Solid State and Solution Studies of Tungsten(VI) Oxotetraalkoxides†

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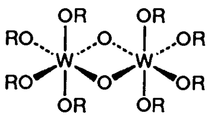
Variable-temperature ^1H NMR studies of the oxoalkoxides, $WO(OR)_4$ (R = Me, Et, Pr^i, or *cyclo*-C_6H_{11}), show these compounds to be dynamic in solution. For R = Me or Et, limiting spectra have been obtained which are consistent with alkoxide-bridged binuclear structures, and for R = Me or *cyclo*-C_6H_{11}, X-ray diffraction studies confirm that these structures are adopted in the solid state. The alkoxide bridges are asymmetric [R = Me, 2.032(7) and 2.242(12) Å (average); R = *cyclo*-C_6H_{11}, 2.044(4) and 2.250(4) Å] and coplanar with the terminal oxo groups, the longer W–OR bonds being *trans* to the short W=O bonds. Tungsten-183 NMR chemical shifts of the compounds with R = Me, Et, *cyclo*-C_6H_{11}, Bu^t or $C_6H_3Pr^i_2$-2,6 are very sensitive to the nature of the alkoxo ligand, and range from δ −62.9 for $[\{WO(OMe)_4\}_2]$ to −493.6 for mononuclear $[WO(OC_6H_3Pr^i_2\text{-}2,6)_4]$. Possible solution equilibria are discussed in the light of these NMR results. An attempt to prepare $[WO(OC_6H_4Me\text{-}4)_4]$ yielded $[W(OC_6H_4Me\text{-}4)_6]$, and an X-ray crystal structure determination showed this compound to be octahedral with an average W–O bond length of 1.895(9) Å.

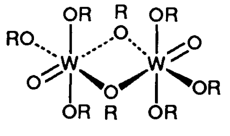
The renewed interest in metal alkoxides as soluble analogues of,[1] or precursors to[2] metal oxides has led to the extensive investigation of homoleptic compounds, $M(OR)_n$, and their hydrolysis to give oxide materials (the so-called 'sol-gel process').[3] Species intermediate between homoleptic alkoxide and oxide, *i.e.* oxoalkoxides, have received less attention, although the polynuclear compounds $[Ti_7O_4(OEt)_{20}]$,[4] $[Nb_8O_{10}(OEt)_{20}]$,[5] and $[Zr_{13}O_8(OMe)_{36}]$[6] have been structurally characterised by X-ray crystallography. The molybdenum compounds $[MoO(OR)_4]$, $[MoO_2(OR)_2]$ (R = Bu^t, Pr^i or CH_2Bu^t), $[Mo_3O(OR)_{10}]$ (R = Pr^i or CH_2Bu^t) and $[Mo_6O_{10}(OPr^i)_{12}]$ have also been prepared.[7]

Because of our interest in the non-aqueous chemistry of polyoxotungstates, $W_xO_y^{n-}$, we were attracted to tungsten(VI) oxoalkoxides as soluble precursors with the possibility of following hydrolysis reactions in solution using ^{183}W NMR spectroscopy. Oxotetraalkoxides of W^{VI}, $WO(OR)_4$, were first described in 1960 by Funk, Weiss and Mohaupt[8] who synthesised a range of compounds with R = Me, Et, Pr^n, Pr^i, Bu^n and CH_2Ph from $WOCl_4$ and the respective alcohol in the presence of ammonia. The compounds were characterised by microanalysis but no spectroscopic properties were reported and the authors did not discuss the structures of these molecules. In 1968, the hydrolysis of $WO(OMe)_4$ in alcohol solutions containing $[NR_4]OH$ (R = Et, Pr^n, Bu^n) to give $[NR_4]_2[W_6O_{19}]$ was reported by Jahr, Fuchs and Oberhauser.[9] We felt that this system warranted a more detailed study, but we wanted first to understand more fully the structures and solution properties of the alkoxide starting materials, and the results of our investigations in this area are described here.

It is well established that the association of co-ordinatively unsaturated metal alkoxide fragments by alkoxide bridge formation is sensitive to the steric bulk of the alkoxide group.[10] Hence, methoxides are often polymeric materials whereas lower co-ordination numbers can be stabilised by very bulky alkoxide ligands. In the case of tungsten oxotetraalkoxides, dimerisation of the five-co-ordinate $[WO(OR)_4]$ species could in principle occur through either oxo or alkoxo bridges to give edge-shared bioctahedral structures such as **I** or **II**. With the bulkier alkoxides, mononuclear $[WO(OR)_4]$ could be square pyramidal (**III**) or trigonal bipyramidal (**IV**). It is also worth noting that an alternative, polymeric structure might involve linear, asymmetric oxo bridges of the type found in the solid state structure of $WOCl_4$ and analogous to the nitrido-bridged, polymeric $WN(OBu^t)_3$.[11] Since the related compounds $[MoO\{OC(CF_3)_3\}_4]$,[12] $[WS(OBu^t)_4]$,[13] and $[WO(OC_6H_3Pr^i\text{-}2,6)_4]$[14] containing bulky groups adopt distorted square-pyramidal structures in the solid state, we expected $WO(OBu^t)_4$ to behave similarly, but it was not clear which structures would be adopted by the compounds with less bulky alkoxide groups.



I



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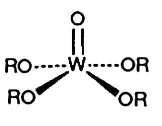
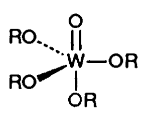


III



IV

Another aspect of alkoxide chemistry is that structures in solution are often not static, whereupon the dynamic processes involved in the interchange of alkoxo groups may provide access to the metal for incoming ligands. The reactivity of $WO(OR)_4$ (*e.g.* towards hydrolysis) might therefore be expected to vary with the lability of bridging bonds in binuclear species, or with the steric bulk of R in mononuclear complexes where access to the vacant co-ordination site may be prevented in extreme cases.

