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Synthesis, structure, and redox properties of the molybdenum(VI) complexes [Mo(η^5-C_5Ph_4R)O_2X] (R = 2,5-dimethoxyphenyl; X = Br or alkoxide)

Wendy M. Harrison, Charles Saadeh, Stephen B. Colbran* and Donald C. Craig

School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia

The first high-oxidation-state, molybdenum complexes with a pentaarylcyclopentadienyl ligand have been prepared. Oxidation of [Mo(C_5Ph_4R)$(CO)_3$Br] (R = 2,5-dimethoxyphenyl) with dioxygen in boiling toluene provides a high yield route to the 16-electron, molybdenum(VI) complex [Mo(C_5Ph_4R)O_2Br]. Reactions of this complex with aliphatic alcohols (R″OH), but not with phenols, afforded the alkoxide complexes [Mo(C_5Ph_4R)O_2(OR″)]. The complexes are unstable to hydrolysis; the cyclopentadiene C_5Ph_4RH is isolated from reactions with water. Crystal structure analyses of the cyclopentadiene C_5Ph_4RH and of [Mo(C_5Ph_4R)O_2(OMe)] were made. The orientation of the dimethoxyphenyl substituent, with the *o*-methoxy group directed either towards or away from the metal centre, leads to proximal and distal rotamers for each complex. The proximal rotamer of [Mo(C_5Ph_4R)O_2(OMe)] crystallises. The NMR spectra of the complexes show peaks for the proximal and distal rotamers. A variable-temperature ^{1}H NMR study of [Mo(C_5Ph_4R)O_2Br] allowed calculation of the rotational barrier for the dimethoxyphenyl substituent: $\Delta G^\ddagger = 68.6 \pm 0.8$ kJ mol^{-1}. A Mo^{VI}–Mo^{V} couple is observed for [Mo(C_5Ph_4R)O_2Br] at −0.55 V (*vs.* the ferrocene–ferrocenium couple), and the corresponding couples for the alkoxide complexes occur at *ca.* −1.55 V.

The recent resurgence in interest in pentaarylcyclopentadienyl transition-metal complexes and their chemistry[1–5] is driven by three observations: (1) these complexes are often considerably more stable than their much more common and studied C_5H_5 or C_5Me_5 analogues; this kinetic stabilisation results from the ligand bulk;[1,2] (2) these complexes often exhibit a wider variety of accessible oxidation states than their C_5H_5 or C_5Me_5 analogues, presumably reflecting the ability of the aryl substituents to buffer electronic changes at the metal centre;[4] (3) the chemistry of pentaarylcyclopentadienyl complexes and their simpler cyclopentadienyl analogues can be very different.[1,2,5]

To our knowledge, there are no previous reports of pentaarylcyclopentadienyl complexes of transition metals in high oxidation states (M^{V}–M^{VII}). Herein, we report the preparations, structures, redox properties, and reactions of some d^0 molybdenum(VI) complexes of the η^5-(2,5-dimethoxyphenyl)tetraphenylcyclopentadienyl (C_5Ph_4R) ligand.

Results and Discussion

Syntheses

The complexes [Mo($C_5R'_5$)O_2X] (R′ = H or Me, X = Cl or Br) have been prepared by a variety of methods.[6–10] For example, preparations of [Mo(C_5Me_5)O_2Cl] include treatment of [{Mo(C_5Me_5)$_2O_2$}$_2$(μ-O)] with PCl_5 in carbon disulfide,[7] as a by-product of the oxidation of [{Mo(C_5Me_5)$_2$(CO)$_2$}$_2$] upon exposure of a chloroform solution to air,[8] more deliberately by oxidation of [{Mo(C_5Me_5)$_2$(CO)$_2$}$_2$] by air in a chloroform–hydrochloric acid mixture,[9] and by irradiation of [Mo(C_5Me_5)(CO)$_3$Cl] in a dioxygen atmosphere.[10] The last reaction suggested an entry point to high-oxidation-state C_5Ph_4R complexes starting from the complexes [M(C_5Ph_4R)(CO)$_3$Br] (M = Mo or W) which were available from our previous studies.[5,11] The targeted molybdenum(VI) complex, [Mo(C_5Ph_4R)O_2Br], was obtained by heating a toluene solution of [Mo(C_5Ph_4R)(CO)$_3$Br] [ν(CO) 2047, 1979 and 1960 cm^{-1}] at reflux under a dioxygen atmosphere until the carbonyl bands disappeared from the IR spectrum. Orange, crystalline [Mo(C_5Ph_4R)O_2Br] was crystallised from toluene–hexanes and obtained in 88% overall yield. The analogous reaction of [W(C_5Ph_4R)(CO)$_3$Br] with dioxygen led to complete decomposition and no tractable compound(s). Partial elemental analysis and NMR spectra of [Mo(C_5Ph_4R)O_2Br] reveal that it co-crystallised with half a molecule of toluene. The mass spectrum showed a molecular ion at *m*/*z* 714 and the most prominent peak at *m*/*z* 634 arises from loss of the bromo ligand from the molecular ion. The IR spectrum featured two prominent bands at 926 and 895 cm^{-1}, values characteristic for terminal Mo=O groups.[6–10] Proton NMR spectra of the complex show double the number of expected peaks. Variable-temperature ^{1}H NMR spectra, which are discussed in detail below, implicate the two rotamers arising from rotation of the dimethoxyphenyl group as the source of the doubling of the peaks.

The complex [Mo(C_5Ph_4R)O_2Br] is considerably more stable than its C_5H_5 and C_5Me_5 analogues. For example, it was stable in air both as a solid and in dichloromethane or toluene solution, and was not affected by light. In contrast, the complexes [Mo($C_5R'_5$)O_2X] (R′ = H or Me, X = Cl or Br) decompose slowly in the solid state and rapidly in solution, with the bromo complexes being less stable;[6–10] Bottomley *et al.*[9] reported that decomposition of [Mo(C_5Me_5)O_2Cl] is accelerated by light and inhibited by dry dioxygen.

In an attempt to synthesize the dimer [{Mo(C_5Ph_4R)O_2}$_2$(μ-O)], the complex [Mo(C_5Ph_4R)O_2Br] was deliberately treated with water. With half an equivalent of water incomplete decomplexation to afford the free cyclopentadiene, C_5Ph_4RH, was observed. With an excess of water the decomplexation to afford the free cyclopentadiene was complete. The hydrolysis reaction was much more rapid in the presence of either acetic acid or the bases triethylamine or sodium carbonate. For example, rapid, complete decomplexation occurred when [Mo(C_5Ph_4R)O_2Br] was treated with water (0.5 equivalent) and either triethylamine or sodium carbonate (1 equivalent). The lability of the bulky C_5Ph_5 ligand has been previously noted and used by Matt and co-workers[12] to generate catalytically active, co-ordinatively unsaturated transition-metal species.

