

Chemistry of *o*-Xylidene–Metal Complexes. Part 3.¹ Tungsten *o*-Xylidene Complexes derived from Tetrachloro(oxo)tungsten(vi) ; X-Ray Crystal Structures of $[W(CH_2C_6H_4CH_2-o)_3] \cdot 0.5C_6H_6$ and $[{W(CH_2C_6H_4CH_2-o)_2O}]_2Mg(C_4H_8O)_4$ *

Michael F. Lappert

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Colin L. Raston, Graham L. Rowbottom, Brian W. Skelton, and Allan H. White

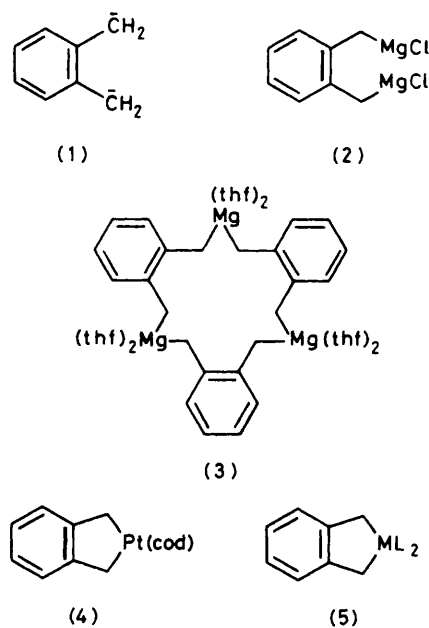
Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands W.A.6009

Reaction of WCl_4O with the di-Grignard reagent $o-C_6H_4(CH_2MgCl)_2$ or the chloride-free '*o*-xylidene' complex $Mg(CH_2C_6H_4CH_2-o)(thf)$ in tetrahydrofuran (thf) yields either the thermally stable

tris(chelate), $[W(CH_2C_6H_4CH_2-o)_3]$ (7), or the W^V complex $[{W(CH_2C_6H_4CH_2-o)_2O}]_2Mg(thf)_4$ (8) (a non-electrolyte in thf), in a manner critically dependent on reaction conditions. In both reactions a reduction step precedes alkylation, as determined by e.s.r., with probable intermediates being $[WCl_4O]^-$, $[WCl_5O]^{2-}$, and $[WCl_3O(thf)_3]$. The complex (7) undergoes reversible one-electron reduction as shown by cyclic voltammetry, $E_{1/2}^{red} = -1.68$ V, and the W^V radical anion, $g_{av.} = 2.005$, is also accessible from (7) and sodium dihydronaphthylide. X-Ray analysis shows that the *o*-xylenediyl ligand (1) behaves as a chelating ligand in both (7) and (8), but in (8) the two ligands (1) are bonded differently. One is typically metallacyclic in nature, $W-C^{\alpha}$ 2.16(2) Å, $W-C^{\alpha}-C(\text{aromatic})$ 109(1)° with a fold angle (Φ) of 42.4°, whereas the other has a larger Φ (66.1°) with $\langle W-C^{\alpha} \rangle$ 2.16(4) Å, and $W-C^{\alpha}-C(\text{aromatic})$ 98(2) and 93(1)°, possibly arising from an aromatic π interaction with the tungsten atom. For the tris(chelate) (7) all ligands are equivalent, the tungsten symmetry is quasi- $3/m$, with a more pronounced $W-\pi$ -arene interaction, possibly of a stabilising influence [$W-C$ 2.21, $W-C(\text{aromatic})$ 2.4₉ Å; $W-C-C(\text{aromatic})$ 82.7°, $\Phi = 83.3^\circ$]. In complex (8), the magnesium atom is octahedrally co-ordinated, with the four thf ligands disposed equatorially; the WO bond is short, 1.71(1) Å.

In Part 1 of the present series we described the preparation and properties of convenient main group metal precursors for metal complexes derived from the *o*-xylenediyl ligand (1).² These were the di-Grignard reagent (2), obtained from *o*-bis(chloromethyl)benzene, magnesium and tetrahydrofuran (thf), and the chloride-free macrometallacycle (3) or $Mg(CH_2C_6H_4CH_2-o)(thf)$. The potential of these reagents for synthesis of *o*-xylidene-containing metallacycles was illustrated by the characterisation of the Pt^{II} complex (4) (cod = cyclo-octa-1,5-diene)² and the metallocene(IV) complexes (5)¹ ($M = Ti, Zr, Hf, \text{ or } Nb, L = \eta-C_5H_5$; $M = Nb, L = \eta-C_5H_4SiMe_3$). [We use the umbrella term '*o*-xylidenemetal complex' to describe, without prejudice as to bonding, all $o-C_6H_4(CH_2)_2$ -metal complexes in which the organic ligand binds in (a) a bridging mode, as in (3); or (b) a chelating mode, whether (i) in bis(σ) fashion, *i.e.*, derived from (1), (ii) an η^4 -manner, *i.e.*, derived from (6), or (iii) in some intermediate state.]

Whereas in much of an earlier work at Sussex on metal alkyls we were concerned with bulky ligands and hence low metal co-ordination numbers (and oxidation states), as in $[Cr\{CH(SiMe_3)_2\}_3]$,³ one of the objectives of our present studies with the ligand (1) is to explore the possibility of stabilising metal complexes in high metal oxidation states. Thus we note that (1) is sterically rather undemanding when functioning as a



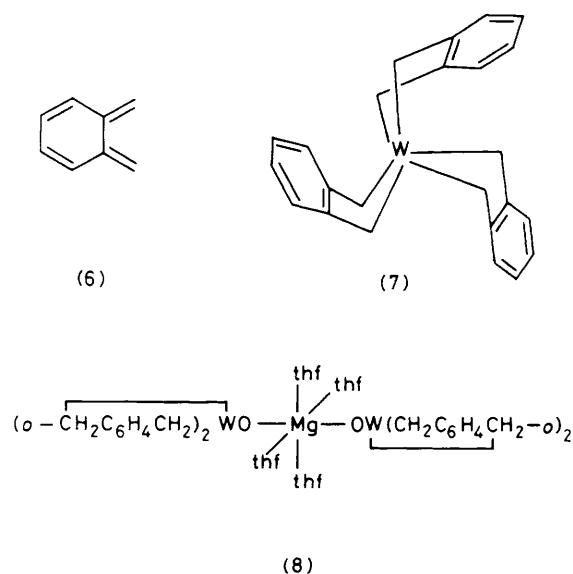
* Tris(*o*-phenylenedimethylene- $C^{\alpha}C^{\alpha}$)tungsten(vi)-benzene (1/0.5) and bis[oxobis(*o*-phenylenedimethylene- $C^{\alpha}C^{\alpha}$)tungsten(vi)]-tetrakis(tetrahydrofuran)magnesium.

Supplementary data available (No. SUP 23776, 21 pp.): structure factors, H-atom co-ordinates, thermal parameters, thf geometries. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii–xix.

Non-S.I. unit employed: 1 Torr = (101 325/760) N m⁻².

