A Metallotricycle: Synthesis, One-electron Reduction, and Crystal Structure of the Thermally Robust Complex Tris-*o*-xylidenetungsten(VI), $[W(CH_2C_6H_4CH_2\text{-}o)_3]$

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Summary Reaction of $[WCl_4(O)]$ with excess of the di-Grignard reagent $o\text{-}C_6H_4(CH_2MgCl)_2$ in tetrahydrofuran (thf) yields $[W(CH_2C_6H_4CH_2\text{-}o)_3]$ (**1**), a thermally robust, reversible one-electron-reducible complex, of *quasi* $3/m$ symmetry with the *o*-xylidene ligand planes aligned parallel to the molecular axis and unusually folded, with significant, and possibly stabilising, W–π interactions, as shown by its *X*-ray structure determination, the mean $W\text{–}C_\alpha H_2$ and $W\text{–}C_\beta$ distances being 2·21 and 2·48 Å respectively.

METALLOBENZOCYCLOPENTENES are now accessible *via* transmetallation involving the di-Grignard reagent $o\text{-}C_6H_4(CH_2MgCl)_2$.[1] In a previous communication we reported the synthesis and structure of the W^V metallocycle $[\{W(CH_2C_6H_4CH_2\text{-}o)_2O\}_2Mg(thf)_4]$ (**2**) (thf = tetrahydrofuran), derived from such a reaction with $[WCl_4(O)]$.[2] By varying the reaction conditions successful synthesis of the elusive metallotricycle (**1**) has now been achieved; the current method for obtaining the optimum yield of (**1**) or (**2**) is shown in the Scheme. The W^{VI} complex (**1**) may originate from disproportionation of a W^V intermediate, since reduction of $[WCl_4(O)]$ to a W^V oxychloride precedes alkylation.[2]

$$\begin{tikzcd}
{[WCl_4(O)]} \arrow[r, "i"] \arrow[ddr, "ii"] & {[\{W(CH_2C_6H_4CH_2\text{-}o)_2O\}_2Mg(thf)_4]} \\
 & \text{(2)} \quad \text{red} \\
{[W(CH_2C_6H_4CH_2\text{-}o)_3]^-} \arrow[r, shift left, "iii"] & {[W(CH_2C_6H_4CH_2\text{-}o)_3]} \arrow[l, shift left, "iv"] \\
 & \text{(1)} \quad \text{orange}
\end{tikzcd}$$

SCHEME. *Reagents and conditions:* i, 3·3 equiv. $o\text{-}C_6H_4(CH_2MgCl)_2$, thf, −78 °C, then <20 °C, 35% yield; ii, >3·5 equiv. $o\text{-}C_6H_4(CH_2MgCl)_2$, thf, −78 °C, then up to 50 °C, 35% yield; iii, $Na[C_{10}H_8]$–thf, 20 °C or iv; iv, cyclic voltammetry in 0·2 M $[NBu^n_4][BF_4]$ in thf at a Pt electrode.

Noteworthy aspects of compound (**1**) are (i) the demonstration that the *o*-xylidene ligand can stabilise a high formal metal oxidation state, +6 in this instance, (ii) its thermal stability, (iii) its ability to undergo one-electron reversible reduction, and (iv) the folding of the *o*-xylidene ligands to approach an *o*-quinodimethide–metal bonding mode (**3a**) which is rigid on the ^1H n.m.r. time scale.† The compound is only the second homoleptic W^{VI} metal alkyl (the other being $[WMe_6]$[3]) and it establishes a new class of organometallic compound, the metallotricycle.

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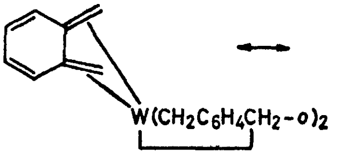
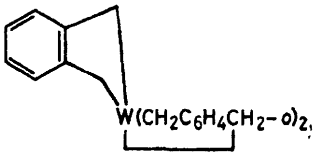
† The ^1H n.m.r. spectrum for complex (**1**) (which gives satisfactory microanalyses) shows an AB pattern for the methylene protons with no coalescence up to 120 °C (C_6D_6); signals at τ 10·39 (d, CH_2), 7·51 (d, J_{HH} 7·3 Hz, CH_2), and 3·03 (m, 2H), and 2·69 (m, 2H) (C_6H_4).



