

Alkylidyne[(pyrazol-1-yl)borato]tungsten Complexes: Metal–Carbon Triple Bonds as Four-electron Donors

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The tungsten complexes $[\text{W}(\equiv\text{CR})(\text{CO})_2(\text{R}'\text{Bpz}_3)]$ ($\text{R} = \text{Me}$ or $\text{C}_6\text{H}_4\text{Me-4}$, $\text{R}' = \text{H}$; $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$, $\text{R}' = \text{pz} = \text{pyrazol-1-yl}$) have been prepared and used to synthesise heteronuclear di- and tri-metal compounds with bridging alkylidyne ligands; the structures of the species $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{Bpz}_4)]$ and $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5(\text{HBpz}_3)]$ have been established by X-ray diffraction.

The ligating properties of the (pyrazolyl)borato anions $[\text{R}'\text{Bpz}_3]^-$ (**1**) are well established,¹ and these species are useful reagents in organometallic chemistry.^{2–4} However, the possibility that these anions might play an important role in metal–alkylidene or –alkylidyne chemistry, a subject of considerable current interest, seems hitherto to have been

overlooked; apart from the discovery of some halogeno-methylidyne–molybdenum and –tungsten complexes involving the tetrakis(pyrazol-1-yl)borato ligand⁵ and the synthesis of the thiocarbonyl–tungsten complex $[\text{W}(\equiv\text{CSMe})(\text{CO})_2(\text{HBpz}_3)]$.⁶

Treatment of the compounds $[\text{W}(\equiv\text{CR})\text{Br}(\text{CO})_4]$ ($\text{R} = \text{Me}$

or C_6H_4Me-4) with $K[HBpz_3]$ afforded in diethyl ether complex (**2a**) and in thf (tetrahydrofuran) complex (**2b**) (70–100%).[†] Compound (**2c**) was similarly prepared from $K[Bpz_4]$, and its structure (Figure 1) established by *X*-ray diffraction.[‡] The $[Bpz_n]^-$ anion functions as a tridentate ligand, as expected, and interestingly the $W\equiv C$ bond distance $[W-C(3) 1.82(1) \text{ \AA}]$ is the same as that in the cyclopentadienyl analogue $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)] [1.82(2) \text{ \AA}]$.⁷ Just as the latter affords many metal cluster compounds on treatment with low-valent metal species,⁸ the complexes (**2**) are also useful precursors to the related metal clusters in which $W(CO)_2(R'Bpz_3)$ fragments replace the $W(CO)_2(\eta-C_5H_5)$ moiety. Compounds (**3**)–(**5**)[†] are examples of di- and tri-metal complexes with bridging alkylidyne ligands prepared from (**2**), and $[Pt(C_2H_4)(PMe_3)_2]$, $[Co_2(CO)_8]$, and $[Rh(CO)_2(\eta-C_9H_7)]$ ($C_9H_7 = \text{indenyl}$), respectively. Important differences between the reactivity patterns of compounds (**2**) and their cyclopentadienyl analogues $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ ($R = Me$ or C_6H_4Me-4) arise.

