Axially Asymmetric Metal Alkyls. Part 4.[1] Synthesis and *X*-Ray Crystal Structure of the Tungsten(V) Metallabicyclic Complex $[\{W[(2\text{-}CH_2C_6H_4)_2]_2O\}_2Mg(C_4H_8O)_4]\cdot CH_2Cl_2$ *

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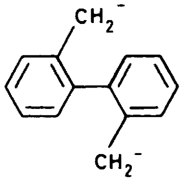
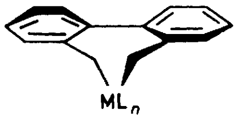
Reaction of the di-Grignard reagent $[\{Mg(thf)_nCl\}_2\{(2\text{-}CH_2C_6H_4)_2\}]$, derived from $[Mg(anth)(thf)_3]$ (anth = anthracene) and $(2\text{-}ClCH_2C_6H_4)_2$, with WCl_4O in tetrahydrofuran (thf) yields a paramagnetic species, shown by an *X*-ray diffraction study to be $[\{W[(2\text{-}CH_2C_6H_4)_2]_2O\}_2Mg(thf)_4]$. Within each molecule the bidentate alkyl ligands have the same chirality, the overall molecular symmetry being approximately *222*. A two-fold axis containing the oxo-groups and metal centres is the only crystallographically imposed symmetry. Oxo-groups are *trans* in the octahedrally co-ordinated magnesium centre [Mg–O(oxo) 2.036(5), 2.029(5) Å; Mg–O(thf) 2.080(3), 2.120(5) Å] and occupy an apical position of square-pyramidally co-ordinated tungsten centres [W–O 1.744(5), 1.726(4) Å; W–CH_2 2.162(5)—2.191(4) Å]. Important angles of the metallacycles are: CH_2–W–CH_2 83.7(2), 85.8(2)°; W–CH_2–C(aryl) 115.3(4)—121.1(4)°; and torsion angles along the biphenyl axes, 52.9 and 63.1°.

In earlier parts of the current series we described the synthesis of an organodilithium complex[2] and a di-Grignard reagent[3] based on the hydrocarbyl dianion $(2\text{-}CH_2C_6H_4)_2{}^{2-}$ (1), and then the synthesis of the metallacycles (2) by treating them with metal or metalloid halides. The metallacycles (2) prepared to date include those where M = Si, L_n = Me_2; M = Sn, L_n = Ph_2;[3] and M = Ti,[4] Zr,[4] Hf,[4] Nb,[1,5] or Ta,[1,5] L_n = $(\eta\text{-}C_5H_5)_2$. Of these the synthesis of the Group 5 metallacycles was limited to the use of the di-Grignard reagent $[\{Mg(thf)_nCl\}_2\{(2\text{-}CH_2C_6H_4)_2\}]$ (3) (thf = tetrahydrofuran), as the lithium complex of (1) favoured reduction and/or the formation of intractable oils. Interestingly, the reaction of (3) with vanadocene dichloride gave the bimetallic complex $[\{V(\eta\text{-}C_5H_5)_2Cl\}_2\{2\text{-}CH_2C_6H_4)_2\}]$ rather than a metallacycle.[1] The di-Grignard reagent (3) that has featured to date[3] is prepared by the classical method of Grignard syntheses. We have now developed a more reliable method of preparing it, and Grignard reagents of other benzylic halides, that involves the treatment of $[Mg(anth)(thf)_3]$ (anth = anthracene) with $(2\text{-}XCH_2C_6H_4)_2$ (X = Cl or Br).[6]

In extending our studies to the Group 6 transition-metal chemistry of (1) we attempt to gain access to bis- or tris-(chelate) tungsten complexes by reacting the di-Grignard reagent (3) with WCl_4O. For such complexes diastereoisomers are possible due to the chirality of the alkyl ligand and thus the presence of two or more chiral centres within each molecule. Transition-metal metallacycles with two or more carbocycles are restricted to the tungsten *o*-xylenediyl complexes $[\{W[(CH_2)_2C_6H_4\text{-}o]_2O\}_2Mg(thf)_4]$ and $[W\{(CH_2)_2C_6H_4\text{-}o\}_3]$, both being prepared from WCl_4O and a di-Grignard reagent.[7] The ligand-to-metal bonding in these complexes has some π character, more so for the tris(chelate) where the overall bonding is best described as intermediate between the η^4 (4) and bis(sigma) (or metallacycle) extremes. Some polyhapto component of bonding in electron-deficient transition-metal complexes of (1) is likely given the relationship between it and the benzyl ligand which readily forms η^3-allyl type complexes,[8] and the metal–hydrocarbyl interaction for each metal centre in $[\{Li(Me_2NCH_2CH_2NMe_2)\}_2\{[2\text{-}CH(SiMe_3)C_6H_4]_2\}]$ which is η^3 (ref. 2).



