Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 53.[1] Alkylidyne(carbaborane)dimetal Complexes with Tungsten–Molybdenum and –Tungsten Bonds; Crystal Structures of the Compounds $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_2B_9H_9Me_2)]$ [M = Mo (Two Isomers) or W] *

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The salts $[N(PPh_3)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9R_2)]$ (R = Me or H) and $[M(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$ (M = Mo or W, C_9H_7 = indenyl) react in CH_2Cl_2 at ambient temperatures to give the dimetal compounds $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9R_2)]$ (**2a**, M = Mo, R = Me; **2b**, M = W, R = Me; **2c**, M = Mo, R = H). *X*-Ray diffraction studies on (**2a**) and (**2b**) showed they were isostructural, with the metal–metal bonds bridged by the *p*-tolylmethylidyne group and by a three-centre two-electron B–H→M bond involving the carbaborane group ligating the tungsten atom. The tungsten atom carries two terminally bound CO groups while the other metal centre (**2a**, Mo; **2b**, W) is bonded by one CO ligand and the indenyl group. Structural parameters for (**2a**) and (**2b**) are essentially identical; for (**2a**), Mo–W 2.657(2), μ-C–Mo 1.95(2), μ-C–W 2.03(1), B–μ-H 1.02, and μ-H–Mo 1.719 Å. In toluene at 80 °C, compounds (**2a**) and (**2b**) isomerise. The isomerisation involves a polytopal rearrangement of the carbaborane ligand, thereby affording the species $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,9\text{-}C_2B_9H_9Me_2)]$ (**3a**, M = Mo; **3b**, M = W). Compound (**3a**) was identified and structurally characterised by an *X*-ray diffraction study. Apart from migration of the carbon atoms within the carbaborane cage, (**3a**) retains the structural features of (**2a**) with the Mo–W bond [2.669(1) Å] bridged by $CC_6H_4Me\text{-}4$ [μ-C–Mo 1.963(4), μ-C–W 2.056(4) Å] and B–H→Mo [μ-H–Mo 1.93(3) Å] groups. Treatment of (**2a**) with $K[BH(CHMeEt)_3]$ followed by $[N(PPh_3)_2]Cl$ gives the salt $[N(PPh_3)_2][MoW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (**4**), with *p*-tolylmethylidene and B–H→Mo groups bridging the Mo–W bond. Reactions of the compounds (**2**) with PMe_3 affords the complexes $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_n(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9R_2)]$ (**5a**, M = Mo, R = Me, *n* = 3; **5b**, M = W, R = Me, *n* = 3; **6**, M = Mo, R = H, *n* = 2). Whereas in (**5a**) and (**5b**) the groups $M(PMe_3)(\eta^5\text{-}C_9H_7)$ are present and *exo*-polyhedral B–H→M bonds are absent, in contrast, in (**6**) the PMe_3 ligand is attached to the tungsten atom and a three-centre two-electron B–H→Mo linkage is present. The latter bridge system is also found in $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ which contains a $W(PMe_3)(\eta^5\text{-}C_9H_7)$ group, and was prepared by displacing the ligand $N_2C(C_6H_4Me\text{-}4)_2$ from $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2\{N_2C(C_6H_4Me\text{-}4)_2\}(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$. Treatment of (**2a**) with dmpm ($Me_2PCH_2PMe_2$) gives the compound $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(\mu\text{-}dmpm)(CO)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$. The n.m.r. data ($^1H$, $^{13}C\text{-}\{^1H\}$, $^{11}B\text{-}\{^1H\}$, and $^{31}P\text{-}\{^1H\}$) for the new complexes are reported, and discussed in relation to structures proposed or established by *X*-ray diffraction.

As part of our interest in polynuclear metal complexes in which the metal–metal bonds are bridged by alkylidyne ligands,[2] we have employed the salts $[N(PPh_3)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9R_2)]$ (**1**, R = Me or H) to prepare dimetal compounds with bonds between tungsten and ruthenium,[1] rhodium, or gold.[3] Herein we report related studies leading to the synthesis of species with tungsten–molybdenum and –tungsten bonds. A preliminary account of some of the work has been given.[4]

Results and Discussion

The salts $[M(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$ (M = Mo or W, C_9H_7 = indenyl) react with alkynes to afford cationic complexes in which the alkynes formally act as four-electron donors.[5] This result suggested that reactions between the salts $[M(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$ and (**1**) should be investigated in view of the isolobal relationship between alkynes and the anions $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9R_2)]^-$. Neutral dimetal products should be obtained. Moreover, there arose the possibility that the new species would be formally electronically unsaturated, if the C≡W group present in (**1**) functioned as a four-electron donor.

Reactions between (**1**) and $[M(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)]$-

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* 1,2,2-Tricarbonyl-1-(η^5-indenyl)-μ-[7′—11′-η-nonahydro-7′,8′-dimethyl-7′,8′-dicarba-*nido*-undecaborato(2−)-$C^{7',8'}$, $B^{9'-11'}$(W), $H^{10'}$(Mo)]-μ-(*p*-tolylmethylidyne)molybdenumtungsten(*Mo*−*W*), 1,2,2-tri-carbonyl-1-(η^5-indenyl)-μ-[7′—11′-η-nonahydro-7′,9′-dimethyl-7′,9′-dicarba-*nido*-undecaborato(2−)-$C^{7',8'}$, $B^{9'-11'}$(W), $H^{10'}$(Mo)]-μ-(*p*-tolylmethylidyne)molybdenumtungsten (*Mo*−*W*), and 1,1,2-tricarbonyl-2-(η^5-indenyl)-μ-[7′—11′-η-nonahydro-7′,8′-dimethyl-7′,8′-dicarba-*nido*-undecaborato-(2−)-$C^{7',8'}$, $B^{9'-11'}$(W^1), $H^{10'}$(W^2)]-μ-(*p*-tolylmethylidyne)ditungsten (*W*−*W*) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

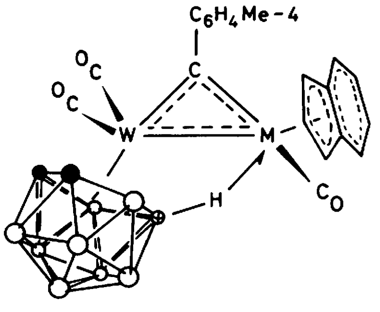
Table 1. Analytical[a] and physical data for the dimetal complexes

	Compound[b]	Colour	Yield (%)	ν(BH)[c]/cm^{-1}	ν(CO)[c]/cm^{-1}	Analysis (%)	
						C	H
(2a)	$[MoW(\mu-CR)(CO)_3(\eta^5-C_9H_7)(\eta^5-7,8-C_2B_9H_9Me_2)]$	Green	55	2 566m	2 002s, 1 956s, 1 933m	38.9 (38.7)	4.0 (3.9)
(2b)	$[W_2(\mu-CR)(CO)_3(\eta^5-C_9H_7)-(\eta^5-7,8-C_2B_9H_9Me_2)]$	Green	39	2 566w	2 002s, 1 952s, 1 929(sh)	34.0 (34.7)	3.8 (3.5)
(2c)	$[MoW(\mu-CR)(CO)_3(\eta^5-C_9H_7)(\eta^5-7,8-C_2B_9H_{11})]$	Green	67	2 577m	2 008s, 1 958s, 1 937m	36.6 (36.9)	3.4 (3.5)
(3a)	$[MoW(\mu-CR)(CO)_3(\eta^5-C_9H_7)(\eta^5-7,9-C_2B_9H_9Me_2)]$	Green	80	2 569m	2 012s, 1 966s, 1 940(sh)	39.2 (38.7)	4.0 (3.9)
(3b)	$[W_2(\mu-CR)(CO)_3(\eta^5-C_9H_7)(\eta^5-7,9-C_2B_9H_9Me_2)]$	Green	70	[d]2 559m	[d]2 012s, 1 966s, 1 950(sh)	35.1 (34.7)	3.4 (3.5)
(4)	$[N(PPh_3)_2][MoW(\mu-CHR)-(CO)_3(\eta^5-C_9H_7)(\eta^5-,7,8-C_2B_9H_9Me_2)]$	Purple	75	2 561m	1 909s, 1 843s, 1 770w	55.2 (56.1)	4.6 (4.7)
(5a)	$[MoW(\mu-CR)(CO)_3(PMe_3)(\eta^5-C_9H_7)(\eta^5-7,8-C_2B_9H_9Me_2)]$	Brown	81	2 551m	1 966s, 1 897s, 1 795m	39.1 (39.5)	4.3 (4.6)
(5b)	$[W_2(\mu-CR)(CO)_3(PMe_3)(\eta^5-C_9H_7)(\eta^5-7,8-C_2B_9H_9Me_2)]$[e]	Brown	40	2 553m	1 960(sh), 1 941vs, 1 838w		
(6)	$[MoW(\mu-CR)(CO)_2(PMe_3)(\eta^5-C_9H_7)(\eta^5-7,8-C_2B_9H_{11})]$	Green	79	2 551m	1 927m, 1 873m	36.7 (37.7)	4.9 (4.5)
(7a)	$[W_2(\mu-CR)(CO)_2(PMe_3)(\eta^5-C_9H_7)-(\eta^5-7,8-C_2B_9H_9Me_2)]$	Red	81	2 554m	1 963s, 1 894s	35.2 (35.6)	4.3 (4.4)
(8)	$[MoW(\mu-CR)(\mu-CO)(\mu-dmpm)-(CO)(\eta^5-C_9H_7)(\eta^5-7,8-C_2B_9H_9Me_2)]$	Brown	81	2 546m	1 923s, 1 765s	[f]36.8 (37.2)	4.8 (4.8)

