

**HYDROBORATION OF CARBON–TUNGSTEN TRIPLE BONDS;
 CRYSTAL STRUCTURES OF $[W_2\{\mu\text{-MeCB(H)Et}\}(CO)_4(\eta\text{-C}_5\text{H}_5)_2]$
 AND $[W\{\eta^3\text{-CH(BC}_8\text{H}_{14})\text{C}_6\text{H}_4\text{Me-4}\}(CO)_2(\eta\text{-C}_5\text{H}_5)]$,
 AND OF RELATED COMPLEXES ***

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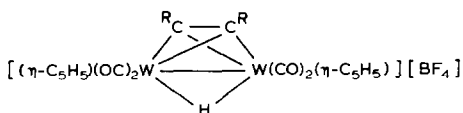
Summary

The compounds $[W(\equiv CR)(CO)_2L]$ ($L = \eta\text{-C}_5\text{H}_5$, $R = \text{Me}$, $\text{C}_6\text{H}_4\text{Me-4}$ or Ph ; $L = \eta\text{-C}_5\text{Me}_5$, $R = \text{C}_6\text{H}_4\text{Me-4}$) react with $\text{BH}_3 \cdot \text{thf}$ to afford the ditungsten compounds $[W_2\{\mu\text{-RCB(H)CH}_2\text{R}\}(CO)_4L_2]$. The structures of the species with cyclopentadienyl ligands and $R = \text{Me}$ and Ph have been established by X-ray diffraction. The reaction between $[W(\equiv \text{CC}_6\text{H}_4\text{Me-4})(CO)_2(\eta\text{-C}_5\text{H}_5)]$ and 9-borabicyclo-[3.3.1]nonane (9-BBN) affords the mononuclear tungsten complex $[W\{\eta^3\text{-CH(BC}_8\text{H}_{14})\text{C}_6\text{H}_4\text{Me-4}\}(CO)_2(\eta\text{-C}_5\text{H}_5)]$. An X-ray diffraction study identified the unusual η^3 -co-ordination mode of the organoboron ligand. Protonation of the complexes $[W_2\{\mu\text{-RCB(H)CH}_2\text{R}\}(CO)_4(\eta\text{-C}_5\text{H}_5)_2]$ ($R = \text{Me}$ or $\text{C}_6\text{H}_4\text{Me-4}$) affords salts $[W_2(\mu\text{-H})\{\mu\text{-RCB(H)CH}_2\text{R}\}(CO)_4(\eta\text{-C}_5\text{H}_5)_2][X]$ ($X = \text{SO}_3\text{CF}_3$ or BF_4). An X-ray diffraction study on the compound with $R = \text{Me}$ failed to locate the two hydrogen atoms associated with the boron but internuclear W–W and B–W separations, together with ^1H NMR studies, suggest that the cation contains a three centre B–H–W bond and a four centre $\mu_3\text{-HBW}_2$ interaction. NMR studies (^1H and $^{13}\text{C}\text{-}\{^1\text{H}\}$) on all the compounds are reported and discussed.

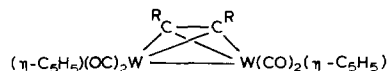
Introduction

Treatment of the alkylidynetungsten compounds $[W(\equiv CR)(CO)_2(\eta\text{-C}_5\text{H}_5)]$ ($R = \text{Me}$ or $\text{C}_6\text{H}_4\text{Me-4}$) with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ gives the salts $[W_2(\mu\text{-H})(\mu\text{-RC}_2\text{R})(CO)_4(\eta\text{-C}_5\text{H}_5)_2][X]$

* Dedicated to Professor Coates on the occasion of his 70th birthday. Professor Coates' initial pioneering work on organometallic chemistry was carried out at Bristol University, and we are pleased to continue the tradition. Moreover, one of us, (F.G.A.S.) was much influenced by the 1956 and 1960 editions of Professor Coates' book "Organometallic Compounds".



(Ia : R = Me ;

Ib : R = C₆H₄Me-4)

(IIa : R = Me ;

IIb : R = C₆H₄Me-4)

C₅H₅)₂][BF₄] (Ia and Ib) [1]. The latter are readily deprotonated, affording the bridged alkyne complexes [W₂(μ-RC₂R)(CO)₄(η-C₅H₅)₂] (IIa and IIb). The ready protonation of [W(≡CR)(CO)₂(η-C₅H₅)] suggested that other electrophilic reagents might react with the alkylidynetungsten compounds, and in this context BH₃ and its derivatives are of particular interest. Any adduct initially formed between a BH₃ group and a C≡W bond would undergo further reaction involving hydride transfer to tungsten, and thus lead to novel structures containing boron. As is well known, carbon-carbon multiple bonds react readily with B-H groups to afford a variety of organoboron compounds in the well established hydroboration chemistry [2]. Similar addition of B-H to carbon-metal multiple bonds could add a new dimension to organoboron chemistry. A preliminary account has been given of some of the work described herein [3].

Results and discussion

Reaction of an excess of BH₃·thf (thf = tetrahydrofuran) with [W(≡CMe)-(CO)₂(η-C₅H₅)] proceeds rapidly (ca. 5 min) to give the orange crystalline compound [W₂{μ-MeCB(H)Et}(CO)₄(η-C₅H₅)₂] (IIIa), characterised by the data given in Tables 1 and 2. In order to establish the structure of this novel product an X-ray diffraction study was carried out. Selected bond distances and angles are listed in Table 3, and the molecule is shown in Fig. 1.

It is immediately apparent that the W-W bond (2.978(2) Å) is transversely bridged by the hitherto unreported MeCB(H)Et ligand (B-C(3) 1.46(1) Å). The molecule has a three-centre two-electron B-H-W bond (B-W(2) 2.41(1), B-H 1.1(1), and W(2)-H 1.8(1) Å). Formally the MeCB(H)Et group, isoelectronic with MeC₂Et, acts as a four electron donor to the W₂(CO)₄(η-C₅H₅)₂ fragment, as do the alkyne ligands in II. Several dimolybdenum compounds [Mo₂(μ-alkyne)-(CO)₄(η-C₅H₅)₂] analogous to the tungsten species II have been prepared, and X-ray diffraction studies have been carried out on those involving the alkynes HC≡CH [4], EtC≡CEt [5], PhC≡CPh [6], and Me₃SiC≡CSiMe₃ [7]. The Mo-Mo separations are very similar to that found for IIIa; molybdenum and tungsten having essentially the same covalent radii. Thus in [Mo₂(μ-Me₃SiC₂SiMe₃)(CO)₄(η-C₅H₅)₂] the metal-metal bond length is 2.952(1) Å. An important structural feature of the dimolybdenum compounds with the bridging ligands RC≡CR (R = H, Et, or Ph) is the presence of a semi-bridging carbonyl group. In the crystal of IIIa, however, all four carbonyl groups are terminally bound (W-C-O 174-177°) as they are in [Mo₂(μ-Me₃SiC₂SiMe₃)(CO)₄(η-C₅H₅)₂]. Nevertheless, the IR spectrum of IIIa, measured in solution, shows a band at 1843 cm⁻¹ (Table 1) indicative

(Continued on p. 190)

