Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 74.[1] Salts of the Anions $[W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ (R = C_6H_4Me-2 or $C_6H_3Me_2$-2,6) as Reagents for the Synthesis of Compounds with Heteronuclear Metal–Metal Bonds: Crystal Structure of $[NEt_4]$-$[FeW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta^5\text{-}C_2B_9H_9Me_2)]$ *

Franz-Erich Baumann, Judith A. K. Howard, Rupert J. Musgrove, Paul Sherwood, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 1TS

The salts $[X][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (X = NEt_4, R = C_6H_4Me-2 or $C_6H_3Me_2$-2,6; X = PPh_4, R = $C_6H_3Me_2$-2,6) have been prepared, and used to synthesise a variety of compounds containing heteronuclear metal–metal bonds. Thus treatment of $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ with $[AuCl(PPh_3)]$ in thf (tetrahydrofuran), in the presence of KPF_6, affords the dimetal compounds $[AuW(\mu\text{-}CR)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$. The reaction between $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) and $[PPh_4][W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ affords the salt $[PPh_4][PtW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(cod)(\eta^5\text{-}C_2B_9H_9Me_2)]$. The latter with $[AuCl(PPh_3)]$ in thf, in the presence of $TlPF_6$, yields the trimetal compound $[AuPtW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(PPh_3)(cod)(\eta^5\text{-}C_2B_9H_9Me_2)]$. Treatment of $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = C_6H_4Me-2) with $[Fe_3(CO)_{12}]$ in thf affords a mixture of the compounds $[NEt_4][FeW(\mu\text{-}CR)(CO)_5(\eta^5\text{-}C_2B_9H_9Me_2)]$, $[NEt_4][FeW\{\mu\text{-}CH(R)\}(\mu\text{-}\sigma{:}\eta^5\text{-}C_2B_9H_8Me_2)(\mu\text{-}CO)(CO)_5]$, and $[NEt_4][Fe_2W(\mu_3\text{-}CR)(\mu_3\text{-}\sigma{:}\sigma'{:}\eta^5\text{-}C_2B_9H_7Me_2)(CO)_8]$. A similar reaction with $[NEt_4][W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ gives $[NEt_4][FeW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta^5\text{-}C_2B_9H_9Me_2)]$ as the only iron–tungsten compound. The structure of the latter has been established by *X*-ray diffraction. The Fe–W bond [2.600(1) Å] is spanned by the $CC_6H_3Me_2$-2,6 group [μ-C–Fe 1.891(5) and μ-C–W 1.976(6) Å]. The iron atom is ligated by three essentially orthogonal CO groups. The tungsten atom is co-ordinated by the pentagonal face of the *nido*-icosahedral fragment $C_2B_9H_9Me_2$, and by two CO groups, one of which semi-bridges the metal–metal bond [W–C–O 165.4(6)°]. The reaction between $[PPh_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = $C_6H_3Me_2$-2,6) and $[Ru(CO)(NCMe)_2(\eta\text{-}C_5H_5)][BF_4]$ in CH_2Cl_2 gives the dimetal compound $[RuW(\mu\text{-}CR)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ which has an exopolyhedral $B\text{–}H\rightharpoonup Ru$ three-centre bond. The n.m.r. spectra (^1H, ^{13}C-$\{^1H\}$, ^{11}B-$\{^1H\}$, and ^{31}P-$\{^1H\}$) of the new compounds are discussed in relation to their structures.

In a series of papers[2] we have described how the salts [X]-$[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ [X = $N(PPh_3)_2$ (**1a**), PPh_4 (**1b**), or $P(CH_2Ph)Ph_3$ (**1c**)] may be used as reagents for preparing complexes in which heteronuclear metal–metal bonds are bridged by the *p*-tolylmethylidyne group. Moreover, in some syntheses a non-spectator role for the carbaborane ligand has been identified. This novel behaviour can take a variety of forms, the scope of which yet remains to be defined. The most common modification of the carbaborane group involves some slippage away from the tungsten so as to form an exopolyhedral $B\text{–}H\rightharpoonup M$ bond with the adjacent metal atom. This is accomplished using a BH fragment in the pentagonal face of the ligand. The metal–metal bond thus becomes bridged both by the carbaborane cage and by the alkylidyne group. Moreover, further transformations can ensure, for example, formation of an exopolyhedral boron–metal σ bond. This apparently arises from transfer of the hydrogen atom of a $B\text{–}H\rightharpoonup M$ moiety to the alkylidyne group to produce a μ-*p*-tolylmethylidene ligand.

In order to extend this area of chemistry, we are investigating reactions of low-valent metal–ligand groups with the salts [X]-$[W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ [X = NEt_4, R = C_6H_4Me-2 (**1d**) or $C_6H_3Me_2$-2,6 (**1e**); X = PPh_4, R = $C_6H_3Me_2$-2,6 (**1f**)]. It was anticipated that the presence in these salts of *ortho* substituents on the benzene ring would introduce modifications in the reactivity patterns of (**1d**)—(**1f**), compared with those of (**1a**)—(**1c**). The increased steric requirements at the co-ordinated alkylidyne-carbon atom of a C_6H_4Me-2 or a $C_6H_3Me_2$-2,6 group, *versus* the less bulky C_6H_4Me-4 fragment could affect the nature of the 'mixed-metal' complexes obtained in reactions of (**1d**)—(**1f**). Moreover, it was hoped that the results might shed light on previously observed modifications of the $\eta^5\text{-}C_2B_9H_9Me_2$ ligand in this chemistry.

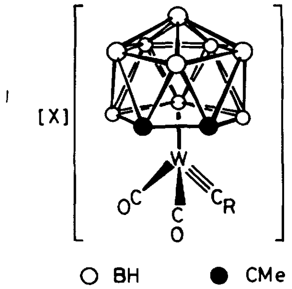
Results and Discussion

The salts (**1d**)—(**1f**) were prepared by treating thf (tetrahydrofuran) solutions of the compounds $[W(\equiv CR)Br(CO)_4]$ (R = C_6H_4Me-2 or $C_6H_3Me_2$-2,6) with $Na_2[7,8\text{-}C_2B_9H_9Me_2]$, followed by addition of NEt_4Cl or PPh_4Cl, as appropriate. Characterising data for (**1d**)—(**1f**), given in Tables 1—2, call for little comment. The i.r. spectra show two peaks in the CO stretching region, that at lower frequency being the more intense. In the ^{13}C-$\{^1H\}$ n.m.r. spectra, characteristic resonances for the alkylidyne-carbon nuclei occur at δ 298.1 for (**1d**) and at 299.2 p.p.m. for (**1e**). In the spectrum of (**1a**) the corresponding signal is at δ 298.3 p.p.m.[2a]

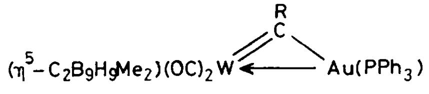
---

* μ-Carbonyl-1,1,1,2-tetracarbonyl-2-[7′—11′-η-nonahydro-7′,8′-dimethyl-7′,8′-dicarba-*nido*-undecaborato(2−)]-μ-*o*-xylylmethylidyne-irontungsten(*Fe–W*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.



	X	R
(1a)	$N(PPh_3)_2$	C_6H_4Me-4
(1b)	PPh_4	C_6H_4Me-4
(1c)	$P(CH_2Ph)Ph_3$	C_6H_4Me-4
(1d)	NEt_4	C_6H_4Me-2
(1e)	NEt_4	$C_6H_3Me_2$-2,6
(1f)	PPh_4	$C_6H_3Me_2$-2,6



	R
(2a)	C_6H_4Me-4
(2b)	C_6H_4Me-2
(2c)	$C_6H_3Me_2$-2,6

Earlier we have shown[2a] that the gold compound [AuCl(PPh$_3$)] reacts with the salt (**1a**) in the presence of TlPF$_6$ to give the gold–tungsten complex (**2a**). The thallium salt was added to facilitate removal of chloride as insoluble TlCl. Treatment of (**1d**) or (**1e**) with [AuCl(PPh$_3$)] in thf, in the presence of KPF$_6$, affords the related products [AuW(μ-CR)(CO)$_2$(PPh$_3$)(η^5-$C_2B_9H_9Me_2$)] [R = C_6H_4Me-2 (**2b**) or $C_6H_3Me_2$-2,6 (**2c**)]. Use of KPF$_6$ rather than TlPF$_6$ in these reactions has the advantage of avoiding a toxic reagent.

Compounds (**2b**) and (**2c**) were characterised by the data given in Tables 1 and 2. Diagnostic doublet resonances for the μ-C nuclei appear in their ^{13}C-{^{1}H} n.m.r. spectra: for (**2b**) at δ 287.7 [d, *J*(PC) 24] and for (**2c**) at δ 284.5 p.p.m. [d, *J*(PC) 24 Hz]. The corresponding resonance in the spectrum of (**2a**) is at δ 292.9 p.p.m. [*J*(PC) 28 Hz].[2a] The structures of the complexes (**2**) are well established, as a consequence of the previously reported[2a] *X*-ray diffraction study on (**2a**). Moreover, in these compounds, as discussed earlier, there are alternative descriptions possible for the electron distribution within the three-membered μ-CAuW ring. Herein we have chosen to involve a formulation with a Au→W donor bond. However, the isolobal relationship existing between the groups Au(PPh$_3$) and H might allow an alternative formulation involving donation of the pair of electrons in the μ-C–Au bond to the tungsten. This bonding mode would be akin to agostic bonding by C–H groups.[3,4]

Although in the solid state, the three compounds (**2**) appear to be comparable in stability, it was observed that in thf solutions (**2b**) partially decomposed, affording solutions containing the anion [W(≡CC_6H_4Me-2)(CO)$_2$(η^5-$C_2B_9H_9Me_2$)]$^-$;