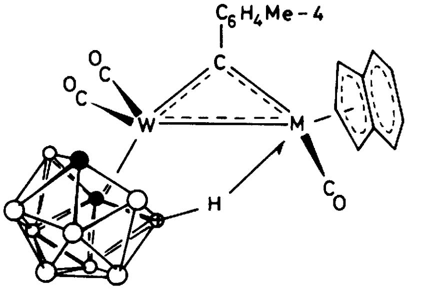
[a] Calculated values are given in parentheses. [b] R = C_6H_4Me-4. [c] In CH_2Cl_2 unless otherwise stated. [d] In Et_2O. [e] Complex unstable, satisfactory microanalytical data not available. [f] Crystallised with a molecule of CH_2Cl_2.

$[N(PPh_3)_2][W(\equiv CC_6H_4Me-4)(CO)_2(\eta^5-7,8-C_2B_9H_9R_2)]$

	R
(1a)	Me
(1b)	H



	M	●	○	⊕
(2a)	Mo	CMe	BH	B
(2b)	W	CMe	BH	B
(2c)	Mo	CH	BH	B



	M	●	○	⊕
(3a)	Mo	CMe	BH	B
(3b)	W	CMe	BH	B

$[BF_4]$ in CH_2Cl_2 at room temperature afforded the green dimetal compounds $[MW(\mu-CC_6H_4Me-4)(CO)_3(\eta^5-C_9H_7)(\eta^5-7,8-C_2B_9H_9R_2)]$ (**2a**, M = Mo, R = Me; **2b**, M = W, R = Me; **2c**, M = Mo, R = H). Analytical and spectroscopic data for these new complexes are summarised in Tables 1—3, and are in accord with the structures shown. Discussion of the spectroscopic data is deferred, however, until the results of *X*-ray crystallographic studies are described.

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

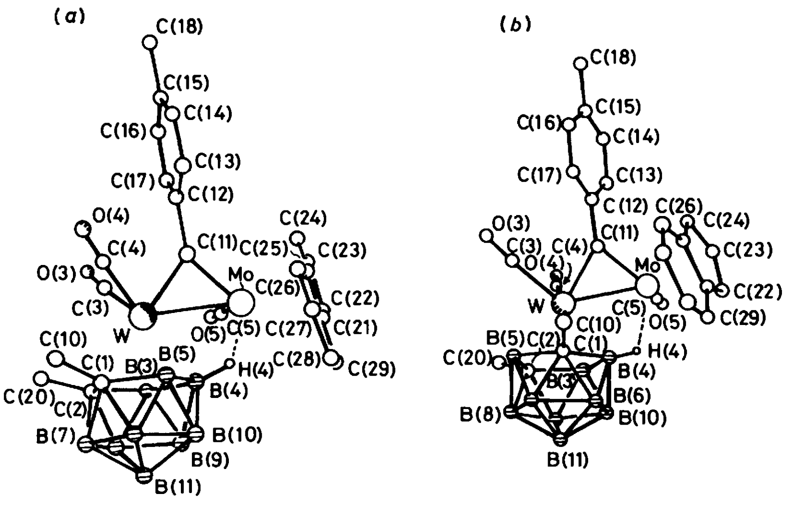
Compound	^1H[b,c] (δ)	^{13}C[d] (δ)
(**2a**)[e]	−7.98 [q, 1 H, Mo(μ-H)B, J(BH) 84], 2.39 (s, 3 H, Me-4), 2.52 (s, 6 H, Me), 5.60—5.91 (m × 3, 3 H, C_9H_7), 6.65—7.45 (m, 8 H, C_6H_4 and C_9H_7)	381.7 [μ-C, J(WC) 98], 226.2, 222.5, 212.9 (CO), 161.0 [$C^1(C_6H_4)$], 136.2—114.0 (C_6H_4 and C_9H_7), 91.4, 90.4, 76.5 (C_9H_7), 31.9, 31.0 (Me), 20.7 (Me-4)
(**2b**)[e]	−8.50 [q, 1 H, W(μ-H)B, J(BH) 65], 2.02 (s, 3 H, Me), 2.10 (s, 3 H, Me), 2.60 (s, 3 H, Me-4), 5.48 (m, 1 H, C_9H_7), 5.80 [t, 1 H, C_9H_7, J(HH) 3], 6.00 (m, 1 H, C_9H_7), 6.72—7.32 (m, 8 H, C_6H_4 and C_9H_7)	[f] 367.6 (μ-C), 221.1 [CO, J(WC) 153], 213.8, 211.4 (CO), 162.2 [$C^1(C_6H_4)$], 135.9—112.1 (C_6H_4 and C_9H_7), 87.3, 85.8, 72.1 (C_9H_7), 32.0, 31.1 (Me), 20.6 (Me-4)
(**2c**)	−7.80 [q, 1 H, Mo(μ-H)B, J(BH) 82], 2.56 (s, 3 H, Me-4), 5.46—5.97 (m × 3, 3 H, C_9H_7), 6.60—7.50 (m, 8 H, C_6H_4 and C_9H_7)	381.9 (μ-C), 226.4, 219.6, 209.2 (CO), 162.1 [$C^1(C_6H_4)$], 136.8—114.3 (C_6H_4 and C_9H_7), 91.9, 90.6, 76.7 (C_9H_7), 21.1 (Me-4)
(**3a**)	−6.91 [q, 1 H, Mo(μ-H)B, J(BH) 83], 0.08 (s, 3 H, Me), 1.37 (s, 3 H, Me), 2.58 (s, 3 H, Me-4), 5.54 (m, 1 H, C_9H_7), 5.57 [t, 1 H, C_9H_7, J(HH) 3], 6.02 (m, 1 H, C_9H_7), 6.78 [$(AB)_2$, 2 H, C_6H_4, J(AB) 8], 7.01—7.09 (m, 3 H, C_9H_7), 7.43 [$(AB)_2$, 2 H, C_6H_4, J(AB) 8], 7.61—7.68 (m, 1 H, C_9H_7)	372.9 (μ-C), 225.2, 216.0, 211.9 (CO), 161.6 [$C^1(C_6H_4)$], 136.9—115.7 (C_6H_4 and C_9H_7), 94.4, 88.2, 78.0 (C_9H_7), 37.7, 33.3 (Me), 21.1 (Me-4)
(**3b**)	−7.57 [br, 1 H, W(μ-H)B], 0.04 (s, 3 H, Me), 1.32 (s, 3 H, Me), 2.62 (s, 3 H, Me-4), 5.54 (m, 1 H, C_9H_7), 5.64 [t, 1 H, C_9H_7, J(HH) 3], 6.12 (m, 1 H, C_9H_7), 6.80—7.62 (m, 8 H, C_6H_4 and C_9H_7)	363.7 (μ-C), 215.4, 212.2, 211.5 (CO), 161.3 [$C^1(C_6H_4)$], 137.5—113.0 (C_6H_4 and C_9H_7), 92.8, 83.8, 70.9 (C_9H_7), 37.2, 33.9 (Me), 22.2 (Me-4)
(**4**)	−8.11 [m, 1 H, Mo(μ-H)B], 1.85 (s, 3 H, Me), 2.34 (s, 3 H, Me), 2.46 (s, 3 H, Me-4), 4.56 (m, 1 H, C_9H_7), 5.02 (s, 1 H, C_9H_7), 5.68 (s, 1 H, C_9H_7), 6.78—7.72 (m, 38 H, C_6H_4, Ph, and C_9H_7), 9.79 (s, 1 H, μ-CH)	[g] 251.6, 250.2 (WCO), 235.1 (MoCO), 161.2 [$C^1(C_6H_4)$], 133.7—111.4 (C_6H_4, Ph, and C_9H_7), 89.5, 86.9, 72.6 (C_9H_7), 33.2, 31.8 (Me), 20.7 (Me-4)
(**5a**)	1.02 [d, 9 H, MeP, J(PH) 10], 2.05 (s, 3 H, Me), 2.11 (s, 3 H, Me), 2.42 (s, 3 H, Me-4), 5.47 (m, 1 H, C_9H_7), 5.56 [t, 1 H, C_9H_7, J(HH) 3], 5.97 (m, 1 H, C_9H_7), 7.06—7.50 (m, 8 H, C_6H_4 and C_9H_7)	[h] 358.1 (μ-C), 159.1 [$C^1(C_6H_4)$], 134.5—122.4 (C_6H_4 and C_9H_7), 105.7, 83.9, 82.6 (C_9H_7), 32.5, 31.4 (Me), 21.0 [d, MeP, J(PC) 21]
(**5b**)	[f] 1.29 [d, 9 H, MeP, J(PH) 10], 1.97 (s, 3 H, Me), 2.24 (s, 3 H, Me), 2.57 (s, 3 H, Me-4), 4.88, 5.76, 5.90, 6.35, 6.82 (m × 5, 5 H, C_9H_7), 7.26—8.26 (m, 6 H, C_6H_4 and C_9H_7)	
(**6**)	−9.45 [m, 1 H, Mo(μ-H)B], 1.22 [d, 9 H, MeP, J(PH) 10], 2.60 (s, 3 H, Me-4), 4.48 (s, 1 H, C_9H_7), 5.73 (s, 1 H, C_9H_7), 5.97 (s, 1 H, C_9H_7), 6.72—7.45 (m, 8 H, C_6H_4 and C_9H_7)	383.2 (μ-C), 238.3 (MoCO), 233.6 [d, WCO, J(PC) 12], 163.0 [$C^1(C_6H_4)$], 135.5—112.6 (C_6H_4 and C_9H_7), 96.1, 91.7, 76.4 (C_9H_7), 21.0 (Me-4), 15.5 [d, MeP, J(PC) 24]
(**7a**)	−7.14 [q, 1 H, W(μ-H)B, J(BH) 70], 1.18 [d, 9 H, MeP, J(PH) 10], 2.03 (s, 3 H, Me), 2.11 (s, 3 H, Me), 2.54 (s, 3 H, Me-4), 4.38 (m, 1 H, C_9H_7), 4.88 [d of d, 1 H, C_9H_7, J(HH) 5, 3], 5.66 (m, 1 H, C_9H_7), 6.84—7.61 (m, 8 H, C_6H_4 and C_9H_7)	353.1 (μ-C), 220.6, 216.3 (CO), 159.4 [$C^1(C_6H_4)$], 137.0—123.8 (C_6H_4 and C_9H_7), 116.6, 111.2, 86.7, 79.3, 67.5 (C_9H_7), 32.1, 31.7 (Me), 21.0 [d, MeP, J(PC) 33], 21.0 (Me-4)
(**8**)	1.19—1.59 (m, 12 H, MeP), 2.01 (s, 3 H, Me), 2.36 (s, 3 H, Me), 2.42 (s, 3 H, Me-4), 2.57 (m, 2 H, CH_2), 5.44 (m, 1 H, C_9H_7), 5.73 (m, 1 H, C_9H_7), 6.11 (m, 1 H, C_9H_7), 6.43—7.47 (m, 8 H, C_6H_4 and C_9H_7)	375.1 (μ-C), 274.8 (μ-CO), 242.1 [d, WCO, J(PC) 18], 164.5 [$C^1(C_6H_4)$], 135.4—114.1 (C_6H_4 and C_9H_7), 100.9, 90.0, 84.4 (C_9H_7), 56.3 [d of d, PCH_2P, J(PC) 31, 31], 31.0, 29.1 (Me), 20.8 (Me-4), 16.5 [d, MeP, J(PC) 36], 16.0 [d, MeP, J(PC) 21]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz, measurements at room temperature unless otherwise stated. [b] Measured in CD_2Cl_2. [c] Proton resonances for B–H groups occur as broad unresolved signals 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] Peaks for major isomer only listed (see text). [f] Measured at −40 °C. [g] Resonance due to μ-*C*H(C_6H_4Me-4) not assigned. [h] Spectrum of poor quality, signals due to CO and Me-4 groups not observed.

