Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 75.[1] Reactions of Octacarbonyldicobalt with the Salts $[X][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (X = NEt_4 or PPh_4; R = Me, Ph, C_6H_4Me-2, or C_6H_4Me-4); Crystal Structure of $[PPh_4][Co_2W(\mu_3\text{-}CPh)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]\cdot 0.5CH_2Cl_2$*

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In CH_2Cl_2, at room temperature, the salt $[NEt_4][W(\equiv CMe)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ reacts with $[Co_2(CO)_8]$ to give the trimetal complex $[NEt_4][Co_2W(\mu_3\text{-}CMe)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]$. The latter is partially decarbonylated *in vacuo* to the hexacarbonyl species $[NEt_4][Co_2W(\mu_3\text{-}CMe)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)]$. In contrast, treatment of the salts $[X][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (X = NEt_4, R = Ph, C_6H_4Me-4, or C_6H_4Me-2; X = PPh_4, R = Ph) with $[Co_2(CO)_8]$ affords the hexacarbonyl–trimetal compounds $[X][Co_2W(\mu_3\text{-}CR)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)]$ *via* the intermediacy of initially formed octacarbonyl products $[X][Co_2W(\mu_3\text{-}CR)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]$. In the presence of carbon monoxide, the hexacarbonyl–trimetal compounds revert to the octacarbonyl, and a single-crystal *X*-ray diffraction study has been carried out on $[PPh_4][Co_2W(\mu_3\text{-}CPh)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]$, which crystallises with half a molecule of CH_2Cl_2 per asymmetric unit. The anion consists of a triangle of metal atoms [Co–Co 2.502(3), Co–W 2.767(2) and 2.769(2) Å] capped by the phenylmethylidyne ligand [μ_3-C–Co 1.89(2) and 1.93(2), μ_3-C–W 2.07(1) Å]. The cobalt atoms each carry three terminal CO groups, but the two CO ligands attached to the tungsten semibridge the Co–W bonds [W–C–O 169(2) and 165(1)°]. The carbaborane ligand is η^5-co-ordinated to the tungsten atom, and lies on the same side of the metal triangle as the μ_3-CPh group. The salts containing the anions $[Co_2W(\mu_3\text{-}CR)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ were shown by n.m.r. studies (^1H, $^{11}B\text{-}\{^1H\}$, ^{11}B, and COSY $^{11}B\text{-}^{11}B$) to have structures in which the carbaborane ligand forms two B–H⇀Co exopolyhedral bonds, one to each cobalt atom.

Salts containing the anions $[W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ (R = alkyl or aryl) are becoming increasingly useful in the synthesis of compounds wherein tungsten is bonded to another transition element.[1,2] The C≡W groups in the alkylidyne–tungsten species can co-ordinate either to neutral or to cationic metal–ligand fragments forming, respectively, anionic or neutral polynuclear metal complexes. Moreover, a most interesting feature of some of these syntheses is the non-spectator role played by the carbaborane ligand. In this paper we further extend this area of chemistry by describing reactions of $[Co_2(CO)_8]$ with the compounds $[X][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**1**; X = NEt_4, R = Me, Ph, C_6H_4Me-4, C_6H_4Me-2, or $C_6H_3Me_2$-2,6; X = PPh_4, R = Ph).[3] The anions present in the salts (**1**) are isolobal with the neutral alkylidyne–tungsten compounds $[W(\equiv CR)(CO)_2L]$ {R = Me, L = η-C_5H_5 or $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate]; R = C_6H_4Me-4, L = η-C_5H_5, η-C_5Me_5, or $HB(pz)_3$}. We have previously reported[4] that the latter react with $[Co_2(CO)_8]$ to afford the trimetallatetrahedrane complexes $[Co_2W(\mu_3\text{-}CR)(CO)_8L]$ (**2**). Hence it was of interest to establish whether related anionic clusters form in reactions between (**1**) and octacarbonyldicobalt.

Results and Discussion

The reaction between (**1a**) and $[Co_2(CO)_8]$ in CH_2Cl_2 at room temperature gave the dark green crystalline salt $[NEt_4][Co_2W(\mu_3\text{-}CMe)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3a**), characterised by the data given in Tables 1 and 2. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum showed a characteristic resonance[1] for a μ_3-C nucleus at δ 290.9 p.p.m. When CH_2Cl_2 solutions of (**3a**) were evaporated *in vacuo*, an oily black product was obtained. Examination of the spectroscopic properties of this material showed that it was a *ca.* 9:1 mixture of (**3a**) and the hexacarbonyl–dicobalt-tungsten species $[NEt_4][Co_2W(\mu_3\text{-}CMe)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4a**). In particular, the ^{11}B n.m.r. spectrum of the mixture showed resonances diagnostic for B–H⇀Co groups at δ 12.79 [*J*(BH) 90] and 9.56 p.p.m. [*J*(BH) 100 Hz]. However, (**4a**) could not be separated from (**3a**), and hence full data on the former compound could not be obtained. The partial decarbonylation of (**3a**) contrasts with the behaviour of related complexes described below.

