Oxidatively induced carbon chain growth at a ditungsten centre

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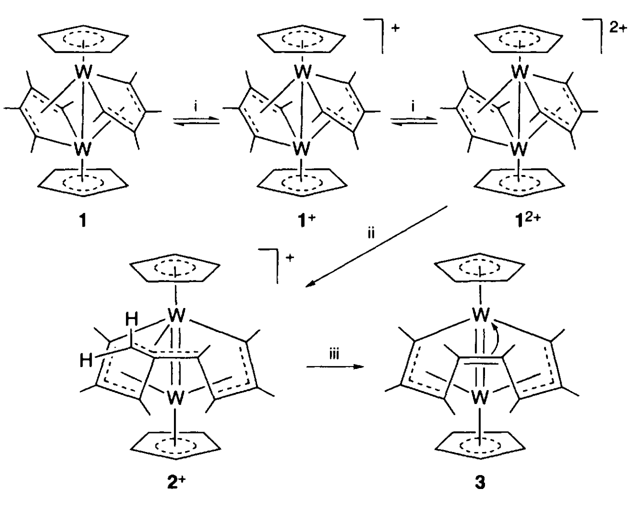
X-Ray structural and EHMO studies show that two electrons are sequentially removed from a W–W δ* orbital on oxidation of the bis(metallacyclopentadiene) complex $[W_2(\mu\text{-}C_4Me_4)_2(\eta\text{-}C_5H_5)_2]$ to $[W_2(\mu\text{-}C_4Me_4)_2(\eta\text{-}C_5H_5)_2]^{z+}$ (z = 1, 2); the dication undergoes C–C coupling and proton loss in boiling MeCN to give $[W_2(\mu\text{-}C_8Me_7CH_2)(\eta\text{-}C_5H_5)_2]^+$ which adds hydride ion to form the metallacyclononatetraene complex $[W_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$.

Recent studies of the mechanism of the reductive oligomerisation of $[Mo(NCMe)(RC{\equiv}CR)_2L]^+$ [R = alkyl, aryl; L = $\eta\text{-}C_5H_5$, $\eta\text{-}C_5Me_5$, $\eta\text{-}C_5HPh_4$, *etc.*] have shown that electron addition is rapidly followed by nitrile loss to give the radical $[Mo(RC{\equiv}CR)_2L]$. For bulky substituents, either on the alkyne or on L, the radical is sufficiently long-lived to be reduced to the monoanion $[Mo(RC{\equiv}CR)_2L]^-$.[1,2] By contrast, $[Mo(MeC{\equiv}CMe)_2(\eta\text{-}C_5H_5)]$ dimerises to give the metallacyclononatetraene complex $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)]$.[3] In order to understand the oligomerisation mechanism more fully, we have studied the reduction of the tungsten complex $[W(NCMe)(MeC{\equiv}CMe)_2(\eta\text{-}C_5H_5)]^+$; dimerisation is observed but the product, the thermally stable bis(metallacyclopentadiene) complex $[W_2(\mu\text{-}C_4Me_4)_2(\eta\text{-}C_5H_5)_2]$, contains pairwise-linked alkynes rather than a C_8 chain.[4] We now show that the C_4 fragments of $[W_2(\mu\text{-}C_4Me_4)_2(\eta\text{-}C_5H_5)_2]$ can be linked to give a metallacyclononatetraene containing a C_8 chain, by a sequence of reactions (Scheme 1) involving double one-electron oxidation to $[W_2(\mu\text{-}C_4Me_4)_2(\eta\text{-}C_5H_5)_2]^{2+}$, thermolysis in boiling MeCN to give $[W_2(\mu\text{-}C_8Me_7CH_2)(\eta\text{-}C_5H_5)_2]^+$, and addition of hydride ion to give $[W_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$. Moreover, we show that oxidation of $[W_2(\mu\text{-}C_4Me_4)_2(\eta\text{-}C_5H_5)_2]$ involves electron loss from a W–W δ* orbital.