Table 1. Analytical[a] and physical data for the complexes

Compound	Colour	Yield (%)	ν(CO)[b]/cm^{-1}	Analysis (%) C	H	N
(**1d**) [NEt$_4$][W(≡CC_6H_4Me-2)(CO)$_2$(η^5-$C_2B_9H_9Me_2$)]	Orange	73	1 959s, 1 858vs	39.2 (41.7)	7.2 (6.7)	2.2 (2.2)
(**1e**) [NEt$_4$][W(≡$CC_6H_3Me_2$-2,6)(CO)$_2$(η^5-$C_2B_9H_9Me_2$)]	Red	80	1 958s, 1 877vs	42.9 (42.7)	7.6 (6.9)	2.2 (2.2)
(**1f**) [PPh$_4$][W(≡$CC_6H_3Me_2$-2,6)(CO)$_2$(η^5-$C_2B_9H_9Me_2$)]	Red	80	1 957s, 1 875vs	54.4 (54.7)	5.7 (5.2)	
(**2b**) [AuW(μ-CC_6H_4Me-2)(CO)$_2$(PPh$_3$)(η^5-$C_2B_9H_9Me_2$)]	Orange	58	[c] 2 004vs, 1 936s	38.7 (39.6)	4.1 (3.9)	
(**2c**) [AuW(μ-$CC_6H_3Me_2$-2,6)(CO)$_2$(PPh$_3$)(η^5-$C_2B_9H_9Me_2$)]	Orange-red	63	2 005vs, 1 936s	41.7 (40.6)	3.9 (4.0)	
(**3c**) [PPh$_4$][PtW(μ-$CC_6H_3Me_2$-2,6)(CO)$_2$(cod)(η^5-$C_2B_9H_9Me_2$)]	Dark red	79	1 918s, 1 710mbr	46.3 (48.7)	4.9 (4.9)	
(**3d**) [PPh$_4$][PtW(μ-$CC_6H_3Me_2$-2,6)(CO)$_2$(PMePh$_2$)$_2$-(η^5-$C_2B_9H_9Me_2$)]	Dark[d] red	100	[e] 1 887s, 1 796mbr			
(**5**) [AuPtW(μ-$CC_6H_3Me_2$-2,6)(CO)$_2$(PPh$_3$)(cod)-(η^5-$C_2B_9H_9Me_2$)]	Brown-Black	55	1 967vs, 1 804mbr	37.6 (38.5)	3.6 (4.0)	
(**6b**) [NEt$_4$][FeW{μ-CH(C_6H_4Me-2)}(μ-σ:η^5-$C_2B_9H_8Me_2$)-(μ-CO)(CO)$_5$]	Dark red	69	2 030s, 1 971 (sh), 1 963vs, 1 950 (sh), 1 892m, 1 759w	38.7 (38.9)	5.5 (5.3)	1.7 (1.8)
(**7b**) [NEt$_4$][Fe$_2$W(μ$_3$-CC_6H_4Me-2)(μ$_3$-σ:σ′:η^5-$C_2B_9H_7Me_2$)-(CO)$_8$]	Dark red	5	2 029s, 1 985vs, 1 975s, 1 961s, 1 932w, 1 922vw, 1 897w	37.2 (36.9)	5.2 (4.4)	1.8 (1.5)
(**8a**) [NEt$_4$][FeW(μ-CC_6H_4Me-2)(CO)$_5$(η^5-$C_2B_9H_9Me_2$)]	Dark brown	57	2 028vs, 1 964s, 1 955s, 1 796wbr	38.7 (38.8)	5.7 (5.4)	1.7 (1.9)
(**8b**) [NEt$_4$][FeW(μ-CC_6H_4Me-2)(CO)$_4$(PMe$_3$)(η^5-$C_2B_9H_9Me_2$)]	Dark brown	14	1 972vs, 1 917s, 1 879m, 1 740wbr	38.9 (39.5)	6.2 (6.3)	1.8 (1.7)
(**8c**) [NEt$_4$][FeW(μ-$CC_6H_3Me_2$-2,6)(CO)$_5$(η^5-$C_2B_9H_9Me_2$)]	Black	30	2 028vs, 1 966s, 1 954s, 1 940 (sh), 1 795mbr	37.9 (39.6)	5.8 (5.6)	1.8 (1.8)
(**10a**) [RuW(μ-$CC_6H_3Me_2$-2,6)(CO)$_3$(η-C_5H_5)(η^5-$C_2B_9H_9Me_2$)]	Black	32	[f] 2 009s, 1 987vs, 1 920s	34.6 (35.4)	4.3 (4.8)	
(**10b**) [RuW(μ-$CC_6H_3Me_2$-2,6)(CO)$_2$(PMe$_2$Ph)(η-C_5H_5)-(η^5-$C_2B_9H_9Me_2$)]	Yellow	34	1 976vs, 1 898s	41.5 (40.9)	4.6 (4.9)	

[a] Calculated values are given in parentheses. [b] Measured in thf, unless otherwise stated. A broad band due to B–H is observed at *ca.* 2 550 cm^{-1}. [c] Complex decomposes in thf (see text). In CH_2Cl_2 bands for (**2b**) are at 2 007vs and 1 938s cm^{-1}. [d] Oil, see text. [e] In CH_2Cl_2. [f] In Et_2O.

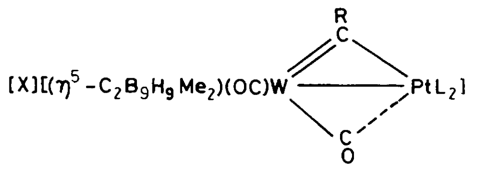
Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the complexes

Compound	^1H (δ)[b,c]	^{13}C (δ)[d]
(1d)	1.52 [t of t, 12 H, $\mathrm{NCH_2}\mathit{Me}$, *J*(HH) 7, *J*(NH) 2], 2.08 (s, 6 H, CMe), 2.55 (s, 3 H, Me-2), 2.99 [q, 8 H, $\mathrm{NC}\mathit{H}_2\mathrm{Me}$, *J*(HH) 7], 7.00—7.48 (m, 4 H, C_6H_4)	298.1 [C≡W, *J*(WC) 198], 227.7 [CO, *J*(WC) 181], 150.1 [$C^1(C_6H_4)$, *J*(WC) 40], 137.9, 130.2, 129.3, 127.9, 125.7 (C_6H_4), 61.8 (br, *C*Me), 52.7 ($\mathrm{N}\mathit{C}\mathrm{H_2Me}$), 29.8 (C*Me*), 20.2 (Me-2), 7.6 ($\mathrm{NCH_2}\mathit{Me}$)
(1e)	1.21 [t of t, 12 H, $\mathrm{NCH_2}\mathit{Me}$, *J*(HH) 7, *J*(NH) 2], 2.09, 2.63 (s × 2, 12 H, CMe, Me_2-2,6), 3.06 [q, 8 H, $\mathrm{NC}\mathit{H}_2\mathrm{Me}$, *J*(HH) 7], 6.96, 7.06 [AB_2, 3 H, C_6H_3, *J*(AB) 11]	299.2 [C≡W, *J*(WC) 199], 228.8 [CO, *J*(WC) 184], 148.2 [$C^1(C_6H_3)$], 139.5, 127.9, 127.6 (C_6H_3), 61.6 (br, *C*Me), 53.0 ($\mathrm{N}\mathit{C}\mathrm{H_2Me}$), 29.9 (C*Me*), 21.3 (Me-2, Me-6), 7.7 ($\mathrm{NCH_2}\mathit{Me}$)
(2b)	2.20 (s, 6 H, CMe), 2.51 (s, 3 H, Me-2), 7.13—7.68 (m, 19 H, C_6H_4, Ph)	287.7 [d, μ-C, *J*(PC) 24], 218.2 [CO, *J*(WC) 163], 150.9 [$C^1(C_6H_4)$], 138.5—126.0 (C_6H_4, Ph), 66. 6 (br, *C*Me), 30.9 (C*Me*), 20.9 (Me-2)
(2c)	2.22, 2.45 (s × 2, 12 H, CMe, Me_2-2,6), 7.11—7.56 (m, 18 H, C_6H_3, Ph)	284.5 [d, μ-C, *J*(PC) 24], 218.4 [CO, *J*(WC) 167], 149.3 [$C^1(C_6H_3)$], 139.5—127.3 (C_6H_3, Ph), 66.7 (br, *C*Me), 30.9 (C*Me*), 21.7 (Me-2, Me-6)
(3c)	1.80—2.60 [m, 8 H, CH_2(cod)], 2.04, 2.18 (s × 2, 12 H, CMe, Me_2-2,6), 3.40—4.80 [m, 4 H, CH(cod)], 6.67—7.00 (m, 3 H, C_6H_3), 7.49—7.87 (m, 20 H, Ph)	312.0 [μ-C, *J*(PtC) 738], 237.1 [CO, *J*(PtC) 107], 156.9 [$C^1(C_6H_3)$, *J*(PtC) 17], 136.1—117.8 (C_6H_3, Ph), 103.6 [CH(cod), *J*(PtC) 127], 94.5 [CH(cod), *J*(PtC) 113], 68.0, 61.2 (*C*Me), 31.0, 30.0, 29.4, 27.0, [CH_2(cod), C*Me*], 22.0 (Me_2-2,6)
(3d)[e]		321.8 [d, μ-C, *J*(PC) 52, *J*(PtC) 282], 241.0 [CO, *J*(PtC) 30], 161.5 [$C^1(C_6H_3)$, *J*(PtC) 23], 139.1—117.4 (C_6H_3, Ph), 64.5, 56.2 (*C*Me), 29.0, 28.0 (C*Me*), 22.1 (Me_2-2,6), 12.2 [d, MeP, *J*(PC) 19], 9.4 [d, MeP, *J*(PC) 22]
(5)	2.20—2.50 [m, 8 H, CH_2(cod)], 2.20, 2.23 (s × 2, 12 H, CMe, Me_2-2,6), 4.20—4.40 [m, 2 H, CH(cod)], 5.50—5.70 [m, 2 H, CH(cod)], 7.43—7.47 (m, 3 H, C_6H_3), 7.56 (m, 15 H, Ph)	337.2 [μ-C, *J*(PtC) 684, *J*(WC) 127], 225.6 [CO, *J*(PtC) 29], 209.9 [CO, *J*(PtC) 54], 155.2 [$C^1(C_6H_3)$, *J*(PtC) 22], 134.2—126.3 (C_6H_3, Ph), 109.3 [CH(cod), *J*(PtC) 98], 106.5 [CH(cod), *J*(PtC) 76], 96.0 [CH(cod), *J*(PtC) 156], 94.4 [CH(cod), *J*(PtC) 132], 66.3, 64.4 (*C*Me), 33.5, 32.4, 31.6, 29.2, 28.4, 27.8 [CH_2(cod), C*Me*], 23.0, 22.9 (Me-2, Me-6)
(6b)	1.27 [t of t, 12 H, $\mathrm{NCH_2}\mathit{Me}$, *J*(HH) 7, *J*(NH) 2], 2.15, 2.28, 2.37 (s × 3, 9 H, CMe, Me-2), 3.12 [q, 8 H, $\mathrm{NC}\mathit{H}_2\mathrm{Me}$, *J*(HH) 7], 6.67—7.30 (m, 4 H, C_6H_4), 7.58 [s, 1 H, $\mu\text{-}\mathrm{C}\mathit{H}(C_6H_4\mathrm{Me}\text{-}2)$]	234.4 [CO, *J*(WC) 140], 214.0 [br, Fe(CO)], 154.8 [$C^1(C_6H_4)$], 135.2, 130.0, 129.7, 126.8, 125.2 (C_6H_4), 116.1 [$\mu\text{-}\mathit{C}\mathrm{H}(C_6H_4\mathrm{Me}\text{-}2)$, *J*(WC) 46], 66.8, 63.8 (*C*Me), 52.4 ($\mathrm{N}\mathit{C}\mathrm{H_2Me}$), 31.7, 31.5 (C*Me*), 21.5 (Me-2), 7.9 ($\mathrm{NCH_2}\mathit{Me}$)
(7b)	1.24 [t of t, 12 H, $\mathrm{NCH_2}\mathit{Me}$, *J*(HH) 7, *J*(NH) 2], 2.29, 2.43, 2.57 (s × 3, 9 H, CMe, Me-2), 3.09 [q, 8 H, $\mathrm{NC}\mathit{H}_2\mathrm{Me}$, *J*(HH) 7], 6.93—7.45 (m, 4 H, C_6H_4)	270.7 (μ_3-C), 222.0 [W(CO), *J*(WC) 158], 210.2 [br, Fe(CO)], 209.9 [br, Fe(CO)], 161.2 [$C^1(C_6H_4)$], 134.2, 130.9, 127.8, 126.5, 125.5 (C_6H_4), 68.1, 64.6 (*C*Me), 53.1 ($\mathrm{N}\mathit{C}\mathrm{H_2Me}$), 33.4, 32.7 (C*Me*), 22.5 (Me-2), 7.8 ($\mathrm{NCH_2}\mathit{Me}$)
(8a)	1.24 [t of t, 12 H, $\mathrm{NCH_2}\mathit{Me}$, *J*(HH) 2], 1.99 [s, 6 H, CMe], 2.10 [s, 3 H, Me-2], 3.09 [q, 8 H, $\mathrm{NC}\mathit{H}_2\mathrm{Me}$, *J*(HH) 7], 6.93—7.50 (m, 4 H, $\mathit{C}_6\mathrm{H}_4$)	387.9 [μ-C, *J*(WC) 141], 247.7 [W(CO)], 216.1 [Fe(CO)], 165.1 [$C^1(C_6H_4)$], 131.8, 129.0, 125.8, 127.4. 121.5 (C_6H_4), 67.5 (br, *C*Me), 53.1 ($\mathrm{N}\mathit{C}\mathrm{H_2Me}$), 29.5 (C*Me*), 21.2 (Me-2), 7.80 ($\mathrm{NCH_2}\mathit{Me}$)
(8b)	1.11 (br, 12 H, $\mathrm{NCH_2}\mathit{Me}$), 1.21 [d, 9 H, PMe_3, *J*(PH) 10], 2.08 (s, 6 H, CMe), 2.56 (s, 3 H, Me-2), 2.94 (br, 8 H, $\mathrm{C}\mathit{H}_2\mathrm{Me}$), 7.03—7.48 (m, 4 H, C_6H_4)	
(8c)	1.28 [t of t, 12 H, $\mathrm{NCH_2}\mathit{Me}$, *J*(HH) 8, *J*(NH) 2], 1.88, 2.10 (s × 2, 12 H, CMe, Me_2-2,6), 3.11 [q, 8 H, $\mathrm{NC}\mathit{H}_2\mathrm{Me}$, *J*(HH) 8], 6.95, 7.14 [AB_2, 3 H, C_6H_3, *J*(AB) 7]	388.4 [μ-C, *J*(WC) 137], 241.1 [W(CO), *J*(WC) 174], 216.2 [Fe(CO)], 164.1 [$C^1(C_6H_3)$], 127.2, 126.9, 125.8 (C_6H_3), 66.9 (*C*Me), 53.1 ($\mathrm{N}\mathit{C}\mathrm{H_2Me}$), 29.7 (C*Me*), 22.1 (Me-2, Me-6), 7.80 ($\mathrm{NCH_2}\mathit{Me}$)
(10a)[f]	−12.00 [br q, 1 H, B–H–Ru, *J*(BH) 76], 2.22, 2.25, 2.32, 2.47 (s × 4, 12 H, CMe, Me_2-2,6), 5.16 (s, 5 H, C_5H_5), 7.09 (m, 3 H, C_6H_3)	276.6 [μ-C, *J*(WC) 143], 227.9 [W(CO), *J*(WC) 177], 223.0 [W(CO), *J*(WC) 177], 198.6 [Ru(CO)], 156.9 [$C^1(C_6H_3)$, *J*(WC) 32], 134.3, 133.4, 128.8, 128.6 128.1 (C_6H_3), 89.4 (C_5H_5), 62.1, 61.7 (br, *C*Me), 30.6, 30.5 (C*Me*), 22.1, 21.8 (Me-2, Me-6)
(10b)	−13.3 [br q, 1 H, B–H–Ru, *J*(BH) *ca.* 50], 1.45 [d, 6 H, MeP, *J*(PH) 8], 2.13, 2.19, 2.86 (s × 3, relative intensity 1:2:1, 12 H, CMe, Me_2-2,6), 4.72 (s, 5 H, C_5H_5), 6.84—7.31 (m, 8 H, C_6H_3, Ph)	297.3 [μ-C, *J*(WC) 150], 234.1 [W(CO), *J*(WC) 187], 224.4 [W(CO), *J*(WC) 167], 158.7 [$C^1(C_6H_3)$, *J*(WC) 47], 139.6—126.5 (C_6H_3, Ph), 85.2 (C_5H_5), 60.1, 59.7 (*C*Me), 30.8, 29.8 (C*Me*), 22.5 (Me-2, Me-6), 16.2 [d, MeP, *J*(PC)]