The complex [Mo(C_5Ph_4R)O_2Br] reacted cleanly with aliphatic alcohols R″OH, but not phenols (no reaction occurred with an excess of 1,4-hydroquinone, phenol or 4-methoxyphenol), to give near-quantitative yields of the corresponding alkoxide complexes, $[Mo(C_5Ph_4R)O_2(OR'')]$ ($R'' = Me$, Et, Pr^i or Bu^t), presumably according to equation (1). Reaction of the

$$[Mo(C_5Ph_4R)O_2Br] + 2R''{-}OH \longrightarrow [Mo(C_5Ph_4R)O_2(OR'')] + R''{-}Br + H_2O \quad (1)$$

liberated HBr with the aliphatic alcohol may provide the driving force for the reactions. Most likely phenols do not react because either they are not sufficiently nucleophilic to attack the electrophilic, formally 16-electron molybdenum(VI) centre or the driving force for the reaction is lost because phenols do not scavenge the liberated HBr as efficiently as the aliphatic alcohols do.

The new alkoxide complexes were all pale yellow, microcrystalline solids which were thermally and air stable. However, like $[Mo(C_5Ph_4R)O_2Br]$ (see above), in solution the complexes are unstable to hydrolysis, so much so that special care had to be taken to dry solvents for NMR spectroscopy. If 'ordinary' solvents were used for NMR spectroscopy (or if reagent-grade alcohols were used in the preparations of the complexes), extra peaks for a common hydrolysis product (two methoxy peaks for this product are most easily identified and with $CDCl_3$ as the solvent occur at δ 3.31 and 3.07) and the free alcohol appeared in the NMR spectra of the complexes. A tentative description of the hydrolysis, based on hydrolyses of transition-metal alkoxides to form oxo-bridged dimers,[13,14] is given in equations (2) and (3). However, despite several attempts, we were unable

$$[Mo(C_5Ph_4R)O_2(OR'')] + H_2O \rightleftharpoons [Mo(C_5Ph_4R)O_2(OH)] + R''OH \quad (2)$$

$$[Mo(C_5Ph_4R)O_2(OR'')] + [Mo(C_5Ph_4R)O_2(OH)] \rightleftharpoons [\{Mo(C_5Ph_4R)O_2\}_2(\mu\text{-}O)] + R''OH \quad (3)$$

to isolate the hydrolysis product. Reactions of $[Mo(C_5Ph_4R)O_2(OMe)]$ with varying amounts of water were tried and (unless an excess of water was used) invariably gave mixtures of the starting complex, $[Mo(C_5Ph_4R)O_2(OMe)]$, the hydrolysis product and the free cyclopentadiene. The complexes in the mixtures decomposed on silica or alumina chromatographic supports (only the free cyclopentadiene, C_5Ph_4RH, eluted from the columns) and could not be separated by repeated crystallisation. Deliberate reactions of $[Mo(C_5Ph_4R)O_2(OMe)]$ with an excess of water (in order to force the hydrolysis reaction) led to decomposition with C_5Ph_4RH being isolated in high yield. The cyclopentadiene was also isolated when $[Mo(C_5Ph_4R)O_2(OMe)]$ was treated with 1.0 equivalent of acetic acid {an attempted synthesis of $[Mo(C_5Ph_4R)O_2(O_2CMe)]$} or with 4-methoxyphenol and 1.0 equivalent of triethylamine {an attempted synthesis of $[Mo(C_5Ph_4R)O_2(OC_6H_4OMe\text{-}4)]$}. These reactions illustrate the proclivity for these molybdenum(VI) complexes to lose the bulky pentaarylcyclopentadienyl ligand.

The alkoxide complexes were characterised by partial elemental analyses, by mass, IR and ^1H NMR spectroscopies, and by a crystal structure analysis of $[Mo(C_5Ph_4R)O_2(OMe)]$. The ^1H NMR spectra show double the number of expected peaks and are collectively discussed below. Infrared spectra showed three strong peaks in the Mo=O region at *ca.* 918, 910 and 883 cm^{-1}, and prominent molecular ion peaks were observed in electron-impact mass spectra of the complexes.

Crystal structures

C_5Ph_4RH. Proton NMR spectra of the cyclopentadiene, C_5Ph_4RH, always showed two equal-intensity peaks for the cyclopentadiene proton and four methoxy peaks (each three times the intensity of the cyclopentadiene peaks). The spectra are suggestive for only one ring position of the cyclopentadienyl ligand being protonated, with all peaks doubled because the two possible rotamers that arise from the two positions for the dimethoxyphenyl (R) group, either with the *o*-methoxy group proximal or distal relative to the cyclopentadiene proton, are observed. As crystals of the cyclopentadiene were available, the structure was determined unequivocally to determine the relative positioning of the cyclopentadiene proton and the dimethoxyphenyl group.

The cyclopentadiene, C_5Ph_4RH, crystallised from dichloromethane–methanol solution in the space group $P\bar{1}$ with two molecules in the unit cell. Fig. 1 presents the molecular structure which is disordered with two positions for the dimethoxyphenyl (R) group observed. The occupancy of minor (unfilled lines in Fig. 1) to major (solid lines in Fig. 1) disorder components refined to 0.28 and 0.72. In both disorder components the dimethoxyphenyl group lies at the 3 position of the planar C_5 ring with the *o*-methoxy group distal with respect to the cyclopentadiene proton. Within the C_5 ring the internal C–C–C angles about the alkenyl carbon atoms are equal within experimental error at 109.1(2)° and that about the sp^3-carbon atom [C(3)] is 103.6(2)°. The bond distances (in Å) within and about the C_5 ring are much as expected and are summarised in Scheme 1. The bond lengths and angles are similar to those found in the structures of tetraphenylcyclopentadiene[16] and pentaphenylcyclopentadiene.[17]

Table 1 Selected bond lengths (Å) and angles (°) for $[Mo(C_5Ph_4R)O_2(OMe)]$ with estimated standard deviations (e.s.d.s) in parentheses