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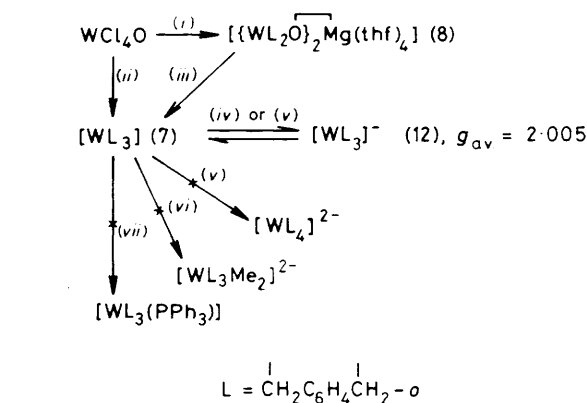
chelating ligand with a relatively small 'bite' angle [*cf.* CH_2-M-CH_2 in (5) = 76.7(2) (Ti), 77.3(2) (Zr), 77.2(4) (Hf), or 72.4(7)° (Nb)]. A ligand isoelectronic with (1) is the catecholate, $o-OC_6H_4O^{2-}$, and it has certainly proved possible to arrange three of these around a metal(III) centre, as in $[M(OC_6H_4O-o)_3]^{3-}$ ($M = Cr$ or Fe).⁴ A related neutral perchloro-complex is known, formally of Mo^VI , $[Mo(OC_6Cl_4O-$



o_3].⁵ Similar compounds which may be regarded as derived from Mo^{VI} are $\{[Mo(O)(OC_6H_2Bu^1-3,5-O-2)_2]_2\}^{6a}$ and $[Mo(NHC_6H_4S-o)_3]$;^{6b} catecholato-metal complexes have been reviewed.⁷ A more detailed problem concerns the precise nature of the mode of bonding of (1) (and the related catecholate) when functioning as a chelating ligand. Thus (1) is the reduced form of 5,6-dimethylenecyclohexa-1,3-diene (6) (*cf.* *o*-quinone) which clearly may behave as an η^4 -chelating ligand; and a complex such as $[W(CH_2C_6H_4CH_2-o)_3]$ (7) may in extreme formulations be regarded as derived either from (1) and W^{VI} or (6) and W^0 . These distinctions are to some extent a matter of semantics. X-Ray data have a bearing and a significant structural parameter is the 'fold angle', Φ , which is defined as the dihedral angle between the $C_6H_4C_2$ and MC_2 planes. We prefer (somewhat arbitrarily) to regard complex (7) as a derivative of W^{VI} because on reduction it gives a tungstate(v) analogue, while the latter is reversibly reoxidised (cyclic voltammetry) to reform (7) (Scheme 1).

An aim of the present work was to prepare the tris(chelate) metal complexes of the Group 6 transition metals, and in particular the tungsten compound (7), which was expected to be the most readily accessible of this family. Possible precursors considered included WCl_6 and WCl_4O . The latter was chosen, partly because the use of a homoleptic chloride $[MCl_4]$ ($M = Ti, Zr, \text{ or } Hf$) had previously¹ led to complexes in which the ligand (1) appeared to behave as a bridging [*e.g.*, as in (3)] rather than a chelating [*e.g.*, as in (4) or (5)] moiety. Thus from the appropriate Group 4 metal(IV) chloride and either (2) or (3) in appropriate stoichiometry there were obtained pyrophoric compounds of empirical formula $M(CH_2C_6H_4CH_2-o)(thf)$ and their lack of hydrocarbon- or ether-solubility was suggestive of an oligomeric structure. By contrast a tris(chelate) such as (7) was expected to be stable (with respect to ring \rightarrow chain isomerisation to give a bridged oligomer) by virtue of its co-ordinative saturation, unlike a Group 4 metal bicycle, $[M(CH_2C_6H_4CH_2-o)_2]$.

There is one previous example of a tungsten(vI) alkyl, WMe_6 (and here there is no ambiguity about oxidation state), which, however, is thermally unstable and begins to decompose after *ca.* 8 d at $-25^\circ C$.⁸ The oxidation state +5 is rather rare for tungsten and hitherto unknown for a W^V alkyl, but is now revealed in the complex (8). Preliminary communic-



Scheme 1. Summary of synthesis and properties of complexes (7) and (8): (i) 3.3 mol equiv. (2), thf, $-78^\circ C$ to $<20^\circ C$; (ii) >3.5 mol equiv. (2), thf, $-78^\circ C$ to *ca.* $50^\circ C$; (iii) 1.0 mol equiv. (2), thf, $50^\circ C$; (iv) $Na(C_{10}H_8)$ in thf, $20^\circ C$; (v) cyclic voltammetry in $[NBu^4][BF_4]$ (0.2 mol dm^{-3}) in thf at a Pt electrode, $-E_3^{red} = 1.68$ V; (vi) 2.2 mol equiv. LiMe, OEt_2 -thf (1:1); (vii) 1.1 mol equiv. PPh_3 , C_6H_6

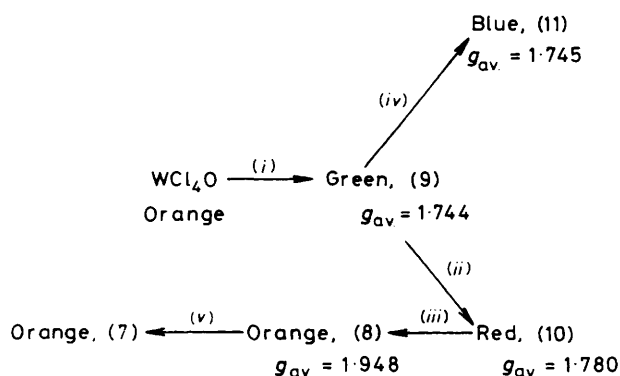
ations have dealt with some aspects of the 'tungsten(vI)' [(7)]⁹ and tungsten(v) [(8)]¹⁰ metallacycles.

Results and Discussion

The nature of the complex derived from reaction of the magnesium reagent (2) or $Mg(CH_2C_6H_4CH_2-o)(thf)$ with WCl_4O appears to be critically dependent on the reaction conditions. The optimum yield for isolation of the reduced species $\{[W(CH_2C_6H_4CH_2-o)_2O]_2Mg(thf)_4\}$ (8) was achieved by adding 3.3 mol equiv. of (1), in the form of the alkylating agent (2) or $Mg(CH_2C_6H_4CH_2-o)(thf)$ in thf solution, to WCl_4O in thf at $-78^\circ C$, followed by removal of solvent *in vacuo* at ambient temperature. A reaction temperature above *ca.* $20^\circ C$

gave mixtures of (8) and $[W(CH_2C_6H_4CH_2-o)_3]$ (7). The use of less than 3.3 mol equiv. resulted in reduced yields of (8), from *ca.* 35% to traces at 3.0 mol equiv., and no product at all for less than this value. Reproducible procedures for the synthesis of the tris(chelate) (7), typically in 35% yield, required the use of greater than *ca.* 3.5 mol equiv. of (1), but there was no improvement in the yield at >4 mol equiv. Optimum yield of (7) was achieved by warming the reaction mixture to *ca.* $50^\circ C$ prior to solvent removal, with other experimental procedures as before. It is noteworthy that a prerequisite for a successful alkylation required that the di-Grignard solution (2) be obtained in almost quantitative yield based on *o*-bis(chloromethyl)benzene, with yields less than 90% giving little or no product (7) or (8). For complex (8) one of the thf molecules was readily lost by drying *in vacuo*.