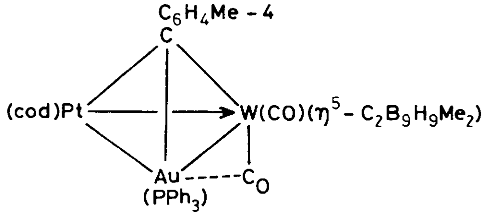
[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in CD_2Cl_2. [c] Proton resonances for B–H groups occur as broad unresolved resonances in the range δ 0–3. [d] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$, with measurements in CD_2Cl_2–CH_2Cl_2. [e] Hydrogen-1 spectrum not measured. See text for ^{31}P-{^1H} and ^{195}Pt-{^1H} n.m.r. data. [f] Minor isomer present, see text.

the associated cation presumably being $[Au(thf)_x(PPh_3)]^+$. Moreover, (**2c**) decomposed in the presence of $PMePh_2$ yielding solutions containing $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ and $[Au(PR_3)_x]^+$ (PR_3 = PPh_3 or $PMePh_2$). These observations suggest that with the compounds (**2**) an increase in the steric requirements of the μ-CR ligand results in some loss of stability.

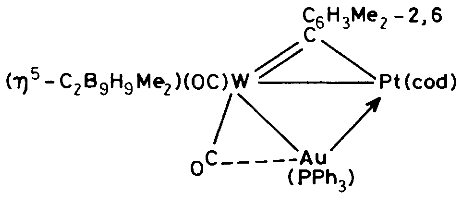
We have previously reported[2f] that the compound $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) reacts with the salt (**1c**) to give the platinum–tungsten complex (**3a**), and that treatment of the latter with two equivalents of $PMePh_2$ affords (**3b**). Similarly, (**1f**) and $[Pt(cod)_2]$, in ethylene-saturated thf solutions, give the compound $[PPh_4][PtW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(cod)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3c**). With $PMePh_2$ in CH_2Cl_2, the latter affords $[PPh_4][PtW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(PMePh_2)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3d**). However, this species was obtained as a red oil which failed to crystallise. Data for the complexes (**3c**) and (**3d**) are given in Tables 1 and 2. The spectroscopic properties are similar to those of (**3a**) and (**3b**), respectively. The ^{31}P-{^1H} n.m.r. spectrum of (**3d**) showed characteristic signals for the presence of a *cis*-$Pt(PMePh_2)_2$ group {δ 3.42 [d, *J*(PP) 7, *J*(PtP) 3 846, *J*(WP) 24] and 8.54 p.p.m. [d, *J*(PP) 7, *J*(PtP) 3 280 Hz]}. From the *J*(PtP) and *J*(WP) values, it may be concluded that the signal at δ 3.42 p.p.m. is due to the transoid W–Pt–$PMePh_2$ group, and that at 8.54 p.p.m. to the cisoid W–Pt–$PMePh_2$ fragment.



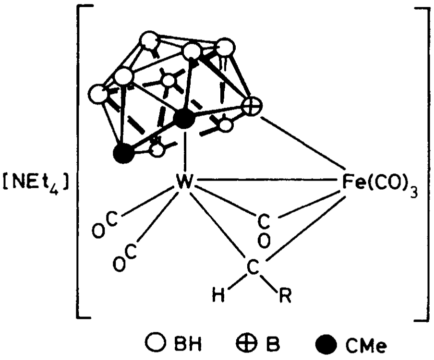
	X	R	L$_2$
(3a)	P(CH$_2$Ph)Ph$_3$	C$_6$H$_4$Me-4	cod
(3b)	P(CH$_2$Ph)Ph$_3$	C$_6$H$_4$Me-4	(PMePh$_2$)$_2$
(3c)	PPh$_4$	C$_6$H$_3$Me$_2$-2,6	cod
(3d)	PPh$_4$	C$_6$H$_3$Me$_2$-2,6	(PMePh$_2$)$_2$



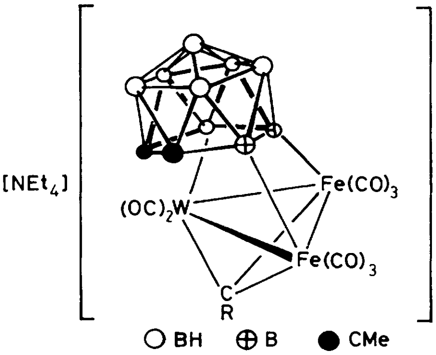
(4)



(5)



(6a) C$_6$H$_4$Me-4
(6b) C$_6$H$_4$Me-2



(7a) C$_6$H$_4$Me-4
(7b) C$_6$H$_4$Me-2

Attempts to obtain isolable neutral complexes by protonating (**3c**) or (**3d**) failed, as they had previously with (**3a**) and (**3b**).[2f] However, (**3c**) underwent an interesting reaction with $[\mathrm{AuCl(PPh_3)}]$ in thf, in the presence of $\mathrm{TlPF_6}$. We have previously shown[2f] that a similar reaction with (**3a**) affords the trimetal compound $[\mathrm{AuPtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(cod)(\eta^5\text{-}C_2B_9H_9Me_2)}]$ (**4**). A closely related complex $[\mathrm{AuPtW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(PPh_3)(cod)(\eta^5\text{-}C_2B_9H_9Me_2)}]$ (**5**) is obtained from (**3c**), but the n.m.r. data show that the structures of (**4**) and (**5**) are different, as shown in the structural formulae.