We therefore chose to study the effect of increasingly bulky alkoxo groups on the structure and solution dynamics of $WO(OR)_4$ by comparing the compounds with R = Me **1**, Et **2**, Pr^i **3**, cyclohexyl **4** and Bu^t **5**.[15]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

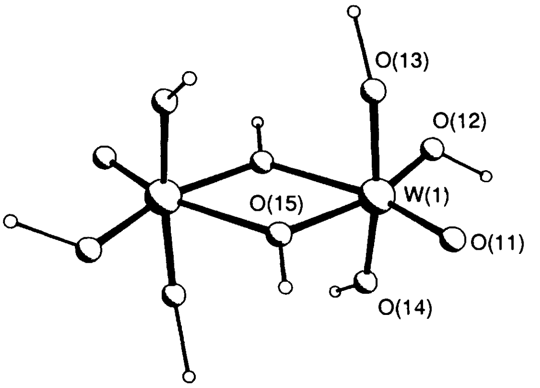


Fig. 1 A view of the molecular structure of one of the two independent molecules of compound **1**

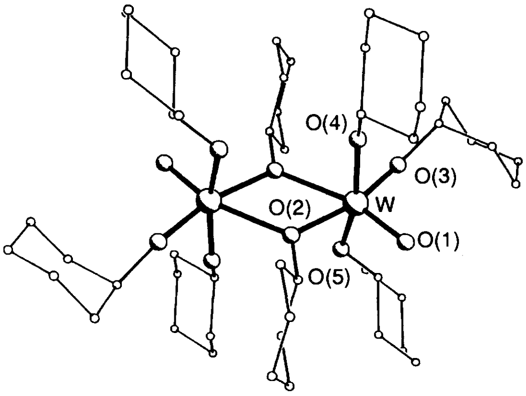


Fig. 2 A view of the molecular structure of compound **4**. Hydrogen atoms are omitted for clarity

Table 1 Bond lengths (Å) and angles (°) for the two independent molecules of compound **1**

Molecule 1		Molecule 2	
W(1)–O(11)	1.702(7)	W(2)–O(21)	1.696(8)
W(1)–O(12)	1.886(7)	W(2)–O(22)	1.902(6)
W(1)–O(13)	1.882(7)	W(2)–O(23)	1.885(8)
W(1)–O(14)	1.892(7)	W(2)–O(24)	1.882(8)
W(1)–O(15)	2.029(7)	W(2)–O(25)	2.035(6)
W(1)–O(15a)	2.254(7)	W(2)–O(25b)	2.230(6)
O(12)–C(12)	1.424(13)	O(22)–C(22)	1.407(20)
O(13)–C(13)	1.441(13)	O(23)–C(23)	1.385(16)
O(14)–C(14)	1.408(15)	O(24)–C(24)	1.414(15)
O(15)–C(15)	1.431(11)	O(25)–C(25)	1.449(11)
O(11)–W(1)–O(12)	105.2(4)	O(21)–W(2)–O(22)	105.4(3)
O(11)–W(1)–O(13)	98.2(3)	O(21)–W(2)–O(23)	97.9(3)
O(12)–W(1)–O(13)	85.3(3)	O(22)–W(2)–O(23)	84.8(3)
O(11)–W(1)–O(14)	95.2(3)	O(21)–W(2)–O(24)	96.0(4)
O(12)–W(1)–O(14)	89.0(3)	O(22)–W(2)–O(24)	89.5(3)
O(13)–W(1)–O(14)	166.5(3)	O(23)–W(2)–O(24)	165.9(3)
O(11)–W(1)–O(15)	93.3(3)	O(21)–W(2)–O(25)	93.6(3)
O(12)–W(1)–O(15)	161.4(3)	O(22)–W(2)–O(25)	160.7(3)
O(13)–W(1)–O(15)	90.8(3)	O(23)–W(2)–O(25)	89.6(3)
O(14)–W(1)–O(15)	90.8(3)	O(24)–W(2)–O(25)	91.6(3)
O(11)–W(1)–O(15a)	162.9(3)	O(21)–W(2)–O(25b)	162.6(3)
O(12)–W(1)–O(15a)	91.9(3)	O(22)–W(2)–O(25b)	92.0(3)
O(13)–W(1)–O(15a)	84.4(3)	O(23)–W(2)–O(25b)	83.6(3)
O(14)–W(1)–O(15a)	83.5(3)	O(24)–W(2)–O(25b)	83.8(3)
O(15)–W(1)–O(15a)	69.7(2)	O(25)–W(2)–O(25b)	69.0(2)
W(1)–O(12)–C(12)	132.5(7)	W(2)–O(22)–C(22)	129.2(8)
W(1)–O(13)–C(13)	137.1(7)	W(2)–O(23)–C(23)	137.2(7)
W(1)–O(14)–C(14)	135.5(7)	W(2)–O(24)–C(24)	138.7(8)
W(1)–O(15)–C(15)	123.7(7)	W(2)–O(25)–C(25)	122.9(6)
W(1)–O(15)–W(1a)	110.3(2)	W(2)–O(25)–W(2b)	111.0(2)
C(15)–O(15)–W(1a)	125.9(7)	C(25)–O(25)–W(2b)	126.1(6)

Symmetry operations: a $1 - x, 1 - y, 2 - z$; b $2 - x, 1 - y, 1 - z$.

Table 2 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
W(1)	6 080.8(3)	5 253.5(3)	9 170.8(3)
W(2)	8 818.2(3)	4 331.5(3)	5 579.8(3)
O(11)	6 337(6)	6 457(5)	8 538(6)
O(12)	7 242(6)	4 160(5)	8 804(7)
C(12)	8 605(10)	4 175(10)	8 805(13)
O(13)	4 845(6)	4 556(5)	8 224(6)
C(13)	4 427(12)	3 409(9)	7 955(12)
O(14)	7 317(6)	5 617(6)	10 270(6)
C(14)	7 961(10)	5 009(11)	11 076(10)
O(15)	4 654(5)	5 985(5)	9 798(5)
C(15)	4 242(11)	7 146(8)	9 635(10)
O(21)	8 919(7)	3 133(6)	6 274(7)
O(22)	7 071(6)	4 829(6)	5 490(7)
C(22)	6 346(12)	5 060(11)	6 240(14)
O(23)	8 255(6)	3 636(6)	4 366(6)
C(23)	7 532(12)	3 945(11)	3 484(11)
O(24)	9 291(7)	5 358(6)	6 616(6)
C(24)	9 225(13)	6 543(11)	6 803(12)
O(25)	10 682(5)	4 213(4)	5 331(5)
C(25)	11 535(10)	3 283(8)	5 699(11)

Table 3 Selected bond lengths (Å) and angles (°) for compound **4**

W–O(1)	1.691(4)	W–O(2)	2.044(4)
W–O(3)	1.893(4)	W–O(4)	1.877(4)
W–O(5)	1.893(4)	W–O(2′)	2.250(4)
O(2)–C(21)	1.452(7)	O(3)–C(31)	1.456(8)
O(4)–C(41)	1.418(6)	O(5)–C(51)	1.433(7)
O(1)–W–O(2)	92.8(2)	O(1)–W–O(3)	101.6(2)
O(2)–W–O(3)	165.8(2)	O(1)–W–O(4)	99.4(2)
O(2)–W–O(4)	89.7(2)	O(3)–W–O(4)	87.4(2)
O(1)–W–O(5)	97.5(2)	O(2)–W–O(5)	92.0(2)
O(3)–W–O(5)	86.8(2)	O(4)–W–O(5)	162.9(2)
O(1)–W–O(2′)	161.6(2)	O(2)–W–O(2′)	69.1(2)
O(3)–W–O(2′)	96.5(2)	O(4)–W–O(2′)	84.2(2)
O(5)–W–O(2′)	80.5(2)	W–O(2)–C(21)	123.6(4)
W–O(2)–W′	110.9(2)	C(21)–O(2)–W′	125.3(4)
W–O(3)–C(31)	131.6(4)	W–O(4)–C(41)	146.7(3)
W–O(5)–C(51)	127.3(4)		

Symmetry operation for primed atoms: $1 - x, 1 - y, 1 - z$.