The cyclic voltammogram (CV) of **1**, at a platinum electrode in CH_2Cl_2, shows two one-electron oxidation waves, the first fully reversible ($E^{0\prime}$ = −0.60 V *vs.* a saturated calomel electrode; $E^{0\prime}$ = −0.09 V for the couple $[Fe(\eta\text{-}C_5Me_5)_2]^{+1/0}$ as an internal standard). Although the second wave [$(E_p)_{ox}$ = 0.49 V] appears irreversible (at a scan rate of 200 mV s^{-1}) chemical studies of the oxidation of **1** show this behaviour to result from the insolubility of the dication $[W_2(\mu\text{-}C_4Me_4)_2(\eta\text{-}C_5H_5)_2]^{2+}$ (as the $[PF_6]^-$ salt) rather than its chemical reactivity. Thus, treatment of **1** with 1 equiv. of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in CH_2Cl_2 gave a good yield of the green paramagnetic cation ($\mathbf{1}^+$), and reaction with 2 equiv. of the same oxidant gave a blue–green precipitate of the dication ($\mathbf{1}^{2+}$) (both were isolated as salts of the $[PF_6]^-$ anion).†



Scheme 1 *Reagents and conditions*: i, $[Fe(C_5H_5)_2]PF_6$, ii, MeCN under reflux; iii, $NaBH_4$

X-Ray analyses‡ of $[\mathbf{1}^+]PF_6$ and $[\mathbf{1}^{2+}][PF_6]_2{\cdot}2MeCN$ show that the three members of the redox series $[W_2(\mu\text{-}C_4Me_4)_2(\eta\text{-}C_5H_5)]^{z+}$ (z = 0,[4] 1, 2) have virtually identical molecular structures. That of $\mathbf{1}^{2+}$ is shown in Fig. 1 together with important bond lengths for $\mathbf{1}^+$ and $\mathbf{1}^{2+}$. The observation of minimal structural change on sequential removal of two electrons from the HOMO of **1** is consistent with electron loss from an orbital which is essentially nonbonding. Notably, the W–W bond is slightly lengthened, by 0.025 and then 0.043 Å on oxidation, while the formal W–W bond order rises from one in 34-electron **1** to two in 32-electron $\mathbf{1}^{2+}$. The nature of the HOMO in **1** is confirmed by EHMO studies which show it has W–W δ* character; each tungsten orbital component lies close to its respective WC_4Me_4 plane (Fig. 2), thereby giving the HOMO near-nonbonding character with respect to W–ligand interactions.

Although $[\mathbf{1}^{2+}][PF_6]_2$ is air-stable in the solid state, the dication undergoes thermolysis in boiling MeCN, and red–purple crystals of $[\mathbf{2}^+]PF_6$ are isolated from the resulting solution. The ^1H NMR spectrum of $\mathbf{2}^+$ shows two cyclopenta-

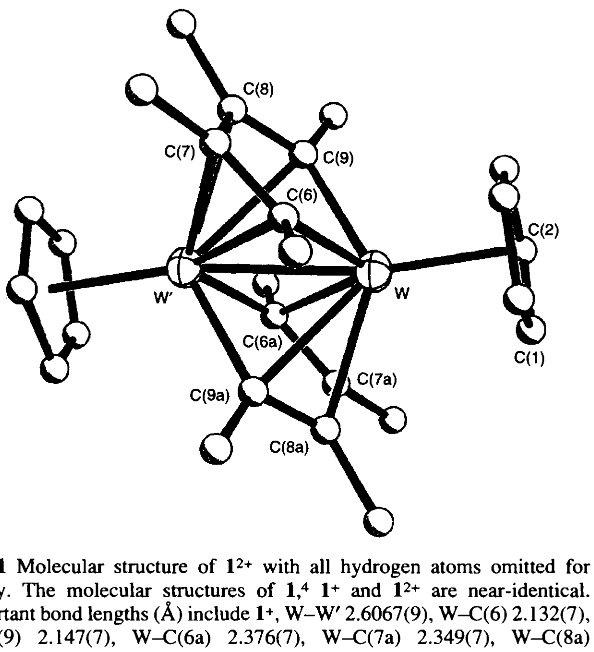


Fig. 1 Molecular structure of $\mathbf{1}^{2+}$ with all hydrogen atoms omitted for clarity. The molecular structures of **1**,[4] $\mathbf{1}^+$ and $\mathbf{1}^{2+}$ are near-identical. Important bond lengths (Å) include $\mathbf{1}^+$, W–W′ 2.6067(9), W–C(6) 2.132(7), W–C(9) 2.147(7), W–C(6a) 2.376(7), W–C(7a) 2.349(7), W–C(8a) 2.375(7), W–C(9a) 2.382(8); $\mathbf{1}^{2+}$, W–W′ 2.6500(14), W–C(6) 2.137(8), W–C(9) 2.126(8), W–C(6a) 2.427(8), W–C(7a) 2.367(8), W–C(8a) 2.365(8), W–C(9a) 2.407(8).

dienyl and seven methyl singlet resonances together with two doublet resonances which may be assigned to the two inequivalent protons of an unsymmetrical methylene group. In the absence of further spectroscopic data an X-ray structural analysis of $\mathbf{2}^{+}$, as its $[BPh_4]^-$ salt, was carried out.