Mo–O(3)	1.708(2)	Mo′–O(3′)	1.708(2)
Mo–O(4)	1.677(3)	Mo′–O(4′)	1.678(3)
Mo–C(1)	2.546(3)	Mo′–C(1′)	2.566(3)
Mo–C(2)	2.599(3)	Mo′–C(2′)	2.606(4)
Mo–C(3)	2.497(3)	Mo′–C(3′)	2.502(4)
Mo–C(4)	2.433(3)	Mo′–C(4′)	2.452(4)
Mo–C(5)	2.398(3)	Mo′–C(5′)	2.425(4)
Mo–O (Me)	1.881(2)	Mo′–O (Me′)	1.881(2)
O(1)–C(31)	1.353(5)	C(2)–C(3)	1.457(5)
O(1)–C(36)	1.404(6)	C(2)–C(12)	1.499(4)
O(2)–C(34)	1.381(7)	C(3)–C(4)	1.423(5)
O(2)–C(37)	1.438(5)	C(3)–C(18)	1.490(5)
C(1)–C(2)	1.428(4)	C(4)–C(5)	1.406(5)
C(1)–C(5)	1.412(5)	C(4)–C(24)	1.493(5)
C(1)–C(6)	1.479(5)	C(5)–C(30)	1.488(4)
O(3)–Mo–O(4)	107.1(2)	O(3′)–Mo′–O(4′)	110.4(4)
O(3)–Mo–O (Me)	101.1(2)	O(3′)–Mo′–O (Me′)	102.8(5)
O(4)–Mo–O (Me)	103.1(1)	O(4′)–Mo′–O (Me′)	106.5(4)
C(31)–O(1)–C(36)	120.1(4)	C(2)–C(3)–C(4)	106.2(3)
C(34)–O(2)–C(37)	116.7(6)	C(3)–C(4)–C(5)	109.0(3)
C(2)–C(1)–C(5)	107.6(3)	C(1)–C(5)–C(4)	109.0(3)
C(1)–C(2)–C(3)	107.9(3)		

Primes indicate the minor disorder component.

$[Mo(C_5Ph_4R)O_2(OMe)]$. The complex crystallised from dichloromethane–methanol solution in the space group $P2_1/c$. The structure is disordered with a complete mirror image of the major disorder component translated by approximately $b/2$ parallel to y. The occupancies of minor and major components refined to 0.24 and 0.76. The two components refined with very similar metrical parameters (Table 1) and those for the major component are discussed below because these are better defined.

Fig. 2 presents a view of the molecule, a typical 'piano-stool' complex with two oxo and one methoxide ligands as 'legs' and a pentaarylcyclopentadienyl 'seat'. Selected bond lengths and angles are listed in Table 1. The Mo–C (cyclopentadienyl) bond lengths average 2.495 Å, considerably longer than the average of 2.381 Å in $[Mo(C_5Me_5)OCl_2]$ (d^1 Mo^V),[18] 2.330 Å in the d^4–d^4

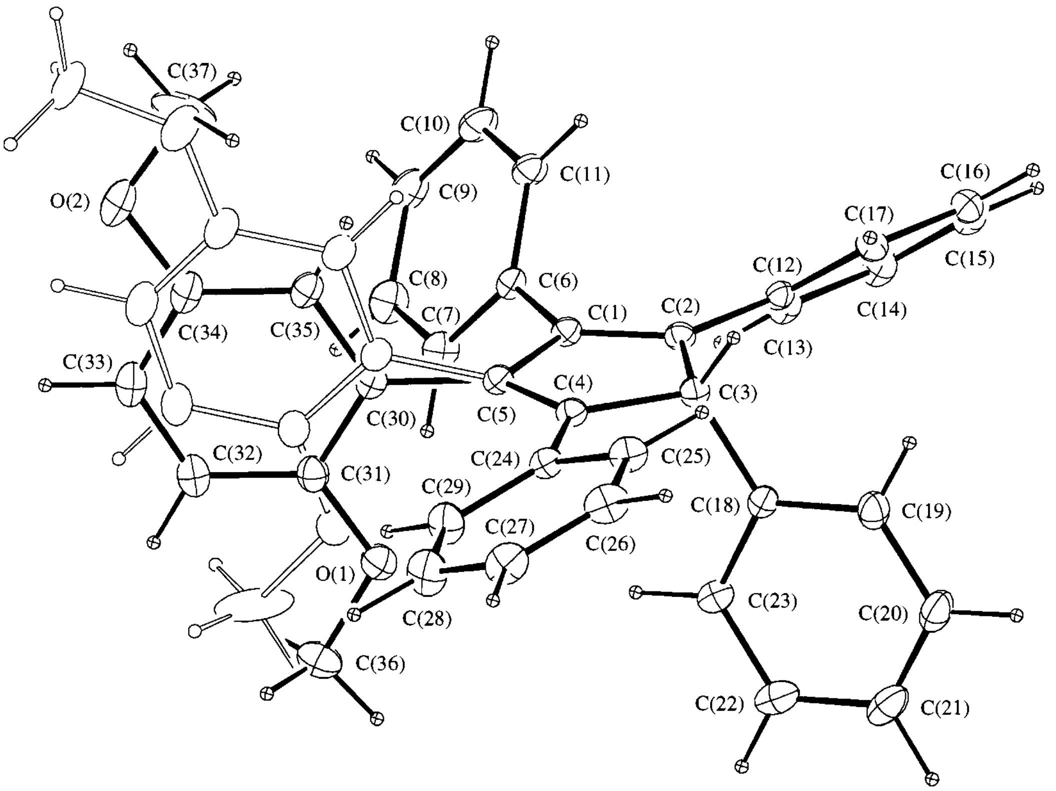
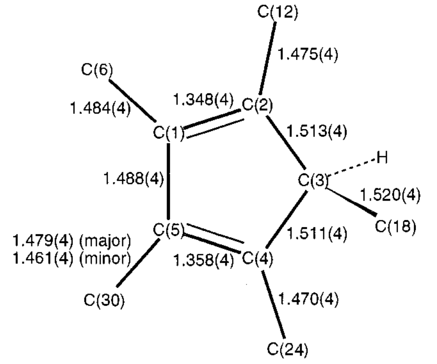


Fig. 1 An ORTEP[15] plot of C_5Ph_4RH showing the two positions for the disordered dimethoxyphenyl substituent (see text). The solid lines indicate the major disorder component. Thermal ellipsoids are drawn at the 10% probability level



Scheme 1

dimer, $[\{Mo(C_5Ph_4R)(\mu\text{-}Br)(\mu\text{-}CO)\}_2]$,[5] and 2.358 Å in the d^3–d^3 dimer, $[\{Mo(C_5Ph_4R)(\mu\text{-}Br)_2\}_2]$.[5] The two dimers have the same cyclopentadienyl ligand as does $[Mo(C_5Ph_4R)O_2(OMe)]$. Therefore, the longer Mo–C (cyclopentadienyl) distances for $[Mo(C_5Ph_4R)O_2(OMe)]$ cannot be attributed to the steric interactions between the metal tripod and the bulky cyclopentadienyl ligand, and, presumably, have an electronic origin. The weaker, relatively longer Mo–C (cyclopentadienyl) distances for $[Mo(C_5Ph_4R)O_2(OMe)]$ accord with the observed lability of the cyclopentadienyl ligand for all the d^0 $[Mo(C_5Ph_4R)O_2X]$ complexes isolated in this study. A propeller-like arrangement is observed for the phenyl substituents of the C_5Ph_4R ligand. The Mo–O (oxo) bond lengths are 1.708(2) and 1.677(3) Å and compare with the Mo–O (methoxide) distance of 1.881(2) Å. The O (oxo)–Mo–O (oxo) angle is 107.1(1)° compared to the O (oxo)–Mo–O (methoxide) angles which are 101.1(1) and 103.1(1)°. These distances and angles are very similar to those found for $[MoO_2(OMe)\{HB(ippz)_3\}]$ [ippz = (3-isopropylpyrazol-1-yl)];[19] for example, in the latter complex the Mo–O (oxo) bond lengths are 1.697(2) and 1.705(2) Å, the Mo–O (methoxide) bond length is 1.865(2) Å, and the O–Mo–O angle is 103.78(8)°. The methoxide ligand in $[Mo(C_5Ph_4R)O_2(OMe)]$ points away from the bulky cyclopentadienyl ligand (model studies reveal that there is insufficient room for it to point towards the bulky cyclopentadienyl ligand). The Mo–O–C (methoxide) angle is 119.6(2)°; presumably the methoxide oxygen atom has rehybridised to place a lone pair in a p orbital of correct symmetry for overlap with a vacant molybdenum d orbital and so maximise the $p_\pi(O) \rightarrow d_\pi(Mo)$ bonding.

