Synthesis and X-Ray Crystal Structure of a W^V Metallocycle

[{$\overline{W(CH_2C_6H_4CH_2\text{-}o)_2O}$}$_2$Mg(tetrahydrofuran)$_4$]

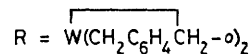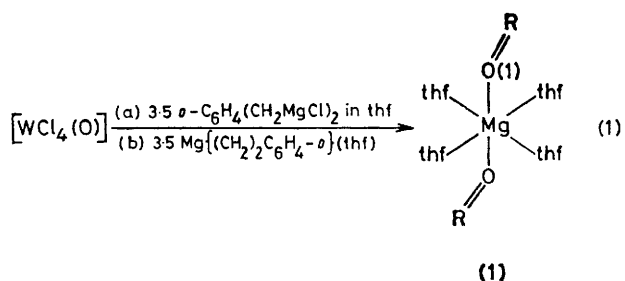By Michael F. Lappert* and Colin L. Raston

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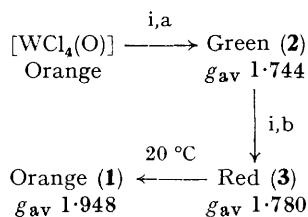
Summary Reaction of [WCl$_4$(O)] with either o-C$_6$H$_4$(CH$_2$MgCl)$_2$ or Mg{(CH$_2$)$_2$C$_6$H$_4$-o}(thf) in tetrahydrofuran (thf) gives the W^V complex [{$\overline{W(CH_2C_6H_4CH_2\text{-}o)_2O}$}$_2$Mg(thf)$_4$], (1) *via* W^V oxochloride intermediates; single crystal *X*-ray diffraction of the complex (1) shows that one of the o-xylidene chelating ligands has a large fold angle (66·1°, *cf.* 42·4° for the other) possibly owing to an aromatic π-interaction with the tungsten atom.

We report (i) two methods for the synthesis of the W^V metallocycle (1) equation (1); (ii) e.s.r. spectroscopic data on its mode of formation from [WCl$_4$(O)] and the di-Grignard reagent[1] o-C$_6$H$_4$(CH$_2$MgCl)$_2$ in tetrahydrofuran (thf), which indicate two d^1 W^V intermediates [see (2) and (3) in the Scheme] and demonstrate that reduction precedes alkylation; and (iii) the molecular structure of complex (1) (see the Figure), which shows *inter alia* that one of the bidentate ligands attached to W differs from the other (the 'fold angles' being 42·4 and 66·1°, respectively) probably to enable some π-interaction to occur between one of the ligands and the metal. As to (i), compound (1) is the first

[WCl$_4$(O)] $\xrightarrow[\text{(b) 3·5 Mg\{(CH}_2\text{)}_2\text{C}_6\text{H}_4\text{-}o\}(thf)}]{\text{(a) 3·5 } o\text{-C}_6\text{H}_4\text{(CH}_2\text{MgCl)}_2\text{ in thf}}$

(1)

(1)

R = $\overline{W(CH_2C_6H_4CH_2\text{-}o)_2}$

stable W^V organometallic compound {other than π-complexes such as[2] [W(η-C$_5$H$_5$)$_2$Cl$_2$]$^+$} and is a rare example of a d^1 metallocycle {the others are [V(η-C$_5$H$_5$)$_2$(LL)] [LL = 2,2′-(C$_6$H$_4$)$_2$, 2,2′-(C$_6$F$_4$)$_2$, or 1,4-C$_4$Ph$_4$],[3] [Nb(η-C$_5$H$_5$)$_2$-{C(CF$_3$)}$_4$][4] and [Nb(η-C$_5$H$_4$SiMe$_3$)$_2$(CH$_2$C$_6$H$_4$CH$_2$-o)], (4)[5]}, and its preparation is a further illustration that the o-

xylidene ligand, $o\text{-}C_6H_4(CH_2^-)_2$, is capable of stabilising high metal-oxidation states [cf., the Ti^{IV}, Zr^{IV}, or Hf^{IV} d° analogues[1] of complex (4)]. A tungsten(VI) oxo-alkyl [$W(CH_2\text{-}CMe_3)_4(O)$] has recently been reported.[6]

$$o\text{-}C_6H_4(CH_2MgCl)_2 \longrightarrow 2e^- + 2Mg^{2+} + 2Cl^- + \text{(structure)} \quad (2)$$

(5)

SCHEME.