The $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum of (**4**)[2f] shows a characteristic resonance for a $\mu_3\text{-}C\mathrm{C_6H_4Me}$-4 nucleus at δ 291.1 p.p.m., and this signal appears as a doublet [J(PC) 15 Hz], with ^{195}Pt satellite peaks [J(PtC) 590 Hz]. Evidence for a *closo*-trimetallatetrahedrane structure for (**4**), rather than a butterfly arrangement of the μ_3-CAuPtW core, is provided by the observation of $^{31}\mathrm{PAu}\text{-}^{195}\mathrm{Pt}$ coupling (100 Hz) in both the $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ and $^{195}\mathrm{Pt}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectra of this species. This coupling is of such a magnitude as to imply the presence of a direct Au–Pt bond. In this respect (**5**) is similar, showing in both the $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ and $^{195}\mathrm{Pt}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectra (see Experimental section) a $^{31}\mathrm{P}\text{-}^{195}\mathrm{Pt}$ coupling of 195 Hz, which corresponds to ^2J(PPt) rather than ^3J(PPt). There is a significant difference, however, between the $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectra of these two trimetal compounds. As mentioned above, for (**4**) the resonance for the ligated alkylidyne-carbon nucleus is a doublet at δ 291.1 p.p.m. This peak is in the chemical shift range for a μ_3-C group. In contrast, in the spectrum of (**5**) the signal for the alkylidyne-carbon is at 337.2 p.p.m. [J(PtC) 684, J(WC) 127 Hz]; a chemical shift value diagnostic for an alkylidyne ligand bridging two metal centres rather than three.[5] Moreover, the observation of ^{195}Pt and ^{183}W satellite peaks on the $\mu\text{-}C\mathrm{C_6H_3Me_2}$-2,6 resonance of (**5**) shows that the ligand bridges the Pt–W bond. Significantly, also the absence of any $^{31}\mathrm{P}\text{-}^{13}\mathrm{C}$ coupling is in accord with there being no direct μ-C–Au bond in this molecule.

Both (**4**) and (**5**) are trimetal species with 44 valence electrons, and thus are formally electronically unsaturated. Although this unsaturation is likely to be distributed to some degree among all three metal centres we have arbitrarily indicated Pt$\rightarrow$W and Au$\rightarrow$Pt donor bonds in (**4**) and (**5**), respectively, in order to assign a filled valence electron shell at each metal centre. The fact that in (**4**) the $\mathrm{CC_6H_4Me}$-4 group is triply-bridging three metal centres, whereas in (**5**) the $\mathrm{CC_6H_3Me_2}$-2,6 ligand is bridging two metal atoms may reasonably be attributed to the greater steric requirements of the *ortho*-xylyl fragment.

Reactions of the two salts (**1d**) and (**1e**) with $[\mathrm{Fe_3(CO)_{12}}]$ were next investigated, in order to compare the nature of the products obtained with those isolated from the reaction between $[\mathrm{Fe_2CO)_9}]$ and the tetraethylammonium salt of the anion $[\mathrm{W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)}]^-$.[2g] The products of the latter reaction were the novel compounds $[\mathrm{NEt_4}][\mathrm{FeW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(\mu\text{-}\sigma{:}\eta^5\text{-}C_2B_9H_8Me_2)(\mu\text{-}CO)(CO)_5}]$ (**6a**) and $[\mathrm{NEt_4}][\mathrm{Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}\sigma{:}\sigma'{:}\eta^5\text{-}C_2B_9H_7Me_2)(CO)_8}]$ (**7a**). These two species were also obtained if $[\mathrm{Fe_3(CO)_{12}}]$ was used instead of $[\mathrm{Fe_2(CO)_9}]$ as a source of the iron carbonyl fragments.

The reaction between (**1d**) and $[\mathrm{Fe_3(CO)_{12}}]$ in thf at room temperature afforded a complex mixture of products, which could not be completely separated by column chromatography on alumina. However, *via* the procedures described in the Experimental section, the three iron–tungsten compounds $[NEt_4][FeW\{\mu\text{-}CH(C_6H_4Me\text{-}2)\}(\mu\text{-}\sigma{:}\eta^5\text{-}C_2B_9H_8Me_2)(\mu\text{-}CO)(CO)_5]$ (**6b**), $[NEt_4][Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}2)(\mu_3\text{-}\sigma{:}\sigma'{:}\eta^5\text{-}C_2B_9H_7Me_2)(CO)_8]$ (**7b**), and $[NEt_4][FeW(\mu\text{-}CC_6H_4Me\text{-}2)(CO)_5(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**8a**) were isolated and characterised. The major product of the reaction was (**8a**), but it was subsequently found that in solution this compound on treatment with a stream of CO gas gave (**6b**) in good yield. The significance of this result is discussed below. Data for (**6b**), (**7b**), and (**8a**) are listed in Tables 1 and 2.

We have previously established the molecular structure of the dimetal compound (**6a**) by *X*-ray diffraction.[2g] The spectroscopic properties of (**6b**) confirm that it is structurally similar to (**6a**). Thus the i.r. spectrum of the former shows a band for the bridging CO group at 1 759 cm^{-1}, while the latter has a similar absorption in its spectrum at 1 755 cm^{-1}, which is also broad and weak. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**6b**) as expected does not show a resonance due to an alkylidyne-carbon nucleus, but there is a peak at δ 116.1 p.p.m. which may be attributed to the $\mu\text{-}CH(C_6H_4Me\text{-}2)$ moiety since $^{183}W\text{-}^{13}C$ coupling (46 Hz) is observed. The corresponding signal in the spectrum of (**6a**) is seen at 119.3 p.p.m. Resonances in the ^1H n.m.r. spectra of (**6a**) (δ 6.39) and (**6b**) (δ 7.58) may be ascribed to the $\mu\text{-}CHR$ fragments.

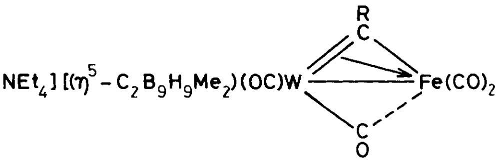
The $^{11}B\text{-}\{^1H\}$ n.m.r. spectra of (**6a**) and (**6b**) are also informative, and are in accord with the two species having similar structures. The spectrum of (**6a**) has been discussed earlier.[2g] It has a signal for the boron atom associated with the B–Fe σ bond at δ 39.6 p.p.m. There is a similar resonance in the $^{11}B\text{-}\{^1H\}$ n.m.r. spectrum of (**6b**) at δ 40.5 p.p.m. No such signal appears in the $^{11}B\text{-}\{^1H\}$ n.m.r. spectra of complexes containing a tungsten-co-ordinated $\eta^5\text{-}C_2B_9H_9Me_2$ group which is not engaged in exopolyhedral bonding. Such species have very broad unresolved signals in the range *ca.* 6 to −20 p.p.m.

The data for compound (**7b**) are very similar to those found previously for (**7a**), and the two di-iron–tungsten compounds must have analogous structures. Moreover, an *X*-ray diffraction study[2g] has firmly established the structure of a closely related compound which differs only in containing a μ_3-CPh ligand capping the Fe_2W triangle. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**7b**) shows a μ_3-C resonance at δ 270.7 p.p.m. The corresponding peak in the spectrum of (**7a**) is seen at 271.8 p.p.m. The $^{11}B\text{-}\{^1H\}$ n.m.r. spectrum of (**7b**) has peaks for the B–Fe groups at δ 45.9 and 56.1 p.p.m., with broad unresolved bands for the other seven boron nuclei occurring from δ −14.0 to −3.2 p.p.m. Moreover, in a ^{11}B spectrum, the resonances at δ 45.9 and 56.1 p.p.m. show no $^1H\text{-}^{11}B$ coupling. In the $^{11}B\text{-}\{^1H\}$ n.m.r. spectrum of (**7a**), the signals for the B–Fe nuclei occur at δ 45.1 and 55.9 p.p.m.[2g]

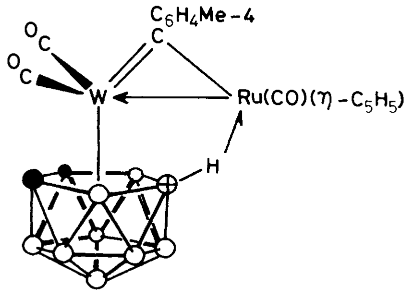
The formation of compound (**8a**) in the reaction between (**1d**) and $[Fe_3(CO)_{12}]$ was of considerable interest, since an analogous product was not obtained in the previous study[2g] using salts containing the anion $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$. Compound (**8a**) is a formally unsaturated 32 valence electron dimetal compound, and in this respect is akin to the compounds $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(L)]$ {L = $\eta\text{-}C_5H_5$, $\eta\text{-}C_5Me_5$, or $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate]} described earlier.[6]

In accord with the electronic unsaturation, the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**8a**) shows a relatively deshielded resonance for the μ-C nucleus at δ 387.9 p.p.m. The signal for the μ-C group in the spectrum of $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5Me_5)]$ is at δ 395.4 p.p.m. These shifts may be compared with the less deshielded signal at δ 341.8 p.p.m. for the alkylidyne-carbon nucleus in the saturated 34 valence electron species $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5Me_5)]$.[6b]

Treatment of (**8a**) with PMe_3 affords the complex $[NEt_4][FeW(\mu\text{-}CC_6H_4Me\text{-}2)(CO)_4(PMe_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**8b**). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum shows a singlet resonance at δ 38.6 p.p.m. with $^{183}W\text{-}^{31}P$ satellite peaks [*J*(WP) 17 Hz]. The small magnitude of the latter shows that substitution of the CO group in (**8a**) to give (**8b**) has occurred at the iron atom. A somewhat similar reaction occurs between $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$ and PMe_3.[6a] The initially formed product $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(PMe_3)\{HB(pz)_3\}]$ readily releases a molecule of CO to give the unsaturated compound $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_3)\{HB(pz)_3\}]$, which like (**8b**) contains a $Fe(CO)_2(PMe_3)$ group.

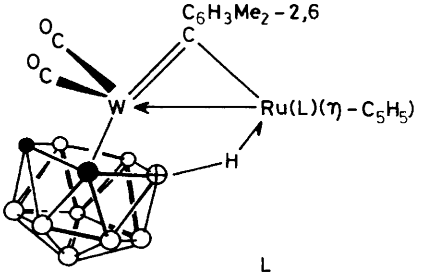


	R	L
(**8a**)	$C_6H_4Me\text{-}2$	CO
(**8b**)	$C_6H_4Me\text{-}2$	PMe_3
(**8c**)	$C_6H_3Me_2\text{-}2,6$	CO



(**9**)

○BH ⊕B ●CMe



	L
(**10a**)	CO
(**10b**)	PMe_2Ph

The reaction between (**1e**) and $[Fe_3(CO)_{12}]$ in thf at room temperature gave only a single iron–tungsten product $[NEt_4][FeW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**8c**). This result is thus in distinct contrast with the reactions of salts of the anions $[W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ (R = $C_6H_4Me\text{-}4$ or $C_6H_4Me\text{-}2$) with iron carbonyls. Data for compound (**8c**) are given in Tables 1 and 2. The formal unsaturation of this compound, with the presence of an $Fe(CO)_3$ group, was established by an *X*-ray diffraction study. Selected internuclear separations and angles are listed in Table 3, and the structure of the anion is shown in the Figure.

