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The d^2/d^3 alkyne redox pair $[WF_2(PhC\equiv CPh)Tp']^z$ (z = +1 or 0): missing links in a 'redox family tree'

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The d^2/d^3 redox pair $[WF_2(PhC\equiv CPh)Tp']^z$ [z = +1 or 0, Tp′ = hydrotris(3,5-dimethylpyrazolyl)borate] is the missing link in a 'redox family tree' relating the d^6 tricarbonyls $[M(CO)_3L]^-$ to the d^2 trihalides $[MX_3L]$ (M = Mo or W, L = Cp or Tp′) by a series of stepwise reactions involving sequential one-electron oxidation followed by ligand substitution.

We have recently reported the synthesis of three related redox pairs, namely $[Cr(CO)_2(\eta\text{-}PhC\equiv CPh)(\eta\text{-}C_6Me_6)]^z$ (z = 0, d^6; z = 1, d^5), $[Mo(CO)_2(\eta\text{-}PhC\equiv CPh)Tp']^z$ (z = 0, d^5; z = 1, d^4)[1] and $[WX(CO)(MeC\equiv CMe)Tp']^z$ (X = F, Cl, Br and I; z = 0, d^4; z = 1, d^3)[2] the structural characterisation of which has shed light on the redox-induced interconversion of two-, three- and four-electron alkyne ligands. In the case of $[WX(CO)(MeC\equiv CMe)Tp']$ the cyclic voltammogram (CV) showed not only the formation of the monocation $[WX(CO)(MeC\equiv CMe)Tp']^+$ but also a second, irreversible, oxidation wave implying the formation of the reactive dication $[WX(CO)(MeC\equiv CMe)Tp']^{2+}$. We now show that two-electron oxidation of $[WF(CO)(RC\equiv CR)Tp']$ (R = Me or Ph) leads to the stable d^2 complex $[WF_2(PhC\equiv CPh)Tp']^+$ which is reduced to paramagnetic, d^3 $[WF_2(PhC\equiv CPh)Tp']$. This d^2/d^3 redox pair is the missing link in a 'redox family tree' which relates the d^6 tricarbonyls $[M(CO)_3L]^-$ (M = Mo or W, L = Cp or Tp′) to the d^2 trihalides $[MX_3L]$ by a series of EC (electrochemical/chemical) reactions. Moreover, we show that such family trees allow the prediction of synthetic routes to hitherto unknown redox-active alkyne complexes.

Treatment of $[WF(CO)(MeC\equiv CMe)Tp']$ with two equivalents of the strong one-electron oxidant $[NO][BF_4]$ in CH_2Cl_2 gave an orange solution from which orange crystals of $[WF_2(MeC\equiv CMe)Tp'][BF_4]$ $\mathbf{1}^+[BF_4]^-$ were isolated. This complex, as well as $[WF_2(PhC\equiv CPh)Tp'][BF_4]$ $\mathbf{2}^+[BF_4]^-$, can also be prepared by reacting $[WF(CO)(RC\equiv CR)Tp']$ with *N*-fluoropyridinium tetrafluoroborate, effectively a source of F^+. Complexes $\mathbf{1}^+[BF_4]^-$ and $\mathbf{2}^+[BF_4]^-$ were characterised† by elemental analysis and by the observation of parent ions (for the cations) in the FAB mass spectra. Each cation shows one resonance in the ^{19}F NMR spectrum [(in CD_2Cl_2): R = Me, δ 178.6 ppm, $J(^{183}W^{19}F)$ 45 Hz; R = Ph, δ 166.5 ppm, $J(^{183}W^{19}F)$ 45 Hz] and four peaks for the methyl groups of the pyrazolyl rings in the ^1H spectrum, consistent with the X-ray structure of $[WF_2(PhC\equiv CPh)Tp'][BF_4]$ $\mathbf{2}^+[BF_4]^-$ (Fig. 1).‡ The four-electron alkyne effectively bisects the WF_2 group {dihedral angles F(1)–W(1)–C(16)–C(17) 59.7, F(2)–W(1)–C(16)–C(17) 50.5°} thereby rendering the two fluorine atoms essentially equivalent; the same alkyne orientation is observed for the isoelectronic complex $[NbCl_2(PhC\equiv CMe)Tp']$.[3]