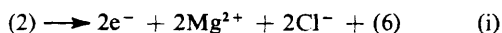
One general route to metal alkyls is *via* transmetallation reactions involving a Grignard reagent or a magnesium dialkyl, as in the present reactions. The metal substrate is generally the chloride, and reactivity is usually restricted to Cl^-/R^- exchange; the oxo-group abstraction with formation of the 'tungsten(vI)' tris(chelate) (7) is therefore surprising. Alkylation with $O^{2-}/2R^-$ exchange is sometimes a feature of reactions of aluminium alkyls, typified by the formation of $ReMe_6$ from $ReMe_5O$ and $(AlMe_3)_2$.¹¹ Attempts to prepare complex (7) from WCl_6 (the tungsten substrate for the neutral homoleptic W^{VI} alkyl, WMe_6)⁸ were unsuccessful, either brown oils or insoluble brown powders being obtained. While WMe_6 can undergo an increase in the metal atom co-ordination number, forming $Li_2[WMe_6]$ with an excess methyl-



Scheme 2. E.s.r. and colour changes during addition of the di-Grignard reagent (2) to WCl_4O in thf; (i) 0.5 mol equiv. (1), $-78^\circ C$; (ii) 2.5–4.0 mol equiv. (1), $-78^\circ C$; (iii) -78 to $+20^\circ C$; (iv) -78 to $+20^\circ C$, 24 h; (v) >3.5 mol equiv. (1), $50^\circ C$. Assignments: (9), $[WCl_4O]^-$; (10), $[WCl_3O]^{2-}$; (11), $[WCl_3O(thf)_3]$

lithium solution, we find that (7) does not form an adduct with excess of (2), $Mg(CH_2C_6H_4CH_2-o)(thf)$, or $(LiMe)_3$. This may be a consequence of steric hindrance at W in (7) which may have an electronic origin, being due to the *o*-xylidene-metal interaction being intermediate between η^4 and metallacyclic bonding. Compound (7) did not react with PPh_3 in benzene at $70^\circ C$, *cf.* formation of $[WMe_6(PMe_3)_3]$ [a better comparison would have been with (7) + PMe_3].¹²

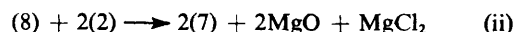
Progressive addition of the di-Grignard reagent (2) in thf (*ca.* 0.075 mol dm^{-3}) to WCl_4O in thf resulted in several intermediate species, as determined by sequential changes in both e.s.r. spectra and colours (Scheme 2). The first, the green complex (9) having g_{av} 1.744, being derived from 0.5 mol equiv. of (1), is conveniently assigned as a W^V chloride and we suggest that reduction from W^{VI} to W^V precedes alkylation, with a possible source of reduction being the corresponding oxidation of the *o*-xylenediyl moiety to give (6), equation (i); this has precedent in the conversion of the isoelectronic catechol dianion to *o*-quinone.¹³ The hydrocarbon (6) is known to be unstable, readily polymerising to $(C_8H_8)_n$.¹⁴ Equation (i)



accounts for the stoichiometric reduction of $W^{VI} \rightarrow W^V$ with 0.5 mol equiv. of (2). We stress that these colour and e.s.r. changes refer to stoichiometric quantities of reagents; effectively (2) may be titrated *versus* WCl_4O .

The exact nature of intermediates (9) (green) and (10) (red) [from 2.5–4.0 mol equiv. of (1)] remains to be determined, but given their low g_{av} values compared with that for (8), and their similarity to those of g_{av} of previously reported oxo(chloro)tungsten(v) species, (9) and (10) may well be mixed oxochlorides. Thus, we note that the ion formulated as $[WCl_3O]^{2-}$ in aqueous HCl had g_{av} 1.773,¹⁵ and the green neutral $[WCl_3(NCMe)_3O]$ in CH_2Cl_2 had g_{av} 1.76.¹⁶ After *ca.* 24 h at *ca.* $20^\circ C$ the green solution (9) turned blue, compound (11), with a similar g_{av} value; this colour is like that of $[WCl_3O(thf)_3]$ for which unfortunately no e.s.r. data are available.¹⁷ If the blue solution (11) is deemed to contain this or a similar W^V species, then a likely sequence is (a) an initial electron transfer whereby WCl_4O is converted into $[WCl_4O]^-$ (9), followed by (b) loss of Cl^- and conversion of (9) to $[WCl_3O(thf)_3]$ (11), with concomitant generation of thf-solvated $MgCl_2$ from the displaced Cl^- and $MgCl^+$ [*cf.* equation (i)]. Alternatively, trapping of Cl^- by the green complex $[WCl_4O]^-$ would result in $[WCl_5O]^{2-}$ and this seems a plausible assignment for the red complex (10).

The dramatic change in g_{av} found by allowing the mixture containing the red complex (10) to warm up from -78 to $20^\circ C$ suggests that alkylation is minimal at lower temperatures. Formation of (7), after warming to *ca.* $50^\circ C$ a solution containing (8) and an excess of the alkylating agent (2), is indicated by the disappearance of the e.s.r. signal corresponding to (8). Moreover we find that it is possible to prepare the tris(chelate) (7) from its W^V precursor (8) and the di-Grignard reagent (2) under similar conditions in *ca.* 40% yield [step (iii) in Scheme 1], and equation (ii) describes the reaction.



Tungsten oxo(alkyl) complexes, derived from WCl_4O and a metal alkyl, have recently received some attention, with emphasis on their role as catalysts for olefin metathesis, as for $[WCl_3O(Me)(OEt)_2]$ ¹⁸ and $[W(CH_2CMe_3)_4O]$.¹⁹ The reduction of W^{VI} to W^V was not observed in the synthesis of either of these complexes, although it was noted that interaction of a strong donor molecule with the former did lead to the formation of a green, reduced tungsten species. In our experiments, the facile reduction may be a consequence of the stronger reducing properties of the *o*-xylenediyl dianion [*cf.* equation (i)] and/or our use of the strong donor solvent thf. In any event, magnesium alkyls or Grignard reagents are known to behave as reducing agents; *e.g.* $[Ti(\eta-C_5H_5)_2Cl_2]$ is reduced, prior to its alkylation, by $Mg\{CH(SiMe_3)_2\}Cl$, ultimately to yield $[Ti(\eta-C_5H_5)_2\{CH(SiMe_3)_2\}]$.²⁰

The tris(chelate) (7) is unusual in being a homoleptic metal alkyl with a co-ordination number (c.n.) greater than four. We attribute this to steric reasons, principally the small ligand bite angle (as has been shown). The only other examples of complexes of c.n. >4 have methyl as the ligand, as in $TaMe_5$,²¹ WMe_6 ,⁸ or $[WMe_6]^{2-}$. The β -hydrogen-free neopentyl-type ligands are too bulky to allow six of them within the inner co-ordination sphere of a metal, *cf.* $[W(CH_2Bu^t)_4(CHBu^t)]$,^{22a} $[W(CH_2Bu^t)_3(CBu^t)]$,^{22b} or $[W(CH_2SiMe_3)_3]_2$.²³

The considerable thermal stability of (7) is demonstrated by its being sublimable at *ca.* $160^\circ C$ (10^{-2} Torr). It is also relatively air stable. By contrast, WMe_6 is not only thermally labile, but is exceedingly air sensitive.⁸ The stability of (7) is attributed to a combination of the chelate effect and steric protection of the metal centre, caused in part by interaction of the π -system of the *o*-xylidene ligand and vacant orbitals of the metal; as a consequence, the ligands occupy a larger cone of the metal co-ordination sphere than might have been expected from consideration of only the ligand bite angle. Indeed (7) has some relationship to tris(η^4 -buta-1,3-diene)tungsten(0), a relatively air- and thermally-stable complex, being sublimable at 50 – $60^\circ C$ (10^{-3} Torr).²⁴

The mass spectrum of the 'tungsten(vi)' tris(chelate) (7) shows a dominant parent peak, P^+ , with the expected isotope pattern, the only other significant peak being $(P - C_8H_8)^+$. However, for the W^V complex (8), tungsten-containing peaks were not found, the observed peaks corresponding to $(C_8H_8)_n^+$ ($n = 2, 4, \text{ or } 6$). For the same complex, conductivity measurements in thf support the hypothesis of a molecular complex, as found in the crystal, rather than dissociation into $[Mg(thf)_n]^{2+}$ and two $[W\{(CH_2)_2C_6H_4\}_2O]^-$ counter ions.