The structural parameters for the anion of (**8c**) may usefully be compared with those of the neutral 32 valence electron iron–tungsten complexes $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$[6a]

Table 3. Selected internuclear distances (Å) and angles (°) for $[NEt_4][FeW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**8c**) with estimated standard deviations in parentheses

W–Fe	2.600(1)	W–C(1)	2.452(6)	W–C(2)	2.361(7)	W–B(3)	2.320(8)
W–B(4)	2.371(10)	W–B(5)	2.415(8)	W–C(5)	1.989(10)	W–C(6)	1.959(7)
W–C(20)	1.976(6)	Fe···C(6)	2.377(7)	Fe–C(7)	1.789(7)	Fe–C(8)	1.770(9)
Fe–C(9)	1.807(9)	Fe–C(20)	1.891(5)	C(1)–C(2)	1.63(1)	C(2)–B(3)	1.70(1)
B(3)–B(4)	1.74(2)	B(4)–B(5)	1.81(2)	B(5)–C(1)	1.68(1)	C(6)–O(6)	1.20(1)
C(7)–O(7)	1.15(1)	C(8)–O(8)	1.14(1)	C(9)–O(9)	1.12(1)		
Fe–W–C(5)	80.2(2)	Fe–W–C(6)	60.9(2)	C(5)–W–C(6)	85.7(3)	Fe–W–C(20)	46.4(1)
C(5)–W–C(20)	90.3(3)	C(6)–W–C(20)	106.7(2)	Fe–W–X	165.2	C(5)–W–X	114.2
C(6)–W–X *	121.4	C(20)–W–X	126.4	W–Fe–C(6)	46.1(2)	W–Fe–C(7)	134.8(2)
C(6)–Fe–C(7)	179.1(3)	W–Fe–C(8)	108.6(2)	C(7)–Fe–C(8)	99.2(4)	W–Fe–C(9)	113.3(3)
C(7)–Fe–C(9)	98.4(3)	C(8)–Fe–C(9)	95.1(4)	W–Fe–C(20)	49.2(2)	C(7)–Fe–C(20)	86.2(3)
C(8)–Fe–C(20)	120.3(3)	C(9)–Fe–C(20)	143.2(4)	W–C(5)–O(5)	177.7(6)	W–C(6)–Fe	73.0(2)
W–C(6)–O(6)	165.4(6)	Fe–C(6)–O(6)	121.6(5)	Fe–C(7)–O(7)	177.5(7)	Fe–C(8)–O(8)	176.2(6)
Fe–C(9)–O(9)	177.1(9)	W–C(20)–Fe	84.5(3)	W–C(20)–C(21)	143.0(3)	Fe–C(20)–C(21)	132.6(4)

* X = Centroid of tungsten-ligated C_2B_3 face of carbaborane ligand.

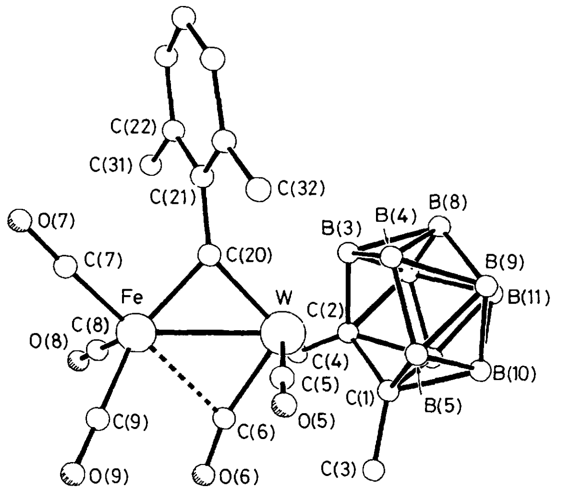
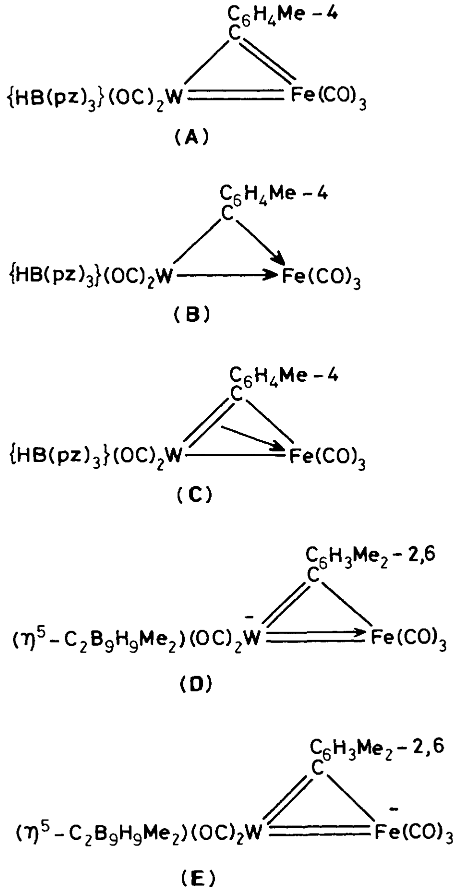


Figure. The structure of the anion of $[FeW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**8c**) showing the crystallographic numbering



Scheme.

and $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PBu^t_2H)(\eta\text{-}C_5H_5)]$.[7] In the last two compounds the $L(OC)_2W{\equiv}CC_6H_4Me\text{-}4$ [$L = HB(pz)_3$ or $\eta\text{-}C_5H_5$] fragment, isolobal with an alkyne, can be regarded as functioning as a four-electron donor to the 14-electron $Fe(CO)_3$ or $Fe(CO)_2(PBu^t_2H)$ groups, respectively. This is shown in the accompanying Scheme for the hydrotris(pyrazol-1-yl)borate complex by (**A**), or the equivalent representations (**B**) or (**C**).[6a] The ability of alkynes to act as four-electron donors is well established.[8,9]

In principle the pattern of bonding within the μ-CFeW ring in (**8c**) could be similarly represented by a structure like (**A**), or its equivalent representations (**B**) or (**C**). However, the W–Fe bond distance [2.600(1) Å] in (**8c**) is significantly shorter than those in either $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$ [2.612(2) Å] or $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PBu^t_2H)(\eta\text{-}C_5H_5)]$ [2.614(1) Å]. Moreover, the W–C(20) separation [1.976(6) Å] in (**8c**) is also shorter than the corresponding distances in $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$ [2.025(7) Å] and $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PBu^t_2H)(\eta\text{-}C_5H_5)]$ [2.018(5) Å]. The reverse situation occurs with the μ-C–Fe distances. That in (**8c**) [1.891(5) Å] is longer than those in $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$ [1.826(6) Å] or $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PBu^t_2H)(\eta\text{-}C_5H_5)]$ [1.850(4) Å]. The disparity between the structural parameters can possibly be explained in terms of the anionic nature of (**8c**). If a formulation similar to (**A**) were applied, the negative charge would be formally localised on the $W(\eta^5\text{-}C_2B_9H_9Me_2)$ fragment. It seems likely that the true electron distribution would involve some contribution from resonance structures in which the negative charge is transferred to the iron centre, as in (**D**) and (**E**) of the Scheme. This feature would result in an increase in the μ-C–W bond order and a decrease in the μ-C–Fe bond order compared with the canonical form (**A**); as is observed for (**8c**). The resonance hybrids (**D**) and (**E**) offer an explanation for the presence of the semi-bridging carbonyl ligand [W–C(6)–O(6) 165.4(6)°, W–C(6) 1.959(7), Fe $\cdots$ C(6) 2.377(7) Å]. Semi-bridging CO groups are often associated with dative metal–metal interactions,[10] and in (**8c**) the semi-bridging C(6)O(6) group may serve partially to remove negative charge at the iron centre [formulation (**E**) of the Scheme].

The xylyl ring in (**8c**) is approximately orthogonal to the μ-C(20)FeW ring, with the torsion angle W–C(20)–C(21)–C(22) 103(1)°. This feature may well be sterically imposed. In [FeW(μ-CC$_6$H$_4$Me-4)(CO)$_5${HB(pz)$_3$}] the *p*-tolyl ring is not orthogonal to the μ-CFeW ring, the corresponding torsion angle being 154(1)°. The carbaborane ligand does not show any significant distortion. The parameters θ, φ, and Δ, as defined elsewhere,[11] are small and have values of 1.4°, 0.9°, and 0.12 Å, respectively. The value of Δ reflects the displacement of the projection of the tungsten atom onto the plane defined by B(6)B(7)B(8)B(9)B(10) from the centroid of these atoms. The direction of the slippage is towards B(3). This is in contrast with the results for electron-rich metal–ligand fragments where the distortion usually occurs towards B(4).

The spectroscopic data for (**8c**) are in complete agreement with the structure established by *X*-ray diffraction. The i.r. spectrum in the carbonyl region (Table 1) shows a band for a strongly semi-bridging CO ligand at 1 795 cm^{-1}. In the ^{13}C-{^{1}H} n.m.r. spectrum (Table 2) there are resonances for the W(CO)$_2$ and Fe(CO)$_3$ groups at δ 241.1 and 216.2 p.p.m., respectively. Evidently site-exchange of these ligands on the n.m.r. time-scale occurs at each metal centre, but not between the metal centres. The resonance for the μ-*C*C$_6$H$_3$Me$_2$-2,6 group occurs at 388.4 p.p.m. in the range expected for a 32 valence electron dimetal complex.[6]

The formation of (**8c**), the only product of the reaction between (**1e**) and [Fe$_3$(CO)$_{12}$], was of considerable interest, as was the observation that with CO gas the analogous complex (**8a**) was converted to (**6b**). Moreover, since (**6b**) and (**8a**) were both formed, together with (**7b**), in the reaction between (**1d**) and [Fe$_3$(CO)$_{12}$], these observations indicate that (**8a**) is an intermediate in the formation of (**6b**). It follows also that in the reactions between iron carbonyls and salts of the anion [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$)]$^-$, studied previously,[2g] formation of (**6a**) involves an intermediate structurally related to (**8a**) and (**8c**), but this precursor was not isolated. In the case of (**1e**) the presence of the bulky C$_6$H$_3$Me$_2$-2,6 fragment evidently results in the reaction proceeding no further than (**8c**). With salts containing W≡CC$_6$H$_4$Me-4 or W≡CC$_6$H$_4$Me-2 groups, however, and in the presence of free CO derived from iron carbonyl fragments, the complexes (**6**) are formed. In an alternative pathway, addition of an Fe(CO)$_4$ fragment to an unsaturated intermediate of type (**8**), with concomitant loss of CO, would afford the trimetal species (**7**). The pathways leading to (**6**) or (**7**) from species of type (**8**) are likely to involve intermediates with B–H⟶Fe bridges. Formation of (**6**) probably involves a metal assisted hydride transfer to the alkylidyne group, while the route to the trimetal compounds (**7**) must involve loss of hydride in some form. In this context it is noteworthy that significant amounts of [NEt$_4$][Fe$_3$H(CO)$_{11}$] were formed in the reactions.