Results and Discussion

Two methods were used to prepare the alkoxides: (*a*) a modification of the alcoholysis procedure of Funk *et al.*[8] and (*b*) chloride metathesis with lithium alkoxide. On occasions, when method (*b*) was used for **3** or **4**, the products after filtration and removal of the solvent, although not fully characterised, appeared to be bimetallic species incorporating lithium, as in the dimeric rhenium oxo compound $[\{ReO(OPr^i)_5Li_2Cl(thf)_2\}_2]$[16] (thf = tetrahydrofuran) and its tungsten organoimido cyclohexoxide analogue, $[\{W(NC_6H_4Me\text{-}4)(OC_6H_{11})_5Li_2Cl(C_6H_{11}OH)_2\}_2]$.[17] Hence, method (*a*) was used for all except **5** [although **1** and **3** can be obtained by sublimation from the initial solid product using method (*b*)].[18] Crystals of **1** and **4** suitable for X-ray diffraction were obtained by recrystallisation from toluene or hexane respectively, but repeated attempts to grow single crystals of the isopropoxide **3** were unsuccessful. What appeared to be single crystals of the *tert*-butoxide **5** were obtained, but these gave only poor diffraction.

Solid State Structures of $[\{WO(OMe)_4\}_2]$ **1** *and* $[\{WO(OC_6H_{11})_4\}_2]$ **4**.—Both compounds **1** and **4** adopt distorted edge-shared bioctahedral geometries featuring asymmetric alkoxo bridges which are coplanar with terminal oxo ligands. The structures are shown in Figs. 1 and 2 with relevant bond distances and angles in Tables 1 and 3 and atomic coordinates in Tables 2 and 4 respectively. There are two independent

Table 4 Atomic coordinates (× 10^4) for compound **4**

Atom	*x*	*y*	*z*
W	4946.6(2)	4150.6(1)	4926.1(1)
O(1)	3925(4)	3620(2)	5212(2)
O(2)	4130(3)	4919(2)	5333(2)
C(21)	3034(6)	4867(4)	5697(3)
C(22)	1903(5)	5071(4)	5416(3)
C(23)	776(6)	5002(5)	5771(3)
C(24)	932(8)	5180(5)	6397(3)
C(25)	2075(6)	4972(4)	6674(3)
C(26)	3209(6)	5047(4)	6305(3)
O(3)	5986(4)	3599(2)	4484(2)
C(31)	6854(7)	3101(4)	4665(3)
C(32)	7675(7)	2928(4)	4109(4)
C(33)	6878(10)	2574(6)	3656(3)
C(34)	6232(12)	2044(5)	3899(4)
C(35)	5467(7)	2186(4)	4430(4)
C(36)	6186(8)	2519(5)	4875(3)
O(4)	6147(3)	4129(2)	5521(1)
C(41)	6389(5)	4119(3)	6135(2)
C(42)	5695(6)	3600(4)	6448(3)
C(43)	6021(8)	3580(5)	7098(3)
C(44)	7397(8)	3514(4)	7181(3)
C(45)	8104(6)	4026(4)	6869(3)
C(46)	7780(5)	4040(4)	6219(2)
O(5)	4103(3)	4317(2)	4212(1)
C(51)	3497(5)	3858(3)	3840(2)
C(52)	3844(7)	3967(4)	3213(2)
C(53)	3211(7)	3482(5)	2807(3)
C(54)	1838(8)	3509(5)	2891(3)
C(55)	1465(8)	3415(5)	3526(3)
C(56)	2104(5)	3891(4)	3926(3)

Table 5 O≡W–O–C Torsion angles (°) in the structures of **1** and **4**

$[\{WO(OMe)_4\}_2]$ **1**		
Molecule (1)	Molecule (2)	$[\{WO(OC_6H_{11})_4\}_2]$ **4**
53.5 to O(12)	54.2 to O(22)	−1.6 to O(2)
152.2 to O(13)	152.2 to O(23)	−67.7 to O(3)
−163.9 to O(14)	−162.8 to O(24)	−42.0 to O(4)
−1.1 to O(15)	1.9 to O(25)	−42.1 to O(5)

molecules in the structure of the methoxide, and data for both are given in Tables 1 and 2. The molecules of **1** and **4** have crystallographic inversion symmetry. The W–O bond lengths for the terminal oxo ligands in all of these molecules lie within the range of values found in other tungsten oxo compounds and are indicative of multiple bonding.[19] For mono-oxo complexes this is normally regarded as being a triple bond, although in these oxoalkoxides it is, in principle, possible that the alkoxo ligands could compete with the oxo group for metal π orbitals, thereby reducing the W–O_{oxo} bond order. Chisholm[20] has discussed the relationship between M–O bond length and the degree of π bonding for terminal alkoxides in a range of Mo and W complexes by considering single-bond covalent radii of M, C and O. When these criteria are applied to the terminal alkoxides in **1** and **4**, the W–OR bond lengths, which are all in the range 1.87–1.90 Å, are indicative of some W–OR π bonding. Defining the *z* axis to be coincident with the tungsten-oxo bond, then the d_{xy} orbital is available for this type of interaction. The question now arises as to whether there is any π interaction between the alkoxides and the d_{xz} or d_{yz} orbitals which would lower the W≡O bond order. If so, then the slightly shorter tungsten-oxo bond lengths in gaseous, square-pyramidal WOX_4 [1.666(4), X = F;[21] 1.684(4), X = Cl;[22] 1.684(3), X = Br[23]] and those in $[(WOF_4)_2(\mu\text{-}F)]^-$ [1.57(3)][24] may be a result of the weaker π-bonding abilities of halides compared with alkoxides.

