

Structure and bonding in the d⁴/d³ alkyne redox pairs [WX(CO)(MeC≡CMe)Tp']^z (X = F, Cl, Br and I; z = 0 and 1): halide stabilisation of electron deficient metal alkyne complexes

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X-Ray structural and EPR spectroscopic studies of the redox-related pairs [WX(CO)(MeC≡CMe)Tp']^z (X = F, Cl, Br and I; z = 0 and 1) [Tp' = hydrotris(3,5-dimethylpyrazolyl)borate] are consistent with the HOMO of the d⁴ (z = 0) species being π -bonding with respect to the W–CO bond, π -antibonding with respect to the W–X bond, and δ -bonding with respect to the W–alkyne bond.

We have recently shown¹ that the oxidation of [Cr(CO)₂(η -PhC≡CPh)(η -C₆HMe₅)] (d⁶) to [Cr(CO)₂(η -PhC≡CPh)(η -C₆HMe₅)]⁺[PF₆]⁻ (d⁵), and of [Mo(CO)₂(η -PhC≡CPh)Tp'] (d⁵) to [Mo(CO)₂(η -PhC≡CPh)Tp']⁺[PF₆]⁻ (d⁴) is accompanied by structural changes consistent with stepwise removal of two electrons from the antibonding M–alkyne π _⊥ orbital (of the d⁶ alkyne complex). In this series, the alkyne effectively acts as an electron-sink. We now describe an unexpected and remarkable extension of this work wherein the d⁴ complexes [WX(CO)(MeC≡CMe)Tp'] (X = F, Cl, Br and I) undergo one-electron oxidation affording isolable d³ complexes [WX(CO)(MeC≡CMe)Tp']⁺[BF₄]⁻. The halide both influences the ease of oxidation and allows stabilisation of the resulting electron deficient d³ metal alkyne complexes.

Treatment of [W(CO)₂(MeC≡CMe)Tp']⁺[BF₄]⁻ with [NBu₄]⁺X⁻ (X = F, Br or I) or [N(PPh₃)₂]Cl in CH₂Cl₂ gives the neutral complexes [WX(CO)(MeC≡CMe)Tp'] **1** (X = F, Cl, Br or I)[†] in 40–60% yield. Each complex undergoes reversible one-electron oxidation, at a Pt electrode in CH₂Cl₂, followed by a second, irreversible, oxidation process at a more positive potential (Table 1). The potential for the first oxidation step, E^o₁, becomes more positive and ν (CO) increases in energy in the order X = F < Cl < Br < I (Table 1), manifestations of the

'inverse halide order'³ where the complex of the most electronegative halogen (X = F) has the most electron rich metal centre.

Treatment of **1** with [Fe(η -C₅H₄COMe)Cp][BF₄] in CH₂Cl₂ gives 40–70% yields of the paramagnetic salts [WX(CO)(MeC≡CMe)Tp']⁺[BF₄]⁻ (**1**⁺[BF₄]⁻)[†] which show ν (CO) shifted to very much higher energy, by 160 (X = I) to 189 cm⁻¹ (X = F). In addition, the order ν (CO) = F \approx I < Br < Cl is now more nearly that expected on the basis of inductive effects due to halogen electronegativities (except for F).

The d³ cations in CH₂Cl₂–thf (1:2) show well resolved EPR spectra; parameters are given in Table 1 and the spectra of **1**⁺ (X = F), at 300 and 77 K are shown in Fig. 1. The isotropic metal coupling, <A^W>, decreases in the order F > Cl > Br suggesting a smaller metal contribution and larger participation of the halogens in the HOMO of **1** on descending the halogen group. The increase in <g> in the series F to I suggests a smaller metal contribution and a larger heavy halogen participation in the LUMO as well.⁴

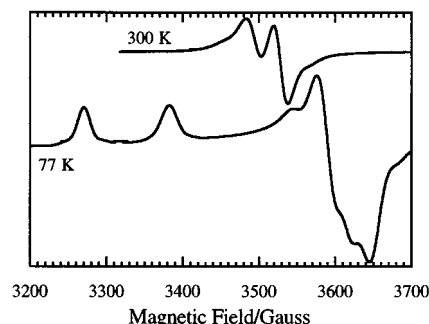


Fig. 1 EPR spectra of [WF(CO)(MeC≡CMe)Tp']⁺ at 300 and 77 K in CH₂Cl₂–thf (1:2).