TABLE 1
ANALYTICAL AND OTHER DATA

Compound	Colour	Yield (%)	ν_{\max} (CO) ^a		Found (calcd.)(%)	
			(cm ⁻¹)		C	H
[W ₂ { μ -MeCB(H)Et}(CO) ₄ (η -C ₅ H ₅) ₂] ^b (IIIa)	Orange	80	1990m, 1843m	1920vs,	31.8 (31.9)	2.7 (2.8)
[W ₂ { μ -(4-MeC ₆ H ₄)CB(H)CH ₂ C ₆ H ₄ Me-4)-(CO) ₄ (η -C ₅ H ₅) ₂] (IIIb)	Red	79	1985mbr, 1920msh, 1847msh	1944s,	43.4 (43.4)	3.4 (3.3)
[W ₂ { μ -PhCB(H)CH ₂ Ph}(CO) ₄ (η -C ₅ H ₅) ₂] ^c (IIIc)	Crimson	64	1990mbr, 1922msh, 1850msh	1945s,	41.6 (41.9)	2.9 (2.9)
[W ₂ { μ -(4-MeC ₆ H ₄)CB(H)CH ₂ C ₆ H ₄ Me-4)-(CO) ₄ (η -C ₅ Me ₅) ₂] (IIIId)	Brown	45	1961w, 1850m,	1926vs,	48.6 (49.5)	4.2 (4.9)
[W{ η^3 -CH(BC ₈ H ₁₄)C ₆ H ₄ Me-4}(CO) ₂ - (η -C ₅ H ₅)] ^d (IV)	Maroon	88	1936s,	1843m	51.9 (52.1)	5.0 (5.1)
[W ₂ (μ -H){ μ -MeCB(H)Et}(CO) ₄ (η -C ₅ H ₅) ₂] [SO ₃ CF ₃] (Va)	Orange	90	2058s, 1995sh,	2011s,	27.8 (27.6)	2.6 (2.4)
{W ₂ (μ -H){ μ -(4-MeC ₆ H ₄)CB(H)CH ₂ C ₆ H ₄ - Me-4}(CO) ₄ (η -C ₅ H ₅) ₂ }[BF ₄] (Vb)	Yellow	87	2063s, 1997sh,	2016s,	39.0 (39.2)	3.5 (3.1)
[W ₂ { μ -(4-MeC ₆ H ₄)CB(AuPPh ₃)CH ₂ C ₆ H ₄ - Me-4}(CO) ₄ (η -C ₅ H ₅) ₂] (VII)	Brown	51	1928w, 1845s ^e	1896s,	43.7 (44.6)	4.5 (3.3)

^a Measured in CH₂Cl₂, unless otherwise stated. ^b Mol. wt. (mass spectrum). Found 678 (calcd. 678).

^c Mol. wt. (mass spectrum). Found 802 (calcd. 802). ^d Mol. wt. (mass spectrum). Found 530 (calcd. 530).

^e Measured in tetrahydrofuran.

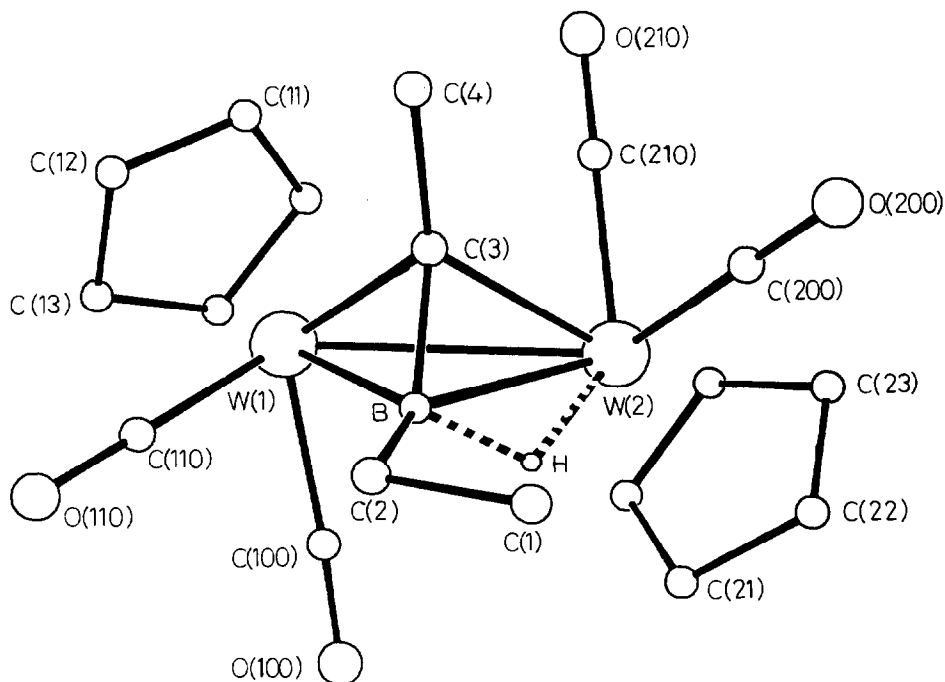


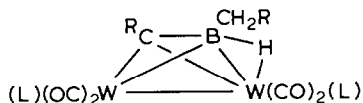
Fig. 1. Molecular structure of [W₂{ μ -MeCB(H)Et}(CO)₄(η -C₅H₅)₂] (IIIa).

TABLE 2
 NMR DATA^a

Compound	$\delta(^1\text{H})^b$	$\delta(^{13}\text{C})^c$	$\delta(^{11}\text{B})^d$
IIIa	-10.13 (sbr, 1 H, BHW), 0.79 [t, 3 H, CH ₂ Me, <i>J</i> (HH) 7], 1.18 (mbr, 2 H, BCH ₂), 2.92 (s, 3 H, CMe), 5.27 (s, 5 H, C ₅ H ₅), 5.49 (s, 5 H, C ₅ H ₅)	222.0 [CO, <i>J</i> (WC) 149], 219.0, 217.7 (CO), 205.1 [CO, <i>J</i> (WC) 167], 110.0 (BC), 88.8, 86.9 (C ₅ H ₅), 31.2 (CMe), 13.7 (BCH ₂ Me), 5.5 (BCH ₂ Me)	-30.2
IIIb	-10.43 (s, 1 H, BHW), -10.04 (s, 1 H, BHW), 2.20 (s, 3 H, Me-4), 2.25 (s, 3 H, Me-4), 2.36 (s, 6 H, Me-4), 2.35 [d, 1 H, BCH ₂ , <i>J</i> (HH) 12], 2.60 [d, 2 × 1 H, BCH ₂ , <i>J</i> (HH) 12], 2.87 [d, 1 H, BCH ₂ , <i>J</i> (HH) 12], 4.95 (s, 5 H, C ₅ H ₅), 5.22 (s, 5 H, C ₅ H ₅), 5.25 (s, 5 H, C ₅ H ₅), 5.42 (s, 5 H, C ₅ H ₅), 6.44, 6.66 [(AB) ₂ , 4 H, C ₆ H ₄ , <i>J</i> (AB) 8], 6.79-7.10 (m, 12 H, C ₆ H ₄)	222.8, 222.2, 221.3, 217.9, 217.6, 216.3 (CO), 213.6 [CO, <i>J</i> (WC) 158], 201.3 [CO, <i>J</i> (WC) 167], 152.1, 150.7, 143.4, 142.2 [C ¹ (C ₆ H ₄)], 134.0-128.6 (C ₆ H ₄), 107.7 (BC), 92.5, 89.2, 88.2, 85.8 (C ₃ H ₅), 69.3 (BC), 21.1 (4 × Me-4), 19.9 (2 × BCH ₂)	-25.4
IIIc	-10.47 (s, 1 H, BHW), -10.07 (s, 1 H, BHW), 2.33 [d, 1 H, BCH ₂ , <i>J</i> (HH) 12], 2.68 [d, 2 × 1 H, BCH ₂ , <i>J</i> (HH) 12], 2.94 [d, 1 H, BCH ₂ , <i>J</i> (HH) 12], 4.94 (s, 5 H, C ₅ H ₅), 5.22 (s, 5 H, C ₅ H ₅), 5.27 (s, 5 H, C ₅ H ₅), 5.44 (s, 5 H, C ₅ H ₅), 6.40-7.30 (m, 20 H, Ph)	222.5, 222.1, 220.6, 217.9, 217.3, 215.7, 213.3, 200.5 (CO), 155.4, 154.1, 146.8, 145.5 [C ¹ (Ph)], 131.6-122.8 (Ph), 106.9 (BC) 92.4, 89.3, 88.1, 85.9 (C ₅ H ₅), 68.6 (BC) 21.6, 20.3 (BCH ₂)	-25.0
IIIId	-9.33 (s, 1 H, BHW), 1.84 (s, 15 H, C ₅ Me ₃), 1.99 (s, 15 H, C ₅ Me ₃), 2.26 (s, 3 H, Me-4), 2.28 (s, 3 H, Me-4), 2.27 [d, 1 H, BCH ₂ , <i>J</i> (HH) 7], 2.78 [d, 1 H, BCH ₂ , <i>J</i> (HH) 7], 6.88-7.13 (m, 8 H, C ₆ H ₄)	230.4 [CO, <i>J</i> (WC) 184], 225.5 [CO, <i>J</i> (WC) 165], 224.7 [CO, <i>J</i> (WC) 175], 221.8 [CO, <i>J</i> (WC) 160], 148.9, 142.3 [C ¹ (C ₆ H ₄)], 133.9-128.7 (C ₆ H ₄), 102.2, 101.8 (C ₅ Me ₃), 78.4 (BC), 21.1 (2 × Me-4), 19.6 (BCH ₂), 11.0, 9.9 (C ₅ Me ₃)	-27.0