(1)



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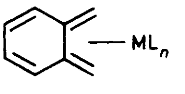

(4)

Unlike the *o*-xylenediyl ligand, ligand (1) is of variable bite due to the possibility of torsion along the biphenyl axis. Surprisingly the O-centred ligand $(2\text{-}OC_6H_4)_2{}^{2-}$, isoelectronic with (1), has been little studied, in contrast to the O-centred analogue of the *o*-xylenediyl ligand, *viz.* the ubiquitous catecholate ligand. Indeed, to our knowledge the only complex reported of the type $[M\{(2\text{-}OC_6H_4)_2\}_xL_n]$ ($x \geq 2$) is a binuclear complex $[Fe_2\{(2\text{-}OC_6H_4)_2\}_4]^{2-}$ (ref. 9).

Results and Discussion

Preparative Chemistry.—Treating a thf solution of freshly sublimed WCl_4O at −78 °C with *ca.* 3.3 mol equiv. of the di-Grignard reagent $[\{Mg(thf)_nCl\}_2\{(2\text{-}CH_2C_6H_4)_2\}]$ (3), in thf gave, after reaction work-up, the oxobis(chelate) complex $[\{W[(2\text{-}CH_2C_6H_4)_2]_2O\}_2Mg(thf)_4]$ (5). It was crystallized as a methylene chloride solvate and authenticated using *X*-ray diffraction techniques. The method of preparing the Grignard reagent was found to affect greatly the yield of (5). That

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* Bis[bis(biphenyl-2,2′-ylenedimethylene-$C^{\alpha},C^{\alpha'}$)tungstenio(V)oxo]-tetrakis(tetrahydrofuran)magnesium–dichloromethane (1/1).

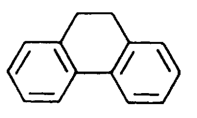
Supplementary data available (No. SUP 56438, 9 pp.): thermal parameters, H-atom co-ordinates, ligand geometries. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. units employed: mmHg = 133 Pa, G = 10^{-4} T.

prepared by the classical route, (**3a**) (elemental magnesium and the appropriate organic chloride),[3] gave < 10% of the product (**5**), based on WCl_4O, whereas that prepared by treating $(2\text{-}ClCH_2C_6H_4)_2$ with $[Mg(anth)(thf)_3]$ in thf,[6] (**3b**), gave reproducible yields of (**5**) close to 45%. Formation of (**3b**) is almost quantitative, as are other Grignard reagents of benzylic type halides that we have prepared using $[Mg(anth)(thf)_3]$. Yields of (**3a**), however, are usually lower at 80—85%, which correlates with solutions of (**3a**) giving lower yields of the tungsten complex (**5**). Interestingly, on reacting WCl_4O with a related di-Grignard reagent, $[o\text{-}\{(thf)_nClMgCH_2\}_2C_6H_4]$ (**6**), (prepared using the classical route) little or no product could be isolated when using Grignard solutions of < 90% yield of the di-Grignard. Thus there is a similarity to the present reaction in the variation in yield of tungsten complexes with the yield of the Grignard reagent.