Single crystal X-ray diffraction studies[‡] on the two redox pairs [WX(CO)(MeC≡CMe)Tp']^z (X = Cl and Br, z = 0 and 1) show the structural effects of oxidation. The gross structures of the four complexes are generally similar; that of [WCl(CO)(MeC≡CMe)Tp'] **1** (X = Cl) is shown in Fig. 2 as a representative example. In each case the alkyne is aligned approximately parallel to the W–CO bond. However, there are significant changes in metal–ligand bond lengths on oxidation (Table 2). Thus, for both pairs there is a significant shortening of the W–X bond (by ca. 0.09 Å), and a considerable lengthening of the W–C(O) bond [by 0.15–0.17 Å, consistent with the very large increase in ν (CO)]. In contrast to the shortening of the M–C_{alkyne} bonds in the d⁶/d⁵ and d⁵/d⁴ pairs noted above (ca. 0.10–0.11 Å on oxidation), there is a very small lengthening of the W–C_{alkyne} bonds (average ca. 0.02 Å) on oxidation of **1**.

The structural changes are consistent with the HOMO of **1** being largely d_{yz} in character but π -antibonding with respect to the W–X bond, π -bonding with respect to the W–C(O) bond, and weakly δ -bonding with respect to the W–alkyne bond (see

Table 1 Spectroscopic and electrochemical data for [WX(CO)(MeC≡CMe)Tp']^z

X	z	Electron configuration	ν (CO)/cm ⁻¹ (in CH ₂ Cl ₂)	E ^o ₁ /V ^a	<g> ^b	<A ^W >, <A ^X > ^{b,c}
F	0	d ⁴	1876	0.30 (1.48)	1.924 ^d	61.4, 31.3
	1	d ³	2065			
Cl	0	d ⁴	1896	0.45 (1.63)	1.936 ^e	51.7, –
	1	d ³	2076			
Br	0	d ⁴	1899	0.46 (1.60)	1.957 ^f	49.6, 16.1
	1	d ³	2074			
I	0	d ⁴	1904	0.47 (1.57)	2.002 ^g	<100, 22.8
	1	d ³	2064			

^a Potentials are relative to the saturated calomel electrode. Oxidation peak potential, at a scan rate of 200 mV s⁻¹, for the second, irreversible, oxidation process in parentheses. Under the experimental conditions, E^o₁ for the one-electron oxidation of [Fe(η -C₅H₄COMe)₂] is 0.97 V. ^b Isotropic EPR parameters for d³ complexes in CH₂Cl₂–thf (1:2) at 300 K. ^c All hyperfine coupling constants in units of 10⁻⁴ cm⁻¹. ^d 77 K: g₁ = 2.031, g₂ = 1.875, g₃ = 1.858, A₁^W = 40, A₂^W = 70, A₃^W = 72, A₁^F = 106, A₂^F = 22, A₃^F = 18. ^e 77 K: g₁ = 2.035, g₂ = 1.905, g₃ = 1.868, A₂^W = 83. ^f 77 K: g₁ = 2.036, g₂ = 1.954, g₃ = 1.874, A₁^{Br} = 60, A₃^{Br} = 52. ^g 77 K: g₁ = 2.050, A₁^W = 30, A₁^I = 79.

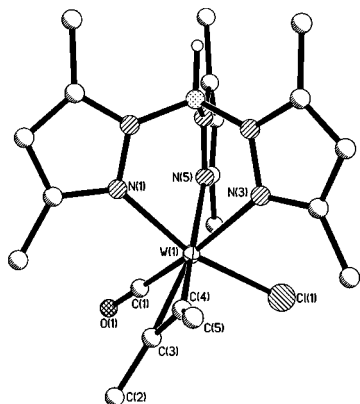


Fig. 2 Structure of $[\text{WCl}(\text{CO})(\text{MeC}\equiv\text{CMe})\text{Tp}']$ (hydrogen atoms omitted for clarity); important bond lengths are given in Table 2.