The X-ray analysis‡ shows $\mathbf{2}^{+}$ to be isostructural with $[Mo_2(\mu\text{-}C_8Me_7CH_2)(\eta\text{-}C_5H_5)_2]^{+}$,[5] as illustrated in Fig. 3, in which there is the C_8 chain structure observed in $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$. The $C_8Me_7CH_2$ ligand in $\mathbf{2}^{+}$ binds to the W_2 moiety through one η^3-allyl [C(4,5,12)] and two μ-allylidene [C(1–3) and C(6–8)] functions. It is not known whether the C_8 chain present in $\mathbf{2}^{+}$ is formed from the two C_4 fragments in $\mathbf{1}^{2+}$ by C–C coupling before or after proton loss. However, the former seems more likely given that the molybdenum analogue $[Mo_2(\mu\text{-}C_8Me_7CH_2)(\eta\text{-}C_5H_5)_2]^{+}$ is formed by proton loss from $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]^{2+}$ (after double one-electron oxidation of $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$).[5,6]

On treatment with $Na[BH_4]$, $\mathbf{2}^{+}$ undergoes hydride addition to give $[W_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$ **3**† which is formulated as a metallacyclononatetraene complex on the basis of elemental analysis, mass spectrometry, and the close similarity of its ^1H NMR spectrum with that of $[Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2]$.[3] The isolation of **3** therefore completes a sequence of reactions in which the two alkyne ligands of $[W(NCMe)(MeC{\equiv}CMe)_2(\eta\text{-}C_5H_5)]^{+}$ are linked by reduction, to give **1**, and then further linked *via* oxidation, thermal C–C coupling to give $\mathbf{2}^{+}$, and hydride addition to give the final metallacyclononatetraene product **3**.

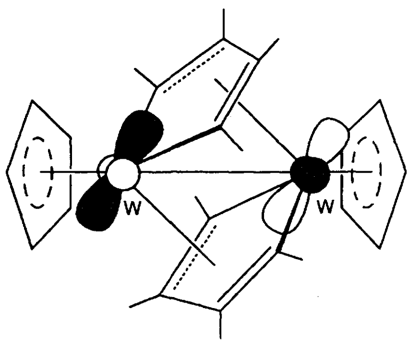


Fig. 2 The HOMO of **1**: the W···W δ* orbital depopulated on formation of $\mathbf{1}^{+}$ and $\mathbf{1}^{2+}$ from **1**

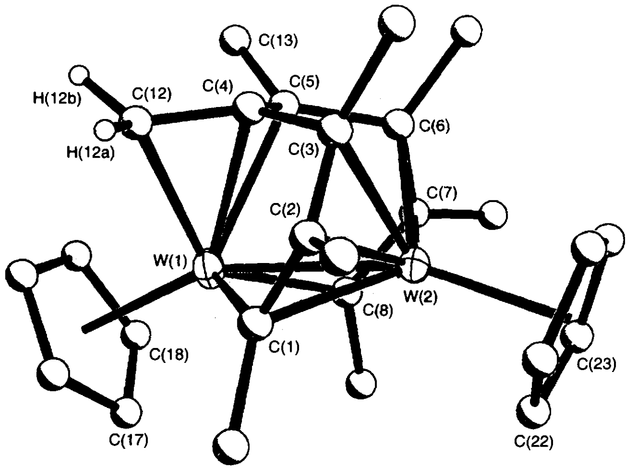


Fig. 3 Molecular structure of $\mathbf{2}^{+}$ with methyl and cyclopentadienyl hydrogen atoms omitted for clarity. Important bond lengths (Å) include: W(1)–W(2) 2.6648(3), W(1)–C(1) 2.101(5), W(1)–C(4) 2.296(5), W(1)–C(5) 2.324(5), W(1)–C(8) 2.136(5), W(1)–C(12) 2.362(6), W(2)–C(1) 2.265(5), W(2)–C(2) 2.314(5), W(2)–C(3) 2.238(5), W(2)–C(6) 2.322(5), W(2)–C(7) 2.351(5), W(2)–C(8) 2.218(5), C(4)–C(12) 1.374(8).

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Footnotes

† All new complexes gave satisfactory elemental analyses (C and H). $[\mathbf{1}^{+}]PF_6$. Green crystals, yield 53%. EPR (CH_2Cl_2–thf, 2 : 1); 200 K, $g_{iso} = 2.037$; 77 K, $g_1 = 2.095$, $g_2 = 2.027$, $g_3 = 1.991$, $g_{av} = 2.038$.