Treatment of (**1b**) with $[Co_2(CO)_8]$ did not lead us to the isolation of the compound $[NEt_4][Co_2W(\mu_3\text{-}CPh)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3b**), an intermediate analogous to (**3a**). Instead, the product isolated was the hexacarbonyl–trimetal compound $[NEt_4][Co_2W(\mu_3\text{-}CPh)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4b**). However, treatment of CH_2Cl_2 solutions of the latter at room temperature with CO gas resulted in a quantitative conversion to (**3b**). In an attempt to obtain crystals suitable for *X*-ray diffraction studies, the tetraphenylphosphonium salts $[PPh_4][Co_2W(\mu_3\text{-}CPh)(CO)_n(\eta^5\text{-}C_2B_9H_9Me_2)]$ [n = 8 (**3c**) or 6 (**4c**)] were similarly prepared from (**1c**). In practice, among all the complexes, only (**3c**) afforded crystals of sufficient quality,

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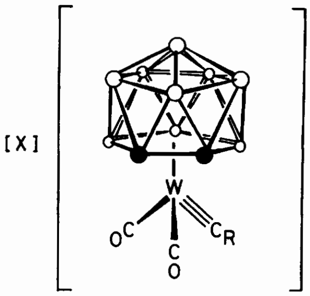
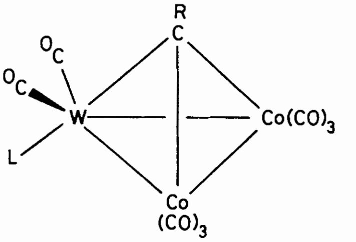
* Tetraphenylphosphonium 1,1,1,2,2,2,3,3-octacarbonyl-3-[7′—11′-η-nonahydro-7′,8′-dimethyl-7′,8′-dicarba-*nido*-undecaborato(2−)]-μ_3-phenylmethylidyne-*triangulo*-dicobalt-tungstate–dichloromethane (2/1).

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

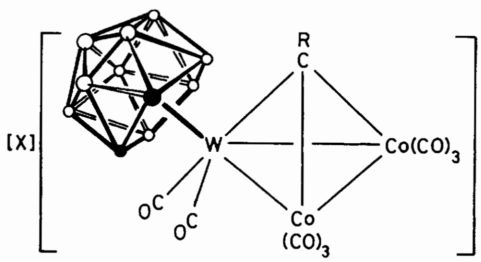


○ BH ● CMe

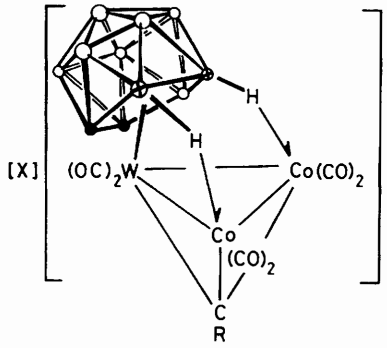
	X	R
(1a)	NEt$_4$	Me
(1b)	NEt$_4$	Ph
(1c)	PPh$_4$	Ph
(1d)	NEt$_4$	C$_6$H$_4$Me-4
(1e)	NEt$_4$	C$_6$H$_4$Me-2
(1f)	NEt$_4$	C$_6$H$_3$Me$_2$-2,6



	R	L
(2a)	Me	η-C$_5$H$_5$
(2b)	C$_6$H$_4$Me-4	η-C$_5$H$_5$
(2c)	C$_6$H$_4$Me-4	η-C$_5$Me$_5$
(2d)	Me	HB(pz)$_3$
(2e)	C$_6$H$_4$Me-4	HB(pz)$_3$



	X	R
(3a)	NEt$_4$	Me
(3b)	NEt$_4$	Ph
(3c)	PPh$_4$	Ph
(3d)	NEt$_4$	C$_6$H$_4$Me-4
(3e)	NEt$_4$	C$_6$H$_4$Me-2



● CMe ○ BH ⊕ B

	X	R
(4a)	NEt$_4$	Me
(4b)	NEt$_4$	Ph
(4c)	PPh$_4$	Ph
(4d)	NEt$_4$	C$_6$H$_4$Me-4
(4e)	NEt$_4$	C$_6$H$_4$Me-2

and the results of the *X*-ray diffraction work are described later.

Data characterising (**3b**), (**3c**), (**4b**), and (**4c**) are listed in Tables 1 and 2, together with those for the related compounds [NEt$_4$][Co$_2$W(μ_3-CR)(CO)$_8$(η^5-C$_2$B$_9$H$_9$Me$_2$)] [R = C$_6$H$_4$Me-4 (**3d**) or C$_6$H$_4$Me-2 (**3e**)] and [NEt$_4$][Co$_2$W(μ_3-CR)(CO)$_6$(η^5-C$_2$B$_9$H$_9$Me$_2$)] [R = C$_6$H$_4$Me-4 (**4d**) or C$_6$H$_4$Me-2 (**4e**)] prepared from the salts (**1d**) and (**1e**), respectively. In all the syntheses, except that which afforded (**3a**), it was evident that the species (**4**) were the thermodynamically more stable products, but on treatment with CO the initially formed complexes (**3**) could be regenerated. The interesting observation was also made that no reaction occurred between [Co$_2$(CO)$_8$] and the salt (**1f**). Presumably the presence of the two *ortho*-substituted methyl groups on the arene ring makes it difficult to afford a structure of type (**3**) in an initial step.

The results of the *X*-ray diffraction study on (**3c**) are summarised in Table 3, and the structure of the anion is shown in the Figure. Interesting comparisons may be made with the previously determined structure of compound (**2b**),[4a] but the lower quality of the data for (**3c**) precludes detailed discussion. Whereas (**2b**) has exact mirror symmetry, crystallographically imposed, compound (**3c**) has only approximate mirror symmetry, excluding the C$_2$B$_9$H$_9$Me$_2$ ligand. In both structures a Co$_2$W isosceles triangle is capped by an alkylidyne group. However, there is a major conformational difference between the two structures. In (**3c**) the orientation of the W(CO)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$) fragment is rotated by 180° about the vector through the W atom and the mid-point of the μ_3-CCo$_2$ triangle compared with the orientation of the isolobal W(CO)$_2$(η-C$_5$H$_5$) group in (**2b**). Moreover, whereas in (**2b**) the W–C–O groups are essentially linear, in (**3c**) the carbonyl ligands of the W(CO)$_2$ moiety semibridge the W–Co bonds (Table 3). This is not possible in (**2b**) because of the different conformation. Perhaps in (**3c**) the semibridging carbonyl groups represent a mechanism for delocalising the anionic charge on the cluster. In both structures the cobalt atoms each carry three linear and essentially orthogonal CO groups, and the arene ring lies parallel to the Co–Co bond.

