithium salts of the anionic three- and four-coordinate complexes of the tri-*tert*-butylmethoxide ligand [23]. In the five coordinate com-

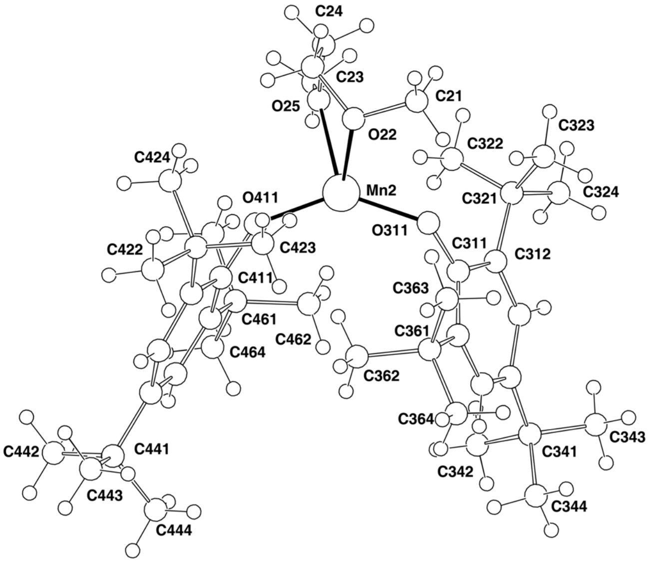

Figure 2. Molecular projection of [Mn$\{C_6H_2(Me_3C)_3$-2,4,6-O$\}_2$(DME)] (**3**) (molecule 2).

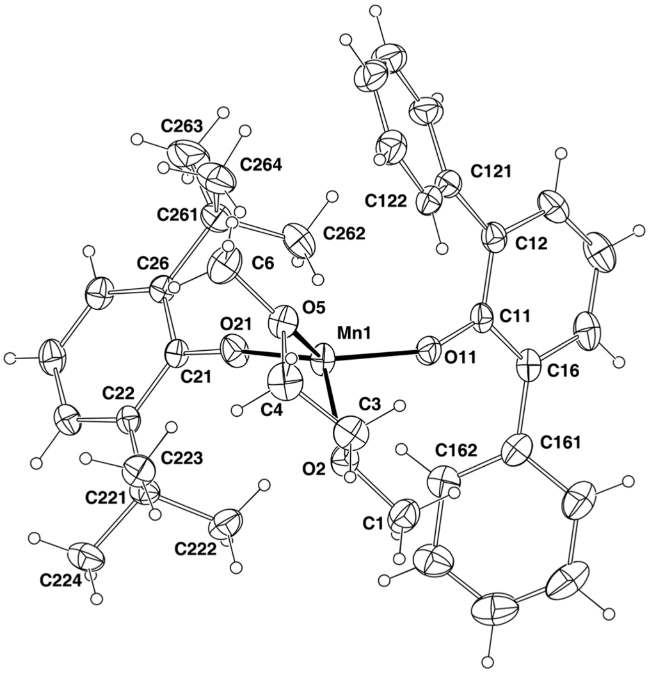

Figure 3. Molecular projection of [Mn$\{C_6H_3(C_6H_5)_2$-2,6-O$\}\{C_6H_3(Me_3C)_2$-2,6-O$\}$(DME)] (**4**).

plex [Mn$(C_6H_2(CF_3)_3$-2,4,6-O$)_2(THF)_3$] [18], the aryloxo ligands are *trans* in a *quasi*-square pyramidal environment, Mn–O 1.993(5), 1.997(5) Å, O–Mn–O 155.1(2), Mn–O–C 178.6(5), 162.0(5)°, the longer distances relating to the higher coordination number. However, the Mn–O(THF) bond lengths average 2.19 Å, marginally shorter than 2.21 Å found for four-coordinate **1**, **3** and **4**, consistent with the ready loss of DME from the present complexes. In these present cases, there is no doubt that their monomeric nature is stabilized by the presence of bulky *ortho* substituents on the phenoxides.

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