The molecular structures of both (**2a**) and (**2b**) were established by *X*-ray diffraction. That for (**2a**) is shown in Figure (*a*), and selected data for both species are given in Table 4. Since the two compounds are isostructural with virtually identical internuclear separations and angles only data for (**2a**) are discussed in detail. The Mo–W bond [2.657(2) Å] is spanned by the *p*-tolylmethylidyne group with C(11)–Mo 1.95(2) and C(11)–W 2.03(2) Å. Thus the alkylidyne group is essentially symmetrically placed with respect to the two metal atoms. Moreover, the μ-C–Mo distance is relatively short, and may be compared with those found in the compound [$MoW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2$]. The latter contains two Mo(μ-CC_6H_4Me-4)W ring systems, and the μ-C–Mo separations [2.19(1) Å] are distinctly longer than those for μ-C–W [1.94(1) Å], so that the two *p*-tolylmethylidyne groups do not symmetrically bridge their respective Mo–W bonds.[6] Moreover, the Mo–W distances [2.938(1) Å] in the molybdenumditungsten species are significantly longer than that found [2.657(2) Å] in (**2a**). Thus the dimensions of the μ-C(11)MoW ring in the latter suggests multiple bond character in the metal–metal and μ-C–metal bonds.

As expected, the molybdenum atom carries the indenyl group, and there are three essentially linearly bound carbonyl ligands, two attached to the tungsten and one to the molybdenum centre. A feature of considerable interest is the bonding mode of the carbaborane cage to the dimetal system. The open C_2B_3 face of the carbaborane group ligates the tungsten atom, with B(4) almost coplanar (deviation 0.30 Å) with the μ-C(11)MoW ring [B(4)–W 2.26(2), B(4)–Mo 2.49(2) Å] and the B(4)–Mo vector is bridged by a hydrogen atom [H(4)]. There is thus a B–H→Mo three-centre two-electron bond, thereby enabling the carbaborane ligand to function formally as a six-electron donor to the Mo–W system. The compounds (**2a**) and (**2b**) are thus 32 cluster valence electron (c.v.e.) species, and do not possess the 34 c.v.e.s necessary for both metal centres to have 18-electron shells. The 'unsaturation' is reflected in the dimensions of the μ-C(11)MoW ring, discussed above.

The mean plane of C(1)C(2)B(3)B(4)B(5) tips away from the tungsten with increasing bond lengths to the metal away from



(2a) **(3a)**

Figure. Molecular structures of (*a*) $[\mathrm{MoW}(\mu\text{-}\mathrm{CC_6H_4Me\text{-}4})(\mathrm{CO})_3(\eta^5\text{-}\mathrm{C_9H_7})(\eta^5\text{-}7,8\text{-}\mathrm{C_2B_9H_9Me_2})]$ (**2a**), and (*b*) $[\mathrm{MoW}(\mu\text{-}\mathrm{CC_6H_4Me\text{-}4})(\mathrm{CO})_3(\eta^5\text{-}\mathrm{C_9H_7})(\eta^5\text{-}7,9\text{-}\mathrm{C_2B_9H_9Me_2})]$ (**3a**) showing the crystallographic numbering scheme

Table 3. Boron-11 and phosphorus-31 n.m.r. data[a] for the complexes

Compound	^{11}B[b] (δ)	^{31}P[c] (δ)
(**2a**)	−10.9 (br, 8 B), 14.1 [1 B, Mo(μ-H)B]	
(**2b**)	−9.5 (br, 8 B), 16.2 [1 B, W(μ-H)B]	
(**2c**)	−8.8 (br, 8 B), 15.4 [1 B, Mo(μ-H)B]	
(**3a**)	−11.2 (br, 8 B), 13.9 [1 B, Mo(μ-H)B]	
(**3b**)	−12.5 (br, 8 B), 15.0 [1 B, W(μ-H)B]	
(**4**)	−11.1 (br, 8 B), 9.2 [1 B, Mo(μ-H)B]	
(**5a**)	−12.6 (br, 9 B)	1.9(s)
(**5b**)[d]	−8.3 (br, 9 B)	−20.3 [*J*(WP) 368]
(**6**)	−12.4 (br, 3 B), −6.7 (br, 5 B), 14.5 [1 B, Mo(μ-H)B]	−16.8 [*J*(WP) 318]
(**7a**)	−10.9 (br, 8 B), 16.7 [1 B, W(μ-H)B]	−26.3 [*J*(WP) 408]
(**8**)	−9.7 (br, 9 B)	21.6 [d, PMo, *J*(PP) 40], −3.9 [d, PW, *J*(PP) 40, *J*(WP) 389]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz, measurements in CD_2Cl_2 at ambient temperatures unless otherwise stated. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $BF_3{\cdot}Et_2O$ (external). [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of 85% H_3PO_4 (external). [d] Spectra measured at −40 °C.