IV	ϵ -1.20–2.10 (mbr, 28 H, BC ₈ H ₁₄ and *BC ₈ H ₁₄), 2.24* (s, 3 H, Me-4), 2.27 (s, 3 H, Me-4), 2.58 [s, 1 H, CH (BC ₈ H ₁₄)], 3.82* [s, 1 H, CH(B ₈ H ₁₄)], 5.23 (s, 5 H, C ₅ H ₅), 5.47* (s, 5 H, C ₅ H ₅), 5.66 [d, 1 H, H ² , J(H ² H ³) 6], 6.16 [d of d, 1 H, H ² , J(H ² H ³) 9, J(H ² H ⁶) 3], 6.26 [d of d, 1 H, H ³ , J(H ² H ³) 9, J(H ³ H ⁵) 2], 6.64* [d, 1 H, H ³ , J(H ³ H ⁵) 6], 6.76* [d, (AB), 2 H, H ⁵ , H ⁶ , J(H ⁵ H ⁶) 4], 6.84 [d, (AB), 2 H, H ⁵ , H ⁶ , J(H ⁵ H ⁶) 8]	ϵ -234.9 [CO, J(WC) 166], 232.2*, 231.1* (CO), 228.9 [CO, J(WC) 179], 136.5 [C ¹ (C ₆ H ₄)], 131.8 [C ² (C ₆ H ₄)], J(WC) 26], 130.8 [C ³ (C ₆ H ₄)], 128.0 [C ¹ (C ₆ H ₄)], J(WC) 120], 109.8, 103.3 [C ⁵ and C ⁶ (C ₆ H ₄)], 91.3 (C ₃ H ₅), 88.6* (C ₃ H ₅), 73.3 [CH(B ₈ H ₁₄)], 39.0, 34.7, 29.3 [mbr, CH ₂ , (BC ₈ H ₁₄)], 24.1 [br, CH ₂ and CH (BC ₈ H ₁₄)], 21.6 (Me-4)	60.4
Va	ϵ -11.16 (sbr, 2 H, BHW), 0.81 (sbr, 2 H, BCH ₂), 0.92 (m, 3 H, BCH ₂ Me), 3.15 (s, 3 H, CMe), 5.74 (s, 10 H, C ₅ H ₅)	216.1 (CO), 205.5 (2 × CO), 201.1 (CO), 121.1 [q, CF ₃ , J(CF) 32], 107.5 (br, CMe) 91.2, 90.4 (C ₅ H ₅), 33.2 (CMe), 15.0 (BCH ₂ Me), 1.2 (br, BCH ₂ Me)	-59.0 ^g
Vb	-11.90 (s, 1 H, BHW), -10.10 (s, 1 H, BHW), 2.29 (s, 3 H, Me-4), 2.45 (s, 3 H, Me-4), 2.79 ^h [d, 1 H, BCH ₂ , J(HH) 13], 5.32 (s, 5 H, C ₅ H ₅), 5.81 (s, 5 H, C ₅ H ₅), 6.94–7.26 (m, 8 H, C ₆ H ₄)	215.8 [CO, J(WC) 154], 204.9 [2 × CO, J(WC) 151], 199.6 [CO, J(WC) 164], 148.0, 141.6 [C ¹ (C ₆ H ₄)], 136.7–128.0 (C ₆ H ₄), 102.0 (BC), 90.9, 90.7 (C ₃ H ₅) 21.2, 21.1 (Me-4), 15.7 (BCH ₂)	-54.6 ⁱ
VII ^j	ϵ 2.03 (s, 3 H, Me-4), 2.29 (s, 3 H, Me-4), 2.75 (sbr, 2 H, BCH ₂), 5.11 (s, 10 H, C ₅ H ₅), 6.37 (s, 4 H, C ₆ H ₄), 6.96, 6.57 [(AB) ₂ , 4 H, C ₆ H ₄ , J(AB) 8], 7.48 (m, 15 H, PPh ₃)	225.2, 222.7, 221.9, 217.8 (CO), 155.1, 144.8 [C ¹ (C ₆ H ₄)], 135.0–128.0 (C ₆ H ₄ and Ph), 91.6, 83.1 (C ₅ H ₅), 63.7 (BC), 24.3 (BCH ₂), 21.0 (Me-4)	

^a Chemical shifts (δ) in ppm coupling constants in Hz. ^b Measured at -40 °C in CD₂Cl₂ unless otherwise stated. ^c Hydrogen-1 decoupled, measured at -40 °C in CD₂Cl₂/CH₂Cl₂ unless otherwise stated. Chemical shifts are positive to high frequency of SiMe₄. ^d Hydrogen-1 decoupled, measured at room temperature in CD₂Cl₂/CH₂Cl₂ unless otherwise stated. Chemical shifts are positive to high frequency of BF₃·Et₂O external. ^e Measured at room temperature. ^f Peaks due to minor isomer labelled with an asterisk, not all signals for this species observed in ¹³C-¹H spectrum. ^g Measured at -40 °C. ^h Other doublet for BCH₂ obscured by Me-4 signals. ⁱ A resonance for the BF₄⁻ anion is observed at -2.8 ppm. ^j The ³¹P-¹H NMR spectrum shows a singlet signal for the PPh₃ group at δ 63.2 ppm in CD₂Cl₂, rel. to 85% H₃PO₄ (external).



(IIIa : R = Me , L = η -C₅H₅ ;

IIIb : R = C₆H₄Me-4 , L = η -C₅H₅ ;

IIIc : R = Ph , L = η -C₅H₅ ;

III d : R = C₆H₄Me-4 , L = η -C₅Me₅)

of the presence of a semi-bridging CO ligand. It is thus probable that in solution the structure is modified. The spectrum of [Mo₂(μ -Me₃SiC₂SiMe₃)(CO)₄(η -C₅H₅)₂] also shows such a band (1840 cm⁻¹), but in addition nine other CO bands are observed indicating the presence of isomers in solution.

The ¹H and ¹³C-¹H NMR data for IIIa when measured at -40 °C (Table 2) indicate the presence of one isomer and are in agreement with the structure found by X-ray diffraction. In the ¹H NMR spectrum there is a diagnostic resonance for the BHW group at δ -10.13 ppm. In accord with the molecular asymmetry, in both the ¹H and ¹³C-¹H NMR spectra there are two C₅H₅ signals, and in the ¹³C-¹H spectrum there are four CO peaks. The μ -CB resonance is at δ 110.0 ppm. The CH₂B protons are inequivalent, and this should result in the ¹H NMR resonance for the CH₂Me group appearing as a doublet of doublets. A not well resolved triplet is in fact observed, while a broad multiplet is seen for the CH₂Me protons due to ¹¹B-¹H coupling. When the spectra of IIIa are measured at ambient temperatures it is evident that there is the onset of a dynamic process. Thus in the ¹³C-¹H NMR spectrum the CO and C₅H₅ resonances broaden, and in the ¹H spectrum the signals for the C₅H₅ group collapse to a broad singlet. The peak for the μ -H ligand also broadens. This behaviour is discussed further below.

The synthesis of IIIa from [W(\equiv CMe)(CO)₂(η -C₅H₅)] involves cleavage of a W \equiv C bond in formation of the BEt group. This interesting result prompted a study of reactions between the compounds [W(\equiv CR)(CO)₂(η -C₅H₅)] (R = C₆H₄Me-4 or Ph) and BH₃·thf in order to establish whether the substituent R influenced the nature of the observed products. The reaction between [W(\equiv CC₆H₄Me-4)(CO)₂(η -C₅Me₅)] and BH₃·thf was also investigated, in view of the well known propensity of the η -C₅Me₅ group to change reactivity patterns, compared with η -C₅H₅ as a ligand.

In contrast with the behaviour of [W(\equiv CMe)(CO)₂(η -C₅H₅)], the reaction between [W(\equiv CC₆H₄Me-4)(CO)₂(η -C₅H₅)] and BH₃·thf proceeded only very slowly, requiring ca. 18 h for completion at room temperature. That between [W(\equiv CPh)(CO)₂(η -C₅H₅)] and BH₃·thf was more rapid (ca. 15 min), while the reaction between [W(\equiv CC₆H₄Me-4)(CO)₂(η -C₅Me₅)] and the boron reagent required ca. 5 h for completion. The products are the ditungsten compounds [W₂{ μ -RCB(H)CH₂R}(CO)₄L₂] (L = η -C₅H₅, R = C₆H₄Me-4 (IIIb), R = Ph (IIIc); L = η -C₅Me₅, R = C₆H₄Me-4 (III d)), data for which are given in Tables 1 and 2.