Although in the solid state the orientations of the W(CO)$_2$L (L = η-C$_5$H$_5$ or η^5-C$_2$B$_9$H$_9$Me$_2$) groups in (**2b**) and (**3c**) are different, i.r. studies on solutions of (**2b**), and on the other species

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

Compound	Colour	Yield (%)	$\nu_{max.}$(CO)[b]/cm^{-1}	Analysis (%)		
				C	H	N
(3a) [NEt$_4$][Co$_2$W(μ_3-CMe)(CO)$_8$(η^5-C$_2$B$_9$H$_9$Me$_2$)]	Dark green	18	2 072s, 2 033vs, 2 011s, 1 876m, 1 814w	30.2 (31.3)	5.1 (4.5)	1.7 (1.7)
(3b) [NEt$_4$][Co$_2$W(μ_3-CPh)(CO)$_8$(η^5-C$_2$B$_9$H$_9$Me$_2$)]	Dark brown	60	2 075s, 2 036vs, 2 018s, 2 012(sh), 1 878m, 1 816w	35.5 (35.8)	4.6 (4.5)	1.8 (1.6)
(3c) [PPh$_4$][Co$_2$W(μ_3-CPh)(CO)$_8$(η^5-C$_2$B$_9$H$_9$Me$_2$)]	Black	40	2 074s, 2 035vs, 2 017m, 2 006(sh), 1 875m, 1 814w	45.0 (46.3)	3.6 (3.6)	
(3d) [NEt$_4$][Co$_2$W(μ_3-CC$_6$H$_4$Me-4)(CO)$_8$(η^5-C$_2$B$_9$H$_9$Me$_2$)]	Black	60	2 074s, 2 035vs, 2 018s, 2 004(sh), 1 878m, 1 818w	35.9 (36.6)	5.2 (4.9)	1.6 (1.5)
(3e) [NEt$_4$][Co$_2$W(μ_3-CC$_6$H$_4$Me-2)(CO)$_8$(η^5-C$_2$B$_9$H$_9$Me$_2$)][c]	Black	60	2 074s, 2 036vs, 2 018m, 1 998w, 1 875m, 1 819w			
(4a) [NEt$_4$][Co$_2$W(μ_3-CMe)(CO)$_6$(η^5-C$_2$B$_9$H$_9$Me$_2$)][d]	Black	10	[e]1 982m, 1 958s, 1 934w, 1 880w			
(4b) [NEt$_4$][Co$_2$W(μ_3-CPh)(CO)$_6$(η^5-C$_2$B$_9$H$_9$Me$_2$)]	Black	39	2 019m, 1 985s, 1 963vs, 1 937w, 1 877w	35.2 (35.3)	4.9 (4.8)	1.8 (1.7)
(4c) [PPh$_4$][Co$_2$W(μ_3-CPh)(CO)$_6$(η^5-C$_2$B$_9$H$_9$Me$_2$)]	Black	20	[f]2 017m, 1 984s, 1 963s, 1 938w, 1 882w	45.7 (46.5)	4.0 (3.8)	
(4d) [NEt$_4$][Co$_2$W(μ_3-CC$_6$H$_4$Me-4)(CO)$_6$(η^5-C$_2$B$_9$H$_9$Me$_2$)]	Black	17	[f]2 016w, 1 984s, 1 962vs, 1 937w, 1 881w	35.2 (36.2)	5.6 (4.9)	2.0 (1.6)
(4e) [NEt$_4$][Co$_2$W(μ_3-CC$_6$H$_4$Me-2)(CO)$_6$(η^5-C$_2$B$_9$H$_9$Me$_2$)]	Dark brown	40	2 017m, 1 983s, 1 962vs, 1 940(sh), 1 876w	34.9 (36.2)	4.7 (4.9)	1.6 (1.6)

[a] Calculated values are given in parentheses. [b] Measured in CH$_2$Cl$_2$, unless otherwise stated. [c] Obtained as an oil, mixed with **(4e)**, yield estimated by i.r. (see text). [d] Complex detected spectroscopically, in a mixture with **(3a)**, yield estimated by i.r. (see text). [e] Band at *ca.* 2 020 cm^{-1} obscured by absorptions due to **(3a)**. [f] In tetrahydrofuran.

Table 2. Hydrogen-1, carbon-13, and boron-11 n.m.r. data[a] for the cobalt–tungsten compounds