B(4). This 'slippage' of the tungsten atom towards the unique boron has also been observed in the ruthenium–tungsten compound $[\mathrm{RuW}(\mu\text{-}\mathrm{CC_6H_4Me\text{-}4})(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})(\eta^5\text{-}7,8\text{-}\mathrm{C_2B_9H_9Me_2})]$[1] which has an *exo*-polyhedral B–H→Ru three-centre two-electron bond similar to the B–H→Mo linkage in (**2a**). Previously *exo*-polyhedral B–H→Rh bridge bonding has been found in the homonuclear dimetal compounds $[\mathrm{Rh_2(PR_3)_2}(\eta^5\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}})_2]$ (PR_3 = PPh_3, PEt_3, or PMe_2Ph).[7] The 'slippage' of the pentagonal girdle of the *nido*-icosahedral carbaborane ligand is accompanied by a 'folding' of the C_2B_3 face about the two equivalent boron atoms [B(3) and B(5) of Figure (*a*)]. The slip and fold distortions may be related[8] to three parameters: (*i*) a slip distance (Δ) from the perpendicular through the centroid of the non-bonded pentagonal B_5 girdle to the metal atom, and (*ii*) two fold angles θ and φ representing the angles between the perpendicular through the centroid of the B(6)B(7)B(8)B(9)B(10) ring and the planes defined by B(5)C(1)C(2)B(3) and B(3)B(4)B(5) [Figure (*a*)], respectively. For compound (**2a**), the parameters are Δ 0.21 Å, θ 1.7°, and φ 1.1°. The corresponding values for $[\mathrm{RuW}(\mu\text{-}\mathrm{CC_6H_4Me\text{-}4})(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})(\eta^5\text{-}7,8\text{-}\mathrm{C_2B_9H_9Me_2})]$ are Δ 0.24 Å, θ 1.4°, and φ 0.3°. Thus in neither compound does the 'slippage' due to the presence of the B–H→Mo(Ru) bonds produce appreciable distortion of the C_2B_9 fragment.

Having established the molecular structures of (**2a**) and (**2b**), and by implication that of (**2c**) also, it is possible to relate the spectroscopic data to the results of the *X*-ray diffraction studies. In their i.r. spectra all three compounds show three CO stretching bands in the terminal region (Table 1). The ^{1}H n.m.r. spectra (Table 2) provide clear confirmation of the presence of the B–H→Mo(W) *exo*-polyhedral bridge bonds. Each spectrum shows a high-field quartet signal [**2a**, δ −7.98, *J*(BH) 84; **2b**, −8.50, 65; **2c**, −7.80, 82 Hz], corresponding to the presence of this linkage. In confirmation, the ^{11}B-{^{1}H} n.m.r. spectra (Table 3) show signals indicating the presence of a uniquely deshielded boron atom in each molecule (**2a**, δ 14.1; **2b**, 16.2, and **2c**, 15.4 p.p.m.). Moreover, in the ^{11}B spectra of (**2a**) and (**2c**) the signals were observed as doublets, with *J*(BH) 84 and 82 Hz, respectively. This ^{11}B–^{1}H coupling is lower than that observed for two-centre two-electron B–H bonds (*ca.* 130 Hz), and mirrors the reduction in ^{13}C–^{1}H coupling found[9] for C–H→M agostic linkages *versus* C–H bonds. In the ^{1}H n.m.r. spectrum of $[\mathrm{RuW}(\mu\text{-}\mathrm{CC_6H_4Me\text{-}4})(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})(\eta^5\text{-}7,8\text{-}\mathrm{C_2B_9H_9Me_2})]$ the resonance for the B–H→Ru group occurs at δ −11.48 with *J*(BH) 70 Hz, while the signal for the boron nucleus in the ^{11}B-{^{1}H} n.m.r. spectrum is at δ 19.5 p.p.m.[1]

The ^{13}C-{^{1}H} n.m.r. spectra of the compounds (**2**) are also informative. The spectrum of each complex shows resonances for CO ligands in three different environments. The ligated carbon nuclei of the bridging alkylidyne groups display signals at δ 381.7 (**2a**), 367.6 (**2b**), and 381.9 p.p.m. (**2c**). These peaks are at the upper end of the range of chemical shifts generally observed for bridging alkylidyne-carbon nuclei in dimetal compounds. The majority of such complexes display ^{13}C-{^{1}H} n.m.r. resonances for the μ-C groups in the range *ca.* 300—360

Table 4. Selected internuclear distances (Å) and angles (°) for the complexes $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_{25}B_9H_9Me_2)]$ [M = Mo (**2a**), W (**2b**), or Mo (**3a**)]

	(**2a**)	(**2b**)	(**3a**)		(**2a**)	(**2b**)	(**3a**)
W–Mo(W)	2.657(2)	2.660(2)	2.669(1)	W–C(11)	2.03(2)	2.08(2)	2.056(4)
Mo(W)–C(11)	1.95(2)	1.94(2)	1.963(4)	W–C(1)	2.46(2)	2.43(2)	2.368(4)
W–C(2)	2.45(2)	2.45(2)	2.445(5)	W–B(3)	2.35(2)	2.31(4)	2.336(5)
W–B(4)	2.26(2)	2.23(3)	2.245(5)	W–B(5)	2.35(2)	2.38(2)	2.395(5)
Mo(W)–B(4)	2.49(2)	2.44(2)	2.502(5)	B(4)–H(4)[a]	1.02	1.36	1.21(3)
Mo(W)–H(4)[a]	1.719	1.665	1.93(3)	W–C(3)	2.03(2)	1.96(2)	2.011(5)
W–C(4)	2.06(2)	1.97(3)	1.995(5)	Mo(W)–C(5)	2.02(2)	1.96(2)	1.977(5)
Mo(W)–(η^5-C_9H_7)[b]	2.34(2)	2.35(2)	2.352(5)				
W–C(3)–O(3)	177(2)	176(2)	177.7(4)	W–C(4)–O(4)	177(1)	179(1)	177.1(4)
Mo(W)–C(5)–O(5)	175(2)	177(2)	175.4(5)	W–C(11)–C(12)	137(1)	135(1)	141.0(3)
Mo(W)–C(11)–C(12)	139(1)	143(1)	135.8(3)	W–C(11)–Mo(W)	83.7(7)	82.8(8)	83.2(1)
B(4)–H(4)–Mo(W)	129	107	103(2)	C(3)–W–C(4)	81.3(8)	82.4(9)	84.0(2)
W–Mo(W)–C(5)	87.0(5)	88.7(6)	84.6(1)				

[a] H(4) fully refined in (**3a**) only. [b] Mean Mo(W)–C_9H_7.

p.p.m. For example, in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of $[ReW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)_2]$ the μ-C resonance occurs at δ 343.5 p.p.m.[10] The saturated 34 c.v.e. compound $[RuW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$, however, has a $^{13}C\text{-}\{^1H\}$ n.m.r. resonance for the μ-C nucleus at δ 276.7 p.p.m.[1] The appearance of the signal at such a relatively high-field has been attributed to the fact that the *p*-tolylmethylidyne group bridges the ruthenium–tungsten bond asymmetrically to such a degree that the alkylidyne ligand could be regarded as being essentially terminally bound to the tungsten. At the other extreme, the μ-C chemical shift in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of the 32 c.v.e. complex $[FeW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5\{HB(pz)_3\}]$ [$HB(pz)_3$ = tris(pyrazol-1-yl)borate] occurs at δ 408.8 p.p.m.[11] It may well be that the $^{13}C\text{-}\{^1H\}$ n.m.r. shifts for the μ-C nuclei in the compounds (**2**) reflect to some degree the electronic unsaturation associated with these 32 c.v.e. systems. However, caution is required in interpreting the data in this manner. Thus the compounds $[MW_2(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (M = Mo or W),[6] possessing *p*-tolylmethylidyne groups edge-bridging Mo–W or W–W bonds, respectively, and having metal centres with 18-electron valence shells, display resonances for the μ-C nuclei in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra at δ 360.1 (Mo) and 376.2 p.p.m. (W). Whereas the former signal shows the expected trend in being *ca.* 20 p.p.m. less deshielded than that for (**2a**), the latter resonance is *ca.* 8 p.p.m. more deshielded than that for (**2b**).

During ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. studies on the compounds (**2**), signals due to another isomer of each species were observed. In Table 1 only the peaks due to the major isomer (*ca.* 80—90%) are listed. For (**2a**), the minor isomer displayed resonances in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum at δ 390.8 (μ-C), 229.6, 220.9, 211.2 (CO), 161.6 $[C^1(C_6H_4)]$, 33.9, and 31.5 p.p.m. (C*Me*). For (**2c**), peaks for the minor isomer were seen at δ 387.6 (μ-C), 229.1, 219.3, and 208.5 p.p.m. (CO). It is possible that the minor isomer represents a different orientation of the $M(CO)(\eta^5\text{-}C_9H_7)$ (M = Mo or W) fragment with respect to the three-membered ring. Alternatively, the second isomer might correspond to a B–H(3) or B–H(5) interaction with the second metal centre, rather than B–H(4) [see Figure (*a*)]. Whatever the nature of the isomerism there is no exchange at room temperature on the n.m.r. time-scale between the isomers. Studies at more elevated temperatures were not conducted since these result in a further transformation of (2) (see below).

There are several ways of formulating the bonding in the compounds (**2**). In one representation the $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9R_2)]^-$ fragment might be regarded as donating six electrons (four from the C≡W group, and two *via* a B–H→M bond) to a $[M(CO)(\eta^5\text{-}C_9H_7)]^+$ (M = Mo or W) group. This description is formally similar to that suggested[5] for the cations $[Mo(CO)_2(\eta\text{-}RC_2R)(\eta\text{-}C_9H_7)]^+$ (R = alkyl or aryl), in which the alkynes function as four-electron donors. However, an alternative bonding scheme might depict a $[M(\equiv CC_6H_4Me\text{-}4)(CO)(L)(\eta^5\text{-}C_9H_7)]$ (L = B–H→) fragment donating four electrons to a $W(CO)_2(\eta^5\text{-}C_2B_9H_9R_2)$ group. These canonical forms are related by the isobal mapping shown below where M = Mo or W and L = B–H→. However,

$$[M(CO)(L)(\eta^5\text{-}C_9H_7)] \xleftrightarrow{\quad o \quad} [W(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9R_2)]^-$$

the results of the *X*-ray diffraction studies on (**2a**) and (**2b**) revealed that the *p*-tolylmethylidyne groups are essentially symmetrically bridging. This indicates that electron delocalisation occurs within the $\overline{W(\mu\text{-}C)M}$ (M = Mo or W) rings so that the bonding is best described in terms of canonical forms.

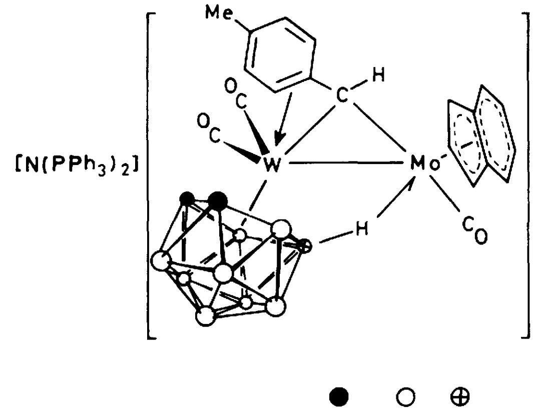
During studies[4] on certain reactions of (**2a**) it was observed that traces of another green complex were produced. Subsequently this new compound (**3a**) was obtained in high yield by heating solutions of (**2a**) in toluene at 80 °C for several hours. A similar complex (**3b**) was obtained from (**2b**). The nature of the compounds (3) was not established until an *X*-ray diffraction study was carried out on (**3a**) which showed it to be an isomer of (**2a**), *viz.* $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,9\text{-}C_2B_9H_9Me_2)]$, with the carbaborane carbon atoms no longer adjacent.

The molecular structure of (**3a**) is shown alongside that of (**2a**) in Figure (*b*), and selected structural parameters are presented in Table 4 in such a manner that they may be compared with those for complexes (**2a**) and (**2b**). It is evident that the structural parameters for (**3a**) and (**2a**) for related connectivities are essentially the same, although in the former the Mo–W separation [2.669(1) Å] is perceptibly longer than in the latter [2.657(2) Å]. Rearrangement within the cage results in bond lengths to tungsten increasing in the order B(4), B(3), C(1), B(5), and C(2). Slippage of the carbaborane ligand to accommodate the B–H→Mo three-centre two-electron bond is small, with Δ = 0.16 Å, θ = 0.9°, and φ = 3.0°. In the electron-rich $[Pt(PEt_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ these parameters are 0.42 Å, 4.7°, and 4.4°, respectively.[8]

The n.m.r. data for the complexes (3) (Tables 2 and 3) are in accord with the structure of (**3a**) established by *X*-ray diffraction. In their ^{1}H n.m.r. spectra, both (**3a**) and (**3b**) show quartet resonances at relatively high field, −6.91 and −7.57 p.p.m., respectively, as expected for the presence of the B–H⇀Mo(W) linkages. In agreement, their ^{11}B-{^{1}H} n.m.r. spectra show a signal for a markedly deshielded boron atom (Table 3). Other resonances in the ^{1}H, ^{13}C-{^{1}H}, and ^{11}B-{^{1}H} spectra are as expected. Interestingly, the spectra of both species showed no evidence for the presence of a second isomer, as found with (**2a**) and (**2b**).

The polyhedral rearrangement whereby compounds (**2a**) and (**2b**) isomerise to (**3a**) and (**3b**), respectively, is a common feature of metallacarbaborane chemistry.[12] However, generally these polytopal rearrangements require higher temperatures (*ca.* 300 °C) than that (*ca.* 80 °C) necessary to convert (**2**) into (**3**). There are, nevertheless, a few metallacarbaboranes known to rearrange under mild conditions, like (**2a**) and (**2b**). For example, in refluxing toluene, [IrH(PPh$_3$)$_2$(η^5-7,8-C$_2$B$_9$H$_{10}$-Ph)] isomerises to [IrH(PPh$_3$)$_2$(η^5-7,9-C$_2$B$_9$H$_{10}$Ph)].[13]

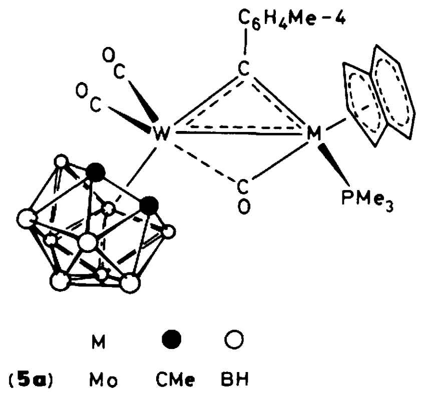
We have previously reported[14] the synthesis of the salt [N(PPh$_3$)$_2$][ReW{µ-CH(C$_6$H$_4$Me-4)}(µ-dmpm)(CO)$_7$] (dmpm = Me$_2$PCH$_2$PMe$_2$), and shown that on protonation it affords a novel neutral complex [ReW(µ-CH$_2$C$_6$H$_4$Me-4)(µ-dmpm)(CO)$_7$] containing an asymmetrically bridging *p*-tolylmethyl group with an agostic C–H⇀W interaction. In view of this result, we studied the reaction of (**2a**) with K[BH(CHMeEt)$_3$] in the expectation of obtaining an anionic dimetal complex with a bridging µ-CH(C$_6$H$_4$Me-4) ligand. It was hoped that if such a product were obtained, protonation would afford a neutral Mo–W species containing a bridging CH$_2$C$_6$H$_4$Me-4 group and an agostic C–H⇀M interaction. Treatment of (**2a**) in thf (tetrahydrofuran) with one equivalent of K[BH(CHMeEt)$_3$], with subsequent addition of [N(PPh$_3$)$_2$]Cl gave the desired purple salt [N(PPh$_3$)$_2$][MoW{µ-CH(C$_6$H$_4$Me-4)}(CO)$_3$(η^5-C$_9$H$_7$)(η^5-7,8-C$_2$B$_9$H$_9$Me$_2$)] (**4**), characterised in the usual manner (Tables 1—3). In agreement with the formation proposed, there was a resonance in the ^{1}H n.m.r. spectrum at δ 9.79, as expected for the µ-CH fragment, and a signal at δ −8.11 for the B–H⇀Mo group. The ^{13}C-{^{1}H} n.m.r. spectrum showed, as expected, the absence of a peak due to a bridging alkylidyne-carbon nucleus. However, the resonance for the µ-*C*H(C$_6$H$_4$-Me-4) group was not observed, probably being masked among the many peaks in the 133.7—111.4 p.p.m. region (Table 2). The µ-CH(C$_6$H$_4$Me-4) group present in (**4**) has also been found in the compounds [PtW(µ-H){µ-CH(C$_6$H$_4$Me-4)}(CO)$_2$-(PMe$_3$)$_2$(η-C$_5$H$_5$)], [PtW{µ-CH(C$_6$H$_4$Me-4)}(µ-CO)(PMe$_3$)$_2$-(η-MeC$_2$Me)(η-C$_5$H$_5$)][BF$_4$],[15] [N(PPh$_3$)$_2$][W$_2${µ-CH(C$_6$-H$_4$Me-4)}(CO)$_7$(η-C$_5$H$_5$)], [AuW{µ-CH(C$_6$H$_4$Me-4)}(CO)$_2$-(PPh$_3$)(η-C$_5$H$_5$)],[16] [N(PPh$_3$)$_2$][MRe{µ-CH(C$_6$H$_4$Me-4)}-(CO)$_9$] (M = Cr, Mo, or W), and the above mentioned species [N(PPh$_3$)$_2$][ReW{µ-CH(C$_6$H$_4$Me-4)}(µ-dmpm)(CO)$_7$].[14]