(3a)



(3b)

Compared with $[WMe_6]$, complex (**1**) is surprisingly thermally robust, being sublimable at 160 °C and 10^{-2} Torr with minimal decomposition (and yielding a parent molecular ion in the mass spectrum) whereas $[WMe_6]$ decomposes slowly at −35 °C.[3] This enhanced stability may be an artefact of the chelate effect or, more convincingly, a consequence of the folding of the *o*-xylidene ligand to allow significant $W(d^0)$–π interaction [see (**3a**) and the Figure]. [Interactions involving the aromatic π electrons are thought to contribute to the stability of $[M(CH_2Ph)_4]$ (M = Ti, Zr, or Hf).[4]] It also has the effect of co-ordinatively saturating the metal, thus blocking otherwise accessible decomposition pathways. This is not unrealistic since $[WMe_6]$ forms a thermally stable adduct, $Li_2[WMe_8].(dioxan)_2$.[3]

Electrochemical reduction of complex (**1**) is reversible down to 10 mV s^{-1} ($-E_{\frac{1}{2}}^{red}$, 1·68 V *vs.* standard calomel electrode). Reduction using $Na[C_{10}H_8]$ in thf generates a persistent e.s.r. singlet, g_{av} = 2·005 [$a(^1H)$ not observed], supporting the electrochemical reduction product as the d^1 anion of formula (**1**).

The crystal structure‡ of complex (**1**) consists of discrete molecules of $[W(CH_2C_6H_4CH_2\text{-}o)_3]$, the tungsten lying in a site of symmetry 3, the overall molecular symmetry being likewise 3 and a good approximation to point symmetry C_{3h} together with a benzene solvate also lying on the three-fold axis. There is a considerable folding of the ligands, all in the same direction (Figure), when compared with the other structurally characterised *o*-xylidene metallocycles, the W^V complex,[2] $[Zr(CH_2C_6H_4CH_2\text{-}o)(\eta\text{-}C_5H_5)_2]$,[1] and $[Nb(CH_2C_6H_4CH_2\text{-}o)(\eta\text{-}C_5H_4SiMe_3)_2]$;[5] mean W–$C_\alpha$ and W–C_β distances are respectively 2·21 and 2·48 Å, *cf. e.g.*, 2·16(2), 3·01(2) and 2·16(2), 2·73(2) Å for the two independent *o*-xylidene ligands in complex (**2**). This suggests that the W–π interaction in complex (**1**) is more pronounced than in (**2**), previously noted as possibly possessing such an interaction,[2] indicative of a bonding mode somewhere between a metallocycle (**3b**) and a π-η^4-ligand (**3a**). A similar situation has recently been reported in $[Zr(\textit{cis}\text{-}2,3\text{-dimethylbutadiene})(\eta\text{-}C_5H_5)_2]$.[6]

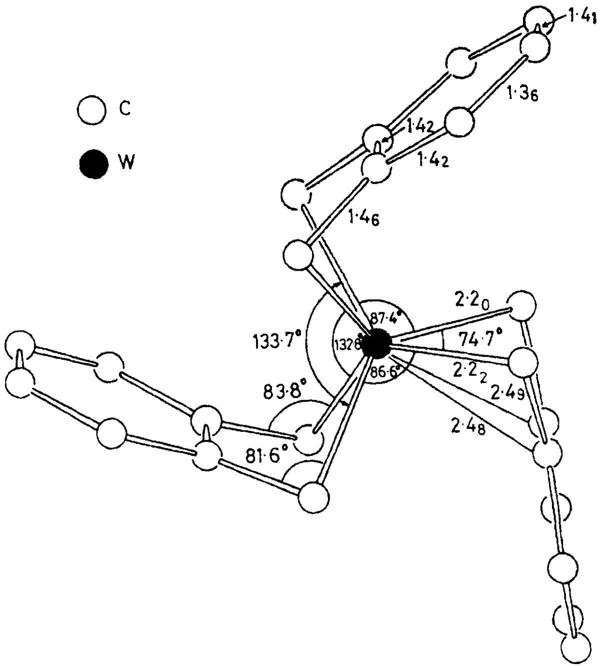


FIGURE. Molecular projection of $[W(CH_2C_6H_4CH_2\text{-}o)_3]$ (**1**), showing important distances (Å) and angles (degrees); the tungsten atom lies on a site of symmetry 3.

We thank the S.R.C. for support.

(*Received, 20th February* 1981; *Com.* 191.)

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‡ *Crystal data:* $C_{24}H_{24}W\cdot C_6H_6$, rhombohedral, space group $R\bar{3}$, a = 10·125(2) Å, α = 91·65(2)°, Z = 2. The structure was determined at room temperature, 295(1) K, from 952 independent 'observed' diffractometer reflections (Mo-K_α radiation). The current R value is 0·046. Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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