Complexes IIIb and IIIc were initially considered to be structurally different from IIIa on account of the number of CO absorptions seen in their IR spectra.

TABLE 3

SELECTED INTERNUCLEAR DISTANCES (Å) AND ANGLES (°) FOR $[W_2\{\mu\text{-MeCB(H)Et}\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (IIIa)

W(1)–W(2)	2.978(2)	W(1)–B	2.39(1)
W(2)–B	2.41(1)	B–C(3)	1.46(1)
C(2)–C(1)	1.52(2)	W(2)–H	1.8(1)
W(1)–C(110)	1.93(1)	W(2)–C(210)	1.94(1)
W(2)–C(cp) ^a	2.34	W(2)–C(3)	2.17(1)
W(1)–C(3)	2.14(1)	B–C(2)	1.57(2)
C(3)–C(4)	1.54(2)	W(1)–C(100)	1.96(1)
B–H	1.1(1)	W(1)–C(cp) ^a	2.34
W(2)–C(200)	1.98(1)		
W(1)–W(2)–B	51.4(3)	W(1)–B–W(2)	76.6(3)
W(2)–B–C(3)	62.7(6)	W(1)–C(3)–B	80.9(7)
B–W(2)–C(3)	36.6(4)	W(2)–W(1)–C(3)	46.8(3)
W(2)–C(3)–C(4)	133.4(7)	B–C(3)–C(4)	127(1)
W(2)–H–B	111(8)	W(1)–B–C(2)	137.8(8)
C(110)–W(1)–C(100)	81.0(5)	W(1)–C(100)–O(100)	176(1)
W(2)–C(200)–O(200)	174(1)	W(1)–B–C(3)	62.1(6)
W(2)–W(1)–B	52.0(3)	B–W(1)–C(3)	37.0(4)
W(2)–C(3)–B	80.7(7)	W(1)–C(3)–C(4)	129.5(8)
W(1)–W(2)–C(3)	45.9(3)	B–W(2)–H	26(4)
C(2)–B–C(3)	130(1)	W(2)–B–C(2)	145.2(9)
W(2)–B–H	42(5)	W(1)–C(110)–O(110)	176(1)
C(200)–W(2)–C(210)	84.8(5)		
W(2)–C(210)–O(210)	177(1)		

^a Mean distance to cyclopentadienyl carbon atoms.

Thus whereas IIIa showed only three CO stretching bands in its IR spectrum (Table 3), compounds IIIb and IIIc showed five bands. Moreover, examination of the NMR spectra of IIIb and IIIc at room temperature and at -40°C revealed very clear evidence for dynamic behaviour. Hence an X-ray diffraction study was required on one or other of these compounds. It was impossible to grow suitable crystals of IIIb, but fortunately those of IIIc were satisfactory.

The results of the X-ray diffraction study are summarised in Table 4, and the molecule is shown in Fig. 2. The structure of IIIc is similar to that of IIIa, with the $\mu\text{-MeCB(H)Et}$ group in the latter replaced by the $\mu\text{-PhCB(H)CH}_2\text{Ph}$ group in the former. The structural parameters for the two species are essentially the same. Hence the observed differences in spectroscopic properties must be due to IIIb and IIIc existing in solution as an equilibrium mixture of isomers.

At -40°C , limiting low temperature spectra of IIIb and IIIc are obtained. Thus in the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra of each complex eight CO resonances and four C_5H_5 signals are observed (Table 2). The ^1H spectra also show four C_5H_5 peaks, and significantly two BHW resonances are seen in each spectrum. Thus in both the low temperature $^{13}\text{C}\{-^1\text{H}\}$ and ^1H NMR limiting spectra of IIIb and IIIc twice the number of peaks are observed, based on the number anticipated from the structure of IIIc established by X-ray diffraction. A somewhat surprising feature of the $^{13}\text{C}\{-^1\text{H}\}$ spectra of the isomers of IIIb and IIIc is the ca. 40 ppm chemical shift difference between the $\mu\text{-CB}$ signals. Thus for the two isomers of IIIb these occur at δ 107.7 and 69.3 ppm, and for IIIc at δ 106.9 and 68.6 ppm. In contrast, in the room

TABLE 4

SELECTED INTERNUCLEAR DISTANCES (Å) AND ANGLES (°) FOR $[\text{W}_2\{\mu\text{-PhCB}(\text{H})\text{CH}_2\text{Ph}\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (IIIc)

W(1)–W(2)	2.981(1)	W(1)–B(1)	2.371(1)
W(2)–B(1)	2.407(8)	B(1)–C(22)	1.51(1)
C(15)–C(16)	1.50(1)	W(2)–H(1)	1.9(1)
W(1)–C(2)	1.97(1)	W(2)–C(4)	1.99(1)
W(2)–C(cp) ^a	2.34	W(2)–C(22)	2.144(6)
W(1)–C(22)	2.158(7)	B(1)–C(15)	1.60(1)
C(22)–C(23)	1.49(1)	W(1)–C(1)	1.94(1)
B(1)–H(1)	1.1(1)	W(1)–C(cp) ^a	2.36
W(2)–C(3)	2.00(1)		
W(1)–W(2)–B(1)	50.9(2)	W(1)–B(1)–W(2)	77.2(2)
W(2)–B(1)–C(22)	61.4(3)	W(1)–C(22)–B(1)	78.3(4)
B(1)–W(2)–C(22)	38.3(3)	W(2)–W(1)–C(22)	45.9(2)
W(2)–C(22)–C(23)	139.5(6)	B(1)–C(22)–C(23)	123.4(5)
W(2)–H(1)–B(1)	105(5)	W(1)–B(1)–C(15)	139.3(6)
C(1)–W(1)–C(2)	78.7(3)	W(1)–C(1)–O(1)	176(1)
W(2)–C(3)–O(3)	172(1)	W(1)–B(1)–C(22)	63.1(4)
W(2)–W(1)–B(1)	52.0(2)	B(1)–W(1)–C(22)	38.7(3)
W(2)–C(22)–B(1)	80.3(4)	W(1)–C(22)–C(23)	126.5(5)
W(1)–W(2)–C(22)	46.3(2)	B(1)–W(2)–H(1)	27(2)
C(15)–B(1)–C(22)	127.9(6)	W(2)–B(1)–C(15)	143.4(5)
W(2)–B(1)–H(1)	48(4)	W(1)–C(2)–O(2)	176(1)
C(3)–W(2)–C(4)	87.5(3)		
W(2)–C(4)–O(4)	180(1)		

^a Mean distance to cyclopentadienyl carbons.