In theory, it is also possible that M–O–C angles in terminal alkoxides could reflect the degree of π donation to the metal, although Rothwell and co-workers[25] have found no correlation between M–OR bond distances and M–O–C angles in bulky aryloxides of Nb^V and Ta^V. Thus, although in the structures of **1** and **4** larger angles are associated with shorter W–OR bonds, this angular variation is not necessarily a reflection of the electronic properties of the W–OR bond and may simply be caused by steric compression. In this regard, it is noticeable that the variation in W–O–C angles is smaller in **1**. A parameter more likely to provide information regarding the nature of W–OR π bonding is the O≡W–O–C torsion angle. The optimum values for interaction between OR and d_{xy} are 0 or 180°, whereas the corresponding values for d_{xz} or d_{yz} are ±90°. The observed torsion angles for **1** and **4** are given in Table 5, and these show that for **1** two of the terminal methoxo groups [O(13), O(14) in molecule 1, or O(23), O(24) in molecule 2] are oriented to interact preferentially with d_{xy} whereas the other [O(12) or O(22)] is in an intermediate position with a slight preference for interaction with d_{xz} or d_{yz}. In the cyclohexoxide **4**, however, all the terminal alkoxo groups are in intermediate orientations, with O(3) in a slightly better position for interaction with d_{xz} or d_{yz}. While these orientations are not necessarily electronic in origin and may be the result of steric interactions, they do not exclude the possibility of some π interaction between terminal OR groups and metal d_{xz} or d_{yz} orbitals, which would lower the tungsten–oxo bond order from three and increase the susceptibility of the oxo ligand to electrophilic attack. This may be relevant to the formation of hexaalkoxides, $[W(OR)_6]$, which we will mention later. Competitive π bonding of this type has also been invoked to explain the orientation of the dimethylamido ligands in the crystal structure of $[W(NPh)(NMe_2)_4]$.[26]

Of particular interest with respect to the solution behaviour of these compounds are the bridging W–O bonds which in both compounds are asymmetric, reflecting the marked *trans* influence of the oxo ligand.[19] An important feature of these structures is that there are no significant differences between the bridging W–O bond distances of the methoxide complex **1** and the corresponding distances in the cyclohexoxide **4**. This implies that the increase in size of the alkyl group from methyl to cyclohexyl does not affect the strength of the bridging W–O bonds, which seems initially to contradict the results from the ^1H NMR solution studies, and this point is discussed in the next section.

Solution NMR Studies of Compounds **1**–**5**, *and of* $[WO(OC_6H_3Pr^i_2\text{-}2,6)_4]$ **6**.—(*i*) *Variable-temperature* ^1H *NMR*. At ambient temperature, the ^1H NMR spectrum of $[\{WO(OMe)_4\}_2]$ **1** contains three peaks in the ratio 2:1:1, and is consistent with the solid-state structure shown in Fig. 1. However, we noticed that these peaks were somewhat broadened, suggesting that the dimeric structure is not static in solution. This is indeed the case, and the results of a variable-temperature ^1H NMR experiment are shown in Fig. 3. It is interesting that before the peaks start to broaden appreciably, the chemical shift of one of them is much less temperature-dependent than the other two. This may reflect electronic redistribution at the ligands prior to bond dissociation. An impurity peak is often present at δ 4.7–4.8 due to small (and variable) amounts of $[W(OMe)_6]$ in samples of **1**.

For the ethoxide, $[\{WO(OEt)_4\}_2]$ **2**, single, broad resonances due to the methylene and methyl protons are observed in the ^1H NMR spectrum at 295 K. These sharpen at higher temperatures, and at lower temperatures eventually resolve to give a spectrum consistent with structure **II**, analogous to the methoxide **1** and cyclohexoxide **4** solid-state structures. The ^1H NMR spectra for **2** are shown in Fig. 4, the low-temperature limiting spectrum clearly demonstrating the diastereotopic methylene protons of the axial, terminal OEt groups. The coalescence temperature is, as expected from steric considerations, lower for **2** than for **1**. As in the case of the methoxide **1**, samples of **2** contained a small amount of an impurity, possibly $[W(OEt)_6]$, having δ_{Me} 1.42.

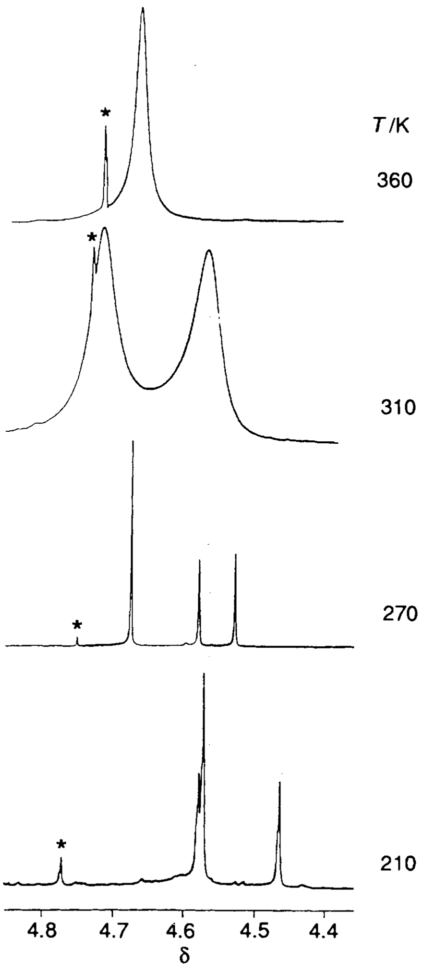


Fig. 3 Variable-temperature 500 MHz ^1H NMR spectra of **1** in [$^2H_8$]toluene. The peak indicated by an asterisk is due to [$W(OMe)_6$]

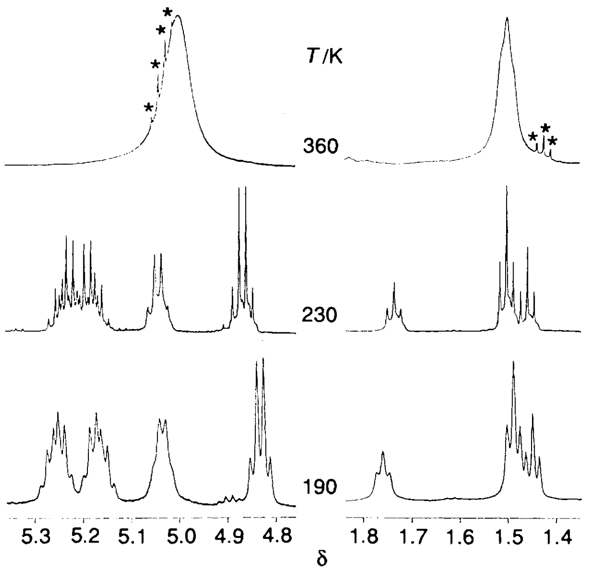


Fig. 4 Variable-temperature 500 MHz ^1H NMR spectra of compound **2** in [$^2H_8$]toluene. The peaks indicated by asterisks at 360 K are tentatively assigned to [$W(OEt)_6$]