The reactions of (**3**) or (**6**) with WCl_4O differ only in that further alkylation to a tris(chelate) complex is possible for (**6**). The reaction of WCl_4O with *ca.* 3.3 mol equiv. of (**6**) gives the *o*-xylenediyl analogue of (**5**), *viz.* $[\{W[(CH_2)_2C_6H_4\text{-}o]_2O\}_2Mg(thf)_4]$ (**7**), and with ⩾3.5 mol equiv. formation of an oxo-free species $[W\{(CH_2)_2C_6H_4\text{-}o\}_3]$ (**8**) occurs,[7] there being no other precedent for removal of an oxo-group by an alkylmagnesium reagent. We find no evidence for such a reaction of WCl_4O with (**3**) (⩾3.5 mol equiv.) even under more forcing conditions than that for the formation of (**8**). Furthermore, previously isolated (**5**) when dissolved in thf did not react with (**3**) [*cf.* (**7**) + (**6**) $\longrightarrow$ (**8**)].[7] The inability to form a tris(chelate) complex using (**3**) may be a consequence of the greater steric hindrance of (**1**) compared to that of $o\text{-}(CH_2)_2C_6H_4{}^{2-}$. They are respectively large and small 'bite' chelating alkyl ligands. As in the reaction of WCl_4O with (**6**) there were noticeable colour changes, and the formation of d^1 species throughout the reaction. Addition of 0.5 mol equiv. of (**3**) at −78 °C gave a *green* solution of $[WCl_4O]^-$ (ref. 7) [$g_{av.}$ 1.746, *cf.* 1.744 for (**6**)], the starting material being *orange*. Further addition yielded a *red* solution, most likely containing $[WCl_5O]^{2-}$ (ref. 7) [$g_{av.}$ 1.778, *cf.* 1.780 for (**6**)], and finally an *orange* solution on warming to 20—50 °C [$g_{av.}$ 1.900, *cf.* 1.948 for (**6**)]. A possible source of reduction, $W^{VI} \longrightarrow W^{V}$, preceding alkylation, is the oxidation of (**3**) to 9,10-dihydrophenanthrene, equation (1).[3]

$(3) + 2WCl_4O \longrightarrow$



$+$

$2Mg^{2+} + 2[WCl_4O]^- \quad (1)$

All e.s.r. signals including that obtained for (**5**) in thf ($g_{av.}$ 1.900) and CH_2Cl_2 ($g_{av.}$ 1.928) were broad singlets (linewidths/2 ~ 15 G), characteristic of d^1 W^V species.

Only one diastereoisomer based on (**5**) was isolated. It has high symmetry, *222* (see below), with four axially asymmetric ligands of the same chirality in each molecule. Dissociation–recombination of (**5**) involving $[Mg(thf)_n]^{2+}$ and $[W\{(2\text{-}CH_2\text{-}C_6H_4)_2\}_2O]^-$, stereospecific formation of the metallacycles within (**5**), or inversion of (**1**) ligands *via* torsion along their biphenyl axes, could account for both the high symmetry and the apparent formation of only one isomer. A discussion of the inversion process is given in Part 2 in relation to $Si\{(2\text{-}CH_2\text{-}C_6H_4)_2\}Me_2$.[3] The amount of dissociation must be small since thf solutions of (**5**) were found to be non-conducting.

A sharp peak in the i.r. spectrum of (**5**) at 934 cm^{-1} has been assigned to the W=O stretching mode on account of its closeness to the corresponding band in (**7**) [ν(W=O) 936 cm^{-1}][6] and to some tungsten oxo–neopentylidene complexes, *e.g.* $[\{WO(CHBu^t)(OBu^t)_2\}_2]$, ν(W=O) 940 cm^{-1}.[10]

Table 1. Metal-atom environments. The first column in each matrix is the metal–ligand atom distance (Å). Other entries are the angles (°) subtended at the metal by the relevant atoms at the head of the row and column. Italicized atoms are generated by the intramolecular two-fold rotor [O(11,21) belong to tetrahydrofurans 1,2 respectively]

(*i*) Magnesium

	r	O(2)	O(11)	O(21)	*O(11)*	*O(21)*
O(1)	2.036(5)	180.0(–)	91.4(1)	87.9(1)	91.4(1)	87.9(1)
O(2)	2.029(5)		88.6(1)	92.1(1)	88.6(1)	92.1(1)
O(11)	2.080(3)			90.7(1)	177.1(2)	89.4(1)
O(21)	2.120(5)				89.4(1)	175.8(2)

(*ii*) W(1)–ligand

	r	C(1)	C(1′)	*C(1)*	*C(1′)*
O	1.744(5)	104.5(1)	117.6(1)	104.5(1)	117.6(1)
C(1)	2.188(5)		83.7(2)	150.9(2)	83.0(2)
C(1′)	2.162(5)			83.0(2)	124.8(2)

(*iii*) W(2)–ligand

	r	C(1)	C(1′)	*C(1)*	*C(1′)*
O	1.726(4)	108.8(1)	110.7(1)	108.8(1)	110.7(1)
C(1)	2.172(6)		85.8(2)	142.4(2)	81.1(2)
C(1′)	2.191(4)			81.1(2)	138.5(2)