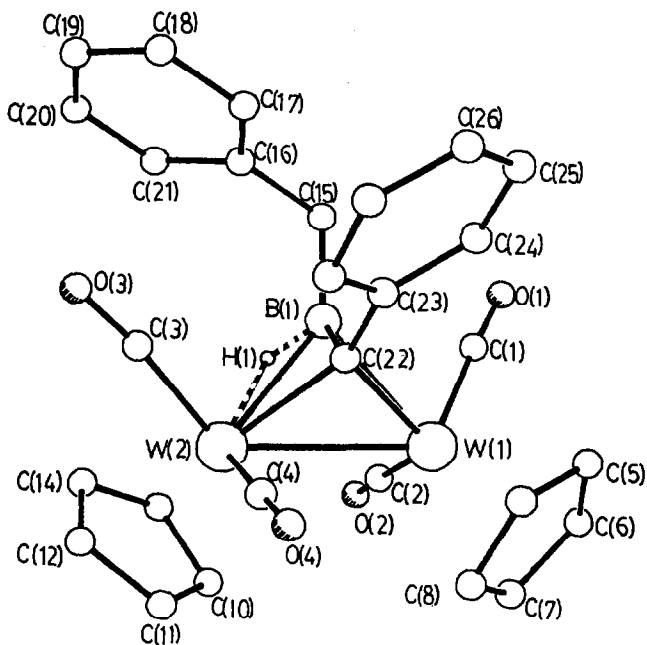
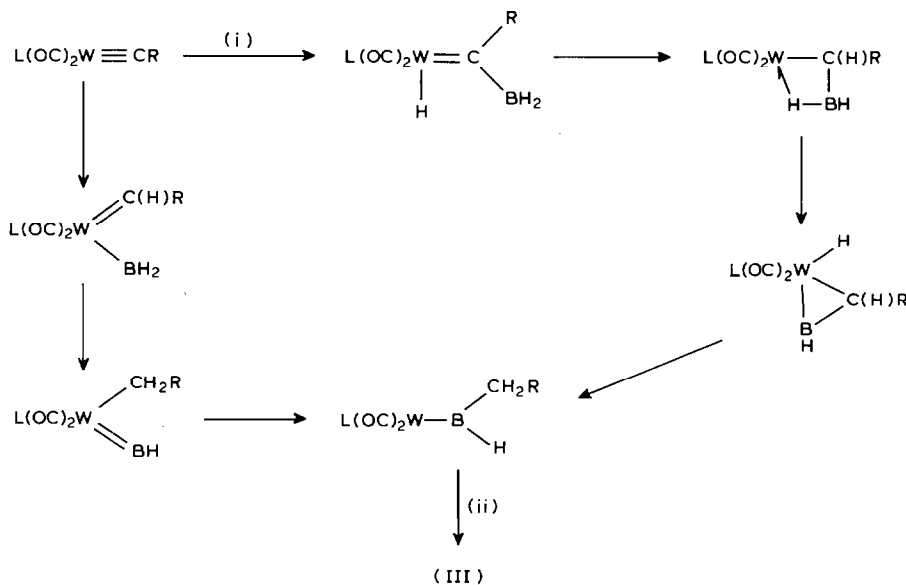


Fig. 2. Molecular structure of $[\text{W}_2\{\mu\text{-PhCB}(\text{H})\text{CH}_2\text{Ph}\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (IIIc).

temperature ^1H spectrum of IIIb only one broad C_5H_5 resonance occurs, while the spectrum of IIIc shows two broad signals. Moreover, for IIIc only one broad BHW peak (-10.8 ppm) is seen in the room temperature spectrum. Evidently in solution two isomers of each species occur which interconvert on the NMR time scale.

The peak intensities for each isomer of IIIb and IIIc are approximately of equal intensity, indicating that the species are present in solution in about equal amounts. Interestingly, NMR studies on IIIId at -40°C reveal the presence of only one isomer in solution (Table 2). Thus there is one high-field BHW resonance at $\delta -9.33$ ppm, and two $\eta\text{-C}_5\text{Me}_5$ peaks at $\delta 1.84$ and 1.99 ppm. As mentioned above, IIIa also exists as one isomer at low temperatures, but with some evidence of an exchange process at ambient temperatures.

The compounds II and the aforementioned dimolybdenum species $[\text{Mo}_2(\mu\text{-RC}_2\text{R})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{R} = \text{H}, \text{Et}$ or Ph) are unsymmetrical, on account of the semi-bridging carbonyl ligand. The molybdenum compounds have variable temperature NMR spectra interpreted in terms of a low-energy CO exchange process which generates C_2 symmetry, and a higher energy process which produces C_{2v} symmetry [6]. It is likely that the low energy C_2 -generating process proceeds via an intermediate without a semi-bridging carbonyl, as has been discussed elsewhere [7] in the context of the structure of $[\text{Mo}_2(\mu\text{-Me}_3\text{SiC}_2\text{SiMe}_3)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$. Similar dynamic processes are also possible with compounds III. However, although the latter are structurally akin to the di-molybdenum and -tungsten bridged-alkyne complexes they are more unsymmetrical, leading to a greater range of isomer possibilities and other rearrangement processes. Thus the $\text{W}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ fragments may adopt different orientations with respect to the B-H-W bridge, leading to the presence of different rotamers in solution. Moreover, the bridging hydride may shift between the two tungsten centres. It would appear from the data presented here that for IIIb



SCHEME 1. $\text{L} = \eta\text{-C}_5\text{H}_5$ or $\eta\text{-C}_5\text{Me}_5$, $\text{R} = \text{alkyl}$ or aryl ; (i) $+\text{BH}_3 \cdot \text{thf}$, (ii) $+\text{L}(\text{OC})_2\text{W}\equiv\text{CR}$.

and IIIc several dynamic processes occur. With IIIId, however, the one isomer formed does not show variable temperature NMR spectra, implying static behaviour, which is perhaps a consequence of the bulky C_5Me_5 groups.

The pathway by which the compounds III are formed is at present obscure. However, two possible routes are indicated in Scheme 1. These differ according to whether in an initial step a B-C or a B-W bond is formed. In either route transfer of hydrogen from boron to carbon occurs to afford a coordinatively and electronically unsaturated species $L(OC)_2WB(H)CH_2R$ which could react with the reagents $[W(\equiv CR)(CO)_2L]$ present to yield III.

In the formation of the species III all three hydrogens of the BH_3 group are incorporated in the products, two being transferred to a carbyne-carbon atom while the third forms a B-H-W bridge. This result prompted a study involving the reagent 9-borabicyclo[3.3.1]nonane (9-BBN) [2], a hydroborating reagent containing only one active B-H bond per molecule. The complexes $[W(\equiv Cr)(CO)_2(\eta-C_5H_5)]$ ($R = Me$ or C_6H_4Me-4) both react with 9-BBN in refluxing thf, but only the *p*-tolylmethylidynetungsten compound affords a stable product. The latter was identified as $[W\{\eta^3-CH(B_8H_{14})C_6H_4Me-4\}(CO)_2(\eta-C_5H_5)]$ (IV) only after an X-ray diffraction study (Table 5 and Figure 3). Compound IV contains an unusual organoboron ligand η^3 -bonded to the tungsten via carbon atoms C, C(1) and C(2), the last two being part of the tolyl group, and C being the original carbyne-carbon now carrying a hydrogen and the bicyclo-boron substituent. The η^3 co-ordination to tungsten via the arene ring in IV has been observed previously in the compounds $[M\{\eta^3-CH_2C_6H_4Me-4\}(CO)_2(\eta-C_5H_5)]$ ($M = Mo$ or W) [8,9]. Indeed we have prepared the tungsten complex via addition of HI to $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ to give $[WI(=C(H)C_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$, followed by treatment of the latter with $K[BH(CHMeEt)_3]$ [1]. Moreover, a series of structurally related compounds $[W\{\eta^3-CH(R)C_6H_4Me-4\}(CO)_2(\eta-C_5H_5)]$ ($R = Et, Pr^i, Ph$ or $CH_2C_6H_4Me-4$) has been obtained by reactions of $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ with organozinc compounds or $[CrPh_3(thf)_3]$ [10]. In these reactions also, as in the formation of IV, the $W\equiv C$ bond is reduced.

Examination of the 1H and $^{13}C\{-^1H\}$ NMR spectra of IV (Table 2) revealed the presence of two isomers, formed in the ratio ca. 4/1. These isomers probably differ according to whether the tungsten is ligated by C, C(1) and C(2), as found in the crystal (Fig. 3), or by C, C(1) and C(6).

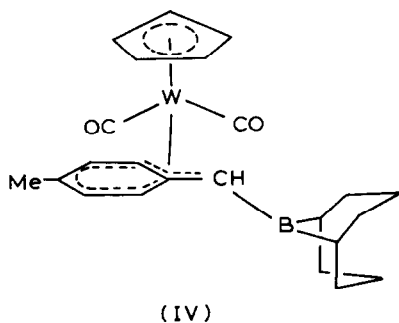


TABLE 5

SELECTED INTERNUCLEAR DISTANCES (Å) AND ANGLES (°) FOR $[\text{W}(\eta^3\text{-CH}(\text{BC}_8\text{H}_{14})\text{C}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (IV)

W-C	2.275(8)	W-C(2)	2.613(8)
C(1)-C(2)	1.43(1)	C(3)-C(4)	1.37(1)
C(5)-C(6)	1.37(1)	C(1)-C	1.47(1)
W-C(01)	1.971(9)	W-C(cp) ^a	2.34
W-C(1)	2.355(8)	C-B	1.52(1)
C(2)-C(3)	1.43(1)	C(4)-C(5)	1.41(1)
C(6)-C(1)	1.42(1)	C-H	1.00(8)
W-C(02)	1.951(9)		
C-W-C(1)	37.0(3)	C(1)-W-C(2)	32.9(2)
C-W-C(02)	91.4(3)	C(1)-W-C(02)	115.8(3)
C(2)-W-C(02)	102.1(3)	W-C-B	102.7(5)
W-C-C(1)	74.4(4)	B-C-C(1)	130.4(7)
W-C(1)-C(2)	83.5(5)	W-C(01)-O(1)	177.3(9)
C-W-C(2)	61.1(3)	C-W-C(01)	124.9(4)
C(1)-W-C(01)	100.7(4)	C(2)-W-C(01)	68.4(4)
C(01)-W-C(02)	78.6(4)	W-C-H	116(4)
B-C-H	115(5)	W-C(1)-C	68.5(4)
W-C(02)-O(2)	170.1(8)	W-C(2)-C(1)	63.6(4)

^a Mean distance to cyclopentadienyl carbon atoms.