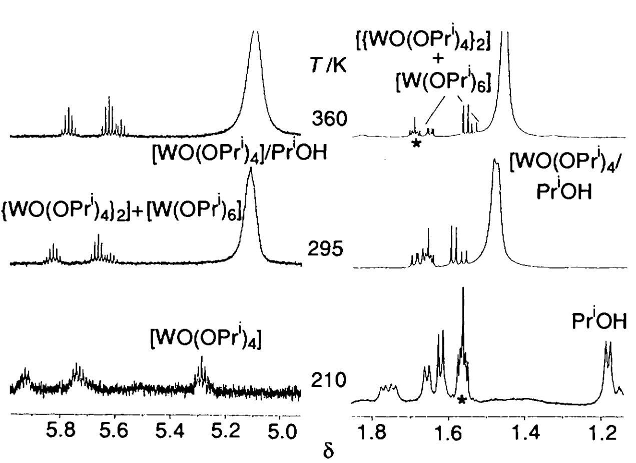


Fig. 5 Variable-temperature 500 MHz ^1H NMR spectra of **3** in [$^2H_8$]toluene. The peaks indicated by asterisks are due to thf. At 210 K the methine resonance of Pr^{i}OH is present as a broad peak at δ 3.85

Table 6 Tungsten-183 NMR data[a] for the oxoalkoxides, $WO(OR)_4$

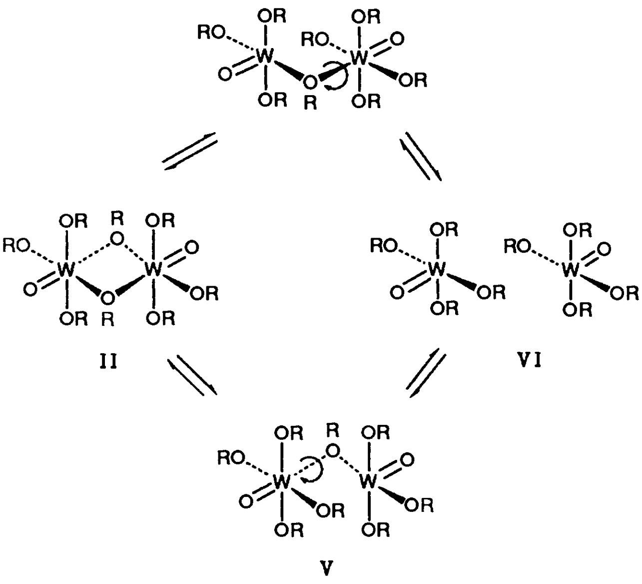
	R	δ_W	$w_{\frac{1}{2}}$	T/K	Solvent
1	Me[b]	−62.9	9.0	295	Toluene–[$^2H_8$]toluene
		−272.4	2.0	370	Toluene–[$^2H_8$]toluene
2	Et[c]	−126.3	40.0	293	Toluene–[$^2H_8$]toluene
4	*cyclo*-C_6H_{11}[b]	−140.3	28.0	298	C_6H_6–C_6D_6
5	Bu^t[b]	−386.9	23.5	300	Toluene–[$^2H_8$]toluene
6	$C_6H_3Pr^i{}_2$-2,6[b]	−493.6	2.5	295	$CDCl_3$

[a] Chemical shifts in ppm referenced to 2 mol dm^{-3} aqueous Na_2WO_4, linewidths in Hz. [b] Measured at 12.5 MHz. [c] Measured at 20.8 MHz.

For [{$WO(OPr^i)_4$}$_2$] **3**, ^1H NMR spectra show that, even after recrystallisation, samples were not pure. The variable-temperature spectra can be interpreted in terms of a dimer–monomer equilibrium in the presence of [$W(OPr^i)_6$] and Pr^{i}OH. At low temperatures, peaks due to [{$WO(OPr^i)_4$}$_2$] with structure **II** are visible, as well as higher field methine resonances which we assign to [$WO(OPr^i)_4$] and Pr^{i}OH. As the temperature is raised, signals due to the monomer increase in intensity at the expense of those due to the dimer, and at *ca.* 300 K coalesce with the Pr^{i}OH signals, indicating rapid exchange between the alcohol and the monomer. It is difficult to assess the concentration dependence of these spectra because of the limited solubility of **3** at lower temperatures. The [$W(OPr^i)_6$] resonances overlap with those of dimeric **3**. A selection of these spectra is shown in Fig. 5.

The ambient temperature ^1H NMR spectrum of [{$WO(OC_6H_{11})_4$}$_2$] **4**, which on steric grounds would be expected to behave in a similar fashion to **3**, contains a complex set of peaks between δ 1.5 and 2.3 due to the ring methylene protons and one main broad resonance at δ 4.9 together with some much lower intensity resonances between δ 5.2 and 5.6 for the methine protons. At lower temperatures the spectra are complex due to conformational changes within the cyclohexyl rings, and we were unable to identify the species present. A fully resolved spectrum consistent with the structure shown in Fig. 2 could not be obtained at temperatures down to 208 K.

(*ii*) ^{183}W *NMR*. We have measured the ^{183}W NMR spectra of the more soluble complexes discussed above and of [$WO(OC_6H_3Pr^i{}_2$-2,6$)_4$] **6**, which has been shown by an X-ray diffraction study to be mononuclear,[14] and the results are shown in Table 6. Although it would be inappropriate to draw any firm conclusions from these few observations regarding the factors affecting ^{183}W chemical shifts, a definite trend emerges. As the steric bulk of the alkyl substituent is increased, δ_W decreases (*i.e.* moves to lower frequency). Given that the methoxide **1** is binuclear and the aryloxide **6** is mononuclear at ambient temperature, the two extreme δ_W values in Table 6 may reflect the six-co-ordinate **1** *vs.* five-co-ordinate **6** metal environment. This would seem to correlate with trends in ^{51}V chemical shifts, where shielding has been shown to increase with increasing electronegativity of the ligand set, and to decrease with increasing co-ordination number of the metal centre.[27]



Scheme 1

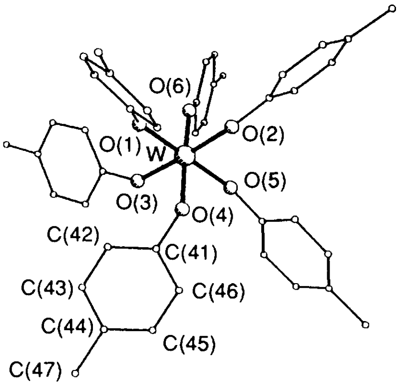


Fig. 6 A view of the molecular structure of compound **7**. Hydrogen atoms are omitted for clarity

Table 7 Selected bond lengths (Å) and angles (°) for compound **7**

W-O(1)	1.894(4)	W-O(2)	1.887(3)
W-O(3)	1.896(3)	W-O(4)	1.889(3)
W-O(5)	1.913(3)	W-O(6)	1.891(3)
O(1)-C(11)	1.378(5)	O(2)-C(21)	1.360(6)
O(3)-C(31)	1.353(5)	O(4)-C(41)	1.364(6)
O(5)-C(51)	1.372(6)	O(6)-C(61)	1.363(5)
O(1)-W-O(2)	86.9(1)	O(1)-W-O(3)	89.5(1)
O(2)-W-O(3)	176.3(2)	O(1)-W-O(4)	91.3(2)
O(2)-W-O(4)	92.9(1)	O(3)-W-O(4)	87.9(1)
O(1)-W-O(5)	176.4(1)	O(2)-W-O(5)	90.7(1)
O(3)-W-O(5)	93.0(1)	O(4)-W-O(5)	86.1(1)
O(1)-W-O(6)	94.7(1)	O(2)-W-O(6)	90.5(1)
O(3)-W-O(6)	89.0(1)	O(4)-W-O(6)	173.3(1)
O(5)-W-O(6)	88.0(1)	W-O(1)-C(11)	139.9(3)
W-O(2)-C(21)	147.3(3)	W-O(3)-C(31)	144.6(3)
W-O(4)-C(41)	136.6(3)	W-O(5)-C(51)	137.9(3)
W-O(6)-C(61)	145.5(3)		