Distal (**A**) and proximal (**B**) rotamers are possible for each $[Mo(C_5Ph_4R)O_2X]$ complex. It is immediately obvious that $[Mo(C_5Ph_4R)O_2(OMe)]$ crystallises as the proximal rotamer with O(1), the *o*-methoxy oxygen atom of the dimethoxyphenyl substituent, directed towards the formally 16-electron, molybdenum(VI) centre (the *o*-methoxy group lies between the two oxo ligands and is *trans* to the methoxide ligand). In all previous structures of C_5Ph_4R complexes[4,20] the *o*-methoxy group of the dimethoxyphenyl substituent points away from the metal centre (*i.e.* the distal rotamer has crystallised). This includes the dimers $[\{Mo(C_5Ph_4R)(\mu\text{-}CO)(\mu\text{-}Br)\}_2]$ and $[\{Mo(C_5Ph_4R)(\mu\text{-}Br)_2\}_2]$,[5] both prepared in a single step from $[Mo(C_5Ph_4R)(CO)_3Br]$ which also provides the entry point to the $[Mo(C_5Ph_4R)O_2X]$ species reported herein. That the aforementioned dimers and $[Mo(C_5Ph_4R)O_2(OMe)]$ have a common precursor, $[Mo(C_5Ph_4R)(CO)_3Br]$, but different orientations for the dimethoxyphenyl substituent, strongly suggests that this substituent can rotate about its bond with the cyclopentadienyl group. The Mo···O(1) distance at 3.025 Å is too long to be (formally) considered a bond. However, the electrostatic interaction between the electropositive molybdenum(VI) centre and the lone pairs on O(1) may well favour the proximal rotamer and contribute to the overall stability of the complex. In this regard, it may be noteworthy that the cyclopentadienyl ring is tilted from perpendicular to the C_5 ring centroid-to-Mo axis in a manner that lessens the distance between the *o*-methoxy group and the molybdenum atom. As a result, the shortest Mo–C bond length is 2.398(3) Å for Mo–C(5) [the dimethoxyphenyl substituent bonds to C(5)], and the longest is 2.599(3) Å for Mo–C(2) [C(2) and C(3) are the two ring carbon atoms furthermost from C(5)].

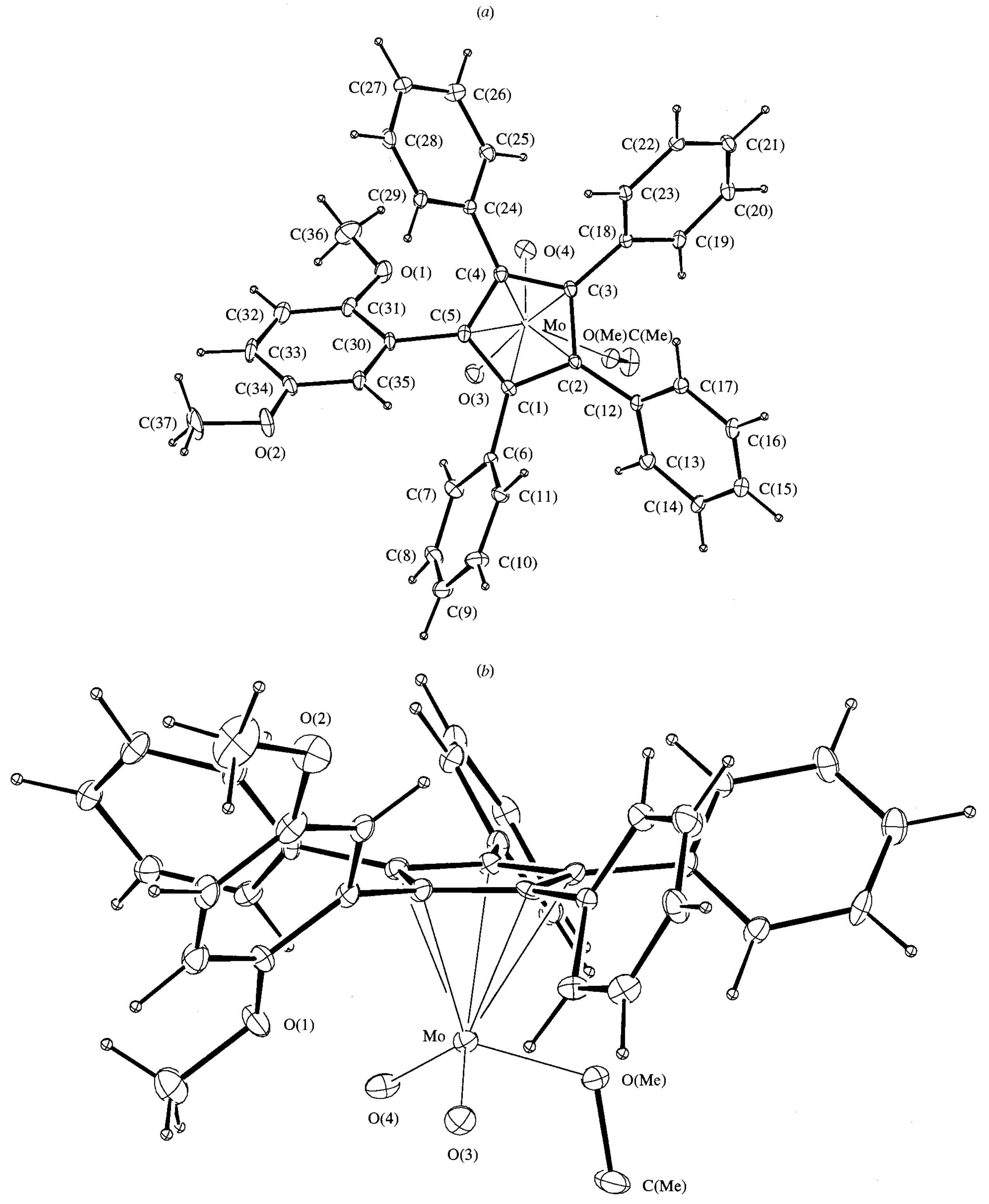


Fig. 2 The ORTEP plots of the major disorder component (see text) of [Mo(C_5Ph_4R)O_2(OMe)] showing (*a*) the atom labelling scheme and (*b*) the positioning of the dimethoxyphenyl substituent and the methoxide ligand relative to the metal centre. Thermal ellipsoids are drawn at the 10% probability level