[†] Selected and representative spectroscopic data ($^{13}C\{-^1H\}$ n.m.r. in $CD_2Cl_2-CH_2Cl_2$, coupling constants in Hz): compound (**2a**), yellow crystals, i.r. ν_{CO} (max) at 1983s and 1899s cm^{-1} (hexane); $^{13}C\{-^1H\}$ n.m.r.: δ , 295.2 $[C\equiv W, J(WC) 189]$ and 223.3 p.p.m. $[WCO, J(WC) 169]$. Compound (**2b**), orange, i.r. ν_{CO} (max) at 1986s and 1903s cm^{-1} (hexane); $^{13}C\{-^1H\}$ n.m.r.: δ , 284.8 $[C\equiv W, J(WC) 189]$ and 224.9 p.p.m. $[WCO, J(WC) 167]$. Compound (**2c**), orange, i.r. ν_{CO} (max) at 1986s and 1903s cm^{-1} (hexane); $^{13}C\{-^1H\}$ n.m.r.: δ , 286.4 $[C\equiv W, J(WC) 190]$ and 224.7 p.p.m. $[WCO, J(WC) 170]$. Compound (**3a**), red, i.r. ν_{CO} (max) at 1914s and 1764m cm^{-1} (hexane); $^{13}C\{-^1H\}$ n.m.r.: δ , 332.0 [d, $\mu-CC_6H_4Me-4, J(PC) 54, J(PtC) 644]$ and 234.4 p.p.m. $[WCO, J(WC) 162]$. Compound (**3b**), pink, i.r. ν_{CO} (max) at 2018s, 1937s, and 1823m cm^{-1} (hexane); $^{13}C\{-^1H\}$ n.m.r.: δ , 322.4 [$\mu-CC_6H_4Me-4, J(PtC) 657$], 231.7 $[WCO, J(WC) 140]$, and 197.9 p.p.m. $[PtCO, J(PtC) 1422]$. Compound (**4a**), green, $^{13}C\{-^1H\}$ n.m.r. ($-50^\circ C$): δ , 263.4 [$\mu_3-CMe, J(WC) 83$], 228.5 $[WCO, J(WC) 152]$, 219.9 $[WCO, J(WC) 154]$, 202.8, 201.3, 199.2, and 194.0 p.p.m. (CoCO). Compound (**5a**), black, i.r. ν_{CO} (max) at 1873s and 1799m cm^{-1} (CH_2Cl_2); $^{13}C\{-^1H\}$ n.m.r.: δ , 329.9 [t, $\mu_3-CR, J(RhC) 24$], 233.0 $[WCO, J(WC) 156]$, and 220.4 p.p.m. [t, $RhCO, J(RhC) 52]$. Compound (**9a**), purple, i.r. ν_{CO} (max) at 2046s, 1980s, 1959s, 1923m, and 1848m cm^{-1} (CH_2Cl_2); $^{13}C\{-^1H\}$ n.m.r. ($-40^\circ C$): δ , 425.8 [$\mu-CMe, J(WC) 128$], 226.5 $[WCO, J(WC) 153]$ and 214.4 p.p.m. (FeCO). Compound (**11**), purple, i.r. ν_{CO} (max) at 2054s, 1993s, 1975s, 1943m, and 1885m cm^{-1} (hexane); $^{13}C\{-^1H\}$ n.m.r.: δ , 392.5 [$\mu-CC_6H_4Me-4, J(WC) 153$], 221.4 $[WCO, J(WC) 174]$ and 214.6 p.p.m. (FeCO).

[‡] The 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.

Crystal data for (**2c**): $C_{22}H_{10}BN_8O_2W$, $M = 622.2$, monoclinic, $a = 8.738(4)$, $b = 23.827(14)$, $c = 10.896(6) \text{ \AA}$, $\beta = 97.27(4)^\circ$, $U = 2250(2) \text{ \AA}^3$, $Z = 4$, $D_c = 1.84 \text{ g cm}^{-3}$, $F(000) = 1208$, space group $P2_1/n$ (no. 14, non-standard setting), Mo- K_α *X*-radiation, graphite monochromator, $\lambda = 0.71069 \text{ \AA}$, $\mu(\text{Mo-}K_\alpha) = 52.8 \text{ cm}^{-1}$. $R 0.035$ ($R_w 0.034$) for 3381 absorption corrected reflections [190 K, $2\theta \leq 55^\circ$, $I \geq 3\sigma(I)$].