$[\mathbf{1}^{2+}][PF_6]_2$. Dark blue–green crystals, yield 77%. ^1H NMR (CD_3NO_2): δ 6.71 (s, 10 H, C_5H_5), 2.89 (s, 12 H, Me), 2.11 (s, 12 H, Me).

$[\mathbf{2}^{+}]PF_6$. Red–purple crystals, yield 46%. ^1H NMR (CD_2Cl_2): δ 5.89 (s, 5 H, C_5H_5), 4.68 (s, 5 H, C_5H_5), 2.88 (s, 3 H, Me), 2.81 (s, 3 H, Me), 2.76 (s, 3 H, Me), 2.57 (s, 3 H, Me), 2.42 (s, 3 H, Me), 1.97 (s, 3 H, Me), 1.17 (s, 3 H, Me), 0.82 [d, $J(^1H^1H)$ 1.5 Hz, 1 H, CH_2], −0.40 [d, $J(^1H^1H)$ 1.5 Hz, 1 H, CH_2]. MS (FAB): *m/z* 713.

3. Purple crystals, yield 61%. ^1H NMR (C_6D_6): δ 5.23 (s, 5 H, C_5H_5), 3.95 (s, 5 H, C_5H_5), 2.43 (s, 6 H, Me), 2.40 (s, 6 H, Me), 2.08 (s, 6 H, Me), 1.40 (s, 6 H, Me). MS (FAB): *m/z* 714.

‡ *Crystal data*: $[W_2(\mu\text{-}C_4Me_4)_2(\eta\text{-}C_5H_5)_2][PF_6]$, $[\mathbf{1}^{+}][PF_6^{-}]$: $C_{26}H_{34}F_6PW_2$, $M = 859.20$, monoclinic, space group $P2_1/n$ (no. 14), $a = 8.628(3)$, $b = 10.183(4)$, $c = 14.597$ Å, $\beta = 100.89(3)°$, $U = 1259.4(8)$ Å^3, $Z = 2$, $D_c = 2.266$ Mg m^{-3}, $\bar{\lambda} = 0.71073$ Å, $\mu = 9.25$ mm^{-1}, $F(000) = 814$, $T = 200$ K. Data were collected on a Siemens R3m/V diffractometer for $1.5 < \theta < 25.0°$. The structure was solved by direct and Fourier methods and refined by least squares against F^2 to $R1$ 0.0292 ($wR2 = 0.0609$) for 1833 unique intensity data with $I > 2\sigma(I)$ corrected for absorption.

For $[W_2(\mu\text{-}C_4Me_4)_2(\eta\text{-}C_5H_5)_2][PF_6]_2\cdot 2MeCN$, $[\mathbf{1}^{2+}][PF_6^{-}]_2\cdot 2MeCN$: $C_{30}H_{40}F_{12}N_2P_2W_2$, $M = 1086.2$, triclinic, space group $P\bar{1}$ (no.2), $a = 9.578(2)$, $b = 9.775(2)$, $c = 10.603(2)$ Å, $\alpha = 94.43(3)$, $\beta = 106.28(3)$, $\gamma = 107.02(3)°$, $U = 897.4(3)$ Å^3, $Z = 1$, $D_c = 2.010$ Mg m^{-3}, $\bar{\lambda} = 0.71073$ Å, $\mu = 6.58$ mm^{-1}, $F(000) = 520$, $T = 293(2)$ K. Data were collected on a Siemens SMART diffractometer for $2.0 < \theta < 23.25°$. The structure was solved by Patterson and Fourier methods and refined by least squares against F^2 to $R1$ 0.0450 ($wR2 = 0.1266$) for 2439 unique observed intensity data with $I > 2\sigma(I)$ corrected for absorption.

For $[W_2(\mu\text{-}C_8Me_7CH_2)(\eta\text{-}C_5H_5)_2][BPh_4]$. $[\mathbf{2}^{+}][BPh_4^{-}]$: $C_{50}H_{53}BW_2$, $M = 1032.43$, monoclinic, space group $P2_1/n$ (no. 14), $a = 14.547(3)$, $b = 18.761(2)$, $c = 14.642(3)$ Å, $\beta = 103.308(11)°$, $U = 3888.8(1)$ Å^3, $Z = 4$, $D_c = 1.763$ Mg m^{-3}, $\bar{\lambda} = 0.71073$ Å, $\mu = 5.947$ mm^{-1}, $F(000) = 2024$, $T = 173(2)$ K. Data were collected on a Siemens SMART diffractometer for $2.0 < \theta < 25.0°$. The structure was solved by direct and Fourier methods and refined by least squares against F^2 to $R1$ 0.0301 ($wR2 = 0.0771$) for 6288 unique observed intensity data with $I > 2\sigma(I)$ corrected for absorption.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/159.

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