NMR spectroscopy and fluxional behaviour

As noted above, NMR spectra of the [Mo(C_5Ph_4R)O_2X] complexes showed double the number of peaks expected for each complex. Fig. 3 shows spectra from a variable-temperature ^1H NMR study of [Mo(C_5Ph_4R)O_2Br] in C_6D_5Cl. Four methoxy peaks (a pair for one methoxy group at δ 3.39 and 3.29 and a pair for the other at δ 3.14 and 2.98) are seen in the limiting low-temperature spectrum obtained at 300 K. On raising the temperature these peaks broaden and then the pairs coalesce and give rise to two peaks at δ 3.38 and 3.12 (at 370 K). Accompanying changes are also apparent in the phenyl region. The changes in the spectra with temperature were completely reversible suggesting that exchange between two conformers for the complex is observed. Independent calculations for both methoxy groups of the barrier for exchange between the two sites using the coalescence-point analysis method of Shanan-Atidi and Bar-Eli[21] both give $\Delta G^{\ddagger} = 68.6 \pm 0.8$ kJ mol^{-1}.

The underlying dynamic process could either be (*i*) exchange between distal and proximal rotamers (**A** and **B** respectively)

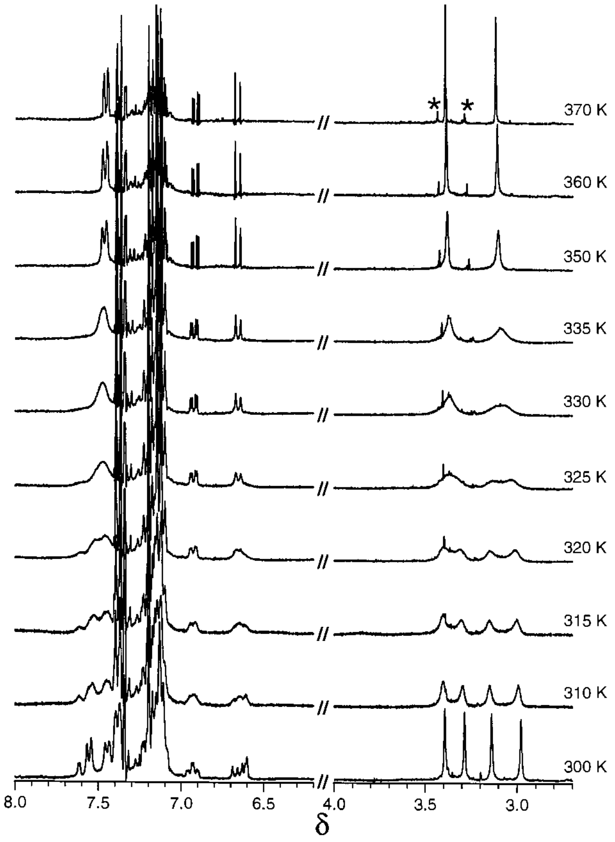
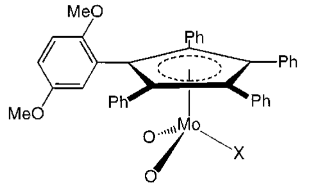
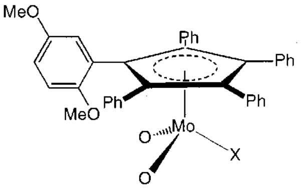


Fig. 3 Temperature-dependent 300 MHz ^{1}H NMR spectra of [$Mo(C_5Ph_4R)O_2Br$] in C_6D_5Cl (the asterisks mark peaks for an impurity)



A



B

arising from the hindered rotation of the dimethoxyphenyl group or (*ii*) rotation of the bulky cyclopentadienyl ligand with respect to the metal–ligand tripod. Rotation of the bulky cyclopentadienyl ligand can be discounted because the values seen for $\Delta G^\ddagger$ are very much larger than reported values of barriers for this process in closely related C_5Ph_5 and C_5Ph_4H complexes, even where the metal–ligand tripod is relatively bulky: for example, ≈38 kJ mol^{-1} for [$Mo(C_5Ph_5)(CO)_2L_2$] [L_2 = 2,3-bis(diphenylphosphino)maleic anhydride radical][22] and 36.4 ± 1.3 kJ mol^{-1} for [$Fe(C_5Ph_5)(CO)(PMe_2Ph)\{C(O)Et\}$].[23] The complexes [$Fe(C_5Ph_4H)_2$][24] and [$Ti(C_5Ph_4H)_2Cl_2$][25] show no evidence for slowed rotation of the cyclopentadienyl ligands down to 178 K. The barrier to phenyl group rotation in the last three complexes is larger than that for cyclopentadienyl rotation. Furthermore, the cations [$Mo(C_5Ph_4R)(CO)_4$]$^+$ and [$Ru(C_5Ph_4R)(CO)_3$]$^+$ display the same dynamic behaviour as does [$Mo(C_5Ph_4R)O_2Br$],[26] ruling out rotation of the cyclopentadienyl ligand with respect to the MoO_2Br tripod as the fluxional mechanism. This suggests that exchange between rotamers **A** and **B**, for [$Mo(C_5Ph_4R)O_2Br$] occurs on the NMR time-scale. It has already been concluded from comparisons of available crystal structures of C_5Ph_4R complexes that the dimethoxyphenyl substituent can rotate thereby giving distal and proximal rotamers (see above).