The salts I may be formed by protonating the complexes II. It was, therefore, of interest to investigate the protonation of the species III. Compound IIIa reacts instantly with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ or $\text{CF}_3\text{SO}_3\text{H}$, but the latter reagent is the more satisfactory producing orange crystals of the salt $[\text{W}_2(\mu\text{-H})\{\mu\text{-MeCB}(\text{H})\text{Et}\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2][\text{SO}_3\text{CF}_3]$ (Va). An analogous complex $[\text{W}_2(\mu\text{-H})\{\mu\text{-(4-MeC}_6\text{H}_4)\text{CBH-4}\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2][\text{SO}_3\text{CF}_3]$ (Vb) has also been prepared.

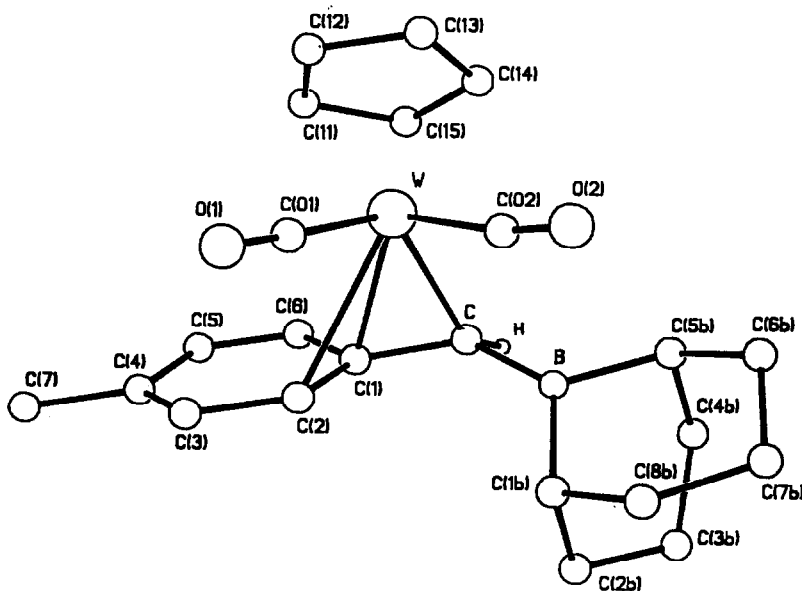
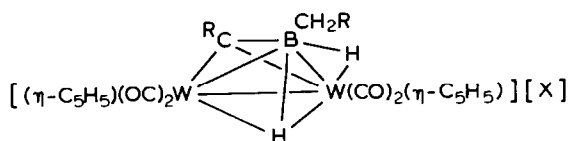


Fig. 3. Molecular structure of $[\text{W}(\eta^3\text{-CH}(\text{BC}_8\text{H}_{14})\text{C}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (IV).



(Va , R = Me , X = SO₃CF₃ ;

Vb , R = C₆H₄Me-4 , X = BF₄)

(CH₂C₆H₄Me-4)(CO)₄(η-C₅H₅)₂[[BF₄]] (Vb) was obtained from IIIb and HBF₄ · Et₂O. Data for these salts are given in Tables 1 and 2. An X-ray diffraction study was carried out on Va (see Table 6 and Fig. 4) in an attempt to locate the added proton but neither bridging hydride ligand could be defined precisely. The results showed, however, that the W–W bond (3.012(1) Å) was longer than that in IIIa (2.978(2) Å) and that W(2)–B (2.44(2) Å) was appreciably longer than W(1)–B (2.35(2) Å). In IIIa the difference between the W–B separations is less.

The NMR data for Va and Vb are structurally informative. The ¹H spectrum of Va at ambient temperatures shows a broad high-field signal at –11.16 ppm, characteristic for BHW. At –50 °C, however, two such resonances are observed at δ –10.21 and –12.07. We tentatively ascribe the former to a three-centre B–H–W bond, and the latter to a hydride triply bridging the BW₂ face in Va, in line with the trend in W–W and B–W separations mentioned above. Evidently, however, the two

TABLE 6

SELECTED INTERNUCLEAR DISTANCES (Å) AND ANGLES (°) FOR [W₂(μ-H){μ-MeCB(H)Et}(CO)₄(η-C₅H₅)₂][SO₃CF₃] (Va)

W(1)–W(2)	3.012(1)	W(2)–B	2.44(2)
W(1)–B	2.35(2)	B–C(15)	1.53(3)
C(17)–C(18)	1.46(3)	W(1)–C(2)	2.07(2)
W(2)–C(4)	2.01(2)	W(2)–C(cp) ^a	2.29
W(2)–C(15)	2.17(2)	W(1)–C(15)	2.10(2)
C(15)–C(16)	1.55(3)	B–C(17)	1.56(3)
W(1)–C(1)	1.99(2)	W(2)–C(3)	2.02(2)
W(1)–C(cp) ^a	2.32		
W(2)–W(1)–B	52.4(5)	W(2)–B–W(1)	77.9(6)
W(1)–B–C(15)	61(1)	W(2)–C(15)–B	81(1)
B–W(1)–C(15)	39.6(7)	W(1)–W(2)–C(15)	44.2(4)
W(1)–C(15)–C(16)	135(1)	B–C(15)–C(16)	127(2)
W(1)–B–C(17)	144(2)	C(1)–W(1)–C(2)	83.2(8)
W(1)–C(2)–O(2)	178(2)	W(2)–C(4)–O(4)	172(2)
W(1)–C(2)–B	49.8(5)	W(2)–B–C(15)	61(1)
W(1)–C(15)–B	79(1)	B–W(2)–C(15)	38(1)
W(2)–W(1)–C(15)	46.0(5)	W(2)–C(15)–C(16)	127(1)
C(17)–B–C(15)	125(2)	W(2)–B–C(17)	138(2)
C(4)–W(2)–C(3)	83.7(8)	W(1)–C(1)–O(1)	179(2)
W(2)–C(3)–O(3)	175(2)		

^a Mean distance to cyclopentadienyl carbons.

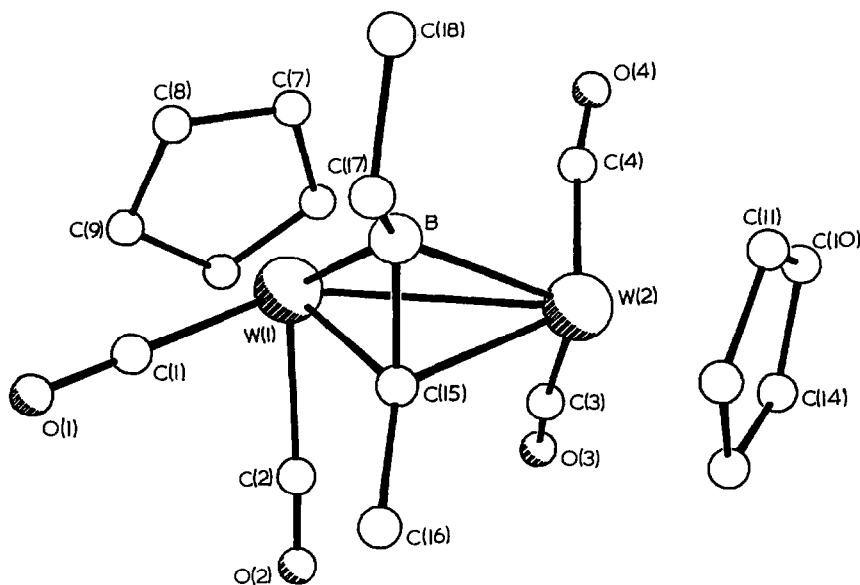
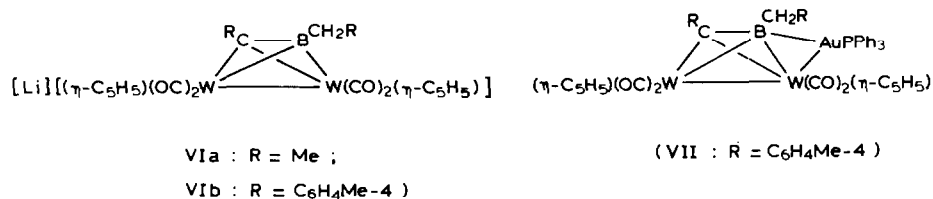


Fig. 4. Molecular structure of the cation $[\text{W}_2(\mu\text{-H})\{\mu\text{-MeCB(H)Et}\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]^+$ (Va).

hydride ligands exchange on the NMR time scale at room temperature. It is noteworthy that the exchange process is of higher energy for Vb since two highfield BHW resonances are observed in both the room temperature spectrum and that measured at -40°C .