The e.s.r. signals characteristic of the d^1 species detected during the formation of complexes (7) and (8) (Scheme 2) or of the radical anion (12) [obtained from (7), Scheme 1], all in thf, show broad linewidths of the order of 15 G with no evident hyperfine coupling to ^{183}W (14.4% abundance, $I = \frac{1}{2}$) or the α -hydrogen atoms (where applicable) even at $-78^\circ C$. The low g_{av} values, 1.744–1.780 for (9)–(11) (Scheme 2), are

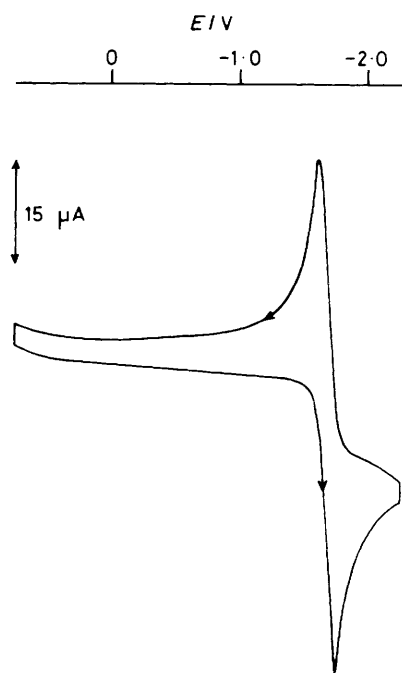


Figure 1. Cyclic voltammogram of $[\text{W}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)_3]$ (7) at a Pt electrode with $0.2 \text{ mol dm}^{-3} [\text{NBu}_4][\text{BF}_4]$ in thf as supporting electrolyte; scan rate, $\nu = 0.1 \text{ V s}^{-1}$; $E_4^{\text{red}} = -1.68 \text{ V}$

characteristic of W^{V} with small delocalisation and large spin-orbit coupling.²⁵

Assignment of the W^{O} stretching mode in the W^{V} complex (8) is uncertain, since co-ordinated thf has $\nu(\text{C}-\text{O}-\text{C})$ in close proximity to the expected $\nu(\text{W}=\text{O})$ range, *ca.* $946\text{--}960 \text{ cm}^{-1}$.^{19,26} However, tentatively we suggest that the sharp peak at 936 cm^{-1} is $\nu(\text{W}=\text{O})$, with the bands at 1032 , 1023 , and 1013 cm^{-1} corresponding to $\nu(\text{C}-\text{O}-\text{C})$ of co-ordinated thf.²⁷ The sharp bands at 442 for (8) and 458 cm^{-1} for (7) are attributed to $\nu(\text{WC}_n)$, by analogy with the $482 \text{ cm}^{-1} \nu_{\text{asy,m}}(\text{WC}_6)$ in WMe_6 .⁸

Attempts to examine the W^{V} complex (8) by cyclic voltammetry were unsuccessful due to its decomposition in the presence of the supporting electrolyte $[\text{NBu}_4][\text{BF}_4]$. The reduction behaviour of the ' W^{VI} ' complex (7) was studied both electrochemically and with the reductant sodium dihydronaphthylide. A one-electron redox change was reversible down to 10 mV s^{-1} with $-E_4^{\text{red}} = 1.68 \text{ V}$ versus a standard calomel electrode. In the cyclic voltammogram, Figure 1, the ratio of anodic to cathodic peaks was unity. However, the system should not be considered rigorously reversible from an electrochemical point of view; the separation of peaks was higher than theoretical (59 mV), with a magnitude dependent upon the scan rate. Reduction of (7) with $\text{Na}(\text{C}_{10}\text{H}_8)$ in thf generated a persistent e.s.r. singlet, $g_{\text{av.}} = 2.005$, suggesting that the electrochemical reduction product is the d^1 anion (12) (Scheme 1). No pure d^1 species could be isolated.

Assignment of ^1H n.m.r. data for the ' W^{VI} ' complex (7) was aided by a comparison with the published data for complexes (13) and (14)²⁸ and the most recently reported complexes (15) ($\text{L} = \text{PMe}_2\text{Ph}$ or PMePh_2).²⁹ The notable feature is a doublet for H_{endo} atoms upfield from SiMe_4 (τ 10.39) and an H_{exo} doublet at τ 7.51, the two methylene groups within each group being equivalent. Complexes (13)—(15) contain η^4 -5,6-dimethylenecyclohexa-1,3-diene ligands whereas in (7) the bonding is intermediate between σ and η^4 , and reminiscent of

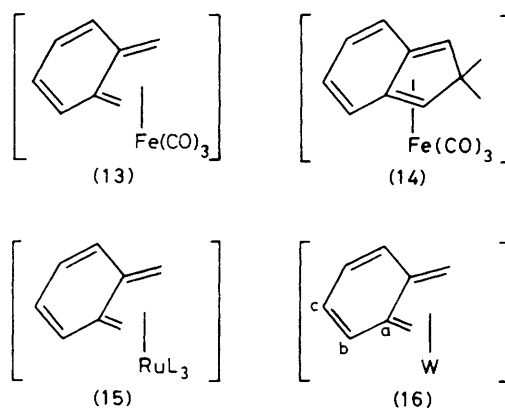


Table 1. Non-hydrogen atomic co-ordinates for $[\text{W}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)_3] \cdot 0.5\text{C}_6\text{H}_6$ (7)

Atom	x	y	z
W	0.194 44(5)	0.194 44(—)	0.194 44(—)
C(1A)	-0.073 9(13)	0.257 5(14)	0.517 5(12)
C(2A)	0.024 9(13)	0.332 2(12)	0.467 6(12)
C(3A)	0.046 7(10)	0.330 7(10)	0.329 3(11)
C(4A)	0.157 0(12)	0.398 8(11)	0.266 4(13)
C(1B)	-0.159 1(11)	0.177 9(12)	0.434 0(13)
C(2B)	-0.140 5(11)	0.172 1(11)	0.300 6(13)
C(3B)	-0.038 2(10)	0.249 9(10)	0.244 2(11)
C(4B)	0.001 0(11)	0.241 7(11)	0.107 2(10)
C(benzene) *	0.436 9(14)	0.610 7(12)	0.453 1(15)

* All six C atoms are identical.

that found in $[\text{Zr}\{\text{CH}_2\text{C}(\text{Me})=\text{C}(\text{Me})\text{CH}_2\}(\eta\text{-C}_5\text{H}_5)_2]$.³⁰ In the latter the 2,3-dimethylbuta-1,3-diene ligand is fluxional, *via* a genuine metallacyclic intermediate, whereas in (7) the 'paddle wheel' is rigid on the n.m.r. time-scale at temperatures greater than 120°C . An important feature of the ^{13}C n.m.r. spectra is a shift upfield from δ *ca.* $130\text{--}150$ (C_a) for metallacycles^{1,2,31} derived from the *o*-xylenediyl ligand (1) to δ 116.9, reflecting a contribution from the 5,6-dimethylenecyclohexa-1,3-diene resonance form (16), as suggested by the structure analysis (see below).

With the exception of complexes containing polyhaptoligands such as $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]^+$,³² the complex (8) is a rare example of a stable W^{V} organometallic compound, unusual in that it is a paramagnetic d^1 -metallacycle; other examples

which have been reported are $[\text{V}(\text{L}')(\eta\text{-C}_5\text{H}_5)_2]$ [$\text{L}' = 2,2'-(\text{C}_6\text{H}_4)_2$, $2,2'-(\text{C}_6\text{F}_4)_2$, or $-\text{C}(\text{Ph})=\text{C}(\text{Ph})\text{C}(\text{Ph})=\text{C}(\text{Ph})-$],³³

$[\text{Nb}\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\}(\eta\text{-C}_5\text{H}_5)_2]$,³⁴ and

$[\text{Nb}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)(\eta\text{-C}_5\text{H}_5)_2]$.¹ Compound (8) is also unique in being the first example of a transition-metal metallabicyclic, and together with (7) and $[\text{W}(\eta\text{-C}_4\text{H}_6)_3]$ ²⁴ provides the foundation of tungstacyclopentene chemistry. Saturated smaller ring congeners, tungstacyclobutanes, are often postulated as intermediates in tungsten-catalysed olefin metathesis.