[$WCl_4(O)$] $\xrightarrow{\text{i,a}}$ Green (2)
Orange g_{av} 1·744

            $\downarrow$ i,b

      20 °C
Orange (1) $\longleftarrow$ Red (3)
g_{av} 1·948 g_{av} 1·780

SCHEME. Titration of [$WCl_4(O)$] in thf against ca. 0·075 M $o\text{-}C_6H_4(CH_2MgCl)_2$ in thf at -78 to $+20$ °C: i, thf, -78 °C, $o\text{-}C_6H_4(CH_2MgCl)_2$: a, 0·5 equiv.; b, 3·5 equiv.

The progressive addition of the di-Grignard reagent (ca. 0·075 M in thf) to [$WCl_4(O)$], equation (1a), may be monitored both by the obvious colour and simultaneous e.s.r. spectral changes (see the Scheme). The end product, complex (1), is obtained as an orange solution in thf or as red crystals, which crumble in vacuo to a red powder of composition {$W(CH_2C_6H_4CH_2\text{-}o)_2O$}$_2$Mg(thf)$_3$ {35% based on [$WCl_4(O)$]}. From the g_{av} values it appears that the first-formed products of reaction (1a) are, successively, the species (2) and (3), which are essentially mixed oxochlorides of W^V, because g_{av} for [$WCl_5(O)$]$^{2-}$ in aq. HCl was reported to be 1·773.[7] The initial $W^{VI} \to W^V$ reduction, whether by reaction (1a) or 1(b), may be concomitant with an intramolecular electron-transfer process in the magnesium reagent, shown in equation (2) for the former case. Thus,
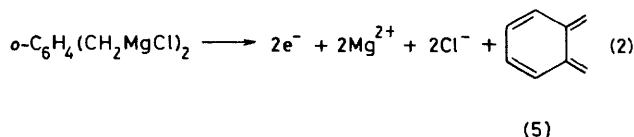
the o-xylidene ligand may have a similar propensity for oxidation to a quinonoid form [in this case the unstable hydrocarbon (5) which polymerises to $(C_8H_8)_n$ [8]] as the isoelectronic catecholate dianion.[9] Consistent with the e.s.r. data, the stoicheiometry of equation (2), and the Scheme, species (2) may be formulated either as [$WCl_4(O)$]$^-$ or [$WCl_5(O)$]$^{2-}$.

The electrical conductivity of complex (1) in thf supports the proposed structure rather than the alternative ionic formulation [$Mg(thf)_4$][$W(CH_2C_6H_4CH_2\text{-}o)_2(O)$]$_2$. The i.r. spectrum shows bands at ν 1032(s), 1023(sh), and 1013(s) cm^{-1}, probably due to ν (W=O) and ν_{asym} (COC) of coordinated thf. The solid complex (1) has g 1·943. It may be recrystallised from thf–PhMe, but in many non-halogenated solvents other than thf it decomposes to give a yellow-orange crystalline complex (currently under investigation).