(**4**)

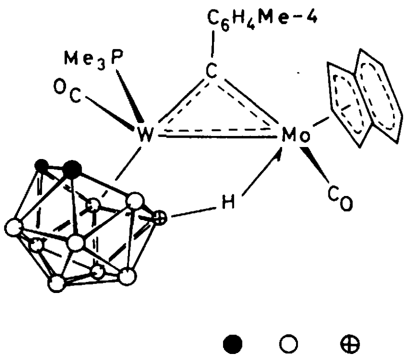
Unfortunately, attempts to protonate (**4**) to form a compound with a bridging CH$_2$C$_6$H$_4$Me-4 ligand, or bridging H and CH(C$_6$H$_4$Me-4) groups were unsuccessful, since decomposition resulted. Reaction of (**4**) with [AuCl(PPh$_3$)], in the presence of TlPF$_6$, in order to introduce a Au(PPh$_3$)$^+$ group and produce a neutral complex also failed.

Since the complexes (**2**) were unsaturated 32 c.v.e. species we were prompted to study reactions with PMe$_3$ and dmpm. Treatment of (**2a**) in CH$_2$Cl$_2$ with PMe$_3$ at room temperature afforded, after chromatography on alumina, yellow-brown crystals of the complex [MoW(µ-CC$_6$H$_4$Me-4)(CO)$_3$(PMe$_3$)-(η^5-C$_9$H$_7$)(η^5-7,8-C$_2$B$_9$H$_9$Me$_2$)] (**5a**). The ditungsten complex (**5b**) was similarly prepared, and data for both species are given in Tables 1—3. The i.r. spectrum of (**5a**) showed three carbonyl stretching bands at 1 966, 1 897, and 1 795 cm^{-1}, the latter indicating the presence of a bridging or strongly semi-bridging CO ligand. The ^{1}H n.m.r. spectrum showed no high-field signal corresponding to the B–H⇀Mo group present in the precursor (**2a**), but the ^{13}C-{^{1}H} n.m.r. spectrum retained the characteristic signal (δ 358.1 p.p.m.) for the µ-*C*C$_6$H$_4$Me-4 nucleus. The latter spectrum was, however, of poor quality and resonances for the CO groups could not be assigned with certainty. The ^{31}P-{^{1}H} n.m.r. spectrum (Table 3) was especially informative since the singlet signal showed no ^{183}W satellite peaks. This established that the PMe$_3$ group was ligating the molybdenum rather than the tungsten centre. For the ditungsten complex (**5b**) the ^{31}P-{^{1}H} resonance showed the characteristic strong ^{31}P–^{183}W coupling (368 Hz) for the

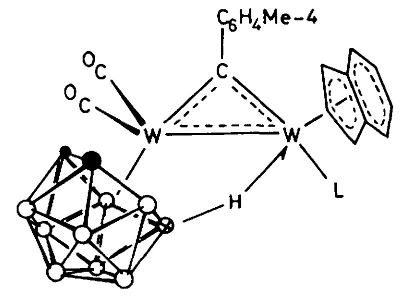


(**5a**)

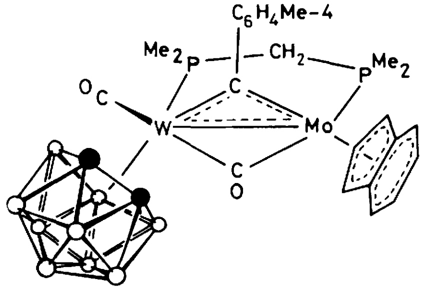
(**5b**)



(**6**)



	L	●	○	⊕
(7a)	PMe_3	CMe	BH	B
(7b)	$N_2(C_6H_4Me\text{-}4)_2$	CMe	BH	B



	●	○
(8)	CMe	BH

Table 5. Data for crystal-structure analyses[a]

	(2a)	**(2b)**	**(3a)**
Molecular formula	$C_{24}H_{29}B_9MoO_3W$	$C_{24}H_{29}B_9O_3W_2$	$C_{24}H_{29}B_9MoO_3W$
M	742.6	830.5	742.6
Crystal colour, shape	Black, irregular	Black, rhomb	Green, rhomb
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	14.178(5)	14.187(11)	15.507(8)
b/Å	16.346(7)	16.321(5)	13.054(3)
c/Å	14.526(8)	14.560(12)	14.087(6)
β/°	113.62(4)	113.76(2)	88.21(4)
U/Å^3	3 085(3)	3 086(3)	2 850(2)
Z	4	4	4
D_c/g cm^{-3}	1.60	1.79	1.73
F(000)	1 431	1 573	1 431
μ(Mo-K_α)/cm^{-1}	42.29	76.37	45.75
T/K	293	293	293
2θ range/°	$3 \leqslant 2\theta \leqslant 40$	$3 \leqslant 2\theta \leqslant 45$	$3 \leqslant 2\theta \leqslant 50$
Approx. crystal size (mm)	0.50 × 0.40 × 0.30	0.30 × 0.25 × 0.10	0.40 × 0.30 × 0.20
Data recorded	3 219	4 344	5 493
No. of unique data	2 883	3 979	5 041
No. of data used	2 516	3 135	4 427
Criterion for observed, n [$I \geqslant n\sigma(I)$]	1.0	2.0	2.0
Refinement:			
Solution method	Patterson	Patterson	Patterson
Anisotropic atoms	C, B, O, Mo, W	C, B, O, W	C, B, O, Mo, W
Isotropic atoms	H	H	H
H atoms refined	All BH	H(4)	All
Final $R(R')$[b]	0.054 (0.057)	0.067 (0.067)	0.026 (0.025)
g	0.0005	0.000 75	0.000 15
Largest final difference electron-density features (e Å^{-3})	±1.65	±2.44	±0.36

[a] Data collected using graphite monochromated Mo-K_α X-radiation, $\bar{\lambda} = 0.710\,69$ Å; diffractometer Nicolet $P3m$ in a θ-2θ scan mode. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$; $w^{-1} = [\sigma_c^2(F_o) + g|F_o|^2]$, $\sigma_c(F_o)$ = e.s.d. in $|F_o|$ due to counting statistics; g chosen to minimise variation in $\Sigma w(|F_o| - |F_c|)^2$ with $|F_o|$.

W(PMe_3) group which is necessarily present in this species. Compound (**5b**) is somewhat unstable in solution and hence its $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum was not measured.

The reaction between (**2c**) and PMe_3 gave the complex [$MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})$] (**6**) in which the PMe_3 group ligates the tungsten atom, as revealed by the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum (Table 3) since the resonance at δ −16.8 p.p.m. shows strong $^{31}P\text{-}^{183}W$ coupling (318 Hz). Moreover, for (**6**) both the ^1H (Table 2) and $^{11}B\text{-}\{^1H\}$ n.m.r. spectra (Table 3), with signals in the two spectra at δ −9.45 and 14.5 p.p.m., respectively, are in accord with the presence of a B–H→Mo group. As with the other complexes reported herein, the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum showed a characteristic resonance (δ 383.2 p.p.m.) for the μ-C nucleus.