The preparation and characterisation of the complexes (7), (8), and (12) demonstrates the potential of the *o*-xylenediyl ligand (1) to stabilise high (W^{VI}) and unusual (W^{V}) oxidation states, as predicted in 1980.³⁵

Structural Commentary.—(a) *The 'tungsten(vi)' tris(chelate)* (7). The unit-cell contents comprise a 2 : 1 ratio of discrete complex molecules of stoichiometry $[\text{W}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)_3]$

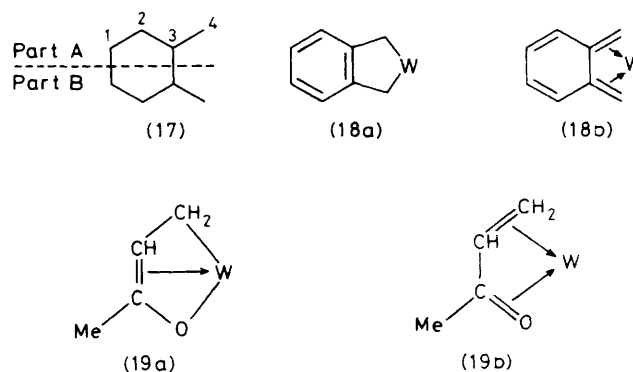
Table 2. Non-hydrogen atom co-ordinates for $[\{W(CH_2C_6H_4CH_2O)_2\}_2Mg(thf)_4]$ (8)

Atom	x	y	z
Mg	0	0	0
Tetrahydrofuran a			
O	0.108 2(7)	-0.000 4(8)	-0.051 4(11)
C(1)	0.148 8(21)	-0.068 2(23)	-0.072 4(26)
C(2) *	0.214 1(37)	-0.033 8(42)	-0.136 9(46)
C(2') *	0.231 0(24)	-0.047 8(27)	-0.080 9(28)
C(3) *	0.213 2(24)	0.036 9(26)	-0.120 9(29)
C(3') *	0.232 5(33)	0.029 0(38)	-0.060 0(40)
C(4) *	0.142 2(28)	0.066 2(31)	-0.102 7(34)
C(4') *	0.163 2(29)	0.054 9(33)	-0.035 6(39)
Tetrahydrofuran b			
O	0.045 6(9)	-0.023 2(9)	0.120 3(9)
C(1) *	0.029 8(33)	0.018 6(34)	0.200 0(35)
C(1') *	0.107 2(30)	0.030 2(34)	0.153 8(36)
C(2)	0.100 9(2)	0.002 9(22)	0.248 9(27)
C(3) *	0.135 2(26)	-0.066 3(30)	0.219 6(31)
C(3') *	0.053 3(27)	-0.049 8(30)	0.264 0(35)
C(4) *	0.090 7(29)	-0.086 7(33)	0.148 5(35)
C(4') *	0.021 6(32)	-0.078 2(32)	0.176 4(35)
O(1)	0.010 1(7)	0.121 7(8)	0.020 9(8)
W	0.030 66(5)	0.217 92(6)	0.048 95(6)
Ligand a			
C(1A)	-0.186 7(14)	0.209 1(19)	0.270 6(16)
C(2A)	-0.108 4(12)	0.210 9(18)	0.267 2(14)
C(3A)	-0.073 4(13)	0.242 4(17)	0.196 9(16)
C(4A)	0.009 1(12)	0.241 3(13)	0.182 7(14)
C(1B)	-0.224 5(13)	0.233 6(17)	0.202 7(17)
C(2B)	-0.191 3(12)	0.260 7(15)	0.127 2(15)
C(3B)	-0.117 2(12)	0.263 9(13)	0.125 1(15)
C(4B)	-0.069 1(12)	0.288 8(14)	0.049 4(16)
Ligand b			
C(1A)	0.110 5(13)	0.488 3(17)	0.061 5(21)
C(2A)	0.085 0(11)	0.437 3(15)	-0.002 1(15)
C(3A)	0.101 1(12)	0.356 9(14)	0.004 9(14)
C(4A)	0.069 0(12)	0.296 1(13)	-0.049 6(16)
C(1B)	0.150 8(14)	0.461 8(15)	0.128 7(21)
C(2B)	0.164 3(14)	0.383 9(18)	0.135 7(17)
C(3B)	0.138 6(12)	0.327 5(15)	0.074 8(13)
C(4B)	0.146 8(13)	0.238 1(14)	0.080 3(15)

* Denotes population 0.5.

and benzene solvent molecules. Both complex and solvent molecules lie disposed about three-fold crystallographic axes; the solvent molecule is disposed about the inversion centre of this axis and thus has symmetry $\bar{3}$ imposed, while the symmetry of the complex molecule disposed about the tungsten atom is 3. Consideration of the disposition of the ligands about the tungsten shows, however, that the actual atom array does not deviate significantly from point symmetry $3/m$ (C_{3h}). Atom numbering is shown in structure (17).

The nature of the interaction of the tungsten with the organic ligand is of interest. We find that the tungsten atom approach is almost normal to the ligand plane, so that a close approach is made to C(3) as well as C(4), $\langle W-C(4) \rangle$ being 2.2 Å, slightly shorter than $\langle W-C(3) \rangle$, 2.4 Å. The six carbon atoms of the phenyl ring are coplanar ($\sigma = 0.008$ Å; $\chi^2 = 2.8$); C(4A,4B) deviate by 0.11 and 0.17 Å, respectively and the tungsten by 1.89 Å. It seems likely that the deviation



of C(4A) from the phenyl ring plane is real; with these two C(4) atoms included in the plane calculation, χ^2 rises to 86. Within the organic ligand, we find appreciable, significant, and consistent deviations from ideal aromatic phenyl geometry. C(1)-C(2) is less than the usual aromatic value of ca. 1.40 Å, while all other bonds in the ring are longer. C(3)-C(4) is reduced well below the usual C(aromatic)-C(aliphatic) distance and the structure overall provides good evidence for the contribution of resonance forms of the type (18a) and (18b).

With very few exceptions the co-ordination geometry of a tris(symmetrical bidentate ligand)metal complex has point symmetry $32 (D_3)$;³⁶ however, it is generally realised that complexes having 1,3-diunsaturated ligands, in which the potential exists for π - as well as σ -bonding, constitute an important exception to this generalisation, as exemplified in the quasi-isoelectronic systems $[W(CH_2=CH-CH=CH_2)_3]$,^{24,37} $[Mo(CH_2=CH-CH=CH_2)_3]$,²¹ $[W(CH_2=CH-COMe)_3]$,³⁸ and $[Mo(phenq)_3]$ (phenq = phenanthrene-9,10-quinone).³⁹ Of particular interest in the present context is the structure of $[W(CH_2=CH-COMe)_3]$, formally a compound of tungsten(0) rather than tungsten(vi). In complex (7), W-C(4A,4B) are 2.20 and 2.22 Å, respectively; cf. 2.11(2) and 2.42(2) Å for W-O and W-CH₂ in $[W(CH_2=CH-COMe)_3]$.³⁸ Consideration of the bond lengths in the ligand of the latter complex suggests the predominance of a structure of the type (19a) rather than (19b). Perhaps the key indicator of π participation in the ligand-metal bonding in the tris(chelate) (7) is the angle $\langle W-C(4)-C(3) \rangle$ which, being 82.7°, is well removed from the tetrahedral limit.