Difficulty was encountered in obtaining NMR spectra of the alkoxide complexes [$Mo(C_5Ph_4R)O_2(OR'')$] free from peaks for the free alcohol and hydrolysis product(s). Great care had to be taken to rigorously dry all solvents and glassware. The spectra show double the expected number of peaks, which are attributed to the proximal and distal rotamers arising from the orientation of the dimethoxyphenyl substituent as described above for [$Mo(C_5Ph_4R)O_2Br$]. Unlike [$Mo(C_5Ph_4R)O_2Br$], the peaks for the two rotamers were no longer of equal intensity. In $CDCl_3$ solution at 298 K the major conformer (A) for each [$Mo(C_5Ph_4R)O_2(OR'')$] complex displayed methoxy peaks at δ ≈3.52 and ≈2.96 whereas the minor conformer (B) has one methoxy peak at δ ≈3.33–3.29 and a second at δ ≈3.12–3.08. The methoxy peaks for the minor conformer (B) were readily distinguished from those for the hydrolysis product (these occur at δ 3.31 and 3.07 exactly, see above) by judicious addition of undried $CDCl_3$ (trace water) to the sample and watching the peaks for the hydrolysis product grow as those for conformers A and B decreased in intensity (the peaks for the hydrolysis product are close to but clearly resolved from those of conformer B). From the integrals of the methoxy peaks, the relative populations of the major conformer (A) to minor conformer (B) at 298 K for each [$Mo(C_5Ph_4R)O_2(OR'')$] complex are: R″ = Me, 1.0(A): 1.05(B); Et, 1.0(A): 0.9(B); Pr^i, 1.0(A): 0.4; Bu^t, 1.0(A): 0.1(B). The steady decline in the relative population of the minor conformer as the steric bulk of the alkoxide ligand increases strongly suggests that the minor conformer is the proximal isomer (*i.e.* **B**). It follows that in the limiting low-temperature spectrum of [$Mo(C_5Ph_4R)O_2Br$], Fig. 3, the outermost pair of methoxy peaks arise from the distal isomer (**A**) and the innermost pair from the proximal isomer (**B**).

Table 2 Cyclic voltammetry data for the [$Mo(C_5Ph_4R)O_2X$] complexes; potentials are in volts *vs.* the ferrocenium–ferrocene couple

	Mo^{VI}–Mo^{V} couple	
X	$E_{\frac{1}{2}}$	i_{pa}/i_{pc}
Br*	−0.55	0.96
OMe	−1.52	0.84
OEt	−1.53	0.83
OPr^i	−1.59	0.77
OBu^t	−1.53	0.82

* Also, E_p −1.04 V.

Electrochemistry

The electrochemistry of the [$Mo(C_5Ph_4R)O_2X$] complexes was characterised by cyclic voltammetry, Table 2. Cyclic voltammograms of the complexes show a reduction couple with peak currents and peak-to-peak separations comparable to those for the ferrocene–ferrocenium couple when measured *in situ* on solutions containing equimolar amounts of ferrocene and molybdenum(VI) complex. This is consistent with the reduction couples being diffusion-controlled (Nernstian) one-electron processes and, therefore, they are attributed to the Mo^{VI}–Mo^{V} couple, equation (4). The peak current ratios, $i_{pa}:i_{pc}$, reveal the

$$[Mo(C_5Ph_4R)O_2X] \pm e \rightleftharpoons [Mo(C_5Ph_4R)O_2X]^{\bullet -} \quad (4)$$

couples to be almost but not completely chemically reversible. That for the bromo complex is the most chemically reversible, showing the 17-electron molybdenum(V) species, [$Mo(C_5Ph_4R)O_2Br$]$^{\bullet -}$, to have some stability. In contrast, reduction of [$Mo(C_5Ph_4R)(CO)_3Br$] is irreversible because electron transfer to the metal centre is accompanied by concomitant scission of bromide ion; the high-energy 19-electron molybdenum(I) intermediate, [$Mo(C_5Ph_4R)(CO)_3$]$^{\bullet -}$, is not observed.[11] The Mo^{VI}–Mo^{V} couple for [$Mo(C_5Ph_4R)O_2Br$] at −0.55 V is about ≈1.0 V positive of those for the alkoxide complexes consistent with the harder, π-donor alkoxide ligands stabilising Mo^{VI}, the higher oxidation state, much more effectively than the softer, π-donor bromo ligand.

Cyclic voltammograms of [Mo(C_5Ph_4R)O_2Br] also revealed a second reduction peak at −1.04 V. The reduction process was irreversible and the peak height was consistent with a multi-electron process. The exact number of electrons involved was not determined. No other reduction processes before the solvent discharge were seen in cyclic voltammograms of the alkoxide complexes.

Conclusion

Oxidation of [Mo(C_5Ph_4R)$(CO)_3$Br] with dioxygen provides a high-yield entry to d^0 molybdenum(VI) complexes of the type [Mo(C_5Ph_4R)O_2X] (X = Br or alkoxide ligand). Analogues of the alkoxide complexes with simpler cyclopentadienyl ligands have not been reported. It seems likely that the bulk of the tetraarylcyclopentadienyl ligand leads to [Mo(C_5Ph_4R)O_2Br] being more stable than its C_5Me_5 analogue, and makes the alkoxide complexes sufficiently stable to be isolated. The dimethoxyphenyl substituent in the [Mo(C_5Ph_4R)O_2X] complexes can rotate about its bond with the cyclopentadienyl ring with both proximal and distal isomers observed in NMR spectra. The barrier for exchange between these rotamers for [Mo(C_5Ph_4R)O_2(OMe)] has been estimated; the proximal rotamer of this complex is the one that crystallises, perhaps because of stabilising interactions between the lone pairs on the *o*-methoxy group and the electron-deficient molybdenum(VI) centre.

Experimental

Except where stated, reactions were carried out under an atmosphere of dry dinitrogen using standard Schlenk and cannula techniques. Solvents were routinely distilled from the appropriate drying agent under dinitrogen immediately prior to use: tetrahydrofuran and toluene from purple sodium–benzophenone solutions, hexanes from sodium wire; dichloromethane from P_2O_5; methanol from magnesium methoxide; ethanol, Pr^iOH and Bu^tOH from the corresponding sodium alkoxide; acetone from anhydrous B_2O_3. Triethylamine was dried and stored over BaO. All other chemicals were used as obtained from commercial sources (usually Aldrich).

Infrared spectra were recorded on a Perkin-Elmer 500B spectrometer, ^1H NMR spectra on Bruker AM500 (500 MHz) or AC300 (300 MHz) spectrometers (data are listed from spectra acquired on the 300 MHz instrument operating at 298 K). Cyclic voltammetry experiments employed a BAS 100B electrochemical analyser interfaced with a 486 IBM compatible computer for data analysis and display. A standard three-electrode configuration was used with a Ag–AgCl reference electrode (BAS), a freshly polished platinum working electrode (BAS) and a single platinum wire as the auxiliary electrode. The solvent $(CH_2Cl)_2$ was highest quality HPLC grade sealed under argon (Aldrich) and distilled from CaH_2 under nitrogen immediately prior to use. The supporting electrolyte was 0.1 M [NBu^n_4][PF_6] (dried as the solid *in vacuo* at 100 °C). Solutions were purged with high-purity nitrogen (presaturated with solvent) prior to each experiment and then blanketed with a cover of nitrogen for the duration of the experiment. An electrochemical scan of the solvent electrolyte system was always recorded before the addition of the compound to ensure that there were no spurious signals. All potentials are quoted relative to the ferrocene–ferrocenium couple [≈0.45 V *vs.* Ag–AgCl in $(CH_2Cl)_2$] recorded as an internal standard by adding ferrocene to each solution after the cyclic voltammetric measurements were complete.