The linewidths shown in Table 6 are also interesting since ^{183}W resonances are usually sharp, often with linewidths <1 Hz.[28] Assuming that the line broadening is due to the dynamic processes occurring in solution, the relative values can be explained in terms of the bond dissociation in binuclear species except, perhaps, for the broadened $[WO(OBu^t)_4]$ resonance, and these points are addressed below. Another noteworthy feature is that at a temperature above that required for coalescence in the ^1H NMR spectrum of methoxide **1**, the ^{183}W resonance for this compound is shifted upfield and is much sharper than at ambient temperature. Clearly, ^{183}W NMR spectroscopy is a powerful technique for studying dynamic as well as static systems in tungsten co-ordination chemistry, but further work is necessary in order to rationalise variations in spectral parameters such as those discussed above.

Solution Dynamics of **1–5**.—It is apparent from our NMR studies that the solution behaviour of the W^{VI} oxoalkoxides, $WO(OR)_4$, is in many ways similar to that of the Group 5 homoleptic alkoxides, $M(OR)_5$ (M = Nb or Ta).[10] If we represent the possible bond dissociation processes as in Scheme 1, then the normal alkoxide complexes are present as dimers (**II**) which undergo facile intramolecular alkoxide exchange, presumably *via* **V**, and no monomer (**VI**) is observed. Rotation about W–O bonds as indicated would exchange terminal and bridging OR groups without complete dissociation. The major difference between $[M_2(OMe)_{10}]$ (M = Nb, Ta) and $[\{WO(OR)_4\}_2]$ (R = Me, Et) is that in the Group 5 compounds terminal alkoxide exchange occurs before bridge–terminal exchange whereas in **1** and **2** this is not the case, presumably because of the strong W≡O π bond.

For the secondary alkoxides the situation is somewhat different; dimeric (**II**) *and* monomeric (**VI**) complexes are present in equilibrium, with higher temperatures favouring the monomeric form. If free alcohol is present, exchange occurs readily with the alkoxo ligands of the monomer but not with those of the dimer. This dependence of the solution behaviour on the nature of the alkoxide groups, which is also observed for the Group 5 pentaalkoxides, merits further consideration. Since in the solid-state structures there is no significant difference in length between the longer W–OR bridging bond of the methoxide **1** and that of the cyclohexoxide **4**, the complete dissociation in solution of alkoxides with secondary and tertiary alkyl groups is not likely to be due to dissociation enthalpy differences, but can be understood by considering the species **V** shown in Scheme 1. It is evident from molecular models that the rotations required for bridge/terminal exchange are much more sterically hindered when R = Pr^i than when R = Me or Et. Consequently, after initial bond dissociation in the isopropoxide either the bridge bond is reformed without bridge–terminal exchange or, rather than a rotation resulting in steric compression, further dissociation occurs to monomeric **VI**.

It is interesting that in the analogous organoimido compound $[\{W(NC_6H_4Me\text{-}4)(OPr^i)_4\}_2]$, which also has a binuclear solid-state structure, the single Pr^i resonance in the ^1H NMR spectrum at ambient temperature resolves at lower temperatures into the pattern expected for the dimeric structure. No resonances due to a monomer are observed.[17] It would seem that in this case the bridge bonding is stronger than in the oxo compound and rotation occurs rather than a second bond dissociation. This is consistent with the oxo ligand exerting a larger *trans* influence than the arylimido ligand.

Although we have not recorded the variable-temperature ^1H NMR spectra of $WO(OBu^t)_4$, Bradley *et al.*[15] reported that the spectrum is invariant down to 193 K suggesting a mononuclear structure which does not dimerise. This would not explain the broadened ^{183}W resonance for this compound but, given the sensitivity of δ_W to co-ordination environment, a square pyramidal–trigonal bipyramidal fluxional process (which cannot be frozen out in the ^1H NMR spectrum) may be responsible.

The Formation of Hexaalkoxides, $[W(OR)_6]$.—The hexaalkoxides $[W(OR)_6]$ (R = Me, Et, Pr^n, Pr^i and allyl) have previously been prepared from $[W(NMe_2)_6]$ and the respective alcohol.[15] The hexamethoxide $[W(OMe)_6]$ has also been synthesised by treatment of WX_6 (X = F or Cl) with $Si(OMe)_4$[29] and its structure has been determined by gas-phase electron diffraction.[30] A range of analogous hexaaryloxides,

Table 8 Atomic coordinates (× 10^4) for compound **7**

Atom	*x*	*y*	*z*
W	2204.6(1)	4184.8(1)	4110.7(1)
O(1)	2088(2)	4254(2)	5352(2)
C(11)	2638(3)	4318(3)	6220(3)
C(12)	3580(3)	4168(3)	6382(3)
C(13)	4108(3)	4241(3)	7261(3)
C(14)	3723(4)	4476(3)	7984(4)
C(15)	2779(4)	4616(4)	7795(4)
C(16)	2232(4)	4541(3)	6926(4)
C(17)	4334(4)	4557(5)	8936(4)
O(2)	3213(2)	4863(2)	4422(2)
C(21)	3574(3)	5549(2)	4280(3)
C(22)	3286(3)	5942(3)	3474(3)
C(23)	3693(3)	6628(3)	3357(4)
C(24)	4380(3)	6934(3)	4032(4)
C(25)	4649(3)	6536(3)	4841(3)
C(26)	4251(3)	5850(3)	4973(3)
C(27)	4854(4)	7663(3)	3877(4)
O(3)	1171(2)	3518(2)	3872(2)
C(31)	261(3)	3438(2)	3901(3)
C(32)	−191(3)	3952(3)	4347(3)
C(33)	−1130(4)	3870(3)	4316(4)
C(34)	−1629(4)	3292(3)	3853(5)
C(35)	−1156(4)	2765(3)	3441(4)
C(36)	−212(3)	2830(3)	3471(4)
C(37)	−2672(4)	3233(5)	3781(7)
O(4)	2983(2)	3329(2)	4375(2)
C(41)	2867(3)	2566(3)	4391(3)
C(42)	2358(4)	2252(3)	4968(4)
C(43)	2230(4)	1477(3)	4957(4)
C(44)	2602(3)	1015(3)	4388(4)
C(45)	3135(3)	1344(3)	3837(3)
C(46)	3274(3)	2115(3)	3838(3)
C(47)	2427(5)	173(3)	4355(5)
O(5)	2405(2)	4105(2)	2885(2)
C(51)	3070(3)	3823(3)	2451(3)
C(52)	3996(3)	4025(3)	2738(4)
C(53)	4635(3)	3740(3)	2265(4)
C(54)	4399(3)	3270(3)	1522(4)
C(55)	3477(4)	3094(3)	1256(4)
C(56)	2816(3)	3357(3)	1708(3)
C(57)	5118(4)	2981(4)	1014(5)
O(6)	1384(2)	4996(2)	3704(2)
C(61)	742(3)	5284(3)	2991(3)
C(62)	522(3)	6037(3)	3030(4)
C(63)	−89(3)	6363(3)	2299(4)
C(64)	−492(3)	5957(3)	1546(4)
C(65)	−277(4)	5202(3)	1520(4)
C(66)	341(3)	4860(3)	2239(3)
C(67)	−1150(5)	6324(4)	745(5)