Crystal data for (**9b**): $C_{22}H_{17}BN_6O_5FeW$, $M = 695.9$, monoclinic, $a = 8.959(7)$, $b = 22.610(17)$, $c = 12.415(8) \text{ \AA}$, $\beta = 103.85(6)^\circ$, $U = 2442(3) \text{ \AA}^3$, $Z = 4$, $D_c = 1.90 \text{ g cm}^{-3}$, $F(000) = 1344$, space group $P2_1/n$ (no. 14), $\mu(\text{Mo-}K_\alpha) = 54.5 \text{ cm}^{-1}$, $R 0.045$ ($R_w 0.047$) for 4563 absorption corrected reflections [190 K, $2\theta \leq 58^\circ$, $I \geq 4\sigma(I)$].

Intensity data were collected (θ - 2θ scans) on Nicolet P3m diffractometers. The structures were solved by conventional heavy atom (Patterson and Fourier) methods, and were refined using a blocked-cascade full matrix least-squares procedure.

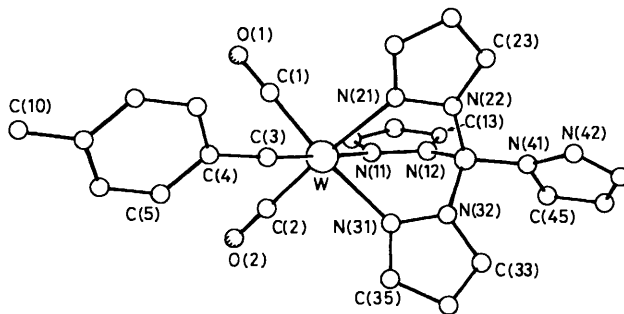
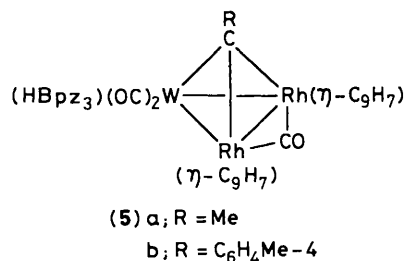
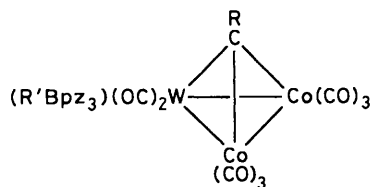
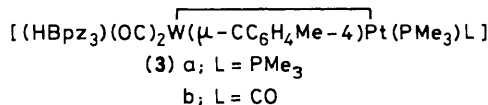
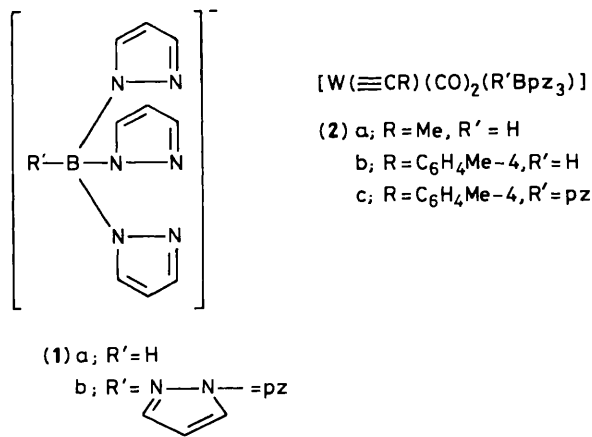


Figure 1. Molecular structure of $[W(\equiv CC_6H_4Me-4)(CO)_2(Bpz_4)]$ (**2c**). Dimensions: $W-C(3) 1.821(7)$, $W-N(11) 2.284(6)$, $W-N(21) 2.219(6)$, $W-N(31) 2.186(5) \text{ \AA}$; mean $W-C-O 177(1)^\circ$.