An attempt was made to remove a proton from IIIa and IIIb with butyllithium. These reactions afforded extremely air and moisture sensitive salts presumed to be $[\text{Li}][\text{W}_2(\mu\text{-RCBCH}_2\text{R})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (VIa, R = Me; VIb, R = $\text{C}_6\text{H}_4\text{Me-4}$). It was not possible to obtain microanalytical data for these species which were reprotoneated to give IIIa and IIIb, respectively, even by NMR solvents. Treatment of VIa with one equivalent of $\text{CF}_3\text{CO}_2\text{D}$ afforded $[\text{W}_2\{\mu\text{-MeCB(D)Et}\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (^2H NMR, δ -10.1 ppm, B-D-W).

Finally, treatment of a thf solution of VIb with $[\text{AuCl}(\text{PPh}_3)]$ in the presence of TIPF_6 affords a complex formulated as $[\text{W}_2\{\mu\text{-(4-MeC}_6\text{H}_4)\text{CB}(\text{AuPPh}_3)\text{CH}_2\text{-C}_6\text{H}_4\text{Me-4}\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (VII), data for which are given in Tables 1 and 2. Compound VII shows no high-field B-H-W resonance in its ^1H NMR spectrum, and the isolobal relationship between the groups H and AuPPh_3 leads us to propose the structure indicated for VII, which is related to that of IIIb. Compound VII is relatively unstable, and crystals could not be grown for an X-ray diffraction study.



The results presented herein suggest that the addition of various borane fragments, or even the boranes themselves, to carbon–metal triple bonds could be a promising area for study. Metal promoted hydrogen transfer from boron to carbon, demonstrated in this study, could result in the formation of new types of metallaboron compound.

Experimental

All experiments were carried out under oxygen-free nitrogen, using Schlenk tube techniques. Light petroleum refers to that fraction of b.p. 40–60 °C. The compounds $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ ($R = Ph, C_6H_4Me-4$ [11] or Me [12]) and $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5Me_5)]$ [13] were made by methods described in the literature. The borane complexes $BH_3 \cdot thf$ and 9-BBN were commercial samples from Aldrich. Data for the new compounds are given in Tables 1 and 2.

Hydroboration of the Complexes $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ ($R = Me, C_6H_4Me-4$ or Ph)

(i) A thf (30 cm^3) solution of $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$ (1.0 g, 3.0 mmol) was treated with $BH_3 \cdot thf$ (4 cm^3 of a 1.0 mol dm^{-3} solution in thf), and the mixture stirred for 5 min. Solvent was removed in vacuo and the residue dissolved in Et_2O (ca. 15 cm^3) and chromatographed on an alumina column (10 \times 2.5 cm). Elution with the same solvent gave a red-orange eluate. Removal of solvent in vacuo afforded orange crystals of $[W_2\{\mu-MeCB(H)Et\}(CO)_4(\eta-C_5H_5)_2]$ (IIIa) (0.82 g).

(ii) Similarly, $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ (0.50 g, 1.2 mmol) in thf (30 cm^3) was treated with the $BH_3 \cdot thf$ reagent (2 cm^3), and the mixture stirred for 18 h. Solvent was removed in vacuo, and the residue dissolved in Et_2O (ca. 10 cm^3) and chromatographed on alumina. Elution with Et_2O gave a red eluate. Solvent was removed in vacuo affording red crystals of $[W_2\{\mu-(4-MeC_6H_4)CB(H)CH_2C_6H_4Me-4\}(CO)_4(\eta-C_5H_5)_2]$ (IIIb) (0.40 g).

(iii) A thf (10 cm^3) solution of $[W(\equiv CPh)(CO)_2(\eta-C_5H_5)]$ (0.25 g, 0.63 mmol) was treated with $BH_3 \cdot thf$ (1 cm^3) and the resulting red-brown solution stirred for ca. 1 h. Solvent was removed in vacuo, and the residue dissolved in CH_2Cl_2 /light petroleum (5 cm^3 , 2/1) and chromatographed. Elution with the same solvent mixture gave a red eluate. Removal of solvent in vacuo, and recrystallisation of the residue from CH_2Cl_2 /light petroleum (10 cm^3 , 1/5) yielded red crystals of $[W_2\{\mu-PhCB(H)CH_2Ph\}(CO)_4(\eta-C_5H_5)_2]$ (IIIc) (0.16 g).

Hydroboration of the Complex $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5Me_5)]$

The compound $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5Me_5)]$ (0.25 g, 0.52 mmol) in thf (10 cm^3) was treated with $BH_3 \cdot thf$ (1 cm^3). After 5 h, solvent was removed in vacuo and the residue dissolved in Et_2O /light petroleum (5 cm^3 , 1/9) and chromatographed on alumina (column ca. 20 \times 2.5 cm). Slow elution with the same solvent mixture removed unreacted $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5Me_5)]$ (orange) followed by an unidentified yellow product. Continued elution afforded a red-brown eluate which, after removal of solvent in vacuo gave brown crystals of $[W_2\{\mu-(4-MeC_6H_4)CB(H)CH_2C_6H_4Me-4\}(CO)_4(\eta-C_5Me_5)_2]$ (IIIId) (0.11 g).

Reaction of [W(\equiv CC₆H₄Me-4)(CO)₂(η -C₅H₅)] with 9-Borabicyclo[3.3.1]nonane

A mixture of [W(\equiv CC₆H₄Me-4)(CO)₂(η -C₅H₅)] (0.50 g, 1.2 mmol) and 9-BBN (0.20 g, 1.6 mmol) in thf (20 cm³) was refluxed for ca. 2 h. Solvent was removed in vacuo, and the residue dissolved in Et₂O/thf (5 cm³, 1/1) and chromatographed on alumina, eluting with the same solvent mixture. Solvent was removed in vacuo from the red eluate, and the residue recrystallised from Et₂O/light petroleum (10 cm³, 1/4) to give maroon crystals of [W(η ³-CH(BC₈H₁₄)C₆H₄Me-4)(CO)₂(η -C₅H₅)] (IV) (0.58 g).

Protonation studies

(i) A Et₂O (20 cm³) solution of IIIa (0.20 g, 0.30 mmol) at room temperature was treated dropwise over ca. 5 min with CF₃SO₃H (0.1 cm³). Immediate precipitation of orange crystals of [W₂(μ -H){ μ -MeCB(H)Et}(CO)₄(η -C₅H₅)₂][SO₃CF₃] (Va) (0.25 g) was observed. The product was washed with Et₂O (3 \times 5 cm³) and dried in vacuo.

(ii) Similarly, IIIb (0.20 g, 0.24 mmol) in Et₂O (20 cm³) with HBF₄·Et₂O (0.1 cm³) gave an immediate precipitation of orange crystals of [W₂(μ -H){ μ -(4-MeC₆H₄)CB(H)CH₂C₆H₄Me-4}(CO)₄(η -C₅H₅)₂][BF₄] (Vb) (0.19 g). The product was washed with Et₂O (3 \times 5 cm³) and dried in vacuo.