Table 2 Important bond lengths (Å) for $[\text{WX}(\text{CO})(\text{MeC}\equiv\text{CMe})\text{Tp}']^z$

X	z	Electron configuration	W-C _{alkyne}	W-X	W-C(O)	C-O	W-N (av.)
Cl	0	d ⁴	2.050(6) 2.002(6)	2.429(1)	1.941(6)	1.174(6)	2.223(8)
Cl	1 ^a	d ³	2.067(3) 2.035(3)	2.343(1)	2.087(3)	1.114(4)	2.179(3)
Br	0	d ⁴	2.053(7) 2.010(7)	2.595(1)	1.941(7)	1.164(8)	2.235(9)
Br	1 ^a	d ³	2.076(4) 2.027(4)	2.503(1)	2.118(5)	1.080(5)	2.184(6)

^a As the $[\text{BF}_4]^-$ salt.

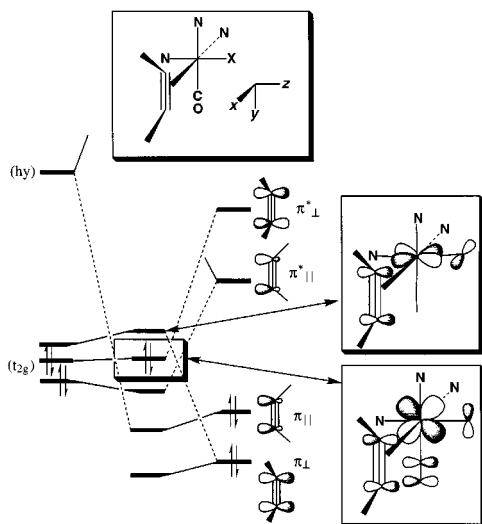


Fig. 3 Schematic diagram of the orbital interactions in d⁴ $[\text{WX}(\text{CO})(\text{MeC}\equiv\text{CMe})\text{Tp}']$ (hy = σ -hybrid orbital).

Fig. 3). This pattern of interactions, and the magnitude of the orbital contributions to the SOMO suggested by the EPR parameters, are reproduced by EHMO calculations on **1**.

As noted above, the variations in both $E_{1'}^{\circ}$ and $\nu(\text{CO})$ indicate an 'inverse halide order' for the set of complexes **1**; X = F < Cl < Br < I. The sequence of $\nu(\text{CO})$ for **1** (Table 1) indicates strongest M-C bonding in **1** (X = F) and weakest in **1** (X = I) and by implication greatest metal π -donor ability (or electron releasing ability) in **1** (X = F). The $\nu(\text{CO})$ data show a decreasing sensitivity of the carbonyl ligand in **1** to the effect of oxidation, in the order F > Cl > Br > I. The implication is that the contribution of the carbonyl ligand to the HOMO of **1** is greatest for X = F and least in X = I. This trend is also

reproduced in EHMO calculations which show that more electronegative halogens make contributions preferentially to the lower energy molecular orbitals.

The inverse halide order has been noticed previously during electrochemical studies^{5,6} or organometal halide complexes, and attributed to variation in either X-to-M $p_{\pi}-d_{\pi}$ ⁷ or M-to-X $d_{\pi}-d_{\pi}$ ^{3,6} donation. In most previous studies, the absence of data on the fluoride complex has hindered distinction between these two possibilities. For **1**, it is clear that the inverse halide order also encompasses the fluoride member of the series yet M-F $d_{\pi}-d_{\pi}$ overlap is impossible. A recent study⁷ revealed an inverse halide order for the series $[\text{FeX}(\text{dppe})(\eta\text{-C}_5\text{Me}_5)]^z$ ($z = 0$ and 1; X = F to I) where changes in bond dissociation energies (from electrochemical studies) showed that the HOMO/SOMO is significantly M-X bonding. This, is clearly different from **1** where oxidation is accompanied by W-X bond shortening, indicating that the HOMO is W-X antibonding (at least for X = Cl and Br). The π -donation of the halides is apparently the key to their ability to stabilise electron deficient species such as **1**⁺. The EHMO-computed halogen atomic orbital participation in the HOMO of **1** rises in the sequence F < Cl < Br < I while the metal contribution falls monotonically.