The tungsten environment in complex (1) is square pyramidal (Figure) with the oxygen occupying the apical position at 1·71(1) Å, typical of strong π-bonding {cf. l(W–O$_{terminal}$) 1·72 Å in $Ba[W^V_2O_4(C_{10}H_{12}N_2O_8)].3H_2O^{10}$}. Two bidentate o-xylidene ligands ('a' and 'b') span the basal-plane positions with one ligand 'folded' towards the oxygen atom while the other is directed away. The fold angle, defined as the angle between the ligand plane and the WC$_2$ plane, for ligand 'a' appears to be 'normal' (42·4°) as the W–C–C angles are close to tetrahedral values. However, for
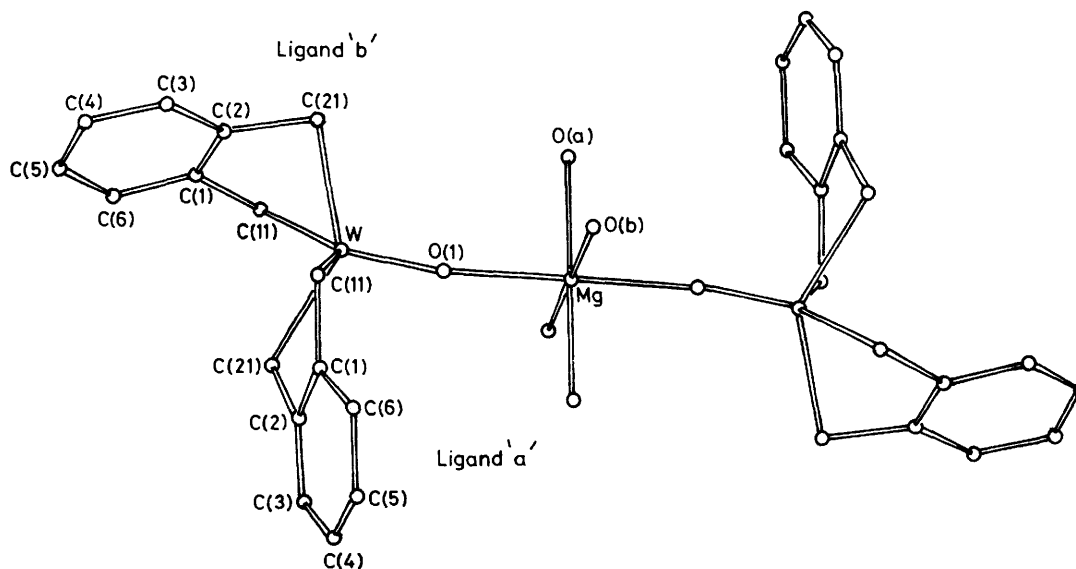

FIGURE. Molecular structure of [{$W(CH_2C_6H_4CH_2\text{-}o)_2O$}$_2$Mg (thf)$_4$], (1); for clarity the disordered carbon atoms of the thf ligands are not shown. Unique distances and angles defining the magnesium environment are Mg–O(1) 2·07(1), Mg–O(a) 2·11(1), Mg–O(b) 2·09(1) Å; O(1)–Mg–O(a) 88·9(5), O(1)–Mg–O(b) 90·4(6), O(a)–Mg–O(b) 88·7(6)°. Similarly for the tungsten environment, W–O(1) 1·71(1), W–C(11a) 2·16(2), W–C(21a) 2·16(2), W–C(11b) 2·14(2), W–C(21b) 2·18(2) Å; C(11a)–W–C(21a) 75·3(9), C(11b)–W–C(21b) 75·8(9), C(11a)–W–C(11b) 85·6(8), C(21a)–W–C(21b) 86·3(9), C(11)–W–C(11) 130·1(9), C(21)–W–C(21) 135·8(9), O(1)–W–C(11a) 112·3(7), O(1)–W–C(11b) 117·6(8), O(1)–W–C(21a) 109·8(7), O(1)–W–C(21b) 114·4(8)°.

ligand 'b' the fold angle (66·1°) and the reduced W–C–C angles, together with the short W- - - - -C(11) and C(21) distances [2·74(2) and 2·71(2) Å; *cf.* 3·01(2) and 3·02(2) Å for 'a'] suggest some π-interaction between the aromatic ring and the metal. The angle subtended by the oxygen bridging the tungsten and magnesium centres is 170·4(8)°. The magnesium atom is in an approximately octahedral environment.

Crystal data: $C_{48}H_{64}MgO_6W_2$, $M = 1129\cdot1$, orthorhombic, space group *Pbca*, $a = 18\cdot061(5)$, $b = 16\cdot759(5)$, $c = 15\cdot637(5)$ Å, $U = 4733(2)$ Å^3, $Z = 4$, $D_c = 1\cdot58$ g cm^{-3}, $\mu(\text{Mo–}K_\alpha) = 66\cdot1$ cm^{-1}, $F(000) = 2240$, $\lambda(\text{Mo–}K_\alpha) = 0\cdot71069$ Å, specimen size: $0\cdot28 \times 0\cdot22 \times 0\cdot14$ mm, $T = 295(1)$ K. The crystal structure was solved from 1102 'observed' reflections after absorption corrections and refined to $R = 0\cdot047$, $R' = 0\cdot050$.†

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