$[W(OR)_6]$ have been prepared from $WOCl_4$ and ROH, although by varying the solvent for the reaction $WO(OR)_4$ (R = aryl) can be obtained.[31]

We have noticed that in the preparation of the oxoalkoxides **1**–**4** the hexaalkoxide $[W(OR)_6]$ is often present in small amounts as an impurity, although in some cases higher yields have been obtained. For example, in one attempted preparation of $[\{WO(OMe)_4\}_2]$, sublimation of the product gave colourless hexagonal crystals of $[W(OMe)_6]$, which unfortunately did not diffract X-rays. Similarly, an attempted preparation of $[WO(OC_6H_4Me\text{-}4)_4]$ from $WOCl_4$ and $NaOC_6H_4Me$-4 resulted in the isolation of the hexaaryloxide, $[W(OC_6H_4Me\text{-}4)_6]$ **7**.

X-Ray Crystal Structure of $[W(OC_6H_4Me\text{-}4)_6]$ **7**.—The results of an X-ray diffraction study of this complex are shown in Fig. 6 and Tables 7 and 8 and, to our knowledge, this is the first solid-state structural determination of a homoleptic tungsten(VI) $[W(OR)_6]$ compound (although the tris-diolate, $[W(O_2C_2H_4\text{-}1,2)_3]$ has been structurally characterised).[32]

The metal has close to octahedral co-ordination geometry with a mean W–O bond length of 1.895(9) Å, which is similar to those in $[W(OMe)_6]$ [1.902(3) Å] and $[W(O_2C_2H_4\text{-}1,2)_3]$ [1.908(15) Å], but shorter than in the tungsten(V) compound, $[NEt_4][W(OPh)_6]$ [1.943(10) Å][33] and longer than in the chloroalkoxides, $[W(OC_6H_3Pr^i_2\text{-}2,6)_3Cl_3]$ [1.839(7) Å][34] and $[W(OC_6H_3Ph_2\text{-}2,6)_2Cl_4]$ [1.846(6) Å].[35] These differences are as expected for the different oxidation states, and for a smaller degree of W–O π bonding in the homoleptic aryloxide compared with the chloro complexes. The W–O–C angles span a range of 11° with a mean value of 142(4)°. This compares with 132.5(5)° and 139(3)° for $[W(OMe)_6]$ and $[NEt_4][W(OPh)_6]$ respectively.

The formation of **7** as described above is probably due to the presence of the phenol in the reaction mixture ($NaOC_6H_4Me$-4 was prepared from the phenol and sodium metal). Protonation of the oxo ligand in these complexes should become easier as the chlorines are replaced because of the extra π donation from the alkoxides, and it appears that phenols are sufficiently acidic for this to occur. In the preparation of $WO(OR)_4$ (R = Me, Et or Pr^i), however, it is more likely to be HCl which reacts with the oxoalkoxide, generating a small amount of chloroalkoxide which is then converted to the hexaalkoxide. It is clear that in the case of **1** methanol itself is not sufficiently acidic to achieve this reaction, since we have shown that no $[W(OMe)_6]$ is formed when a methanolic toluene solution of $[\{WO(OMe)_4\}_2]$ is heated under reflux.

Having established the solution behaviour of the oxoalkoxides **1**–**5**, we have now begun to investigate their hydrolysis reactions, particularly in the presence of WO_4^{2-}, in an attempt to elucidate the oligomerisation processes involved and to develop syntheses of new organic-soluble isopolytungstates. Results obtained so far suggest that this approach should provide access to a wide range of new, soluble, molecular oxides. Our work in this area will be the subject of future publications.

Experimental

All manipulations were carried out under dry, oxygen-free nitrogen using standard Schlenk techniques, or in a dry-box fitted with a recirculation system. Hydrocarbon and ether solvents were dried over and distilled from sodium–benzophenone immediately prior to use. Methanol was distilled from magnesium methoxide. Ethanol, propan-2-ol, and cyclohexanol were distilled from the corresponding sodium alkoxides and stored over 4 Å molecular sieves. Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 598 spectrometer, NMR spectra on Bruker WP 200 (^1H and ^{13}C), WM 300 (^1H, ^{13}C, ^{183}W, and variable-temperature ^1H) or AMX 500 (variable-temperature ^1H) spectrometers. Elemental analyses were performed by the microanalytical service, the Department of Chemistry, University of Newcastle upon Tyne. The compound $WOCl_4$ was prepared from $WO_3\cdot H_2O$ and $SOCl_2$ and purified by sublimation *in vacuo*.

Preparations.—$[\{WO(OMe)_4\}_2]$ **1**. Methanol (1.40 cm^3, 34.56 mmol) was added to a solution of $WOCl_4$ (2.54 g, 7.46 mmol) in tetrahydrofuran (thf, 80 cm^3) with stirring. Nitrogen and then ammonia were bubbled through the solution for 5 min and 20 min respectively. The white precipitate of NH_4Cl was filtered off and the solvent was removed from the filtrate under reduced pressure. After extraction into hot toluene and evaporation of the solvent, the solid residue was washed with hexane and pumped dry. Yield 2.37 g, 98%. The compound can