Also: W(1)–C(2,2′) 3.230(5), 3.213(4) Å
W(2)–C(2,2′) 3.131(6), 3.191(5) Å

Compound (**5**) and the *o*-xylenediyl analogue (**7**) are the only examples of transition-metal metallabicyclic species. Both are also unusual in being paramagnetic tungsten(V)–alkyl complexes; the only other example reported is $[W\{(CH_2)_2C_6H_4\text{-}o\}_3]^-$ (ref. 7). Interestingly d^1 oxoalkyls of rhenium, namely $[ReR_4O]$ (R = Me or CH_2SiMe_3), have been known for a decade from the work of Wilkinson and co-workers.[11] d^0 Oxotetra-alkyls of tungsten that are oxidized open-chain analogues of (**5**) [and (**7**)], are known, *e.g.* $[W(CH_2CMe_3)_4O]$.[12] With the inability to prepare a tris(chelate) tungsten complex for the ligand (**1**), compounds (**8**) and WMe_6[13] remain as the only examples of homoleptic alkyl–tungsten(VI) complexes.

Formation of (**5**) and not a tris(chelate) complex using the di-Grignard derived from $[Mg(anth)(thf)_3]$ rather than that formed from elemental magnesium demonstrates a significant difference in the chemistry of (**1**) and the related *o*-xylenediyl moiety.[7]

Structural Commentary.—The unit-cell contents comprise a 1:1 ratio of $[\{W[(2\text{-}CH_2C_6H_4)_2]_2O\}_2Mg(thf)_4]$ and methylene chloride molecules. Both lie disposed about two-fold crystallographic axes that in the complex molecules pass through the three metal and two oxo-oxygen centres. The angles subtended by the oxygens at the magnesium centre and at the oxygens by magnesium and tungsten centres are thus 180°. Corresponding angles in the related complex $[\{W[(CH_2)_2C_6H_4\text{-}o]_2O\}_2Mg(thf)_4]$ (**7**) are 170.4(8) and 180° respectively.[7] Consideration of the arrangement of the thf groups, and the chiral bidentate ligands within each molecule, which are all of the same chirality, shows that the overall molecular symmetry of the complex is close to *222* (Figure); close examination of angles of the two tungsten environments and W–CH_2–C(aryl) angles (Table 1) for the related sections of each molecule reveals a small perturbation from this symmetry. The arrangement of ligands