It has been previously shown[2b] that in CH$_2$Cl$_2$ the salts (**1a**) and [Ru(CO)(NCMe)$_2$(η-C$_5$H$_5$)][BF$_4$] react to give the neutral ruthenium–tungsten complex [RuW(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η-C$_5$H$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**9**). In the structure of the latter, established by *X*-ray crystallography, there is a B–H⟶Ru three-centre two-electron bridge bond. The boron atom forming this bond lies in the pentagonal face of the η^5-C$_2$B$_9$H$_9$Me$_2$ ligand, and it is the central boron of the B–*B*–B–C–C ring. The reaction between the salt (**1f**) and [Ru(CO)(NCMe)$_2$(η-C$_5$H$_5$)][BF$_4$] was investigated as part of the work reported herein. The major product was a compound [RuW(μ-CC$_6$H$_3$Me$_2$-2,6)(CO)$_3$(η-C$_5$H$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**10a**), formed together with a small amount (*ca.* 10%) of an isomer of the latter.

Although comparison of the data for (**10a**) (Tables 1 and 2) with that obtained earlier for (**9**) showed that these compounds had very similar structures, it became apparent from a ^{11}B–^{11}B COSY n.m.r. spectrum of (**10a**) that the structures of the two species were subtly different. The ^{11}B-{^{1}H} n.m.r. spectrum of (**9**) shows a resonance for the unique boron atom forming the B–H⟶Ru bond at δ 19.5 p.p.m.[2b] The spectrum of (**10a**), measured at 128 MHz, shows a similar peak at 17.57 p.p.m., which becomes a doublet in a proton-coupled ^{11}B n.m.r. spectrum [*J*(BH) 68 Hz]. A ^{11}B–^{11}B COSY spectrum, however, revealed only three cross peaks associated with this low-field resonance of relative intensity 1:1:1 at δ −6.18, −7.16, and −8.51 p.p.m. The observation of only three cross peaks on the low-field signal suggests that the boron atom forming the B–H⟶Ru bond is sited adjacent to a carbon in the pentagonal face of the η^5-C$_2$B$_9$H$_9$Me$_2$ ligand. If the boron atom involved in the three-centre B–H⟶Ru bond were the central boron of the B–*B*–B–C–C ring it would have a connectivity with four other boron nuclei, rather than three, and thus gives rise to four cross peaks.

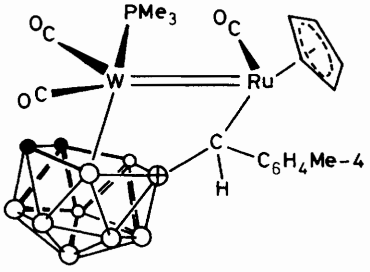
The ^{1}H n.m.r. spectrum of (**10a**) shows a resonance for the proton of the B–H⟶Ru group as a broad quartet at δ −12.00 [*J*(BH) 70 Hz]. The corresponding signal in the spectrum of (**9**) is at −11.48 [*J*(BH) 76 Hz]. The ^{13}C-{^{1}H} n.m.r. spectrum of compound (**9**) shows a characteristic peak for the alkylidyne-carbon nucleus at δ 276.7 p.p.m. [*J*(WC) 132 Hz]. The ^{13}C-{^{1}H} n.m.r. spectrum of the new complex (**10a**) has a resonance for the μ-C nucleus with a virtually identical chemical shift (Table 2).

As mentioned above, the synthesis of (**10a**) is accompanied by formation of a minor isomer which could not be separated and unambiguously identified. This species revealed itself in both the i.r. and ^{13}C-{^{1}H} n.m.r. spectra of the mixture. In thf solution, the i.r. spectrum shows three CO stretching bands at 2 009s, 1 987vs, and 1 920s cm^{-1}. When measured in light petroleum additional bands appear (2 015m, 2 007vw, 1 992vs, 1 929w, and 1 922s cm^{-1}). The weak bands are attributed to the minor isomer. In the ^{13}C-{^{1}H} n.m.r. spectrum of (**10a**) there are peaks of *ca.* 10% the intensity of the signals for the major component at δ 274.5 (μ-C), 228.0, 222.8 (WCO), 199.6 (RuCO), 156.2 [C^1(C$_6$H$_3$)], 90.8 (C$_5$H$_5$), 31.8, and 30.0 p.p.m. (C*Me*). It seems probable that the minor isomer of (**10a**) has a structure similar to that of (**9**) with the B–H⟶Ru interaction involving the central boron atom of the pentagonal C$_2$B$_3$ ring.

Treatment of (**10a**) with PMe$_2$Ph affords the complex [RuW(μ-CC$_6$H$_3$Me$_2$-2,6)(CO)$_2$(PMe$_2$Ph)(η-C$_5$H$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**10b**), a simple replacement of the carbonyl group on the ruthenium atom of (**10a**) having occurred. Complex (**10b**) was characterised by the data given in Tables 1 and 2. The ^{31}P-{^{1}H} n.m.r. spectrum showed a singlet peak at δ 13.82 p.p.m., the absence of ^{183}W–^{31}P coupling confirming the presence of a Ru(PMe$_2$Ph) group. The ^{11}B-{^{1}H} n.m.r. spectrum displayed a resonance for the B–H⟶Ru group at δ 18.94 p.p.m. [*J*(BH) 45 Hz]. In the ^{11}B–^{11}B COSY spectrum this signal shows again three cross peaks to signals at δ −4.05, −7.13, and −8.51 p.p.m., in 1:1:1 intensity.

The reaction which afforded (**10b**) is readily reversed. Passage of CO gas through solutions of (**10b**) in thf gave (**10a**). It is interesting to compare these results with the earlier work.[2b] Treatment of (**9**) with PMe$_3$ affords complex (**11**), resulting from insertion of the *p*-tolylmethylidyne ligand into the B–H⟶Ru bond of the precursor. The tertiary phosphine co-ordinates to the tungsten centre in a reaction that is not reversed with CO.

During the studies described therein, it was found that the ruthenium–tungsten compound (**10a**) could be obtained by an



(11)

alternative method. The unsaturated iron–tungsten complex (**8c**) was treated with $[Ru(CO)(NCMe)_2(\eta\text{-}C_5H_5)][BF_4]$ in the hope of obtaining a neutral trimetal compound having a μ_3-$\overline{\mathrm{CFeRuW}}$ trimetallatetrahedrane core. Addition of metal–ligand fragments to complexes containing unsaturated three-membered dimetalla ring systems provides a well established route to trimetal compounds with capping alkylidyne ligands.[12] However, the reaction between (**8a**) and $[Ru(CO)(NCMe)_2(\eta\text{-}C_5H_5)][BF_4]$ resulted in loss of the iron carbonyl fragment, and formation of (**10a**). A similar attempt to add a $Au(PPh_3)$ fragment to (**8c**), *via* treatment of the latter with $[AuCl(PPh_3)]$ in thf in the presence of $TlPF_6$, also failed, giving instead the dimetal compound (**2c**). We believe that the failure to obtain trimetal compounds in these reactions of (**8c**) is due to the presence of the bulky $C_6H_3Me_2$-2,6 fragment as the substituent on the alkylidyne-carbon atom.

The results described in this paper have shown that the reactivity pattern of the salts (**1d**)—(**1f**) is distinctly different from that of salts of the anion $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$.

Experimental

The techniques and equipment used have been described in earlier papers in this series.[2] Light petroleum refers to that fraction of b.p. 40—60 °C. All experiments were carried out using Schlenk-tube techniques, under oxygen-free nitrogen. Unless otherwise stated, alumina (Brockman activity II) was used for chromatography columns. Analytical and other data for the new compounds are given in Table 1. Boron-11 n.m.r. spectra were recorded in CD_2Cl_2 and chemical shifts (p.p.m.) are positive to high frequency of $BF_3\cdot Et_2O$ (external). Phosphorus-31 n.m.r. spectra were measured in CD_2Cl_2 and chemical shifts are positive to high frequency of H_3PO_4 (external). Platinum-195 n.m.r. spectra, measured in CD_2Cl_2, were recorded with chemical shifts to high frequency of $\Xi(^{195}Pt) = 21.4$ MHz. The (alkylidyne)bromo(tetracarbonyl)-tungsten complexes $[W(\equiv CR)Br(CO)_4]$ ($R = C_6H_4Me$-2 or $C_6H_3Me_2$-2,6) were prepared by the method previously reported for $[W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$.[13] For $[W(\equiv CC_6H_3Me_2\text{-}2,6)Br(CO)_4]$ a modification in the procedure was employed in that a light petroleum–CH_2Cl_2 mixture (2:1) was used as solvent, with the synthesis carried out at room temperature so that the preparation was complete within *ca.* 90 min. All volatile material was then removed *in vacuo* and the product washed with light petroleum (−20 °C). The compounds $[NHMe_3][7,8\text{-}C_2B_9H_{10}Me_2]$,[14] $[Pt(cod)_2]$,[15] and $[Ru(CO)(NCMe)_2(\eta\text{-}C_5H_5)][BF_4]$[16] were prepared by methods previously described.

Synthesis of the Salts $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ ($R = C_6H_4Me$-2 *or* $C_6H_3Me_2$-2,6).—(*i*) A solution of $Na_2[7,8\text{-}C_2B_9H_9Me_2]$ was prepared by refluxing $[NHMe_3][7,8\text{-}C_2B_9H_{10}Me_2]$ (2.45 g, 11.0 mmol) with an excess of NaH (*ca.* 2 g) in thf (110 cm^3) for 14 h, under a slow stream of nitrogen. The solution obtained was added slowly (10—20 cm^3 portions) to a thf (10 cm^3, at −20 °C) solution of $[W(\equiv CC_6H_4Me\text{-}2)Br(CO)_4]$ (4.68 g, 10.2 mmol) with rapid stirring of the mixture. Carbon monoxide is evolved, and the solution turned dark red. After warming to room temperature, NEt_4Cl (2.5 g) was added, and stirring was continued for *ca.* 30 min. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2 (20 cm^3). Water (*ca.* 20 cm^3) was added to remove sodium salts. The organic phase was removed with a syringe, and the aqueous phase was extracted with CH_2Cl_2 (2 × 10 cm^3). The combined extracts, and the organic phase initially obtained, were chromatographed (3 × 10 cm column). Elution with CH_2Cl_2 removed a trace of $[W(CO)_6]$ and other impurities which were discarded. Continued elution gave an orange eluate. The latter was concentrated to *ca.* 15 cm^3 and Et_2O (80 cm^3) added, precipitating a red oil. The mixture was stirred rapidly (10 min), and then cooled to *ca.* −20 °C. After several hours orange *microcrystals* of $[NEt_4][W(\equiv CC_6H_4Me\text{-}2)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**1d**) (4.70 g) (m.p. 94—96 °C) were obtained, and washed with Et_2O (2 × 10 cm^3).