The CV of $[WF_2(RC\equiv CR)Tp']^+$ shows a reversible one-electron reduction wave ($E^{o\prime}$ = −0.11 V, R = Me; $E^{o\prime}$ = −0.04 V, R = Ph; *vs.* SCE) corresponding to the formation of $[WF_2(RC\equiv CR)Tp']$ (the Ph complex also shows a second, apparently reversible, reduction wave at −1.61 V). Accordingly, the neutral d^3 complex $[WF_2(PhC\equiv CPh)Tp']$ **2** was prepared as dark red crystals by treating a suspension of the salt $[WF_2(PhC\equiv CPh)Tp'][BF_4]$ in toluene with $[CoCp_2]$, removing the precipitate of $[CoCp_2][BF_4]$, evaporating the purple filtrate to dryness, and crystallising the residue using thf–*n*-hexane. The identity of **2** was confirmed by elemental analysis and by cyclic voltammetry which showed a reversible oxidation wave at a potential identical to that for the reduction of $\mathbf{2}^+$.

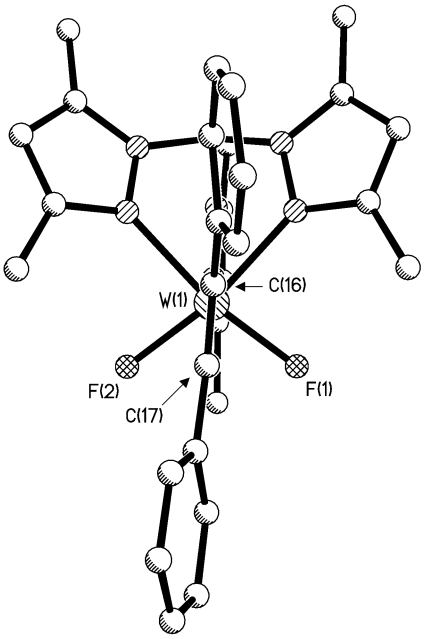

Fig. 1 Structure of the cation of $[WF_2(PhC\equiv CPh)Tp'][BF_4]$ $\mathbf{2}^+[BF_4]^-$ (hydrogen atoms omitted for clarity). Important bond lengths (Å) and angles (°): W–F(1) 1.886(2), W–F(2) 1.894(2), W–C(16) 2.062(4), W–C(17) 2.037(5), C(16)–C(17) 1.340(6); F(1)–W–F(2) 101.6(1).

The room temperature EPR spectrum of $[WF_2(RC\equiv CR)Tp']$ (**1**, R = Me; **2**, R = Ph) shows a single broad line (R = Me, g_{iso} = 1.789; R = Ph, g_{iso} = 1.772). In frozen solution the spectrum is nearly axial (R = Me, g_1 = 1.956, g_2 = 1.771, g_3 = 1.718, g_{av} = 1.815; R = Ph, g_1 = 1.928, g_2 = 1.740, g_3 = 1.685, g_{av} = 1.784) with coupling to *one* fluorine [R = Me, $A_1(^{19}F)$ = 74.0, $A_2(^{19}F)$ = 67.9 G, $A_3(^{19}F)$ (unresolved) (Fig. 2); R = Ph, $A_1(^{19}F)$ = 69.9, $A_2(^{19}F)$ = 71.0, $A_3(^{19}F)$ 50 G] suggesting that the alkyne is more closely aligned with one W–F bond. Such an alignment was confirmed in the solid state by an X-ray structural analysis of **2** (Fig. 3) which showed a very similar

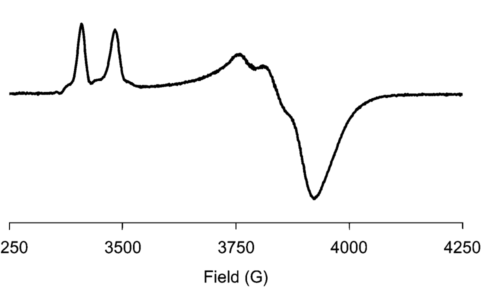

Fig. 2 The frozen solution EPR spectrum of **1** in thf–CH_2Cl_2 (2:1) at 110 K.