(b) *The bis-tungsten(v) bicycle, (8).* The structure determination confirms the stoichiometry to be $[\{W(CH_2C_6H_4CH_2O)_2\}_2Mg(thf)_4]$, one half of the formula unit comprising the asymmetric unit of the structure. The magnesium atom is located at the origin of the unit cell and has crystallographically imposed $\bar{1}$ symmetry. Its environment comprises six oxygen atoms arranged in a distribution approaching octahedral, with $\langle Mg-O \rangle$ 2.09 Å, comparable with other octahedral Mg-O distances in complexes with oxygen σ -donor ligands such as thf or H₂O; e.g., in $[NH_4]_2[Mg(OH_2)_6][SO_4]_2$, $\langle Mg-O \rangle$ is 2.08 Å.⁴⁰ Four of the oxygen atoms are derived from the thf molecules, only two being independent, and both seriously disordered beyond the co-ordinated oxygen; the nature of the disorder and the presence of the tungsten preclude deconvolution of these solvent molecule geometries to any high degree of precision. The four thf oxygen atoms lie in a centrosymmetric equatorial plane about the magnesium, $\langle Mg-O \rangle$ 2.10 Å; the apical oxygen atoms (Mg-O 2.07 Å) belong to the inner co-ordination sphere of each tungsten atom.

Atom numbering is shown in (17) for each *o*-C₆H₄(CH₂)₂ moiety, the carbon atoms of thf are numbered C(1)-C(4) starting at a carbon adjacent to oxygen. The W environment

Table 3. Molecular non-hydrogen geometry for $[\text{W}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)_3]\cdot 0.5\text{C}_6\text{H}_6$ (7) (the two values in each entry are for sections A and B of the ligand). For numbering see (17)

Distances (Å)	
W-C(3)	2.48(1), 2.49(1)
W-C(4)	2.22(1), 2.20(1)
C(1)-C(1)	1.41(2)
C(1)-C(2)	1.35(2), 1.37(2)
C(2)-C(3)	1.42(2), 1.43(2)
C(3)-C(3)	1.42(1)
C(3)-C(4)	1.47(2), 1.45(2)

Angles (°)	
C(1)-C(1)-C(2)	121(1), 120(1)
C(1)-C(2)-C(3)	121(1), 121(1)
C(2)-C(3)-C(4)	125(1), 126(1)
C(2)-C(3)-C(3)	119(1), 119(1)
C(3)-C(3)-C(4)	116(1), 115(1)
C(3)-C(4)-W	81.6(6), 83.7(6)
C(4)-W-C(4)	74.7(4)

Other angles about tungsten: C(4A)-W-C(4A) (z, x, y) 86.6(4), C(4A)-W-C(4B) (z, x, y) 132.6(4), C(4A)-W-C(4B) (y, z, x) 133.7(4), C(4B)-W-C(4B) (z, x, y) 87.4(4).

Table 4. Magnesium environment for $[\{\text{W}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)_2\text{O}\}_2\text{Mg}(\text{thf})_4]$ (8) (independent values only are given; the labels a and b refer to the oxygen atoms of the two W-containing ligands a and b)

Distances (Å)	
Mg-O(1)	2.07(1)
Mg-O(a)	2.11(1)
Mg-O(b)	2.09(1)

Angles (°)	
O(1)-Mg-O(a)	88.9(5)
O(1)-Mg-O(b)	90.4(6)
O(a)-Mg-O(b)	88.7(6)

has no crystallographically imposed symmetry; its point symmetry approximates to m , with a pseudo-mirror plane passing through O, W, and the midpoints of the C(3A)-C(3B) and C(4A)-C(4B) bonds, *i.e.*, the two *o*-xylenediyl ligands (a and b) are symmetrical bidentate ligands with the tungsten lying to one side of the ligand plane. The geometry is determined with lower precision than that of complex (7) because of the disorder in the structure. The tungsten-oxygen bond length, 1.71(1) Å, in spite of its interaction with the magnesium, is typical of a $\text{W}^{\text{V}}=\text{O}$ value, *cf.* 1.72 Å in $\text{Ba}[\text{W}_2\text{O}_4(\text{edta})]\cdot 3.5\text{H}_2\text{O}$ (edta = ethylenediaminetetra-acetate),⁴¹ although as other data (*e.s.r.* and conductivity) clearly point to W^{V} , a W-O-Mg bonding mode seems appropriate. The two W-C(4) bonds do not differ significantly, $\langle \text{W-C}(4) \rangle$ being 2.16 Å, a value much lower than that (2.21 Å) found in (7). In ligand a, $\langle \text{W-C}(4)-\text{C}(3) \rangle$ is 109° (*i.e.*, the tetrahedral angle), but in ligand b it is much reduced, 96°. The W-C(3) distances in ligand a are 3.01(2) and 3.02(2) Å, while for ligand b they are 2.74(2) and 2.71(2) Å. Planes defined by the six carbon atoms of each phenyl ring have σ 0.02 Å in each case; C(4A,4B) deviate from the plane by 0.11 and 0.09 (ligand a) and 0.16 and 0.12 Å (ligand b) towards the tungsten atom in each case, the tungsten deviation being 1.25 and 1.70 Å, respectively. The dihedral angle between the two phenyl ring planes is 84°; the angles between the W-O bond and the plane normals are 16 and 80°, respectively.

Clearly in complex (8) the two ligands a and b differ. Ligand

Table 5. The tungsten environment for $[\{\text{W}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)_2\text{O}\}_2\text{Mg}(\text{thf})_4]$ (8) (the two values in each entry are for ligands a and b, respectively). For numbering see (17)

Distances (Å)	
W-O(1)	1.71(1)
W-C(4A)	2.16(2), 2.14(2)
W-C(4B)	2.16(2), 2.18(2)
C(3A)-C(4B)	1.51(3), 1.45(3)
C(3A)-C(4B)	1.53(3), 1.51(3)
C(3A)-C(3B)	1.42(3), 1.38(3)
C(3B)-C(3B)	1.34(3), 1.42(4)
C(1B)-C(2B)	1.40(3), 1.33(4)
C(1A)-C(1B)	1.33(4), 1.35(4)
C(1A)-C(2A)	1.42(3), 1.39(4)
C(2A)-C(3A)	1.37(3), 1.38(3)

Angles (°)	
O(1)-W-C(4A)	112.3(7), 117.6(8)
O(1)-W-C(4B)	109.8(7), 114.4(8)
C(4A)-W-C(4B)	75.3(9), 75.8(8)
W-C(4A)-C(3A)	109(1), 98(2)
W-C(4B)-C(3B)	109(1), 93(1)
C(4A)-C(3A)-C(3B)	116(2), 114(2)
C(4B)-C(3B)-C(3A)	111(2), 117(2)
C(4A)-C(3A)-C(2A)	125(2), 124(2)
C(4B)-C(3B)-C(2B)	127(2), 126(2)
C(3B)-C(3A)-C(2A)	118(2), 121(2)
C(3A)-C(3B)-C(2B)	122(2), 117(2)
C(3B)-C(2B)-C(1B)	117(2), 123(3)
C(2B)-C(1B)-C(1A)	124(2), 119(3)
C(1B)-C(1A)-C(2A)	118(2), 122(3)
C(1A)-C(2A)-C(2A)	120(2), 118(2)

Other angles: Mg-O-W 170.4(8), C(4Aa)-W-C(4Bb) 130.1(9), C(4Aa)-W-C(4Bb) 85.8(8), C(4Ba)-W-C(4Ab) 86.3(9), C(4Ba)-W-C(4Bb) 135.8(9).

a, lying normal to the W-O bond, has many of the geometrical properties of a σ -bonded ligand with the W-C(4)-C(3) angle exactly tetrahedral and $\text{W}\cdots\text{C}(3)$ very long. Ligand b, by contrast, has W-C(4)-C(3) reduced well below the tetrahedral, and C(3) lies closer to the tungsten; the distance is still much greater than in (7), however, and it is likely that the bonding to the metal is also predominantly σ in character through C(4). In so far as the aromatic ligand geometry is concerned, the precision is insufficient to make any assertions in regard to the effect of the bonding variations consequent upon the different types of metal co-ordination.