Deprotonation studies

Treatment of IIIa (0.10 g, 0.15 mmol) in thf (20 cm³) at -20 °C with LiBuⁿ (0.15 mmol) resulted in an immediate colour change from red to black. Removal of solvent in vacuo gave a purple oil which was dissolved in CH₂Cl₂ (2 cm³) at 0 °C and slowly treated with light petroleum (10 cm³), causing precipitation. The supernatant liquid was removed with a syringe and the residue washed with light petroleum (2 \times 5 cm³). Drying in vacuo gave an extremely air and moisture sensitive purple powder assumed to be [Li][W₂(μ -MeCBEt)(CO)₄(η -C₅H₅)₂] (VIa) (0.09 g, 90%). Attempts to obtain stable NEt₄⁺ or N(PPh₃)₂⁺ salts were unsuccessful.

An identical procedure was used to obtain a purple microcrystalline product [Li][W₂{ μ -(4-MeC₆H₄)CBCH₂C₆H₄Me-4}(CO)₄(η -C₅H₅)₂] (VIb) (0.08 g, 80%) from IIIb (0.10 g, 0.12 mmol) and LiBuⁿ (0.12 mmol) in thf (20 cm³) at -20 °C. For VIb, ν_{\max} (CO), 1924s, 1840s, 1803sh, 1768sh and 1703m cm⁻¹ (in thf).

Synthesis of the Complex [W₂{ μ -(4-MeC₆H₄)CB(AuPPh₃)CH₂C₆H₄Me-4}(CO)₄(η -C₅H₅)₂]

A thf (20 cm³) solution of VIb (0.10 g, 0.12 mmol) was treated with [AuCl(PPh₃)] (0.06 g, 0.12 mmol) and TIPF₆ (0.06 g, 0.18 mmol). There was an immediate colour change from dark red to black. Removal of solvent in vacuo gave a dark brown oil, which was dissolved in CH₂Cl₂ (5 cm³) and chromatographed on alumina. Elution with CH₂Cl₂ gave a dark brown eluate. Removal of solvent in vacuo afforded a brown residue, which was recrystallised from CH₂Cl₂/light petroleum (10 cm³, 1/4) at 0 °C to yield [W₂{ μ -(4-MeC₆H₄)CB(AuPPh₃)CH₂C₆H₄Me-4}(CO)₄(η -C₅H₅)₂] (VII) (0.08 g).

Crystal structure determinations

The crystal and other experimental data for compounds IIIa, IIIc, IV, and Va are summarized in Table 7. All data were corrected for Lorentz, polarisation and X-ray

TABLE 7
DATA FOR CRYSTAL STRUCTURE ANALYSES ^a

Compound	IIIa	IIIc	IV	Va
<i>M</i>	C ₁₈ H ₁₉ BO ₄ W ₂ 677.9	C ₂₈ H ₂₃ BO ₄ W ₂ 802.0	C ₂₃ H ₂₇ BO ₂ W 530.1	C ₁₉ H ₂₀ BF ₃ O ₇ SW ₂ 827.9
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Tetragonal
Crystal habit	Prisms	Prisms	Prisms	Irregular
Space group	<i>P</i> 2 ₁ / <i>n</i> (non- standard setting of No. 14)	<i>P</i> 2 ₁ / <i>n</i> (non- standard setting of No. 14)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (no. 19)	<i>I</i> 4 ₁ / <i>a</i>
<i>a</i> (Å)	12.594(8)	14.977(6)	10.637(4)	15.152(5)
<i>b</i> (Å)	16.114(14)	9.634(2)	13.266(5)	15.152(5)
<i>c</i> (Å)	9.321(5)	18.351(6)	14.181(5)	40.90(2)
β (°)	100.22(5)	111.13(3)	—	—
<i>U</i> (Å ³)	1861(2)	2470(1)	2001(1)	9391(6)
<i>Z</i>	4	4	4	16
<i>D</i> _c (g cm ⁻³)	2.42	2.16	1.76	2.34
<i>F</i> (000)	1248	1504	1040	6174
<i>T</i> (K)	298	298	200	298
μ (Mo- <i>K</i> _α) (cm ⁻¹)	126.37	95.42	59.11	101.53
Crystal size (mm)	0.10 × 0.30 × 0.53	0.60 × 0.30 × 0.20	0.30 × 0.20 × 0.10	0.15 × 0.10 × 0.05
2 θ min : max (°)	3 : 50	3 : 50	3 : 60	3 : 50
Data recorded	3558	4602	3376	5381
Data unique	2031	4452	3214	4639
Data used	1886	3851	2813	2895
<i>n</i> in <i>I</i> ≥ <i>n</i> σ(<i>I</i>)	2.0	3.5	2.0	4.0
Absorption correction method	Numerical (Faces)	Empirical (ψ scans)	Empirical (ψ scans)	Empirical (ψ scans)
Weighting scheme: <i>g</i> in $w^{-1} = [\sigma^2(F_0) + g F_0 ^2]$	0.0006	0.0010	0.0005	0.0004
Final R(<i>R'</i>)	0.040 (0.040)	0.037 (0.041)	0.036 (0.034)	0.062 (0.063)
Largest final difference electron- density features (e Å ⁻³)	1.00	2.00	1.64	1.5

^a Common to all data: graphite-monochromated Mo-*K*_α X-radiation. λ 0.71069 Å. Nicolet *P3m* and *P2*₁ automated diffractometers operating in ω -2 θ scan mode. Refinement was by blocked-cascade least squares.

absorption effects. The structures were solved by Patterson and Fourier methods by which all non-hydrogen atoms were located and refined with anisotropic thermal parameters, with the exception of the SO₃CF₃ anion and C₅H₅ groups in Va, which were disordered and refined isotropically. Hydrogen atoms (with exceptions noted below) were incorporated in calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters equal to 1.2 times the equivalent isotropic thermal parameter of the attached carbon atom. For IIIa and IIIc, B(μ -*H*)W was located and refined isotropically. Location of the B–H hydrogens in Va was not possible. The correctness of the given enantiomorph in IV was checked by refinement. All computa-

tions were carried out with an Eclipse S230 (Data General) computer with the SHELXTL system of programs [14]. Scattering factors were taken from [15], as were the corrections for atomic anomalous dispersion. The atom coordinates, full listing of bond distances and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Structure factors are available from the authors.

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References

- 1 J.A.K. Howard, J.C. Jeffery, J.C.V. Laurie, I. Moore, F.G.A. Stone, and A. Stringer, *Inorg. Chim. Acta*, 100 (1985) 23.
- 2 H.C. Brown and M. Zaidlewicz, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Pergamon Press, 1982, Vol. 7, Sections 45.2–45.5.
- 3 G.A. Carriedo, G.P. Elliott, J.A.K. Howard, D.B. Lewis, and F.G.A. Stone, *J. Chem. Soc., Chem. Commun.*, (1984) 1585.
- 4 W.I. Bailey, D.M. Collins, and F.A. Cotton, *J. Organomet. Chem.*, 135 (1977) C53.
- 5 W.I. Bailey, F.A. Cotton, J.D. Jamerson, and J.R. Kolb, *J. Organomet. Chem.*, 121 (1976) C23.
- 6 W.I. Bailey, M.H. Chisholm, F.A. Cotton, and L.A. Rankel, *J. Am. Chem. Soc.*, 100 (1978) 5764.
- 7 J.A. Beck, S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M.J. Winter, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, (1982) 195.
- 8 R.B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, 88 (1966) 709.
- 9 F.A. Cotton and T.J. Marks, *J. Am. Chem. Soc.*, 91 (1969) 1339. F.A. Cotton and M.D. LaPrade, *ibid.*, 90 (1968) 5418.
- 10 J.C. Jeffery, A.L. Ratermann, and F.G.A. Stone, *J. Organomet. Chem.*, 289 (1985) 367.
- 11 E.O. Fischer, T.L. Lindner, G. Hüttner, P. Friedrich, F.R. Kreissl, and J.O. Besenhard, *Chem. Ber.*, 110 (1977) 3397.
- 12 W. Uedelhoven, K. Eberl, and F.R. Kreissl, *Chem. Ber.*, 112 (1979) 3376.
- 13 E. Delgado, L.J. Farrugia, J. Hein, J.C. Jeffery, A.L. Ratermann, and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, in press.
- 14 G.M. Sheldrick, SHELXTL programs for use with the Nicolet X-ray system, Cambridge, 1976; updated at Göttingen, 1981.
- 15 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, Vol. 4.