Compound	^{1}H(δ)[b]	^{13}C(δ)[c]	^{11}B(δ)[d]
(3a)	1.42 (m, br, 12 H, NCH$_2$*Me*), 2.31 (m, br, 8 H, NC*H*$_2$Me), 2.33 (s, 6 H, CMe), 4.35 (s, 3 H, μ_3-CMe)	290.9 [μ_3-C, *J*(WC) 114], 230.6 [WCO, *J*(WC) 164], 199.8 (br, CoCO), 63.2 (*C*Me), 52.5 (N*C*H$_2$Me), 49.5 (μ_3-C*Me*), 29.9 (C*Me*), 8.7 (NCH$_2$*Me*)	−10.31(m, br)
(3b)	1.21 [t of t, 12 H, NCH$_2$*Me*, *J*(HH) 7, *J*(NH) 2], 2.21 (br, 6 H, CMe), 3.07 [q, 8 H, NC*H*$_2$Me, *J*(HH) 7], 6.93—7.44 (m, 5 H, Ph)	[e]282.0 (μ_3-C), 231.0 [WCO, *J*(WC) 156], 199.7 (br, CoCO), 164.5 [C^1(Ph)], 130.2, 125.8, 125.3 (Ph), 64.1 (*C*Me), 52.6 (N*C*H$_2$Me), 30.0 (C*Me*), 7.7 (NCH$_2$*Me*)	−9.97 (m, br)
(3e)	1.22 [t, 12 H, NCH$_2$*Me*, *J*(HH) 7], 2.20, 2.35, 2.52 (s × 3, 9 H, Me-2, CMe), 3.04 [q, 8 H, NC*H*$_2$Me, *J*(HH) 7], 7.00—7.11 (m, 4 H, C$_6$H$_4$)	283.0 (μ_3-C), 226.2, 222.6 (WCO), 203.5 (br, CoCO), 162.1 [C^1(C$_6$H$_4$)], 134.3, 132.6, 129.4, 125.1, 124.8 (C$_6$H$_4$) 61.1, 59.0 (*C*Me), 52.8 (N*C*H$_2$Me), 33.7, 31.9 (C*Me*), 24.0 (Me-2), 7.5 (NCH$_2$*Me*)	−9.90 (m, br)
(4b)	−7.75 [q, 1 H, B(H)Co, *J*(BH) 90], −7.30 [q, 1 H, B(H)Co, *J*(BH) 92], 1.24 [t, 12 H, NCH$_2$*Me*, *J*(HH) 7], 2.08, 2.53 (CMe), 3.06 [q, 8 H, NC*H*$_2$Me, *J*(HH) 7], 6.90—7.58 (m, br, 5 H, Ph)	302.8 (μ_3-C), 224.3, 222.3 [WCO, *J*(WC) 153], 205.3 (br, CoCO), 164.8 [C^1(Ph)], 128.6, 128.1, 125.1 (Ph), 67.2 (*C*Me), 53.0 (N*C*H$_2$Me), 34.3, 31.5 (C*Me*), 7.41 (NCH$_2$*Me*)	[f]13.94 [B(H)Co, 1 B, *J*(BH) 86], 10.33 [B(H)Co, 1 B, *J*(BH) 92], −6.51 [1 B, *J*(BH) 147], −7.66 [1 B, *J*(BH) 123], −8.95 [1 B, *J*(BH) 159], −10.47 (m, 3 B), −12.87 [1 B, *J*(BH) 146]
(4d)	−7.72 [vbr, 1 H, B(H)Co], −7.15 [vbr, 1 H, B(H)Co], 1.17 (m br, 12 H, NCH$_2$*Me*), 2.08, 2.26, 2.51 (s × 3, 9 H, CMe, Me-4), 2.97 (br, 8 H, NC*H*$_2$Me), 6.96—7.53 (m, 4 H, C$_6$H$_4$)	302.4 (μ_3-C), 224.7, 221.7 (WCO), 205.3 (br, CoCO), 161.7 [C^1(C$_6$H$_4$)], 135.3, 128.9, 128.5 (C$_6$H$_4$), 67.2, 60.2 (*C*Me), 52.5 (N*C*H$_2$Me), 34.2, 31.3 (C*Me*), 21.5 (Me-4), 8.2 (NCH$_2$*Me*)	13.81 [B(H)Co, *J*(BH) 98], 10.58 [B(H)Co, *J*(BH) 78], −9.46 (m, br)
(4e)	−8.60 [vbr, 2 H, B(H)Co], 1.22 [t, 12 H, NCH$_2$*Me*, *J*(HH) 7], 2.07, 2.32, 2.51 (s × 3, 9 H, CMe, Me-2), 3.04 [q, 8 H, NC*H*$_2$Me, *J*(HH) 7.0], 7.01—7.11 (m, 4 H, C$_6$H$_4$)	301.0 (μ_3-C), 223.3, 219.1 (WCO), 204.0 (br, CoCO), 161.0 [C^1(C$_6$H$_4$)], 131.8, 131.1, 129.4, 125.1, 124.0 (C$_6$H$_4$), 63.0, 57.0 (*C*Me), 52.8 (N*C*H$_2$Me), 31.9, 30.2 (C*Me*), 22.9 (Me-2), 7.6 (NCH$_2$*Me*)	15.00 [B(H)Co, *J*(BH) 88], 12.45 [B(H)Co, *J*(BH) 102], −9.80 (m, br)

[a] Chemical shifts in p.p.m., coupling constants in Hz. [b] Measured in CD$_2$Cl$_2$. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of SiMe$_4$. Measurements in CD$_2$Cl$_2$–CH$_2$Cl$_2$. [d] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of BF$_3$·Et$_2$O (external). Measurements in CD$_2$Cl$_2$, at 28 MHz, ^{1}H–^{11}B coupling constants measured from coupled ^{11}B spectra. [e] Measured at −40 °C with solutions saturated with CO (see text). [f] Measured at 128 MHz.

of this type, reveal the existence of stereoisomers.[2] These most likely correspond to molecules with different orientations of their W(CO)$_2$L groups with respect to the vector through the W atom and the mid-point of the μ_3-CCo$_2$ triangle. Interestingly, the i.r. spectrum of **(3c)** in the carbonyl stretching region shows six bands whereas the spectrum of **(2b)** displays ten absorptions. Thus it appears that only one stereoisomer of **(3c)** exists in solution.