Preparations

[Mo(C_5Ph_4R)O_2Br]. **CAUTION**: this reaction involves toluene heated to beyond its flash point (4 °C) under an oxygen atmosphere, and although no problems were encountered appropriate precautions should be taken such as careful exclusion of potential ignition sources and use of safety shields.

A solution of [Mo(C_5Ph_4R)$(CO)_3$Br] (3.1 g, 4.1 mmol) in toluene (200 cm^3) was heated at reflux under an oxygen atmosphere. The reaction was monitored by IR spectroscopy; after 2.5 h the carbonyl peaks for [Mo(C_5Ph_4R)$(CO)_3$Br] [ν(CO) 2047, 1979 and 1960 cm^{-1}] disappeared. The solution was cooled and evaporated to dryness. Recrystallisation of the orange residue from toluene–hexanes afforded the orange microcrystalline product which was filtered off, washed with cold hexane, and dried under vacuum [0.2 mmHg (*ca.* 26.6 Pa), 24 h]. Yield 2.6 g, 88% (Found: C, 64.4; H, 4.4. Calc. for $C_{37}H_{29}BrMoO_4\cdot0.5C_7H_8$: C, 64.1; H, 4.4%). IR (paraffin mull): 2924s, 2800s, 1377m, 1229m, 1042m, 926m, 895m, 816w, 772m, 723m and 698m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.25–6.78 [m, Ph and $C_6H_3(OMe)_2$, 21 H], 6.45 [dd, $C_6H_3(OMe)_2$], 6.22 [d, $C_6H_3(OMe)_2$], 3.55, 3.31, 3.12 and 2.98 (four s, ratio 1 : 1 : 1 : 1, OMe, 6H), and 7.19 (s) and 2.35 (s) (both toluene). EI mass spectrum: *m/z* 714 (M^+, 84), 634 (100) and 619 (32%).

General method for alkoxide complexes [Mo(C_5Ph_4R)O_2(OR″)]. A suspension of [Mo(C_5Ph_4R)O_2Br] (typically 0.1–0.3 g) in the appropriate alcohol (40 cm^3) was heated at reflux for 4 h. Pale yellow solutions formed which were filtered hot through a plug of dry Celite and the solvent then removed under vacuum. Recrystallisation of the yellow to orange residues from solutions of dichloromethane and the appropriate alcohol afforded the pale yellow crystalline products which were collected and dried under vacuum. Yields were high, typically 80–90%.

[Mo(C_5Ph_4R)O_2(OMe)] (Found: C, 67.7; H, 5.0. Calc. for $C_{38}H_{32}MoO_5\cdot0.5CH_3OH$: C, 67.9; H, 5.0%). IR (paraffin mull): 1500m, 1422m, 1270m, 1222s, 1080m, 1075m, 1040s, 1022s, 1018s, 918s, 910s, 883s, 870w, 840w, 800w, 797m, 770m, 719m and 692s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.21–6.58 [m, Ph and $C_6H_3(OMe)_2$, 22 H], 6.29 and 6.06 [two d, $C_6H_3(OMe)_2$, 1 H], 4.38 and 4.36 (two s, OMe, 3 H), 3.52, 3.33, 3.12 and 2.97 [four s, ratio 1.0 : 1.05 : 1.05 : 1.0, $C_6H_3(OMe)_2$, 6H], and 3.49 (s, methanol). ^{13}C-{^1H} NMR ($CDCl_3$): δ 153.28, 152.94, 152.82, 151.62, 151.50, 149.60, 132.15, 132.11, 131.86, 131.71, 131.52, 131.32, 131.09, 131.03, 130.94, 130.52, 130.32, 129.03, 128.11, 127.56, 127.49, 127.41, 127.26, 125.79, 125.13, 124.73, 124.58, 124.13, 124.00, 123.54, 121.56, 121.17, 118.28, 118.09, 117.28, 116.71, 116.26, 116.07, 115.64, 112.41, 111.83, 70.89, 70.26, 55.53, 55.36, 55.19, 54.44 and 50.82 (methanol). EI mass spectrum: *m/z* 666 (M^+, 100), 634 (23), 619 (22), 602 (19), 584 (9) and 537 (65%).

[Mo(C_5Ph_4R)O_2(OEt)] (Found: C, 68.5; H, 5.4. Calc. for $C_{39}H_{34}MoO_5$: C, 69.0; H, 5.1%). IR (paraffin mull): 1500m, 1422m, 1270m, 1222s, 1080m, 1075m, 1040s, 1022s, 1018s, 918s, 910s, 883s, 797m, 770m, 719m and 692s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.20–6.23 [m, Ph and $C_6H_3(OMe)_2$, 23 H], 4.52 (two overlapping q, OEt, 2 H), 3.51, 3.32, 3.11 and 2.97 (four s, ratio 1.0 : 0.9 : 0.9 : 1.0; OMe, 6 H) and 1.26 (two overlapping t, OEt, 3 H). EI mass spectrum: *m/z* 680 (M^+, 25), 619 (10), 506 (62), 381 (30), 303 (40), 167 (100) and 91 (68%).

[Mo(C_5Ph_4R)O_2(OPr^i)] (Found: C, 69.5; H, 5.3. Calc. for $C_{40}H_{36}MoO_5$: C, 69.4; H, 5.2%). IR (paraffin mull): 1501m, 1267m, 1262m, 1099m, 1044m, 941m, 914m, 893s, 839m, 802m and 721m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.21–6.58 [m, Ph and $C_6H_3(OMe)_2$, 22 H], 6.25 [two d, $C_6H_3(OMe)_2$, 1 H], 4.65 (m, OPr^i, 1 H), 3.52, 3.30, 3.08 and 2.96 (four s, ratio 1.0 : 0.4 : 0.4 : 1.0, OMe, 6 H), 1.25 and 1.24 (two overlapping d, ratio 1.0 : 0.4, OPr^i, 6 H). EI mass spectrum: *m/z* 694 (M^+, 30), 621 (12), 506 (68), 181 (53) and 167 (100%).

[Mo(C_5Ph_4R)O_2(OBu^t)] (Found: C, 69.3; H, 5.8. Calc. for $C_{41}H_{38}MoO_5$: C, 69.7; H, 5.4%). IR (paraffin mull): 2970m, 1505m, 1227s, 1180m, 1158m, 1040m, 1025m, 922s, 890s, 880s, 718m and 695s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.19–6.15 [m, Ph and $C_6H_3(OMe)_2$, 23 H], 3.52, 3.29, 3.07 and 2.96 (four s, ratio

1.0 : 0.1 : 0.1 : 1.0, OMe, 6 H), 1.32 and 1.30 (two s, ratio 1.0 : 0.1, OBu^t, 9 H). EI mass spectrum: *m*/*z* 708 (M^+, 15), 652 (13), 584 (30), 506 (40), 289 (30), 265 (40), 165 (52) and 105 (100%).