In considering *o*-xylylenemetal complexes in relation to the fold angle $[\Phi]$, the dihedral angle between $\text{W}(\text{C}^2)_2$ and ligand planes] the metallacyclic form [as in (18a)] possess relatively low Φ values, as found for (i) ligand a in complex (8), 42.4°;

(ii) $[\text{M}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)(\eta\text{-C}_5\text{H}_5)_2]$, $\Phi = 41$ ($\text{M} = \text{Ti}$), $\Phi =$

53.1 ($\text{M} = \text{Zr}$), $\Phi = 53^\circ$ ($\text{M} = \text{Hf}$); and (iii) $[\text{Nb}(\text{CH}_2\text{C}_6\text{H}_4\text{C-H}_2\text{-}o)(\eta\text{-C}_3\text{H}_4\text{SiMe}_3)_2]$, $\Phi = 40.7^\circ$.¹ In these complexes the 'folding' is deemed to be a consequence of the geometrical requirements of incorporating a large metal atom in a five-membered ring. However with increasing resonance contribution of the metal- π -ligand form, as in (18b), the Φ value increases, *cf.* $\Phi = 66.1^\circ$ for ligand b in complex (8) or $\Phi = 83.3^\circ$ in complex (7). At the η^4 extreme [*cf.* (18b)], as in $[\text{Fe}(\eta^4\text{-C}_6\text{H}_6)(\text{CO})_2(\text{PPh}_3)_2]$, where the metal resides equidistant from the four carbon atoms of the η^4 -ligand, the fold angle is $\gg 90^\circ$.⁴²

Non-hydrogen atomic co-ordinates are shown in Tables 1

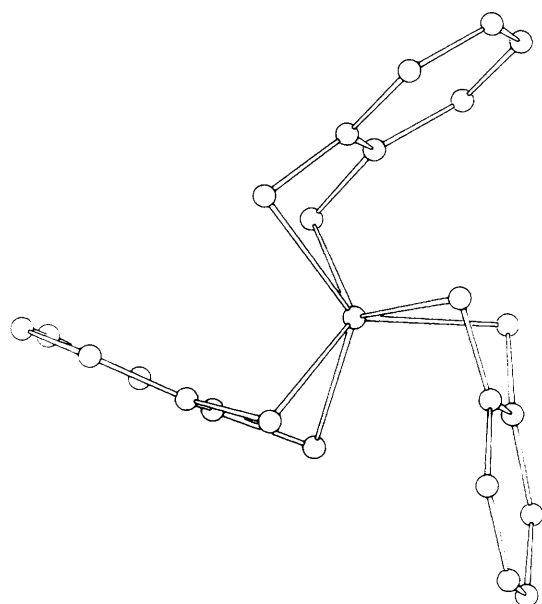


Figure 2. Projection of a single molecule of $[W(CH_2C_6H_4CH_2-o)_3]$ (7)

and 2 for (7) and (8), molecular geometric parameters for complex (7) in Table 3 and for complex (8) in Tables 4 (Mg environment) and 5 [$o-C_6H_4(CH_2)_2$ environment]. Projections of a single molecule of complex (7) and the projection of the tungsten environment down the $W=O$ bond of complex (8) are shown in Figures 2 and 3, respectively.

Experimental

General Procedures.—These have been described in Part 1.² The g_{av} values from e.s.r. spectra were measured relative to polycrystalline diphenylpicrylhydrazyl using a Varian E3 spectrometer. Cyclic voltammetry was carried out in thf with the electrolyte $[NBu^+][BF_4^-]$ (0.2 mol dm^{-3}) and a platinum working electrode under an atmosphere of dinitrogen in accordance with the procedure described in ref. 43. Measurements were made using a Hi-Tek Instruments Ltd. Potentiostat type DT 2101, a Chemical Electronics (Birtley) waveform generator type 01, and recorded on a Philips X-Y recorder type 24000 A4.

Materials.— WCl_4O was prepared by partial hydrolysis of WCl_6 and purified by sublimation at 180°C (10^{-2} Torr).

Preparation of $[W(CH_2C_6H_4CH_2-o)_2O]_2Mg(thf)_n$ [$n = 3$ or $4 \rightleftharpoons$ (8)].—To a stirred solution of freshly sublimed WCl_4O (1.80 g, 5.27 mmol) in thf (30 cm^3) at -78°C was slowly added a thf solution ($0.082 \text{ mol dm}^{-3}$) of the di-Grignard reagent (2)² (212 cm^3 , 17.4 mmol) during ca. 1 h. After a further 20 min at -78°C and gradual warming to room temperature over ca. 1 h, the mixture was taken to dryness *in vacuo*, extracted with warm (50°C) toluene (50 cm^3), and filtered to give an orange-red filtrate and a brown viscous residue. Concentration of the former to ca. 5 cm^3 , followed by cooling to -30°C , gave red crystals of (8) which readily crumbled to a powder *in vacuo* [Found: C, 50.0; H, 5.5. $C_{44}H_{56}MgO_5W_2$ ($n = 3$) requires C, 50.0; H, 5.35%]. Recrystallisation from a thf-toluene mixture (1 : 1, 20 cm^3) at -30°C gave, after drying *in vacuo*, the title compound ($n = 3$) (0.93 g, 35%); electrical conductivity (thf), $\Lambda = 0.27 \text{ S cm}^2 \text{ mol}^{-1}$; g_{av} (thf) = 1.948 or 1.943, for the powdered solid; i.r. (Nujol, KBr plates),

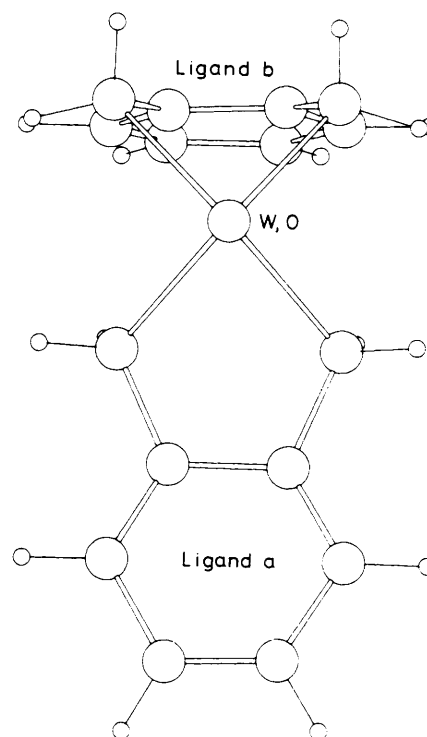


Figure 3. Projection of the tungsten environment of $[W(CH_2C_6H_4CH_2-o)_2O]_2Mg(thf)_4$ (8)

1 292m, 1 209s, 1 032s, 1 023 (sh), 1 013s, 936s, 925 (sh), 915s, 883m, 746s, 727 (sh), 609m, and $442s \text{ cm}^{-1}$.