Although, as mentioned above, we were unable to obtain crystals of any of the compounds (**4**) for an *X*-ray diffraction study, the structures of these species are firmly based on the n.m.r. data given in Table 2. Thus the ^{1}H n.m.r. spectrum (200 MHz) of (**4b**) shows two high-field resonances at δ −7.30 and −7.75, and these appear as quartets [*J*(BH) *ca.* 90 Hz]. These signals are characteristic for the presence of two B–H→Co groups in (**4b**). Similar three-centre two-electron bonding occurs in the compounds [RuW(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η-C$_5$H$_5$)(η^5-C$_2$B$_9$H$_9$Me$_2$)] and [MoW(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η^5-C$_9$H$_7$)(η^5-C$_2$B$_9$H$_9$Me$_2$)], structurally characterised by *X*-ray diffraction.[5] The resonances for the B–H→M (Ru or Mo) groups in these complexes occur as quartets at δ −11.48 [*J*(BH) 70] and −7.98 [*J*(BH) 84Hz], respectively. In accord with the data obtained from the ^{1}H n.m.r. spectrum of (**4b**), a proton-coupled ^{11}B n.m.r. spectrum (128 MHz) revealed two signals at δ 10.33 and 13.94 p.p.m., each with ^{1}H–^{11}B couplings of *ca.* 90 Hz. These resonances are diagnostic for exopolyhedral B–H→M(Co) bonds.[5] There are five ^{11}B resonances (Table 2), due to the other seven boron nuclei, but these occur to higher field, and correspond to BH groups not involved in three-centre bonding to a metal centre. It should be noted that the ^{11}B-{^{1}H} n.m.r. spectra of compounds of type (**3**) are characterised by a very broad unresolved signal at *ca.* −10 p.p.m. Similar spectra are shown by other complexes in which the η^5-C$_2$B$_9$H$_9$Me$_2$ group ligates a single metal centre.[1,2,5]

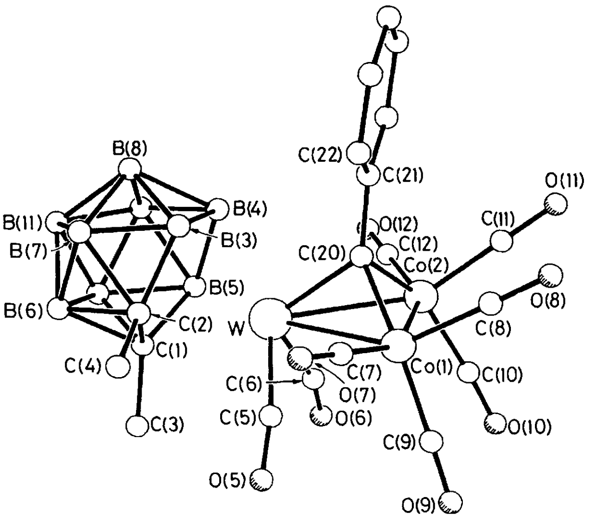


Figure. The structure of the anion of the salt [PPh$_4$][Co$_2$W(μ$_3$-CPh)(CO)$_8$(η^5-C$_2$B$_9$H$_9$Me$_2$)] (**3c**), showing the crystallographic numbering

The ^{11}B–^{11}B two-dimensional COSY n.m.r. spectra for compounds of type (**4**) were also structurally informative. Thus for (**4b**) the signal at δ 10.33 p.p.m. showed cross-peaks with the three resonances of relative intensity 1:1:1 at δ 13.94, −8.95, and −12.87 p.p.m. Moreover, the peak at δ 13.94 p.p.m. showed cross-peaks with the four resonances of relative intensity 1:1:1:1 at δ 10.33, −6.51, −7.66, and −8.95 p.p.m. These results are in agreement with the structural formula for (**4b**) shown. The resonance at 10.33 p.p.m. is evidently due to the boron nucleus of the B–H→Co group adjacent to a CMe fragment, since in this site it has a connectivity with only three other boron atoms. Correspondingly, the signal at 13.94 may be assigned to the boron nucleus of the B–H→Co group having its boron atom located in the central position in the pentagonal $\overline{\mathrm{C{-}C{-}B{-}}\mathit{B}\mathrm{{-}B}}$ ring of the η^5-C$_2$B$_9$H$_9$Me$_2$ ligand. In this site it would have connectivities to four other boron atoms, and display four cross-peaks in the COSY spectrum, as is observed. Moreover, the cross-peak relationship between both low-field signals is in agreement with a direct B–B link between the two B–H→Co groups.

The ^{1}H and ^{11}B n.m.r. spectra of (**4d**) and (**4e**) were not as well resolved as those of (**4b**) since they were measured at lower field (90 and 28 MHz, respectively). Nevertheless, the data (Table 2) show that all three complexes have similar structures. The ^{1}H n.m.r. spectrum of (**4d**) shows two high-field resonances at δ −7.15 and −7.72 for the B–H→Co groups, and in the ^{11}B spectrum these fragments give rise to characteristic peaks at δ 10.58 and 13.81 p.p.m. In the ^{1}H n.m.r. spectrum of (**4e**) there is only one high-field signal (δ −8.60) but it is broad, with a relative intensity corresponding to two protons. The ^{11}B spectrum has the two diagnostic peaks (δ 12.45 and 15.00 p.p.m.) for the B–H→Co groups. The ^{13}C-{^{1}H} n.m.r. spectra of (**4b**), (**4d**), and (**4e**) show characteristic resonances for their μ$_3$-C

Table 3. Selected internuclear distances (Å) and angles (°) for the complex [PPh$_4$][Co$_2$W(μ$_3$-CPh)(CO)$_8$(η^5-C$_2$B$_9$H$_9$Me$_2$)]·0.5CH$_2$Cl$_2$ (**3c**)