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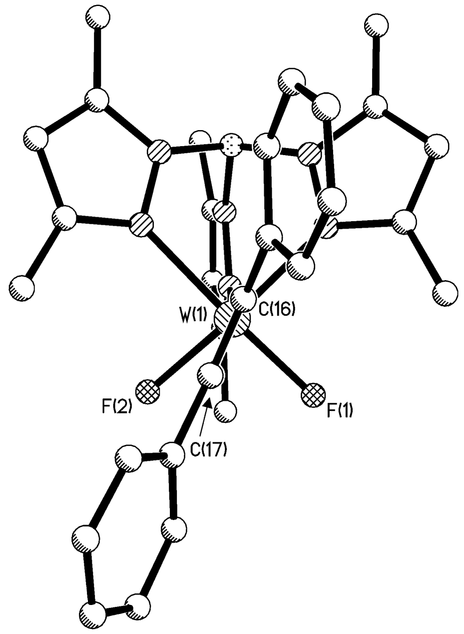
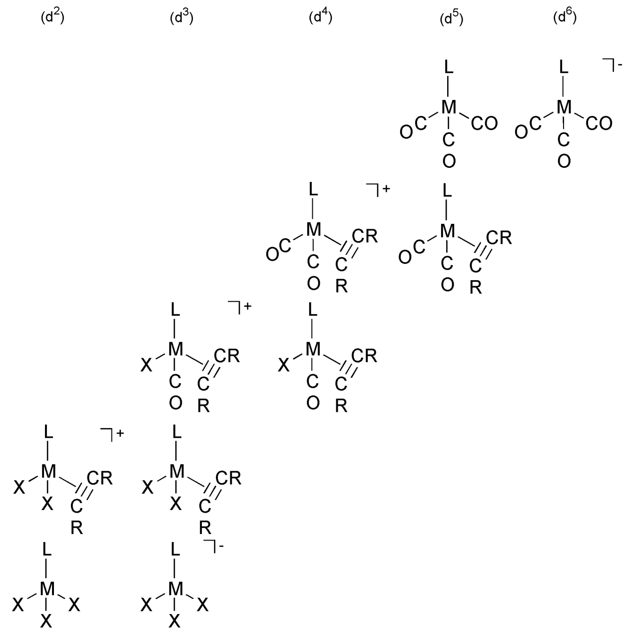


Fig. 3 Structure of [WF_2(PhC≡CPh)Tp′] **2** (hydrogen atoms omitted for clarity). Important bond lengths (Å) and angles (°): W–F(1) 1.940(2), W–F(2) 1.981(2), W–C(16) 2.048(4), W–C(17) 2.025(4), C(16)–C(17) 1.318(6); F(1)–W–F(2) 90.1(1).

structure to that of $\mathbf{2}^+$ but with the alkyne rotated by *ca.* 20° relative to the orientation in $\mathbf{2}^+$ {dihedral angles for **2**: F(1)–W(1)–C(16)–C(17) 73.1, F(2)–W(1)–C(16)–C(17) 27.5°}. The alkyne arrangement in **2** is similar to that observed for d^3 [WX(CO)(MeC≡CMe)Tp′]$^+$ (dihedral angles: X = Cl; OC–W–C_{alkyne}–C_{alkyne} 21.5, Cl–W–C_{alkyne}–C_{alkyne} 73.0°, X = Br; OC–W–C_{alkyne}–C_{alkyne} 22.3, Br–W–C_{alkyne}–C_{alkyne} 70.7°)[2] which, in turn, is rotated by *ca.* 13° away from the arrangement, almost parallel to the W–CO bond, in d^4 [WX(CO)(MeC≡CMe)Tp′] (dihedral angles: X = Cl; OC–W–C_{alkyne}–C_{alkyne} 7.9, Cl–W–C_{alkyne}–C_{alkyne} 88.7°, X = Br; OC–W–C_{alkyne}–C_{alkyne} 6.4, Br–W–C_{alkyne}–C_{alkyne} 88.7°). In marked contrast to **2**, the alkyne bond in isoelectronic [$MoCl_2$(PhC≡CPh)Cp] is aligned parallel to the Cl···Cl vector,[4] most likely reflecting the steric requirements of Tp′ *vs.* Cp. The stability of $\mathbf{1}^+$ and $\mathbf{2}^+$ may also result from the larger size of the Tp′ ligand in that the irreversible oxidation wave observed[4] in the CV of [$MoCl_2$(RC≡CR)Cp] suggests the cyclopentadienyl analogues [$MoCl_2$(RC≡CR)Cp]$^+$ to be unstable.