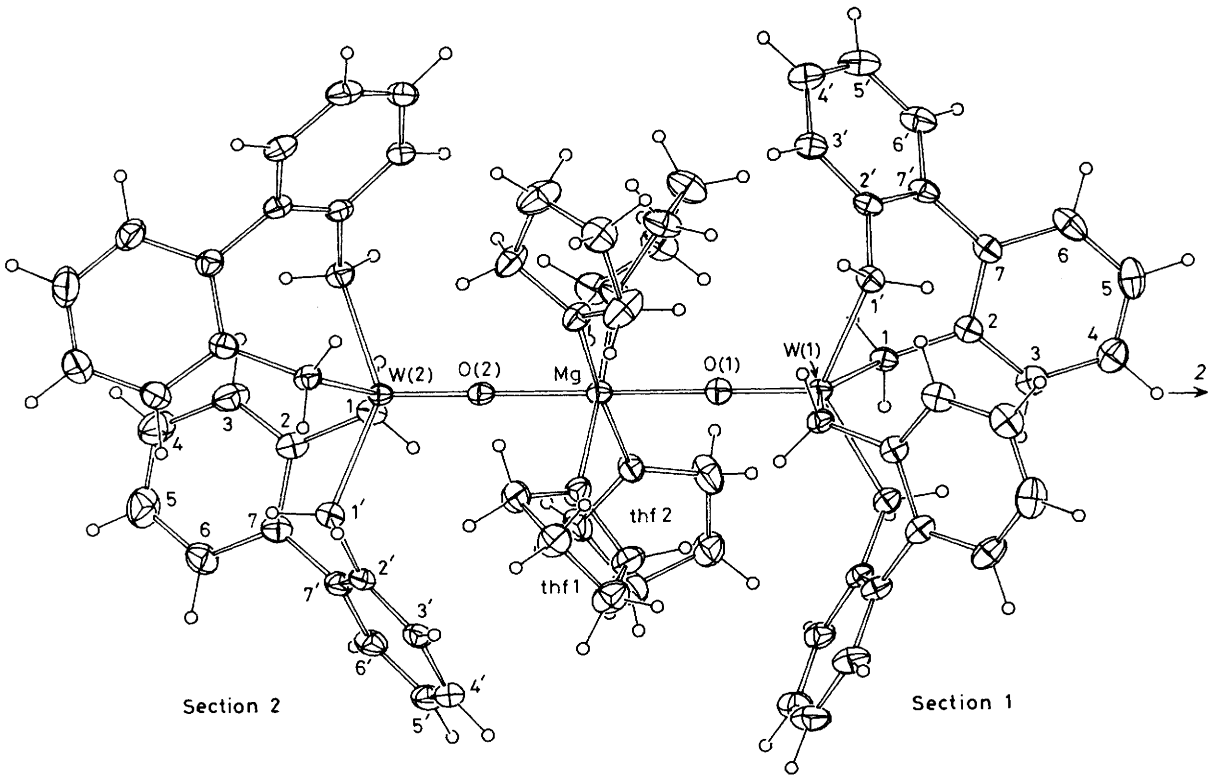


Figure. Molecule projection of [{W[(2-CH$_2$C$_6$H$_4$)$_2$]$_2$O}$_2$Mg(thf)$_4$] (5); 20% thermal ellipsoids are shown for the non-hydrogen atoms, and the hydrogen atoms have an arbitrary radius of 0.1 Å

about each tungsten atom corresponds to a distorted square pyramid for W(1) and a regular square pyramid for W(2), the unidentate ligand being in the apical position for both [unique O=W–CH$_2$ angles 104.5(1), 117.6(1) W(1), 108.8(1), 110.7(1)° W(2); CH$_2$–W–CH$_2$ (interligand) angles 150.9(2), 124.8(2) W(1), 142.4(2), 138.5(2)° W(2)].

A rationale for two slightly different co-ordination polyhedra comes from electron-pair repulsion theory.[14] The normalized ligand 'bite' [1.34 W(1), 1.36 W(2)] and effective bond-length ratios (unidentate:bidentate) [0.80 W(1), 0.79 W(2)] are close to values where the square pyramid and trigonal bipyramid have similar energies.

Tungsten–CH$_2$ and –O distances are similar for the two sections [2.17_5, 1.744(5) Å W(1); 2.18_2, 1.726(4) Å W(2)]. Corresponding values for the structure of the related *o*-xylenediyl complex (7) are 2.16(4) and 1.71(1) Å.[7] In comparing (5) and (7) it should be noted that the structure of (7) was determined with lower precision, a consequence of disorder on the thf ligands. These are well defined in (5), having only slightly higher thermal motion than the rest of the molecule.

While in compound (7) there is some evidence for a W–π interaction, resulting from folding of the *o*-xylenediyl plane relative to the W(CH$_2$)$_2$ plane, in (5) the metal–hydrocarbyl interaction is exclusively of the σ-bonding type [see (2)]; W $\cdots$ C(7,7′), C(2,2′) are > 3.2 Å (Table 1) and the W–CH$_2$–C(7,7′) angles are relatively large, the latter being different for the two tungsten centres [121.1(4), 120.3(4) W(1); 115.3(4), 118.6(3) W(2)] as part of the departure from *222* symmetry mentioned above.

The tungsten–oxygen bond lengths are only marginally longer than typical W=O values, *e.g.* 1.70(2) Å in [W(O)(CHBu^t)(PMe$_3$)$_2$Cl$_2$],[15] *cf.* 1.73_5 Å in (5), and thus a simplified description of oxygen to metal bonding is W=O→Mg. This is also supported by the ν(W=O) stretching frequency (see above).

The *trans*-octahedral arrangement of ligands about the magnesium atom is similar to that in (7);[7] Mg–O(oxo) 2.04_6, *cf.* 2.07 Å (7), Mg–O(thf) 2.10 Å, both compounds. Other magnesium compounds of structural type *trans*-[Mg(ligand)$_2$-(ether type ligand)$_4$] include *trans*-[MgBr$_2$(thf)$_4$],[16] *trans*-[Mg-Br$_2${(OCH$_2$C$_6$H$_4$)$_2$}$_4$],[17] and *trans*-[{Co(PMe$_3$)$_3$NN}$_2$Mg-(thf)$_4$][18] which have Mg–O distances similar to those in (5) and (7).