W–Co(1)	2.769(2)	W–Co(2)	2.767(2)	Co(1)–Co(2)	2.502(3)	W–C(1)	2.48(1)
W–C(2)	2.38(2)	W–B(3)	2.45(3)	W–B(4)	2.38(3)	W–B(5)	2.36(2)
W–C(5)	1.96(3)	W–C(6)	2.03(2)	W–C(20)	2.07(1)	Co(1) ··· C(5)	2.61
Co(1)–C(7)	1.77(2)	Co(1)–C(8)	1.80(2)	Co(1)–C(9)	1.81(3)	Co(1)–C(20)	1.93(2)
Co(2) ··· C(6)	2.60	Co(2)–C(10)	1.80(3)	Co(2)–C(11)	1.76(2)	Co(2)–C(12)	1.82(2)
Co(2)–C(20)	1.89(2)	C(1)–C(2)	1.64(3)	C(2)–B(3)	1.70(4)	B(3)–B(4)	1.80(3)
B(4)–B(5)	1.76(4)	B(5)–C(1)	1.71(3)				
Co(1)–W–Co(2)	53.7(1)	Co(1)–W–C(5)	64.2(5)	Co(2)–W–C(6)	63.4(4)	C(5)–W–C(6)	80.9(9)
Co(1)–W–C(20)	44.1(6)	Co(2)–W–C(20)	43.1(5)	C(5)–W–C(20)	107.8(8)	C(6)–W–C(20)	106.4(7)
Co(1)–W–X*	152	Co(2)–W–X	139	C(5)–W–X	118	C(6)–W–X	115
C(20)–W–X	121	W–Co(1)–Co(2)	63.1(1)	W–Co(1)–C(7)	93.7(6)	Co(2)–Co(1)–C(7)	152.7(8)
W–Co(1)–C(8)	143.2(9)	Co(2)–Co(1)–C(8)	91.0(6)	C(7)–Co(1)–C(8)	101.6(8)	W–Co(1)–C(9)	108.4(5)
Co(2)–Co(1)–C(9)	97.5(6)	C(7)–Co(1)–C(9)	104(1)	C(8)–Co(1)–C(9)	100(1)	W–Co(1)–C(20)	48.2(4)
Co(2)–Co(1)–C(20)	48.5(5)	C(7)–Co(1)–C(20)	106(1)	C(8)–Co(1)–C(20)	95(1)	C(9)–Co(1)–C(20)	143.0(8)
W–Co(2)–Co(1)	63.2(1)	W–Co(2)–C(10)	116.0(7)	Co(1)–Co(2)–C(10)	98.5(8)	W–Co(2)–C(11)	144.0(8)
Co(1)–Co(2)–C(11)	100.8(7)	C(10)–Co(2)–C(11)	98(1)	W–Co(2)–C(12)	88.3(5)	Co(1)–Co(2)–C(12)	150.4(6)
C(10)–Co(2)–C(12)	101(1)	C(11)–Co(2)–C(12)	98(1)	W–Co(2)–C(20)	48.3(4)	Co(1)–Co(2)–C(20)	49.7(6)
C(10)–Co(2)–C(20)	147(1)	C(11)–Co(2)–C(20)	96.2(9)	C(12)–Co(2)–C(20)	105.9(9)	W–C(5)–O(5)	169(2)
W–C(6)–O(6)	165(1)	W–C(20)–Co(1)	87.7(8)	W–C(20)–Co(2)	88.6(7)	Co(1)–C(20)–Co(1)	81.8(9)
W–C(20)–C(21)	133(1)	Co(1)–C(20)–C(21)	125(1)	Co(2)–C(20)–C(21)	125(1)		

* X is the centroid of the tungsten-ligated C$_2$B$_3$ face of the carbaborane ligand.

nuclei at δ 302.8, 302.4, and 301.0 p.p.m., respectively. These signals are somewhat more deshielded than those in the two precursors (**3b**) and (**3e**), appearing at δ 282.0 and 283.0 p.p.m., respectively. The n.m.r. spectra of (**3d**) could not be measured due to the fact that this compound releases CO very readily to give (**4d**). The trend in chemical shifts between the respective compounds (3) and (4), however, suggests that in the latter the alkylidyne ligand asymmetrically bridges the Co_2W triangle, as discussed previously.[6]

Decarbonylation of the complexes (3) to give (4) requires rotation of the $W(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)$ moiety, since in the former species the cage ligand lies on the same side of the Co_2W triangle as the alkylidyne group (Figure). The reverse reaction, in the presence of CO, requires rotation of the $W(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)$ group in the opposite direction. Both electronic and steric effects of the μ_3-CR groups appear to be important in these transformations. As mentioned earlier, compound (**3a**) could only be partially decarbonylated to (**4a**). In contrast, in the reactions between $[Co_2(CO)_8]$ and (**1b**)—(**1e**), the compounds (**3b**)—(**3e**) were only detected by i.r. as intermediates in the formation of (**4b**)—(**4e**), respectively. In the presence of CO, the decarbonylation process affording (**4b**)—(**4d**) could be reversed, leading to the isolation and characterisation of (**3b**)—(**3d**). However, (**4e**) could only be partially converted to (**3e**). The steric effect of the *ortho*-substituted Me group on the arene ring may be responsible for this result. As mentioned earlier, no compounds analogous to (3) or (4) were obtained from (**1b**). Electronic effects of substituents on the aryl ring may also be important. Thus (**3d**) decarbonylates so readily in solution that n.m.r. measurements were not possible. In contrast, such data could be obtained for (**3b**), although the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra had to be measured on CO-saturated solutions at −40 °C. In the solid state, however, (**3c**) did not decarbonylate, thereby allowing the *X*-ray diffraction study.

The results described in this paper, as well as those reported in the previous paper,[1] provide further examples of interesting differences in the reactivity patterns of the species $[W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ compared with the compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$, in their respective reactions with low-valent metal complexes. These differences arise as a consequence of involvement of the carbaborane group in many reactions of the salts (**1**).