The redox pair [WF_2(RC≡CR)Tp′]^z (z = +1 or 0) is the missing link in a ‘redox family tree’ (Scheme 1) which relates the d^2 to d^5 alkyne complexes noted above to the d^6 tricarbonyls [$M(CO)_3L$]$^-$ (M = Mo or W, L = Cp or Tp derivative) and the d^2 trihalides [MX_3L],[5] formally by a sequence of steps involving one-electron oxidation followed by ligand substitution. Although not all members of this family tree have been identified for all of M, X and L there is sufficient evidence to suggest that the missing members may be chemically accessible. More important, however, is the observation that similar ‘redox family trees’ may be proposed for metals in adjacent groups of the periodic table, thereby allowing the existence of hitherto unknown alkyne complexes to be predicted. Thus, in agreement with prediction, preliminary CV studies[6] show that [$Re(CO)_2$(PhC≡CPh)Cp][7] and [Re(dppe)(MeC≡CPh)Cp]$^{2+}$[8] undergo two reversible one-electron oxidation and reduction reactions, respectively, the potentials for which suggest the chemical accessibility of other novel paramagnetic alkyne complexes, namely [$Re(CO)_2$(PhC≡CPh)Cp]$^+$ and [Re(dppe)(MeC≡CPh)Cp]$^+$.



Scheme 1 M = Mo or W, L = Cp or Tp′, X = halide, R = alkyl or aryl.

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Notes and references

† All new complexes had satisfactory elemental analyses (C, H and N). Complex [WF_2(MeC≡CMe)Tp′][BF_4] $\mathbf{1}^+$[BF_4]$^-$; orange crystals, yield 35%; ^{1}H NMR (CD_2Cl_2): δ 5.96 (s, 1H, $C_3N_2\mathit{H}Me_2$); 6.10 (s, 2H, $C_3N_2\mathit{H}Me_2$); 3.34 (s, 3H, MeC≡CMe); 4.44 (s, 3H, MeC≡CMe); 1.84 (s, 6H, $C_3N_2H\mathit{Me}_2$); 2.22 (s, 3H, $C_3N_2H\mathit{Me}_2$); 2.37 (s, 3H, $C_3N_2H\mathit{Me}_2$); 2.41 (s, 6H, $C_3N_2H\mathit{Me}_2$). Complex [WF_2(PhC≡CPh)Tp′][BF_4] $\mathbf{2}^+$[BF_4]$^-$; orange-red crystals, yield 64%; ^{1}H NMR (CD_2Cl_2): δ 5.96 (s, 2H, $C_3N_2\mathit{H}Me_2$); 6.04 (s, 1H, $C_3N_2\mathit{H}Me_2$); 1.53 (s, 6H, $C_3N_2H\mathit{Me}_2$); 2.42 (s, 3H, $C_3N_2H\mathit{Me}_2$); 2.44 (s, 3H, $C_3N_2H\mathit{Me}_2$); 2.53 (s, 6H, $C_3N_2H\mathit{Me}_2$); 6.76–8.07 (m, 10H, C_6H_5). Complex [WF_2(PhC≡CPh)Tp′] **2**; dark red crystals, yield 48%.

‡ X-Ray data were collected on a Bruker SMART diffractometer at 173 K for $\theta < 25°$ with λ = 0.71073 Å. The structures were solved by direct methods and refined by least-squares against all F^2 values.*Crystal data*: [WF_2(PhC≡CPh)Tp′][BF_4] $\mathbf{2}^+$[BF_4]$^-$ (from CH_2Cl_2–diethyl ether): $C_{29}H_{32}B_2F_6N_6W$, M = 783.07, monoclinic, space group $P2_1/c$ (no. 14), a = 12.263(2), b = 12.517(2), c = 20.124(3) Å, β = 99.57(1)°, V = 3045.9(7) Å^3, Z = 4, μ = 3.86 mm^{-1}, R_1 = 0.0275.[WF_2(PhC≡CPh)Tp′] **2** (from thf–n-hexane): $C_{29}H_{32}BF_2N_6W$, M = 692.27, monoclinic, space group $P2_1/c$ (no. 14), a = 9.643(2), b = 32.628(7), c = 9.823(2) Å, β = 113.99(1)°, V = 2823.6(9) Å^3, Z = 4, μ = 4.13 mm^{-1}, R_1 = 0.0317.CCDC reference numbers 172824 and 172825. See http://www.rsc.org/suppdata/cc/b1/b109535h/ for crystallographic data in CIF or other electronic format.

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