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Notes and references

† All new complexes had satisfactory elemental analyses (C, H and N). Complexes $[\text{WX}(\text{CO})(\text{MeC}\equiv\text{CMe})\text{Tp}']$. X = F: blue-purple crystals, yield 60%; X = Cl: royal blue crystals, yield 48%; X = Br: blue crystals, yield 43%; X = I: blue-green crystals, yield 60%. Complexes $[\text{WX}(\text{CO})(\text{MeC}\equiv\text{CMe})\text{Tp}'][\text{BF}_4]$. X = F: green-brown crystals, yield 38%; X = Cl: dark green crystals, yield 41%; X = Br: dark green crystals, yield 47%; X = I: purple crystals, yield 69%.

‡ X-Ray data were collected on a Bruker SMART diffractometer at 173 K for $\theta < 27.5^\circ$ with $\lambda = 0.71073$ Å. The structures were solved by direct methods and refined by least squares against all F^2 values with $F^2 > 3\sigma(F^2)$ corrected for absorption.

Crystal data: $[\text{WCl}(\text{CO})(\text{MeC}\equiv\text{CMe})\text{Tp}']$ (from diethyl ether-*n*-hexane): $\text{C}_{20}\text{H}_{28}\text{BClN}_6\text{OW}$, $M = 598.59$, monoclinic, space group Cc (no. 9), $a = 18.243(4)$, $b = 10.094(2)$, $c = 14.012(2)$ Å, $\beta = 116.552(3)^\circ$, $V = 2308.1(7)$ Å³, $Z = 4$, $\mu = 5.14$ mm⁻¹, $R_1 = 0.0265$. $[\text{WCl}(\text{CO})(\text{MeC}\equiv\text{CMe})\text{Tp}'][\text{BF}_4]$ (from CH_2Cl_2 -*n*-hexane): $\text{C}_{20}\text{H}_{28}\text{B}_2\text{ClF}_4\text{N}_6\text{OW}$, $M = 685.40$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.1371(10)$, $b = 11.7697(25)$, $c = 13.3634(15)$ Å, $\alpha = 87.723(7)^\circ$, $\beta = 84.451(12)^\circ$, $\gamma = 85.235(12)^\circ$, $V = 1268.8(3)$ Å³, $Z = 2$, $\mu = 4.71$ mm⁻¹, $R_1 = 0.0199$.

$[\text{WBr}(\text{CO})(\text{MeC}\equiv\text{CMe})\text{Tp}']\cdot\text{CHCl}_3\cdot 0.75\text{C}_6\text{H}_{14}$ (from CHCl_3 -*n*-hexane): $\text{C}_{25.5}\text{H}_{29}\text{BBrCl}_3\text{N}_6\text{OW}$, $M = 816.7$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.297(3)$, $b = 11.663(2)$, $c = 13.935(2)$ Å, $\alpha = 88.34(1)^\circ$, $\beta = 70.03(2)^\circ$, $\gamma = 78.05(1)^\circ$, $V = 1537.2(5)$ Å³, $Z = 2$, $\mu = 0.57$ mm⁻¹, $R_1 = 0.0363$.

$[\text{WBr}(\text{CO})(\text{MeC}\equiv\text{CMe})\text{Tp}'][\text{BF}_4]$ (from CH_2Cl_2 -*n*-hexane): $\text{C}_{20}\text{H}_{28}\text{B}_2\text{BrF}_4\text{N}_6\text{OW}$, $M = 729.86$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.1498(15)$, $b = 11.8631(19)$, $c = 13.4742(14)$ Å, $\alpha = 89.028(10)^\circ$, $\beta = 85.677(7)^\circ$, $\gamma = 85.247(11)^\circ$, $V = 1294.5(3)$ Å³, $Z = 2$, $\mu = 6.06$ mm⁻¹, $F(000) = 706$, $R_1 = 0.0293$. CCDC 182/1456. See <http://www.rsc.org/suppdata/cc/1999/2403/> for crystallographic files in .cif format.

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