Experimental

The techniques and equipment used have been described previously.[1,7] Light petroleum refers to that fraction of b.p. 40—60 °C. Alumina (Brockman activity II) was used in chromatography columns. Analytical and other data for the new compounds are given in Table 1. The salts $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = Me, Ph, C_6H_4Me-4, C_6H_4Me-2, or $C_6H_3Me_2$-2,6) and $[PPh_4][W(\equiv CPh)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ were prepared by methods described previously.[1,2,7]

Synthesis of the Cobalt–Tungsten Complexes.—(*i*) A mixture of (**1a**) (0.82 g, 1.47) mmol) and $[Co_2(CO)_8]$ (0.58 g, 1.51 mmol) in CH_2Cl_2 (40 cm^3) in a Schlenk tube was stirred under a slow stream of nitrogen for 24 h, after which time an i.r. spectrum revealed that reaction was complete. The dark olive green solution was concentrated to *ca.* 15 cm^3, and chromatographed (2 × 15 cm column) using CH_2Cl_2 as solvent. A fast moving brown band containing $[Co_4(CO)_{12}]$ and $[W(CO)_6]$ (identified by i.r.) was discarded. A broad green band developed, having a light green tail. The latter was shown by i.r. to contain $[NEt_4][Co(CO)_4]$, and should not be allowed to contaminate the major green eluate, which was concentrated *in vacuo* to *ca.* 10 cm^3. Carbon monoxide was bubbled through this solution (*ca.* 10 min), trichloroethylene (40 cm^3) added, and the mixture cooled to *ca.* −20 °C. This treatment afforded dark green *microcrystals* of $[NEt_4][Co_2W(\mu_3\text{-}CMe)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3a**) (0.22 g).

A sample of (**3a**) (0.05 g) in CH_2Cl_2 (10 cm^3) was evaporated *in vacuo*, and the oily residue maintained under vacuum for 1 h. The residue was then redissolved in CH_2Cl_2–CD_2Cl_2, and i.r. (Table 1) and ^{11}B n.m.r. {δ 12.79 [*J*(BH) 90], 9.56 [*J*(BH) 100 Hz], −3.0 to −12.0 p.p.m. (br, m)} measurements revealed the presence of *ca.* 10% of $[NEt_4][Co_2W(\mu_3\text{-}CMe)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4a**).

(*ii*) A mixture of $[Co_2(CO)_8]$ (0.51 g, 1.50 mmol) and (**1b**) (0.93 g, 1.50 mmol) in CH_2Cl_2 (20 cm^3) was stirred under a slow stream of nitrogen for 24 h. Solvent was removed *in vacuo*, and the black residue was redissolved in CH_2Cl_2 (15 cm^3) and chromatographed. Elution with the same solvent removed a brown band, shown by i.r. to contain $[W(CO)_6]$ and $[Co_4(CO)_{12}]$. A second dark brown band consisted of the desired product tailed by a fainter band containing $[NEt_4][Co(CO)_4]$, which should not be allowed to contaminate the main fraction. The dark brown eluate was concentrated to *ca.* 5 cm^3, and light petroleum (40 cm^3) added. This treatment produced a black oil and a yellow supernatant liquid. The latter was discarded, and the oil redissolved in CH_2Cl_2 (10 cm^3). Trichloroethylene (50 cm^3) was added and the mixture cooled to −20 °C. After *ca.* 3 d, black *microcrystals* of $[NEt_4][Co_2W(\mu_3\text{-}CPh)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4b**) (0.50 g) were filtered off, washed with trichloroethylene–light petroleum (5 cm^3, 1:1), and dried *in vacuo*.

A sample of (**4b**) (0.15 g, 0.20 mmol), in CH_2Cl_2 (10 cm^3) at 0 °C, was saturated with a slow stream of CO gas for 90 min, after which time an i.r. spectrum revealed a 100% conversion to (**3b**). Trichloroethylene (20 cm^3) and light petroleum (10 cm^3) were added, and the mixture was left at −20 °C for 2 d to give black-brown *needles* of $[NEt_4][Co_2W(\mu_3\text{-}CPh)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3b**) (0.11 g). The product was washed with light petroleum (10 cm^3) and dried *in vacuo* briefly (*ca.* 5 min). Compound (**3b**) in solution readily releases CO to give (**4b**), and should be kept in a Schlenk tube under CO. For n.m.r. measurements the solvents used should be saturated with CO.

(*iii*) The compounds $[PPh_4][Co_2W(\mu_3\text{-}CPh)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3c**), $[PPh_4][Co_2W(\mu_3\text{-}CPh)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4c**), $[NEt_4][Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)\text{-}(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3d**), and $[NEt_4][Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4d**) were prepared by methods similar to those used to obtain (**3b**) and (**4b**).

The compound $[NEt_4][Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}2)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**4e**) was prepared by the method used for (**4b**). Carbonylation of (**4e**) was only partially successful. A sample of (**4e**) (0.10 g, 0.12 mmol) in CH_2Cl_2 (10 cm^3) was treated with CO gas. After 1 h, i.r. measurements revealed that a 50% conversion to (**3e**) had occurred. Continued treatment with CO gas, however, for *ca.* 2 h produced significant amounts of the salt (**1e**). Addition of light petroleum (30 cm^3) and cooling to −20 °C afforded a black oil, which was recovered and washed with light petroleum (5 cm^3) and dried *in vacuo*. Crystals could not be obtained but spectroscopic data (Tables 1 and 2) revealed the oil to be essentially pure $[NEt_4][Co_2W(\mu_3\text{-}CC_6H_4Me\text{-}2)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]$ (**3e**).