The contrasting behaviour of (**2a**) and (**2c**) towards PMe_3 is of interest, and may reflect the greater steric demands of the $C_2B_9H_9Me_2$ cage *versus* $C_2B_9H_{11}$, so that with (**2a**) addition of PMe_3 occurs at Mo and with (**2c**) it occurs at W. Both (**5a**) and (**6**) are 32 c.v.e. species. Interestingly, we have been able to prepare a ditungsten complex [$W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)$] (**7a**) which possesses both a $W(PMe_3)(\eta^5\text{-}C_9H_7)$ group as in (**5b**) and a three-centre

Table 6. Atomic positional parameters (fractional co-ordinates, × 10^4) for complex (**2a**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
W	821(1)	735(1)	2 330(1)
Mo	1 773(1)	201(1)	4 205(1)
C(11)	1 980(12)	−78(9)	2 993(11)
C(12)	2 685(14)	−642(9)	2 657(13)
C(13)	3 595(13)	−383(13)	2 715(14)
C(14)	4 108(15)	−904(13)	2 342(14)
C(15)	3 806(17)	−1 683(15)	2 040(15)
C(16)	2 891(19)	−1 936(11)	2 058(14)
C(17)	2 292(16)	−1 433(10)	2 361(14)
C(18)	4 435(21)	−2 284(15)	1 661(18)
C(21)	2 788(12)	652(9)	5 843(11)
C(22)	2 312(12)	−91(10)	5 909(12)
C(23)	2 735(14)	−694(11)	5 501(13)
C(24)	3 389(13)	−341(11)	5 131(13)
C(25)	3 454(13)	518(11)	5 372(12)
C(26)	3 969(14)	1 184(15)	5 152(13)
C(27)	3 884(14)	1 940(15)	5 450(16)
C(28)	3 241(18)	2 082(13)	5 943(15)
C(29)	2 694(15)	1 460(13)	6 144(12)
C(3)	150(13)	−222(11)	1 411(13)
O(3)	−209(11)	−772(7)	946(11)
C(4)	1 634(12)	786(10)	1 434(14)
O(4)	2 106(9)	819(8)	993(9)
C(5)	598(15)	−598(11)	3 892(13)
O(5)	−5(12)	−1 080(9)	3 736(12)
C(1)	201(12)	2 129(9)	1 793(12)
C(10)	471(15)	2 348(10)	920(14)
C(2)	−796(12)	1 495(10)	1 556(12)
C(20)	−1 408(14)	1 169(11)	474(12)
B(3)	−672(14)	984(12)	2 619(14)
B(4)	509(14)	1 343(11)	3 576(13)
B(5)	1 038(14)	2 066(11)	2 994(15)
B(6)	175(16)	2 868(12)	2 552(17)
B(7)	−987(16)	2 537(11)	1 652(15)
B(8)	−1 475(16)	1 844(13)	2 202(15)
B(9)	−718(15)	1 735(11)	3 498(14)
B(10)	368(16)	2 396(12)	3 702(15)
B(11)	−903(16)	2 692(14)	2 835(18)

two-electron B–H$\rightarrow$M bond as in (**6**). Compound (**7a**) was obtained by displacing the diazoalkane ligand $N_2C(C_6H_4Me\text{-}4)_2$ in (**7b**) with PMe_3. The precursor (**7b**) is obtained from (**2b**) and $N_2C(C_6H_4Me\text{-}4)_2$, and its structure has been established by *X*-ray diffraction.[17]

Data for (**7a**) (Tables 1—3) are in accord with the structure proposed. A quartet signal in the ^1H n.m.r. at −7.14 [*J*(BH) 70 Hz], and a boron resonance at δ 16.7 p.p.m., established the presence of the B–H$\rightarrow$W group. In the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum, the $W(PMe_3)$ group is revealed by a resonance at δ −26.3 p.p.m. [*J*(WP) 408 Hz].

Treatment of (**2a**) with dmpm in CH_2Cl_2 afforded $[MoW(\mu\text{-}CR)(\mu\text{-}CO)(\mu\text{-}dmpm)(CO)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (**8**), characterised in the usual manner (Tables 1—3). The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum had a $\mu\text{-}CC_6H_4Me\text{-}4$ resonance at δ 375.1 p.p.m., and peaks at δ 274.8 and 242.1 [*J*(PC) 18 Hz] were assigned to the μ-CO and W(CO) groups, respectively. In accord with the proposed structure, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed doublet signals at δ 21.6 [*J*(PP) 40 Hz] and −3.9 p.p.m. [*J*(PP) 40, *J*(WP) 389 Hz] due to the molybdenum and tungsten bound phosphorus nuclei, respectively. There was no spectroscopic evidence for the presence of a B–H$\rightarrow$Mo group in (**8**).

Reactions of the compounds (**2**) or (**7b**) with the tertiary phosphines all afford dimetal complexes with 32 c.v.e. The various processes involve displacement of the B–H$\rightarrow$M (Mo or W) bonds to give (**5**), displacement of CO or $N_2C(C_6H_4Me\text{-}4)_2$ ligands to yield (**6**) and (**7a**), respectively, and displacement of the B–H$\rightarrow$Mo group and CO ligands in the synthesis of (**8**).

The synthesis of the compounds (**2**), and their subsequent reactions with PMe_3 or dmpm provide further examples of the 'non-innocent' role of the carbaborane groups in this new area of chemistry.

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C. Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. The compounds $[N(PPh_3)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_9R_2)]$ (**1**)[3] and $[M(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$ (M = Mo or W)[5] were prepared as described previously. The instrumentation employed for the spectroscopic measurements was reported earlier,[3] together with other techniques relevant to the work herein described. Alumina used for chromatography was Brockman activity II. Analytical and other data for the new compounds are given in Table 1.

Synthesis of the Compounds $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9R_2)]$ (M = Mo *or* W, R = Me; M = Mo, R = H).—(*i*) A mixture of (**1a**) (0.52 g, 0.50 mmol) and $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$ (0.22 g, 0.50 mmol) was stirred in CH_2Cl_2 (10 cm^3) for 30 min. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (30 cm^3, 1:1) and chromatographed on alumina. Elution with the same solvent mixture gave a green eluate. Solvent was removed *in vacuo* and the residue crystallised from Et_2O–light petroleum (10 cm^3, 1:1) at −20 °C affording green *crystals* of $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (**2a**) (0.21 g).

(*ii*) The reactants (**1a**) (1.19 g, 1.14 mmol) and $[W(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$ (0.60 g, 1.14 mmol) were stirred together in CH_2Cl_2 (30 cm^3) for 4 h. Solvent was removed *in vacuo*, the residue extracted with CH_2Cl_2–Et_2O (50 cm^3, 1:1), and the extracts chromatographed on alumina. Elution with the same solvent mixture yielded a green band which was collected. Removal of solvent *in vacuo* and crystallisation from CH_2Cl_2–Et_2O (5 cm^3, 1:3) at −20 °C gave green *prisms* of $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (**2b**) (0.35 g).

(*iii*) In a synthesis similar to that described for (**2a**), the salt (**1b**) (0.51 g, 0.50 mmol) and $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$ (0.22 g, 0.50 mmol) in CH_2Cl_2 (15 cm^3) for 30 min gave green *crystals* of $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ (**2c**) (0.24 g).

Isomerisation of the Compounds $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (M = Mo *or* W).—A toluene (15 cm^3) solution of (**2a**) (0.37 g, 0.50 mmol) was heated at 80 °C for 3 h. Solvent was removed *in vacuo*, the residue dissolved in CH_2Cl_2–light petroleum (15 cm^3, 1:1) and chromatographed on alumina. Elution with the same solvent mixture gave a green solution. Removal of solvent *in vacuo* afforded green *microcrystals* of $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,9\text{-}C_2B_9H_9Me_2)]$ (**3a**) (0.30 g).

The compound $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,9\text{-}C_2B_9H_9Me_2)]$ (**3b**) was similarly prepared from (**2b**) in yields of *ca.* 70%.

Reaction of the Compound $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ *with* $K[BH(CHMeEt)_3]$.—A vigorously stirred thf (10 cm^3) solution of (**2a**) (0.37 g, 0.50 mmol) was treated with $K[BH(CHMeEt)_3]$ (0.50 mmol; 0.5

Table 7. Atomic positional parameters (fractional co-ordinates, × 10^4) for complex (**2b**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
W(1)	824(1)	728(1)	2 331(1)
W(2)	1 760(1)	187(1)	4 206(1)
C(11)	1 992(13)	−117(11)	3 026(13)
C(12)	2 599(15)	−669(11)	2 676(14)
C(13)	3 580(16)	−407(15)	2 706(17)
C(14)	4 135(19)	−947(19)	2 373(16)
C(15)	3 801(21)	−1 729(16)	2 068(17)
C(16)	2 850(22)	−1 943(15)	2 031(20)
C(17)	2 246(17)	−1 455(12)	2 364(15)
C(18)	4 435(28)	−2 292(20)	1 703(25)
C(21)	2 744(14)	701(11)	5 857(13)
C(22)	2 277(16)	−47(13)	5 893(15)
C(23)	2 704(15)	−672(12)	5 526(15)
C(24)	3 378(16)	−352(13)	5 148(15)
C(25)	3 491(15)	512(14)	5 412(14)
C(26)	3 989(17)	1 207(16)	5 120(17)
C(27)	3 907(18)	1 966(16)	5 424(18)
C(28)	3 216(18)	2 091(15)	5 921(15)
C(29)	2 665(18)	1 495(14)	6 140(16)
C(3)	175(14)	−201(12)	1 449(13)
O(3)	−206(14)	−780(9)	976(13)
C(4)	1 617(15)	789(11)	1 494(16)
O(4)	2 096(11)	808(10)	1 007(10)
C(5)	628(16)	−589(13)	3 934(17)
O(5)	−35(12)	−1 066(10)	3 740(12)
C(1)	206(15)	2 107(11)	1 782(14)
C(10)	436(18)	2 365(13)	886(15)
C(2)	−794(14)	1 493(12)	1 556(15)
C(20)	−1 422(14)	1 189(14)	477(13)
B(3)	−641(21)	923(14)	2 625(23)
B(4)	542(16)	1 320(12)	3 573(16)
B(5)	1 073(19)	2 088(12)	2 983(17)
B(6)	202(19)	2 880(13)	2 575(18)
B(7)	−993(18)	2 550(15)	1 649(19)
B(8)	−1 522(18)	1 826(15)	2 192(18)
B(9)	−697(16)	1 716(13)	3 468(16)
B(10)	387(16)	2 417(13)	3 748(17)
B(11)	−905(23)	2 705(14)	2 889(23)