In previous work on ligand (1) we showed that the torsion angle about the bonds between the two phenyl rings is predominantly controlled by the size of the chelated species (or heteroatom). At one extreme the small oxygen heteroatom (O–C 1.45 Å) has a low torsion angle (38.5°)[19] while at the other, larger heteroatoms, *e.g.* Nb in [Nb{(2-CH$_2$C$_6$H$_4$)$_2$}-(η-C$_5$H$_5$)$_2$]^n (Nb–C, 2.32, 2.29, 2.25 Å, $n = -1, 0, +1$ respectively), have large torsion angles (59.0, 62.4, 78.4°, $n = -1, 0, +1$).[1] A secondary effect associated with changing the heteroatom size is a variation in M–CH$_2$–C(aryl) angle, most noticeable for large heteroatoms. This is borne out in the above niobepines [Nb–CH$_2$–C(aryl) 123.2, 118.7, and 120.0°, $n = -1, 0, +1$] and in the present compound; W(1), W(2) torsion angles and W–CH$_2$–C(aryl) angles are respectively 52.9, 121.2 and 63.1, 117.0°.

Experimental

General Procedures, and Physical and Analytic Measurements.—These were detailed in Parts 1,[2] 2,[3] and 3.[1]

Materials.—WCl$_4$O was prepared by partial hydrolysis of WCl$_6$ and purified by sublimation at 110 °C (10^{-2} mmHg). The di-Grignard reagent [{Mg(thf)$_n$Cl}$_2$(2-CH$_2$C$_6$H$_4$)$_2$}] (3) was

Table 2. Non-hydrogen atom co-ordinates

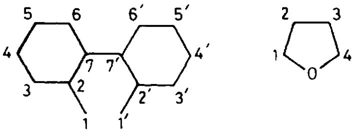
	Section 1			Section 2		
Atom	x	y	z	x	y	z
Mg	0	−0.105 59(11)	$\frac{3}{4}$			
O	0	−0.0134(2)	$\frac{3}{4}$	0	−0.1975(2)	$\frac{3}{4}$
Tetrahydrofuran						
O	−0.095 3(2)	−0.108 0(2)	0.618 2(2)	−0.073 3(2)	−0.102 1(2)	0.800 6(1)
C(1)	−0.162 7(3)	−0.070 0(3)	0.580 8(4)	−0.128 0(3)	−0.148 3(3)	0.787 4(4)
C(2)	−0.198 0(4)	−0.067 4(3)	0.481 7(4)	−0.189 3(4)	−0.117 5(3)	0.790 9(5)
C(3)	−0.142 9(3)	−0.099 9(3)	0.464 7(3)	−0.152 3(4)	−0.063 3(3)	0.848 3(4)
C(4)	−0.100 4(4)	−0.140 7(3)	0.544 0(4)	−0.080 3(4)	−0.054 3(3)	0.851 2(5)
W	0	0.6065 62(1)	$\frac{3}{4}$	0	−0.275 66(1)	$\frac{3}{4}$
Ligand						
C(1)	0.029 5(3)	0.090 5(2)	0.885 8(3)	−0.016 9(3)	−0.307 4(2)	0.855 4(3)
C(2)	0.057 6(3)	0.151 8(2)	0.923 8(3)	−0.048 7(3)	−0.370 8(3)	0.842 7(3)
C(3)	0.007 7(3)	0.193 5(3)	0.925 9(3)	−0.001 3(3)	−0.421 2(3)	0.886 4(4)
C(4)	0.031 2(4)	0.251 2(3)	0.963 0(4)	−0.030 0(4)	−0.480 4(3)	0.874 4(5)
C(5)	0.105 7(4)	0.267 9(3)	1.001 4(4)	−0.107 1(5)	−0.490 2(3)	0.820 2(6)
C(6)	0.158 3(3)	0.227 8(3)	1.001 2(4)	−0.157 0(3)	−0.442 1(3)	0.776 4(4)
C(7)	0.135 4(3)	0.169 2(3)	0.961 9(3)	−0.129 1(3)	−0.382 2(2)	0.786 8(3)
C(1′)	0.107 3(3)	0.111 0(2)	0.790 4(3)	−0.116 2(3)	−0.310 8(2)	0.654 9(3)
C(2′)	0.179 3(3)	0.099 3(2)	0.883 4(3)	−0.178 4(3)	−0.298 7(2)	0.673 2(3)
C(3′)	0.236 8(3)	0.061 8(3)	0.890 1(4)	−0.233 6(3)	−0.253 2(3)	0.625 4(3)
C(4′)	0.304 1(3)	0.050 3(3)	0.970 9(4)	−0.291 2(3)	−0.240 3(3)	0.643 2(4)
C(5′)	0.316 7(3)	0.077 0(3)	1.047 0(4)	−0.293 3(3)	−0.271 3(3)	0.709 0(4)
C(6′)	0.261 3(3)	0.115 5(3)	1.043 8(3)	−0.240 1(3)	−0.318 0(3)	0.756 4(4)
C(7′)	0.191 9(3)	0.127 5(2)	0.963 2(3)	−0.182 8(3)	−0.331 8(2)	0.739 3(3)
Solvent						
C	$\frac{1}{2}$	0.200 3(6)	$\frac{1}{4}$			
Cl	0.441 7(2)	0.155 3(2)	0.270 2(2)			