C_5Ph_4RH. Reactions of [$Mo(C_5Ph_4R)O_2Br$] or [$Mo(C_5Ph_4R)O_2(OMe)$] with water both in the presence or in the absence of acids (acetic acid) or bases (sodium carbonate or triethylamine) gave high yields of the free cyclopentadiene, C_5PhRH. The following reaction is typical. Water (0.5 cm^3) and sodium carbonate (13 mg, 0.12 mmol) were added to [$Mo(C_5Ph_4R)O_2(OMe)$] (72 mg, 0.11 mmol) in methanol (35 cm^3) and the mixture stirred for 18 h. An equal volume of dichloromethane was then added, followed by four volumes of water. The dichloromethane phase was separated, dried with $MgSO_4$, and the solvent removed. Recrystallisation of the white residue from dichloromethane–methanol solution afforded colourless crystals of the cyclopentadiene (42 mg, 77%), m.p. 178–179 °C (Found: C, 87.8; H, 6.2. Calc. for $C_{37}H_{30}O_2$: C, 87.7; H, 6.0%). IR (paraffin mull): 1597m, 1493s, 1410m, 1269m, 1223s, 1177m, 1055m, 1030m, 764m, 745m and 698m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.31–6.95 (m, Ph, 20 H), 6.74–6.50 [m, $C_6H_3(OMe)_2$, 3 H], 5.14 and 5.12 (two s, ratio 1 : 1, HC_5Ph_4R, 1 H), 3.63, 3.55, 3.51 and 3.12 (four s, ratio 1 : 1 : 1 : 1, OMe, 6 H). EI mass spectrum: *m*/*z* 506 (M^+, 100), 191 (42), 182 (88), 165 (70), 105 (72) and 77 (44%).

Crystallography

Crystal data. C_5Ph_4RH. $C_{37}H_{30}O_2$, *M* 506.6, triclinic, space group $P\bar{1}$, *a* 9.911(2), *b* 11.338(2), *c* 14.582(3) Å, α 108.57(1), β 93.81(1), γ 114.87(1)°, *U* 1370.5(6) Å^3, D_c 1.23 g cm^{-3}, *Z* 2, μ_{Cu} 5.43 cm^{-1}. Crystal size 0.07 × 0.17 × 0.41 mm, $2\theta_{max}$ 140°, minimum and maximum transmission factors 0.83 and 0.96. The number of reflections was 3179 considered observed out of 5163 unique data. After refinement on *F*, final residuals *R*, *R′* were 0.059, 0.083 for the observed data.

[$Mo(C_5Ph_4R)O_2(OMe)$], $C_{38}H_{32}MoO_5$, *M* 664.6, monoclinic, space group $P2_1/c$, *a* 10.103(3), *b* 9.040(2), *c* 35.114(9) Å, β 104.16(1)°, *U* 3110(1) Å^3, D_c 1.42 g cm^{-3}, *Z* 4, μ_{Mo} 4.52 cm^{-1}. Crystal size 0.13 × 0.20 × 0.20 mm, $2\theta_{max}$ 50°, minimum and maximum transmission factors 0.92 and 0.95. The number of reflections was 4247 considered observed out of 5436 unique data, with R_{merge} 0.011 for 90 pairs of equivalent *hk*0 reflections. After refinement on *F*, final residuals *R*, *R′* were 0.068, 0.113 for the observed data.

Structure determination. Reflection data were measured at 294 K with an Enraf-Nonius CAD-4 diffractometer in θ–2θ scan mode using nickel-filtered copper radiation (λ 1.5418 Å) for C_5Ph_4RH and graphite-monochromatized molybdenum radiation (λ 0.7107 Å) for [$Mo(C_5Ph_4R)O_2(OMe)$]. Data were corrected for absorption using the analytical method of de Meulenaer and Tompa.[27] Reflections with $I > 3\sigma(I)$ were considered observed. The structures were determined by direct phasing and Fourier methods. Hydrogen atoms were included in calculated positions and assigned thermal parameters equal to those of the atom to which they were bonded.

Reflection weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{\frac{1}{2}}$. The weighted residual is defined as $R' = (\Sigma w\Delta^2/\Sigma wF_o^{\,2})^{\frac{1}{2}}$. Atomic scattering factors and anomalous dispersion parameters were from ref. 28. Structure solutions were by MULTAN 80[29] and refinement used RAELS;[30] ORTEP II[15] running on a Macintosh IIcx computer was used for the structural diagrams, and a DEC Alpha-AXP workstation was used for calculations.

C_5Ph_4RH. Anisotropic refinement of the non-hydrogen atoms converged with *R* 0.083. A Fourier-difference map revealed several small maxima in the vicinity of the dimethoxyphenyl group, indicating probable positional disorder. A second orientation of the group was created relative to a local axial system using the residual peaks as a basis, and the orientation, position and relative occupancy of this was refined along with the parameters of the other atoms. The internal geometry of the minor component was maintained identical with the major one, with the exception of the methyl groups, which were refined independently, but with the O–Me distances lightly constrained to be equal. Thermal motion of the dimethoxyphenyl group was described by a 12-parameter TL rigid-body model (T is the translation tensor and L the libration tensor[31]), with the centre of libration at the cyclopentadienyl carbon of attachment. The methyl groups were allowed additional individual atom anisotropic components to model vibration about the phenyl carbon–oxygen bonds. The occupancies refined to 0.72 and 0.28, and the final *R* was 0.059. Minimum and maximum final residual electron densities were −0.47 and 0.43 e Å^{-3}.

[$Mo(C_5Ph_4R)O_2(OMe)$]. Anisotropic refinement of non-hydrogen atomic parameters converged to *R* 0.135. A Fourier-difference map at this stage revealed a complete image of the structure, related to the original orientation by a combination of reflection normal to *y* with translation parallel to *y* of roughly *b*/2. A molecule relative to a refineable local axial system was generated from the original by an exact mirror operation normal to *y*. This axial system was originally positioned with a translation of *b*/2 along *y*, and its position and the relative occupancy of its related atoms were refined along with the parameters of the original atoms. The ligand was maintained identical for both disorder components, and the positions of the other atoms were allowed to refine, but with corresponding Mo–O distances lightly constrained to approach equality in both orientations. The thermal motion of the minor component was described by a 15-parameter TLX rigid-body model [X is the origin of libration (if refined)[31]], while the atoms of the major component had individual anisotropic vibrational parameters. The occupancies refined to 0.76 and 0.24, and the displacement along *y* to 0.47. The final *R* was 0.068. Minimum and maximum final residual electron densities were −0.99 and 0.97 e Å^{-3} in the vicinity of the Mo atom.

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