Table 9 Crystallographic data

Complex	1	4	7
Formula	$C_8H_{24}O_{10}W_2$	$C_{48}H_{88}O_{10}W_2$	$C_{42}H_{42}O_6W$
M	648.0	1192.9	826.6
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$Pbca$	$P2_1/n$
a/Å	10.449(1)	10.850(1)	14.675(1)
b/Å	11.688(1)	20.728(2)	17.717(2)
c/Å	13.908(1)	22.698(2)	14.882(2)
β/°	98.831(5)		102.07(1)
U/Å^3	1678.4	5104.8	3783.8
Z	4	4	4
D_c/g cm^{-3}	2.564	1.552	1.451
μ/mm^{-1}	14.03	4.65	3.16
$F(000)$	1200	2416	1664
Crystal size/mm	0.10 × 0.58 × 0.63	0.15 × 0.30 × 0.60	0.27 × 0.35 × 0.46
$2\theta_{max}$/°	50	50	45
Transmission factors	0.034–0.456	0.095–0.173	0.239–0.291
Reflections measured	12 951	4696	4939
Unique reflections	2938	4503	4939
Observed reflections	2760	2911	3778
R_{int}	0.057	0.022	
R^a	0.044	0.037	0.028
R'^b	0.055	0.029	0.025
Goodness of fit	1.66	1.42	1.56
No. of parameters	182	272	461
Extinction x	9.2(10) × 10^{-7}	8(2) × 10^{-8}	1.0(2) × 10^{-7}
Mean, max. shift/e.s.d.	0.001, 0.005	0.006, 0.024	0.013, 0.047
Max., min. electron density/e Å^{-3}	2.0, −1.9	1.8, −1.0	0.4, −0.5

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b R' = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{\frac{1}{2}}$.

be recrystallised from hot toluene (Found: C, 14.9; H, 3.6. $C_4H_{12}O_5W$ requires C, 14.8; H, 3.7%). IR: 1160m, 1145(sh), 1112m, 1060s (br), 991s, 961s, 955s, 725w, 589m, 556s, 522s, 481m, 375w and 305s cm^{-1}. δ_C(75.47 MHz, C_6D_6) 64.95 and 63.17.

The same procedure was used to prepare compounds **2**–**4**.

$[\{WO(OEt)_4\}_2]$ **2**. This was prepared from $WOCl_4$ (9.68 g, 28.33 mmol) and EtOH (7.2 cm^3, 122.7 mmol) in thf (100 cm^3). Yield 7.18 g, 67% (Found: C, 24.5; H, 5.1. $C_8H_{20}O_5W$ requires C, 25.3; H, 5.3%). IR: 1148m, 1135(sh), 1095m, 1065s, 970w, 920s, 786s, 724m, 600s, 376w and 342w cm^{-1}.

$[\{WO(OPr^i)_4\}_2]$ **3**. This was prepared from $WOCl_4$ (4.74 g, 13.92 mmol) and Pr^iOH (5 cm^3, 65.3 mmol) in thf (100 cm^3). Yield 4.55 g, 75% (Found: C, 32.2; H, 5.6. $C_{12}H_{28}O_5W$ requires C, 33.0; H, 6.5%). IR: 1340m, 1160m, 1125m, 1110m, 1071w, 1020w, 980s, 855m, 770s, 610s, 450m, 437w, 418w, 345m and 330m cm^{-1}.

$[\{WO(OC_6H_{11})_4\}_2]$ **4**. This was prepared from $WOCl_4$ (2.18 g, 6.38 mmol) and *cyclo*-$C_6H_{11}OH$ (2.7 cm^3, 26.2 mmol) in thf (40 cm^3). Recrystallisation from hexane gave colourless prisms, 2.36 g, 62% (Found: C, 48.1; H, 7.4. $C_{24}H_{44}O_5W$ requires C, 48.3; H, 7.4%). IR: 1368m, 1362m, 1344w, 1333w, 1315w, 1272w, 1252m, 1188w, 1157m, 1132m, 1101s, 1052s, 1035w, 1022m, 1013w, 982s, 947s, 891m, 872w, 857w, 850m, 798m, 722m, 697s, 685m, 632m, 562m, 533m, 521w, 502w, 471m, 451w, 437w, 413m, 391w, 373m, 350w, 317m and 272m cm^{-1}. δ_C(50.32 MHz, C_6D_6, 298 K) 84.56, 35.93, 26.71 and 24.94.

$[WO(OBu^t)_4]$ **5**. The salt $LiOBu^t$ (4.34 g, 54.2 mmol) was added to a solution of $WOCl_4$ (4.43 g, 13.0 mmol) in diethyl ether (60 cm^3) at −70 °C. The resulting white suspension was stirred for 6 h at room temperature and then evaporated to a gum. Extraction with hot toluene (30 cm^3) and removal of the solvent under reduced pressure gave the complex as a white powder. Yield 2.7 g, 62% (Found: C, 38.7; H, 7.3. $C_{16}H_{36}O_5W$ requires C, 39.0; H, 7.4%). IR: 1360m, 1230m, 1170s, 1022w, 940s, 902w, 780m, 720w, 560m and 470w cm^{-1}. δ_H(200.13 MHz, C_6D_6) 1.71 (s). δ_C(50.32 MHz, C_6D_6) 82.77 and 31.29.

$[W(OC_6H_4Me\text{-}4)_6]$ **7**. The salt $NaOC_6H_4Me$-4 [from HOC_6H_4Me-4 (2.46 g, 22.8 mmol) and Na (0.58 g, 25.2 mmol)] was added to $WOCl_4$ (1.94 g, 5.7 mmol) in thf (40 cm^3) at −70 °C and then the reaction mixture was stirred at 25 °C for 24 h. The solvent was removed and the solid extracted into hot toluene (30 cm^3). Recrystallisation from MeCN (20 cm^3) at −20 °C gave the complex as dark red needles, 2.18 g, 46%. IR: 1595w, 1571w, 1298w, 1286w, 1240vs, 1205w, 1163m, 1100m, 1010m, 930w, 892m, 882s, 818s, 798m, 781m, 722s, 641s, 580s, 518w, 463m and 386m cm^{-1}.

Reaction between Compound 1 *and* MeOH.—A solution of compound **1** (0.76 g, 2.3 mmol) and MeOH (1.5 cm^3, 37 mmol) in toluene (20 cm^3) was heated under reflux for 18 h. After removal of the volatiles *in vacuo*, the ^1H NMR spectrum of the residue showed that no $[W(OMe)_6]$ had been formed.

X-Ray Crystallography.—Data were measured at room temperature on a Stoe-Siemens diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Crystallographic data are summarised in Table 9. Cell parameters were refined in each case from 2θ values of 30 reflections (20–25°) measured at $\pm\omega$. Intensities were measured by on-line profile fitting[36] from ω–θ scans; corrections were made for slight intensity decay and for absorption (semiempirically).[37] Atoms were located from Patterson and difference syntheses and refined anisotropically by blocked-cascade least-squares methods on F for reflections with $F > 4\sigma(F)$;[37] weighting was of the form $w = \sigma^2(F)$, with contributions from both counting statistics and an analysis of variance.[38] Hydrogen atoms were included in calculated positions for **4** and **7**, with isotropic thermal parameters. An isotropic extinction parameter x was refined, such that $F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{\frac{1}{4}}$. Atomic scattering factors were taken from ref. 39.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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