Crystal-structure Determination and Refinement.—Crystals of (**3c**) grew slowly from $CHCl{=}CCl_2$–CH_2Cl_2 (3:1) as dark red or black diamond-shaped plates. Diffracted intensities were collected at 293 K from a crystal of dimensions *ca.* 0.35 × 0.33 × 0.10 mm on a Nicolet *P*3*m* diffractometer. Of the 8 701 unique data collected (Wyckoff ω scans, $2\theta \leqslant 50°$), 4 677 had $I \geqslant 2.0\sigma(I)$, and only these were used in the structure solution and refinement. The data were corrected for Lorentz,

Table 4. Atomic positional parameters (fractional co-ordinates, × 10^4) for complex (**3c**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	2 245(1)	2 398(1)	993(1)	C(21)	1 697(10)	1 711(13)	−625(8)
Co(1)	840(2)	1 350(2)	183(1)	C(22)	1 774(13)	686(14)	−746(9)
Co(2)	867(2)	3 149(2)	−149(1)	C(23)	1 883(11)	391(15)	−1 289(9)
C(1)	3 496(10)	2 762(13)	2 112(10)	C(24)	1 942(13)	1 115(21)	−1 719(10)
C(2)	3 493(11)	1 644(12)	1 792(9)	C(25)	1 877(14)	2 115(17)	−1 606(11)
C(3)	3 293(13)	2 884(15)	2 697(10)	C(26)	1 757(11)	2 425(15)	−1 065(8)
C(4)	3 392(14)	636(14)	2 122(10)	P	2 777(3)	8 528(3)	3 918(3)
B(3)	3 385(14)	1 686(15)	980(11)	C(32)	1 533(7)	9 765(8)	3 055(6)
B(4)	3 209(11)	2 999(15)	739(9)	C(33)	748	10 091	2 729
B(5)	3 261(14)	3 624(15)	1 462(14)	C(34)	210	9 587	2 853
B(6)	4 381(14)	2 174(18)	2 396(12)	C(35)	459	8 755	3 304
B(7)	4 318(14)	1 535(21)	1 684(12)	C(36)	1 245	8 429	3 630
B(8)	4 164(12)	2 469(23)	1 054(10)	C(31)	1 782	8 934	3 506
B(9)	4 086(14)	3 597(17)	1 342(12)	C(42)	3 273(6)	10 487(8)	4 271(6)
B(10)	4 223(17)	3 465(17)	2 199(14)	C(43)	3 777	11 304	4 398
B(11)	4 773(14)	2 748(20)	1 944(11)	C(44)	4 404	11 210	4 280
C(5)	1 861(12)	1 641(15)	1 514(10)	C(45)	4 527	10 299	4 035
O(5)	1 718(9)	1 280(11)	1 926(7)	C(46)	4 023	9 482	3 908
C(6)	1 700(11)	3 536(12)	1 190(9)	C(41)	3 396	9 576	4 026
O(6)	1 536(9)	4 174(12)	1 443(7)	C(52)	2 981(8)	6 976(9)	4 839(6)
C(7)	1 285(12)	159(17)	506(10)	C(53)	3 154	6 587	5 486
O(7)	1 582(9)	−615(11)	716(8)	C(54)	3 419	7 227	6 064
C(8)	89(13)	1 047(13)	−711(11)	C(55)	3 513	8 257	5 995
O(8)	−384(10)	830(12)	−1 280(7)	C(56)	3 340	8 647	5 347
C(9)	225(12)	1 531(13)	559(10)	C(51)	3 075	8 006	4 769
O(9)	−156(10)	1 651(11)	811(8)	C(62)	2 228(7)	7 459(10)	2 703(7)
C(10)	147(15)	3 657(15)	39(12)	C(63)	2 278	6 751	2 263
O(10)	−300(11)	3 922(13)	193(11)	C(64)	2 959	6 162	2 513
C(11)	246(12)	3 084(15)	−1 072(12)	C(65)	3 590	6 280	3 203
O(11)	−171(10)	3 070(12)	−1 680(9)	C(66)	3 540	6 988	3 644
C(12)	1 418(11)	4 282(15)	−102(10)	C(61)	2 859	7 577	3 394
O(12)	1 755(8)	4 970(10)	−84(8)	C(70)	5 000	5 000	5 000
C(20)	1 525(10)	2 047(11)	−61(8)	Cl(1)	3 963(9)	4 355(9)	4 513(7)
				Cl(2)	5 097(11)	4 062(11)	4 327(8)

polarization, and *X*-ray absorption effects, the latter by an empirical method based on azimuthal scan data.[8]

Crystal data. $[C_{24}H_{20}P][C_{19}H_{20}B_9Co_2O_8W]\cdot 0.5CH_2Cl_2$, M = 1 157.2 (including solvent), monoclinic, a = 19.705(5), b = 13.238(3), c = 22.224(3) Å, β = 121.22(1)°, U = 4 958(2) Å^3, Z = 4, D_c = 1.55 g cm^{-3}, $F(000)$ = 2 284, space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 31.6 cm^{-1}.

The structure was solved and all the non-hydrogen atoms located by conventional heavy-atom and difference Fourier methods. Anisotropic thermal parameters were refined for the phosphorus atom of the cation, and all non-hydrogen atoms of the anion, with the exception of B(3). Attempts to refine this last atom with anisotropic thermal parameters were unsuccessful, probably reflecting the poor quality of the data obtained from this weakly diffracting crystal. During refinement of the structure the asymmetric unit was found to contain half a molecule of dichloromethane, disordered about a centre of inversion and the chlorine and carbon atoms were included with anisotropic thermal parameters. With the exception of the solvent hydrogen atoms, all hydrogen atoms were included at calculated positions (C–H 0.96, B–H 1.10 Å[9]) with a common refined isotropic thermal parameter for those belonging to methyl groups and fixed isotropic thermal parameters (*ca.* 1.2 × $U_{\text{equiv.}}$ of the atom to which they were attached) for the remaining hydrogen atoms. The phenyl rings of the cation were constrained to rigid hexagonal geometries. Refinement by blocked-cascade least squares led to R = 0.074 (R' = 0.067) and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,4|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks > 1.14 or < -1.15 e Å^{-3}, the largest lying close to the tungsten atom. Scattering factors with corrections for anomalous dispersion were taken from ref. 10. All computations were carried out on a Data General 'Eclipse' computer with the SHELXTL system of programs.[8] Atom 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.

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