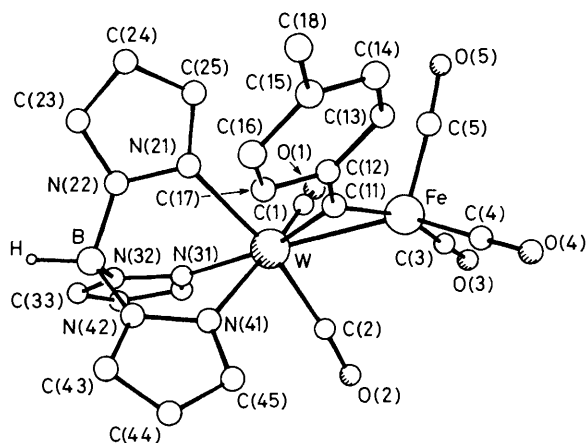
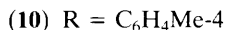
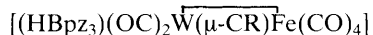
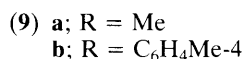
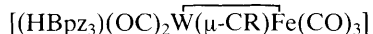
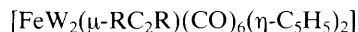
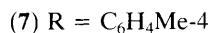
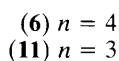
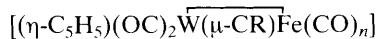


Figure 2. Molecular structure of $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5(\text{HBpz}_3)]$ (**9b**). Dimensions: Fe–W 2.612(2), Fe–C(11) 1.826(6), W–C(11) 2.025(7), W–N(21) 2.217(5), W–N(31) 2.217(6), W–N(41) 2.202(5) Å; W–C(11)–Fe 85.3(3), Fe–C–O mean 177(1), W–C(1)–O(1) 169.6(6), W–C(2)–O(2) 174.3(6)°.



Whereas $[\text{Fe}_2(\text{CO})_9]$ reacts with $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ in diethyl ether to give (**6**), a labile 'Fe(CO)₄' complex which readily affords (**7**) or (**8**),⁹ the compounds (**2a**) and (**2b**) react with di-iron enneacarbonyl to give the stable dimetal species (**9**).[†] The structure of (**9b**), determined by X-ray diffraction (Figure 2),[‡] establishes unambiguously the presence of an Fe(CO)₃ group. This result implies that either the iron atom is in a 16-electron configuration or, as seems more likely, the W≡C bonds in (**2**) can function as four-electron donors, as recognised for alkynes in certain complexes.¹⁰ The idea that W≡C bonds can vary in electron donor

properties, as between (**6**) and (**9**) is supported by the relatively long W–C(11) distance [2.025(7) Å] in (**9b**) compared with W–μ-C separations in several dimetal complexes containing $\overline{\text{W}(\mu\text{-CR})\text{M}}$ ring systems.¹¹ Moreover, in the ¹³C–{¹H} n.m.r. spectra of (**9a**) and (**9b**) the μ-CR resonances are at δ 425.8 and 408.8 p.p.m., respectively, remarkably deshielded compared with the signals for these groups in most species involving the RC≡W(CO)₂(η-C₅H₅) fragment. Thus in the ¹³C–{¹H} spectrum of (**6**) the μ-CR resonance occurs at δ 331.3 p.p.m. Similar low-field shifts have been observed for the ligated carbon atoms of alkynes in complexes in which these groups act as four-electron donors.¹²

Complex (**9b**) reacts with CO to give a species (**10**), believed to be similar to (**6**) on the basis of virtually identical band patterns in the CO region of their i.r. spectra. Under a nitrogen purge, however, solutions of (**10**) revert to (**9b**).

Complexes similar to (**9**) are not limited to species containing the W(CO)₂(HBpz₃) group. Thus treatment of $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ with $[\text{Fe}(\text{CO})_3(\eta\text{-cyclo-octene})_2]$, a source of Fe(CO)₃ fragments,¹³ affords (**11**);[†] the i.r. and n.m.r. data for which are similar to those of (**9b**). The μ-CR resonance in the ¹³C–{¹H} n.m.r. spectrum occurs at δ 392.5 p.p.m., ca. 60 p.p.m. more deshielded than the signal in (**6**). Compound (**11**) is more labile than (**9b**), with CO affording (**6**).

We thank the S.E.R.C. for support and Shell Research Ltd. for a CASE award (to A. P. J.).

Received, 24th August 1984; Com. 1221

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