Preparation of $[W(CH_2C_6H_4CH_2-o)_3]$ (7).—To a solution of freshly sublimed WCl_4O (0.5 g, 1.47 mmol) in thf (10 cm^3) at -78°C was slowly added a thf solution ($0.075 \text{ mol dm}^{-3}$) of the di-Grignard reagent (2)² (78.2 cm^3 , 5.88 mmol). After slowly warming to ca. 50°C during 1 h, the solvent was removed *in vacuo* and the brown residue extracted with diethyl ether (100 cm^3). Concentrating (to ca. 10 cm^3) and cooling (-30°C) afforded orange needles of (7). Recrystallisation (C_6H_6) gave orange prisms (0.26 g, 35%) which readily lost a solvent of crystallisation *in vacuo*, m.p. $>300^\circ\text{C}$ (Found: C, 58.1; H, 4.9. $C_{24}H_{24}W$ requires C, 58.1; H, 4.85%). N.m.r.: 1H (90 MHz) (C_6D_6), τ 2.69 (m, 2 H, C_6H_4), 3.03 (m, 2 H, C_6H_4), 7.51 (d, 2 H_{exo} , J_{HH} 7.3 Hz, CH_2), 10.39 (d, 2 H_{endo} , J_{HH} 7.3 Hz, CH_2); ^{13}C [CD_2Cl_2 , 1H decoupled; for numbering, see (17)], δ 49.9 (s, $W-CH_2$), 116.9 [s, C(3)], 131.2 [s, C(2)], 133.4 [s, C(1)]. Mass spectrum, m/e 496 (P^+), 392 ($P - C_8H_8$)⁺; i.r. (Nujol, KBr plates), 3 472w, 3 400w, 1 345m, 1 217m, 1 160w, 1 153w, 1 038w, 960m, 772s, 764m, 758s, 740s, 726m, 588w, and $458s \text{ cm}^{-1}$.

Syntheses of Complexes (7) and (8) from the Chloride-free Complex $Mg(CH_2C_6H_4CH_2-o)(thf)$.—Each of the complexes (7) and (8) was also prepared using the title magnesium reagent 2 in a similar fashion to that used for the di-Grignard reactions, except that the total thf used was only ca. 25% of that in the di-Grignard experiments. The work-up procedures, after addition of the Mg compound to a thf solution (-78°C) of WCl_4O , were identical to those outlined above. Similar mol ratios of WCl_4O to o -xylenediyl ligand (1) were essential.

Reduction of the 'Tungsten(vi)' Tris(chelate), (7).—Dropwise addition of a thf solution of sodium dihydronaphthylide (≤ 1

mol equiv.), prepared according to ref. 44, to a thf solution of complex (7) at ca. 20 °C generated a red solution. An e.s.r. signal, $g_{av.} = 2.005$, was persistent for days at ca. 20 °C, and was unaffected by addition of $[\text{NBu}_4][\text{BF}_4]$, the electrochemical electrolyte.

Electrochemical reduction of complex (7) in thf was shown to be reversible, $-E_{\frac{1}{2}}^{\text{red}} = 1.68 \text{ V}$ versus a standard calomel electrode, Scheme 1.

E.S.R. Monitoring of the Formation of Complex (8).—The observations are summarised in Scheme 2. In a typical experiment, using the procedure described above for synthesis of complex (8) via the di-Grignard reagent (2), the e.s.r. spectra after addition of successive 0.5 mol equiv. of (2) were measured at -78 °C . Upon addition of 0.5 mol equiv. the colour progressed from orange to green with subsequent rapid change to red upon further addition. After 3.5 mol equiv. addition and warming to ca. 20 °C, there resulted a red to orange colour change. Values of $g_{av.}$ were as follows at -78 °C [mol equiv. of (2) in parentheses]: 1.744 (0.5), 1.720 (1.0), 1.750 (1.5), 1.750 (2.0), 1.786 (2.5), 1.782 (3.0), 1.780 (3.5 or 4.0). At 20 °C, the observed $g_{av.}$ was 1.948 for 2.5, 3.0, 3.5, or 4.0 mol equiv. of (2), but for 0.5 mol equiv. of (2), $g_{av.}$ was 1.745.

Crystallography.—Crystal data for complex (7). $\text{C}_{27}\text{H}_{27}\text{W}$, $M = 535.4$, trigonal, space group $R\bar{3} (C_{3i}, \text{no. } 148)$, $a = 10.125(2) \text{ \AA}$, $\alpha = 91.65(2)^\circ$, $U = 1036.8(4) \text{ \AA}^3$, $Z = 2$, $D_c = 1.71 \text{ g cm}^{-3}$, $F(000) = 526$. Specimen: hexagonal plate, $0.22 \times 0.22 \times 0.084 \text{ mm}$ enclosed in capillary; $\mu_{\text{Mo}} = 54 \text{ cm}^{-1}$.

Crystal data for complex (8). $\text{C}_{48}\text{H}_{64}\text{MgO}_6\text{W}_2$, $M = 1129.1$, orthorhombic, space group $Pbca (D_{2h}^{15}, \text{no. } 61)$, $a = 18.061(5)$, $b = 16.759(5)$, $c = 15.637(5) \text{ \AA}$, $U = 4733(2) \text{ \AA}^3$, $Z = 4$, $D_c = 1.58 \text{ g cm}^{-3}$, $F(000) = 2240$. Specimen size: $0.28 \times 0.22 \times 0.14 \text{ mm}$, enclosed in capillary; $\mu_{\text{Mo}} = 52 \text{ cm}^{-1}$.

Structure determinations. Unique data sets were measured within the limits $2\theta_{\text{max.}} = 50^\circ$ for complex (7), or $2\theta = 50^\circ$ (later truncated at $2\theta = 40^\circ$) for complex (8), using a Syntex P1 four-circle diffractometer in conventional $2\theta/\theta$ scan mode; T was 295 K and monochromatic Mo- K_α radiation ($\lambda = 0.7106 \text{ \AA}$) was used. For complex (7), 1244 independent reflections were measured, for (8) 2216; of these 952 (7) or 1102 (8), with $I > 3\sigma(I)$ were considered 'observed' and used in the structure solution and refinement after absorption correction. Structures were solved by the heavy-atom method and refined by full-matrix least squares [for (7)], or block-diagonal (9×9) least squares [for (8)], with anisotropic thermal parameters for the non-hydrogen atoms. For complex (7), hydrogen atoms were located in difference maps and improved to trigonal positions (aromatic) and tetrahedral positions (α) and constrained in the refinement with $U = 1.25\langle U_{\text{H}}(\text{parent C}) \rangle$. For complex (8), the *o*-xylenediyl hydrogen atoms were treated similarly; however, the tetrahydrofuran situation was ambiguous. As a result of disorder or the use of a space group of unrealistically high symmetry, the thf molecules were found to be disposed over two sets of sites with seemingly equivalent populations. Carbon atom thermal parameters of these (and also those of the *o*-xylenediyl ligand α -carbons) were refined isotropically and the thf carbon populations were set at 0.5. Residuals at convergence were (R, R') 0.046, 0.051 for complex (7), and 0.047, 0.050 for complex (8), reflection weights being set at $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral-atom scattering factors were used throughout, Mg^{2+} excepted, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'').⁴ Calculation was carried out using a local variant of the X-RAY 76 program system implemented on a CYBER 73 computer by S. R. Hall.⁴⁶

Atom numbering in the *o*- $\text{C}_6\text{H}_4(\text{CH}_2)_2$ moieties is as shown in (17); disordered components of the tetrahydrofuran molecules are primed. Hydrogen-atom labelling follows that of the parent carbon; where more than one is concerned, these are designated A,B. Note that in a footnote in ref. 9 the formula of complex (7) was erroneously given as the mono- rather than the hemi-benzene solvate.

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