prepared by the classical method,[3] or using [Mg(anth)(thf)$_3$][6] as detailed in the literature.

Preparation of $[\{W[(2\text{-}CH_2C_6H_4)_2]_2\overline{O\}_2Mg}(thf)_4]\cdot CH_2Cl_2$, (**5**).—To a stirred solution of freshly sublimed WCl$_4$O (1.35 g, 3.95 mmol) in thf (50 cm^3) was added a solution of (**3**) (160 cm^3, 0.083 mol dm^{-3}, 92%) {freshly prepared from [Mg(anth)(thf)$_3$] and 2,2′-bis(chloromethyl)biphenyl} dropwise, at −78 °C, over a period of 2 h. On completion of the addition the solution was warmed to room temperature, the solvent removed *in vacuo*, and the residue extracted with toluene (100 cm^3). The solution was filtered, the volume reduced to *ca.* 10 cm^3, then kept overnight at −30 °C, whereupon a red precipitate of the *title compound* formed. This was recrystallised as dark red prisms from dichloromethane by the slow addition of diethyl ether (1.35 g, 45%), m.p. 168—170 °C (decomp.) (Found: C, 57.5; H, 5.10. Calc. for $C_{73}H_{82}Cl_2MgO_6W_2$: C, 57.75; H, 5.45%). E.s.r.: thf, $g_{av.}$ 1.900 (no hyperfine coupling; CH$_2$Cl$_2$, $g_{av.}$ 1.928 (s, no hyperfine coupling). I.r. (Nujol): 934s cm^{-1} (W=O).

Crystallography.—*Crystal data.* $C_{73}H_{82}Cl_2MgO_6W_2$, M = 1 518.5, monoclinic, space group $C2/c$ (C^6_{2h}, no. 15), a = 20.526(6), b = 22.076(4), c = 17.540(5) Å, β = 122.50(2)°, U = 6 703(3) Å^3, D_c (Z = 4) = 1.50 g cm^{-3}, F(000) = 3 048. Monochromatic Mo-K_α radiation, λ = 0.710 69 Å, μ = 37.7 cm^{-1}. Specimen: 0.07 × 0.07 × 0.38 mm. Transmission coefficients: 0.58—0.67. T = 295 K.

Structure determination. A unique data set was measured to $2\theta_{max.}$ = 65° using a Syntex $P2_1$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode. 12 102 Independent reflections were obtained, 7 052 with $I > 3\sigma(I)$ being considered 'observed' and used in the basically 9 × 9 block-diagonal least-squares refinement after analytical absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms (exception: the solvent carbon which had a very elongated ellipsoid and may be disordered to either side of the two-fold axis); $(x, y, z, U_{iso})_H$ were included as invariants at idealized values. Residuals at convergence R, R' on $|F|$ were 0.037, 0.024 (statistical weights). Neutral-atom complex scattering factors were used;[19] computation used the XTAL 83 program system[20] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Atomic coordinates are given in Table 2. Non-hydrogen atom labelling in the ligand and tetrahydrofuran units is as shown below.



Abnormal features. Initial attempts to determine the structure on a separate batch of crystals prepared from (**3a**) rather than (**3b**) yielded a much less precise model with much less extensive data and disorder, particularly about the solvent and tetrahydrofuran molecules, in a unit cell 4% greater in volume! [a = 19.97(1), b = 24.36(1), c = 16.992(8) Å, β = 122.59(3)°, U = 6 962(5) Å^3].

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