(*ii*) The compound $[W(\equiv CC_6H_3Me_2\text{-}2,6)Br(CO)_4]$ (5.17 g, 10.5 mmol) in thf (20 cm^3) was treated with a thf (60 cm^3) solution of $Na_2[7,8\text{-}C_2B_9H_9Me_2]$ {10.7 mmol, prepared by treating $[NHMe_3][7,8\text{-}C_2B_9H_{10}Me_2]$ (10.7 mmol) with an excess of NaH}. Carbon monoxide evolution occurred, and the mixture became red. After stirring for 20 min, an excess of NEt_4Cl (3.4 g) was added. After a further 30 min, solvent was removed *in vacuo*, and the red oil obtained dissolved in CH_2Cl_2 (20 cm^3) to which water (25 cm^3) was added. The organic layer was removed with a syringe, and the aqueous layer extracted with CH_2Cl_2 (10 cm^3 portions) until the extracts were colourless. The extracts and the organic layer were combined, concentrated to *ca.* 15 cm^3, and chromatographed. The red eluate was reduced in volume to *ca.* 15 cm^3, and Et_2O (50 cm^3) layered above this solution. After cooling to −20 °C for approximately 3 d red *crystals* of $[NEt_4][W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**1e**) (*ca.* 5.4 g) formed, m.p. 108—110 °C.

Red *crystals* of (**1f**), the $[PPh_4]^+$ salt (m.p. 144—146 °C), may be similarly prepared.

Reactions of the Salts $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ *with* $[AuCl(PPh_3)]$.—(*i*) A mixture of (**1d**) (0.20 g, 0.33 mmol), $[AuCl(PPh_3)]$ (0.16 g, 0.33 mmol), and an excess of KPF_6 (0.50 g) was stirred in thf (10 cm^3) for 1 h at 0 °C. Solvent was removed *in vacuo*, and the residue extracted with CH_2Cl_2 (2 × 10 cm^3). The combined extracts were chromatographed (1.5 × 15 cm column), eluting with CH_2Cl_2. The fast moving orange band was collected, and solvent removed *in vacuo*. The residue was dissolved in thf (3 cm^3), and Et_2O (30 cm^3) added. After cooling (*ca.* −20 °C) overnight, orange *microcrystals* of $[AuW(\mu\text{-}CC_6H_4Me\text{-}2)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**2b**) (0.18 g) were isolated. Phosphorus-31 n.m.r.: δ 52.5 p.p.m. [*J*(WP) 15 Hz].

(*ii*) Similarly, (**1e**) (0.33 g, 0.50 mmol), $[AuCl(PPh_3)]$ (0.29 g, 0.58 mmol), and KPF_6 (0.30 g) were mixed in thf (10 cm^3). After 1 h, i.r. measurements indicated that the reaction had gone to completion. Solvent was removed *in vacuo*, and the red-brown residue was extracted with CH_2Cl_2–Et_2O (3 × 25 cm^3, 1:1). The combined extracts were reduced in volume and chromatographed, eluting with the same solvent mixture. The orange eluate was evaporated and the residue dissolved in thf (5 cm^3). Addition of Et_2O (10 cm^3) and light petroleum (40 cm^3) while stirring precipitated orange-red microcrystals. The mixture was maintained at *ca.* −20 °C overnight to complete formation of orange-red *microcrystals* of $[AuW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**2c**) (0.31 g). Phosphorus-31 n.m.r.: δ 50.8 p.p.m. [*J*(WP) 15 Hz].

Preparation of Platinum–Tungsten Complexes.—(*i*) A mixture of (**1f**) (0.43 g, 0.50 mmol) and $[Pt(cod)_2]$ (0.21 g, 0.50 mmol) in thf (10 cm^3) at 0 °C was treated with a stream of C_2H_4 for 10 min, or until an i.r. spectrum showed complete conversion of reactants. Diethyl ether (50 cm^3) was added dropwise (4 h). Part of the product precipitated as a dark red powder, but a black oil also formed. The red solid was filtered off, washed with Et_2O (10 cm^3), and dried *in vacuo*. Solvent was removed from the filtrate *in vacuo* and the residual oil obtained was redissolved in thf (5 cm^3) and treated with Et_2O (50 cm^3). This afforded additional red *microcrystals* of the product $[PPh_4][PtW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(cod)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3c**) (0.46 g). Platinum-195 n.m.r.: δ 580.1 p.p.m. [*J*(WPt) 293 Hz].

(*ii*) Complex (**3c**) (0.12 g, 0.10 mmol) was dissolved in CH_2Cl_2–CD_2Cl_2 (0.2 cm^3, 4:1) in an n.m.r. tube, and treated with $PMePh_2$ (0.30 mmol). The solution was shaken for *ca.* 1 min, after which time i.r. measurements indicated that the reaction had gone to completion. Removal of solvent *in vacuo*, after n.m.r. measurements [$^{13}C\text{-}\{^1H\}$ (Table 2), $^{31}P\text{-}\{^1H\}$, and $^{195}Pt\text{-}\{^1H\}$], afforded $[PPh_4][PtW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(PMePh_2)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3d**) as a red oil, from which it was not possible to obtain crystals. N.m.r.: $^{31}P\text{-}\{^1H\}$ (CD_2Cl_2), δ 23.25 [PPh_4, *J*(CP) 90 and 14], 8.54 [d, $PMePh_2$, *J*(PP) 7, *J*(PtP) 3 280], and 3.42 p.p.m. [d, $PMePh_2$, *J*(PP) 7, *J*(PtP) 3 846, *J*(WP) 24 Hz]; $^{195}Pt\text{-}\{^1H\}$, δ 241.4 p.p.m. [d of d, *J*(PPt) 3 846 and 3 280, *J*(WPt) 215 Hz].

Synthesis of $[AuPtW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(PPh_3)(cod)(\eta^5\text{-}C_2B_9H_9Me_2)]$.—A thf (10 cm^3) solution of (**3c**) (0.35 g, 0.30 mmol) and $[AuCl(PPh_3)]$ (0.16 g, 0.30 mmol) at 0 °C was treated with an excess of $TlPF_6$ (0.30 g), and the mixture stirred. Within 30 min the reaction was complete (i.r.). Solvent was removed *in vacuo*, and the dark brown residue extracted with CH_2Cl_2 (3 × 10 cm^3). The extracts were concentrated *in vacuo* to *ca.* 10 cm^3, and chromatographed (1.5 × 10 cm column), with CH_2Cl_2 as eluant. The yellow-brown eluate was collected, concentrated to *ca.* 3 cm^3, and light petroleum (30 cm^3) layered above the CH_2Cl_2 solution in a narrow-bore Schlenk tube. The latter was cooled to −20 °C overnight, to give brown-black *microcrystals* of $[AuPtW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(PPh_3)(cod)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**5**) (0.211 g), which were washed with light petroleum (2 × 5 cm^3) and dried *in vacuo*. If the product forms as an oil, addition of Et_2O (*ca.* 4 cm^3) and cooling to 0 °C will produce microcrystals. N.m.r.: $^{31}P\text{-}\{^1H\}$ (CD_2Cl_2), δ 47.24 p.p.m. [*J*(PtP) 195, *J*(WP) 15 Hz]; $^{195}Pt\text{-}\{^1H\}$, δ 900 p.p.m. [d, *J*(PPt) 195, *J*(WPt) 215 Hz].

Reaction between $[NEt_4][W(\equiv CC_6H_4Me\text{-}2)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ *and* $[Fe_3(CO)_{12}]$.—A mixture of (**1d**) (1.27 g, 2.0 mmol) and $[Fe_3(CO)_{12}]$ (1.01 g, 2.0 mmol) in thf (40 cm^3) was stirred (24 h) under a slow stream of nitrogen. Solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (15 cm^3) and chromatographed (2.5 × 18 cm column). Elution with CH_2Cl_2 removed excess $[Fe_3(CO)_{12}]$ (green) and $[Fe(CO)_5]$ (identified by i.r.). The second eluate (dark brown) contained (**8a**), and minor amounts of (**6b**) and (**7b**). A slow moving pink eluate contained $[NEt_4][Fe_3H(CO)_{11}]$ (0.14 g), identified by i.r.

The dark brown fraction was reduced in volume to *ca.* 10 cm^3 *in vacuo*, and Et_2O (40 cm^3) layered above this solution. The Schlenk tube was maintained at −20 °C for 2—3 d, giving black *microcrystals* of $[NEt_4][FeW(\mu\text{-}CC_6H_4Me\text{-}2)(CO)_5(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**8a**) (0.86 g). This product generally contains minor amounts of (**6b**) and (**7b**), and these species may be removed by repeated recrystallisation of (**8a**).

A sample of (**8a**) (0.08 g, 0.10 mmol) in thf (10 cm^3) was treated with a slow stream of CO, resulting in the brown solution gradually turning red. Solvent was removed *in vacuo*, and the oily residue was dissolved in CH_2Cl_2 (10 cm^3), and chromatographed (1.5 × 15 cm column). Elution with CH_2Cl_2 gave a red-brown eluate which was reduced in volume to *ca.* 5 cm^3. After addition of Et_2O (35 cm^3) and cooling to −20 °C, dark red almost black *crystals* of $[NEt_4][FeW\{\mu\text{-}CH(C_6H_4Me\text{-}2)\}(\mu\text{-}\sigma{:}\eta^5\text{-}C_2B_9H_8Me_2)(\mu\text{-}CO)(CO)_5]$ (**6b**) (0.055 g) form after *ca.* 2 d. The product was washed with Et_2O (5 cm^3), and dried *in vacuo*, m.p. 128—130 °C (decomp.).

The trinuclear metal compound (**7b**) could only be obtained pure if (**8a**) is removed from the crude reaction with PMe_3. Thus a sample (0.16 g, 0.21 mmol) of the initial product [containing over 90% of (**8a**), estimated spectroscopically], obtained from (**1d**) and $[Fe_3(CO)_{12}]$, was dissolved in thf (10 cm^3) and treated with a light petroleum (10 cm^3) solution of PMe_3 (*ca.* 0.50 mmol). After 1 h, solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2 (5 cm^3) and chromatographed (1.5 × 12 cm column). Elution of the first red-brown band with CH_2Cl_2, followed by concentration to *ca.* 2 cm^3, addition of Et_2O (20 cm^3), and cooling to −20 °C for 2—3 d afforded dark red *microcrystals* of $[NEt_4][Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}2)(\mu_3\text{-}\sigma{:}\sigma'{:}\eta^5\text{-}C_2B_9H_7Me_2)(CO)_8]$ (**7b**) (0.017 g). The second olive-brown band moved very slowly down the column using acetone as solvent. Removal of the volatile material *in vacuo* gave a brown residue which was dissolved in CH_2Cl_2 (5 cm^3) to which Et_2O (30 cm^3) was added. The mixture was then cooled to −20 °C giving, after *ca.* 3 d, dark brown *microcrystals* of $[NEt_4][FeW(\mu\text{-}CC_6H_4Me\text{-}2)(CO)_4(PMe_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**8b**) (0.025 g). Phosphorus-31 n.m.r.: δ 38.6 p.p.m. [*J*(WP) 17 Hz].