Table 8. Atomic positional parameters (fractional co-ordinates, × 10^4) for complex (**3a**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
W	2 540(1)	881(1)	309(1)
Mo	3 051(1)	2 817(1)	522(1)
C(11)	3 071(3)	1 663(3)	1 414(3)
C(12)	3 334(3)	1 512(3)	2 397(3)
C(13)	2 832(3)	1 879(4)	3 146(3)
C(14)	3 092(3)	1 774(4)	4 072(3)
C(15)	3 860(3)	1 327(4)	4 286(3)
C(16)	4 362(4)	967(4)	3 533(4)
C(17)	4 114(3)	1 048(4)	2 601(3)
C(18)	4 123(6)	1 207(7)	5 298(5)
C(21)	4 077(3)	4 063(3)	15(3)
C(22)	3 292(3)	4 550(3)	314(4)
C(23)	3 181(4)	4 381(4)	1 300(4)
C(24)	3 842(4)	3 747(4)	1 618(3)
C(25)	4 428(3)	3 575(3)	837(3)
C(26)	5 234(4)	3 028(4)	733(4)
C(27)	5 643(4)	3 017(4)	−126(5)
C(28)	5 305(4)	3 496(5)	−930(4)
C(29)	4 542(4)	4 003(4)	−877(4)
C(1)	3 332(3)	887(3)	−1 156(3)
C(10)	4 296(3)	929(4)	−949(4)
C(2)	1 700(3)	66(3)	−923(3)
C(20)	1 057(4)	−706(4)	−497(4)
B(3)	1 546(3)	1 355(4)	−824(4)
B(4)	2 627(3)	1 918(3)	−961(3)
B(5)	2 774(3)	−221(4)	−1 034(4)
B(6)	3 036(4)	1 590(4)	−2 132(3)
B(7)	3 131(4)	230(4)	−2 174(4)
B(8)	2 096(4)	−290(4)	−2 037(4)
B(9)	1 342(4)	709(4)	−1 906(4)
B(10)	1 921(4)	1 892(4)	−1 943(4)
B(11)	2 243(4)	849(4)	−2 691(4)
C(3)	3 062(3)	−297(3)	1 011(3)
O(3)	3 374(3)	−943(3)	1 426(3)
C(4)	1 563(3)	709(4)	1 250(3)
O(4)	990(3)	652(4)	1 787(3)
C(5)	1 819(3)	3 089(4)	825(4)
O(5)	1 125(3)	3 267(4)	1 058(4)

cm^3 of a 1.0 mol dm^{-3} solution in thf). After 10 min, $[N(PPh_3)_2]Cl$ (0.29 g, 0.50 mmol) was added and the mixture stirred for a further 15 min. Solvent was removed *in vacuo*, the residue dissolved in CH_2Cl_2–light petroleum (30 cm^3, 1:1) and chromatographed on alumina. Elution with CH_2Cl_2 gave a purple solution. Removal of solvent *in vacuo* and crystallisation of the residue from CH_2Cl_2–light petroleum (10 cm^3, 1:1) at −20 °C gave purple *microcrystals* of $[N(PPh_3)_2][MoW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (**4**) (0.48 g).

Reactions of the Compounds $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9R_2)]$ (M = Mo *or* W, R = Me; M = Mo, R = H) *with* PMe_3.—(*i*) A CH_2Cl_2 (10 cm^3) solution of (**2a**) (0.37 g, 0.50 mmol) was treated with PMe_3 (0.50 mmol; 1.0 cm^3 of a 0.50 mol dm^{-3} solution in light petroleum) and the mixture stirred for 30 min. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (20 cm^3, 1:1) and chromatographed on alumina. Elution with CH_2Cl_2–light petroleum (2:1) afforded a yellow-brown solution. Removal of solvent *in vacuo* gave yellow-brown *microcrystals* of $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9Me_2)]$ (**5a**) (0.33 g).

(*ii*) A CH_2Cl_2 (2 cm^3) solution of (**2b**) (0.07 g, 0.08 mmol) at −70 °C was treated with PMe_3 (0.13 mmol; 0.45 cm^3 of a 0.30 mol dm^{-3} solution in CH_2Cl_2). The solution was warmed to *ca.* −40 °C and Et_2O (2 cm^3), at the same temperature, added. The mixture was cooled to −70 °C. Partial removal of solvent *in vacuo* yielded dark brown *microcrystals* of $[W_2(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)(CO)_3(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (**5b**) (0.03 g).

(*iii*) Addition of PMe_3 (0.50 mmol; 1.0 cm^3 of a 0.50 mol dm^{-3} solution in light petroleum) to a CH_2Cl_2 (10 cm^3) solution of (**2c**) (0.36 g, 0.50 mmol) afforded a dark green solution. Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (20 cm^3, 1:1) and chromatographed on alumina. Elution with the same solvent mixture gave green *crystals* of $[MoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ (**6**) (0.30 g), crystallised from Et_2O–light petroleum (10 cm^3, 1:1) at −20 °C.

Synthesis of the Complex $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$.—A mixture of (**7b**) (0.10 g, 0.098 mmol) and PMe_3 (0.098 mmol, 0.01 cm^3) in CH_2Cl_2 (5 cm^3) was stirred for 1 h. The resulting brown solution was chromatographed on alumina, elution with CH_2Cl_2 yielding a brown solution. Solvent was removed *in vacuo*, and the residue washed with Et_2O (2 × 10 cm^3) giving red-brown *microcrystals* of $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^5\text{-}C_9H_7)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (**7a**) (0.07 g).

Synthesis of the Complex [MoW(μ-CC$_6$H$_4$Me-4)(μ-CO)(μ-dmpm)(CO)(η^5-C$_9$H$_7$)(η^5-7,8-C$_2$B$_9$H$_9$Me$_2$)].—A mixture of compound (**2a**) (0.37 g, 0.50 mmol) and dmpm (0.50 mmol; 0.5 cm^3 of a 1 mol dm^{-3} solution in thf) was stirred in CH$_2$Cl$_2$ (10 cm^3) for 10 h. Solvent was removed *in vacuo*, and the residue dissolved in CH$_2$Cl$_2$–light petroleum (20 cm^3, 1:1) and chromatographed on alumina. Elution with CH$_2$Cl$_2$ afforded a brown solution. Removal of solvent *in vacuo*, and crystallisation from CH$_2$Cl$_2$–light petroleum (10 cm^3, 1:1) at −20 °C gave brown *crystals* of [MoW(μ-CC$_6$H$_4$Me-4)(μ-CO)(μ-dmpm)(CO)(η^5-C$_9$H$_7$)(η^5-7,8-C$_2$B$_9$H$_9$Me$_2$)] (**8**) (0.35 g).

Crystal Structure Determinations and Refinements.—Details of the data collection procedures, and structure solution and refinement are given in Table 5. Data were collected on single crystals mounted under nitrogen in thin-walled glass capillaries and were corrected for Lorentz polarisation and *X*-ray absorption effects, the last by an empirical method based upon azimuthal scan data.[18]

The structures were solved by conventional heavy-atom and difference Fourier methods, and were refined by blocked-cascade least squares. For (**3a**) all hydrogen atoms were refined with a fixed isotropic thermal parameter. For (**2a**) all B–H cage hydrogen atoms were similarly refined, with the remaining hydrogen atoms included in calculated positions (C–H 0.96 Å), with chemically related hydrogen atoms being given common isotropic thermal parameters. For (**2b**), only the hydrogen atom attached to B(4) was located and refined isotropically. All hydrogens attached to carbon atoms were treated as for (**2a**). Scattering factors were from ref. 19. All calculations were carried out on an 'Eclipse' (Data General) computer with the SHELXTL system of programs.[18] Atomic co-ordinates for (**2a**), (**2b**), and (**3a**) are given in Tables 6, 7, and 8, respectively.

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