Preparation of $[NEt_4][FeW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta^5\text{-}C_2B_9H_9Me_2)]$.—A thf (15 cm^3) solution of (**1e**) (1.36 g, 2.10 mmol) was treated with $[Fe_3(CO)_{12}]$ (1.06 g, 2.10 mmol) in the same solvent (1.06 g, 2.1 mmol), and the mixture was stirred at room temperature for *ca.* 15 h. Solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (10 cm^3) and chromatographed (2 × 15 cm column) using the same solvent. A fast moving green band contained $[Fe_3(CO)_{12}]$ and $[Fe(CO)_5]$ (identified by i.r.). A second deep-brown eluate was collected. Solvent was removed *in vacuo*, and the residue was dissolved in thf (5 cm^3) and a layer of Et_2O (*ca.* 80 cm^3) placed on top. Without mixing, the Schlenk tube was cooled to −20 °C, and within 2 d black *crystals* of $[NEt_4][FeW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**8c**) (0.496 g) (m.p. 156—166 °C decomp.) were collected and washed with Et_2O (20 cm^3).

Preparation of $[RuW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$.—A mixture of (**1f**) (0.71 g, 0.83 mmol) and $[Ru(CO)(NCMe)_2(\eta\text{-}C_5H_5)][BF_4]$ (0.33 g, 0.90 mmol) in CH_2Cl_2 (10 cm^3) was stirred for 36 h at room temperature. Solvent was removed *in vacuo* and the brown residue extracted with Et_2O (5 × 10 cm^3). The extracts were chromatographed on a Florisil column (1 × 18 cm), using Et_2O as eluant. A brown eluate was recovered, from which solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2–Et_2O (15 cm^3, 1:2), and light petroleum (30 cm^3) layered above the brown solution. After cooling to *ca.* −20 °C for several hours, black *microcrystals* of $[RuW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**10a**) (0.19 g) (m.p. 136—140 °C decomp.) were obtained, washed with light petroleum (10 cm^3), and dried *in vacuo*.

Treatment of (**10a**) (0.14 g, 0.18 mmol) with PMe_2Ph (0.15 g, 1.1 mmol) in thf (10 cm^3) with stirring for *ca.* 15 h, followed by removal of solvent *in vacuo*, dissolving the residue in CH_2Cl_2 (5 cm^3) and chromatography on Florisil gave ochre-yellow *microcrystals* of $[RuW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(PMe_2Ph)(\eta\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**10b**) (0.05 g) (m.p. 148—150 °C decomp.). Phosphorus-31 n.m.r.: δ 13.82 (s) p.p.m.

Table 4. Atomic positional parameters (fractional co-ordinates, × 10^4) with estimated standard deviations in parentheses for (**8c**)

Atom	*x*	*y*	*z*
W	0	2 957(1)	0
Fe	−1 144(1)	2 514(1)	−1 463(1)
C(1)	770(3)	4 327(6)	1 182(6)
C(2)	403(3)	3 723(6)	1 840(6)
C(3)	574(5)	5 475(7)	665(8)
C(4)	−148(4)	4 274(9)	1 988(7)
B(3)	511(4)	2 332(7)	1 855(7)
B(4)	959(5)	2 041(8)	1 116(10)
B(5)	1 105(4)	3 382(9)	672(8)
B(6)	1 112(4)	4 391(7)	2 644(7)
B(7)	959(5)	3 116(9)	3 080(8)
B(8)	1 326(5)	2 087(7)	2 637(9)
B(9)	1 706(4)	2 729(10)	1 897(9)
B(10)	1 569(4)	4 169(8)	1 914(8)
B(11)	1 711(4)	3 372(9)	3 109(8)
C(5)	119(4)	2 959(5)	−1 421(7)
O(5)	205(4)	2 940(5)	−2 220(5)
C(6)	−588(3)	4 177(6)	−688(6)
O(6)	−833(3)	5 068(5)	−973(5)
C(7)	−1 572(3)	1 276(6)	−2 061(6)
O(7)	−1 834(3)	462(5)	−2 408(6)
C(8)	−1 674(3)	3 140(6)	−1 001(7)
O(8)	−1 986(3)	3 562(6)	−653(6)
C(9)	−1 395(4)	3 316(7)	−2 752(7)
O(9)	−1 537(4)	3 780(7)	−3 565(5)
C(20)	−496(2)	1 579(5)	−479(4)
C(21)	−468(3)	420(5)	−272(5)
C(22)	−768(3)	−60(5)	375(6)
C(23)	−739(4)	−1 194(6)	547(7)
C(24)	−447(5)	−1 876(6)	86(9)
C(25)	−157(4)	−1 443(6)	−560(7)
C(26)	−151(3)	−290(5)	−725(5)
C(31)	−1 128(4)	668(7)	818(7)
C(32)	168(4)	148(6)	−1 402(7)
N	−2 724(3)	−3 268(6)	−2 597(7)
C(41)	−2 469(10)	−2 522(18)	−3 172(13)
C(42)	−1 721(7)	−2 699(15)	−2 742(15)
C(51)	−3 441(7)	−3 071(11)	−3 105(16)
C(52)	−3 766(6)	−3 819(11)	−2 530(14)
C(61)	−2 648(6)	−4 487(10)	−2 956(12)
C(62)	−2 927(6)	−4 712(11)	−4 205(9)
C(71)	−2 486(12)	−3 316(16)	−1 399(14)
C(72)	−2 504(9)	−1 959(14)	−952(15)

Crystal Structure Determination of (**8c**).—Crystals of (**8c**) were grown as dark green plates from thf–Et_2O. Diffracted intensities were collected at 293 K on a Nicolet *P*3*m* diffractometer from a crystal of dimensions *ca.* 0.25 × 0.40 × 0.50 mm. Of the 3 280 unique data collected (ω–2θ scans, 2$\theta \leqslant 55°$), 3 140 had $I \geqslant 2.0\sigma(I)$ and only these were used in structure solution and refinement. The data were corrected for Lorentz, polarisation, and *X*-ray absorption effects, the latter by an empirical method based on azimuthal scan data.[17]

Crystal data. $[C_{18}H_{20}N][C_{18}H_{24}B_9FeO_5W]$, $M = 787.6$, monoclinic, $a = 23.498(4)$, $b = 12.109(2)$, $c = 13.044(3)$ Å, $\beta = 115.33(2)°$, $U = 3\,355(1)$ Å^3, $Z = 4$, $D_c = 1.56$ g cm^{-3}, $F(000) = 1\,568$, space group *Cc* (no. 9), Mo-K_α *X*-radiation (graphite monochromator, $\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 39.7 cm^{-1}.

The structure was solved by conventional heavy-atom methods. Successive difference-Fourier syntheses were used to locate all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atoms were included at calculated positions (C–H 0.96, B–H 1.10 Å).[18] Chemically equivalent groups of methyl hydrogen atoms were assigned common refined isotropic thermal parameters, all remaining hydrogen atoms had fixed isotropic thermal parameters (*ca.* 1.2 × U_{equiv} of the parent atom). Refinement by blocked-cascade least squares led to $R = 0.024$ ($R' = 0.024$) and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,45|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks >0.77 or < -1.27 e Å^{-3}, the largest peaks lying close to either the tungsten atom or $[NEt_4]^+$ counter ion. As the space group *Cc* is chiral, an enantiomeric refinement of the type suggested by Rogers[19] was carried out, and this verified that the assumed absolute configuration was correct. Scattering factors with corrections for anomalous dispersion were taken from ref. 20. All calculations were carried out on a Data General 'Eclipse' computer with the SHELXTL system of programs.[17] Atomic co-ordinates are given in Table 4. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, H-atom co-ordinates, and remaining bond lengths and angles.

Acknowledgements

We thank the Deutscher Akademischer Austauschdienst for the award of a NATO Fellowship (to F-E. B.), the S.E.R.C. for a research studentship (to P. S.), and the USAF Office of Scientific Research (Grant 86-0125) for partial support.

References

1 Part 73, I. J. Hart, J. C. Jeffery, M. J. Grosse-Ophoff, and F. G. A. Stone, preceding paper.

2 (*a*) M. Green, J. A. K. Howard, A. P. James, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 61; (*b*) M. Green J. A. K. Howard, A. N. de M. Jelfs, O. Johnson, and F. G. A. Stone, *ibid.*, p. 73; (*c*) M. Green, J. A. K. Howard, A. P. James, A. N. de M. Jelfs, C. M. Nunn, and F. G. A. Stone, *ibid.*, p. 81; (*d*) J. A. K. Howard, A. P. James, A. N. de M. Jelfs, C. M. Nunn, and F. G. A. Stone, *ibid.*, p. 1221; (*e*) M. J. Attfield, J. A. K. Howard, A. N. de M. Jelfs, C. M. Nunn, and F. G. A. Stone, *ibid.*, p. 2219; (*f*) F-E. Baumann, J. A. K. Howard, O. Johnson, and F. G. A. Stone, *ibid.*, p. 2661; (*g*) F-E. Baumann, J. A. K. Howard, O. Johnson, and F. G. A. Stone, *ibid.*, p. 2917.

3 M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, **250**, 395.

4 R. H. Crabtree and D. G. Hamilton, *Adv. Organomet. Chem.*, 1988, **28**, 299.

5 J. C. Jeffery, M. A. Ruiz, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1988, 1131 and refs. therein.

6 (*a*) M. Green, J. A. K. Howard, A. P. James, A. N. de M. Jelfs, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1986, 1697; (*b*) E. Delgado, L. J. Farrugia, J. Hein, J. C. Jeffery, A. L. Ratermann, and F. G. A. Stone, *ibid.*, 1987, 1191.

7 M. Boual, J. C. Jeffery, and J. G. Lawrence-Smith, unpublished work.

8 L. Ricard, R. Weiss, W. E. Newton, G. J. J. Chen, and J. W. McDonald, *J. Am. Chem. Soc.*, 1978, **100**, 1318.

9 J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc.*, 1980, **102**, 1532, 3288 and refs. therein.

10 F. A. Cotton, *Prog. Inorg. Chem.*, 1976, **21**, 1.

11 D. M. P. Mingos, M. I. Forsyth, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1978, 1363.

12 F. G. A. Stone, *Pure Appl. Chem.*, 1986, **58**, 529; in, 'Inorganic Chemistry: Toward the 21st Century,' ed. M. H. Chisholm, *ACS Symp. Ser.*, 1983, **211**, 383.

13 E. O. Fischer, U. Schubert, W. Kleine, and H. Fischer, *Inorg. Synth.*, 1979, **19**, 164; E. O. Fischer, U. Schubert, and H. Fischer, *ibid.*, p. 172; E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrich, F. R. Kreissl, and J. O. Besenhard, *Chem. Ber.*, 1977, **110**, 3397.

14 M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. C. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 862.

15 J. L. Spencer, *Inorg. Synth.*, 1979, **19**, 213.

16 M. Crocker, M. Green, C. E. Morton, K. R. Nagle, and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1985, 2145.

17 G. M. Sheldrick, SHELXTL programs for use with the Nicolet *X*-Ray System, Revision 5.1, Göttingen, 1986.

18 P. Sherwood, Local program for the calculation of idealised H-atom positions for a *nido*-icosahedral carbaborane fragment, University of Bristol, 1987.

19 D. Rogers, *Acta Crystallogr., Sect. A*, 1981, **37**, 734.

20 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 21*st July* 1987; *Paper* 7/1325