Tricarbonyl(carbaborane) Complexes of the Group 6 Metals as Reagents for preparing Heteronuclear Trimetal Compounds involving Rhodium†

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The reaction between the salt [Rh(NCMe)$_3$(η-C$_5$Me$_5$)][BF$_4$]$_2$ and the reagents Na$_2$[M(CO)$_3$(η^5-7,8-C$_2$B$_9$H$_9$R'$_2$)] (M = Mo or W, R' = H or Me) in tetrahydrofuran affords [Rh(CO)$_2$(η-C$_5$Me$_5$)] and the trimetal complexes [MRh$_2$(μ-H)(μ-CO)(μ-σ:η^5-7,8-C$_2$B$_9$H$_8$R'$_2$)(CO)$_2$(η-C$_5$Me$_5$)$_2$]. An X-ray diffraction study of the compound with M = W and R' = Me revealed a structure based on a triangulated metal core [Rh(1)–Rh(2) 2.859(1), W–Rh(1) 2.736(1), W–Rh(2) 2.822(1) Å] with the Rh–Rh bond bridged by a hydrido ligand. Two of the carbonyl groups are terminally attached to the tungsten atom, while the third [W–C–O 154(1)°] semi-bridges a W–Rh bond. The open pentagonal C$_2$B$_3$ face of the carbaborane framework is η^5 co-ordinated to the tungsten, but the cage also bridges the metal triangle through exopolyhedral B–Rh and B–H$\rightharpoonup$Rh bonds, using boron atoms in the C$_2$B$_3$ ring attached to the tungsten. The B–Rh bond bridges the W–Rh vector which is asymmetrically bridged by the CO group, and involves the boron atom α to the carbons in the CC*B*BB ring. The B–H$\rightharpoonup$Rh three-centre two-electron bond utilises the boron atom which is β to the carbons in the CCB*B*B ring. Examination of the NMR spectra (^{1}H, ^{13}C-{^{1}H}, ^{11}B-{^{1}H}, ^{11}B) of the trimetal complexes revealed that the structures of these molecules at −60 °C were similar to that established in the solid state for M = W and R' = Me. However, at ambient temperatures three of the complexes (M = Mo, R' = H or Me; M = W, R' = Me) isomerised to a structure [MRh$_2$(μ-H)$_2$(μ-CO)(μ-σ:σ':η^5-7,8-C$_2$B$_9$H$_7$R'$_2$)(CO)$_2$(η-C$_5$Me$_5$)$_2$] in which the carbaborane cage bridged the metal triangle *via* two B–Rh bonds.

The dianionic complexes [M(CO)$_3$(η^5-C$_2$B$_9$H$_9$R'$_2$)]$^{2-}$ (M = Mo or W, R' = H or Me)[1] are mapped isolobally with the monoanionic species [M(CO)$_3$(η-C$_5$R'$_5$)]$^-$. However, although salts of the cyclopentadienyl-molybdenum and -tungsten species have been used extensively for the preparation of mixed-metal complexes,[2] there has been little exploitation of salts of [M(CO)$_3$(η^5-C$_2$B$_9$H$_9$R'$_2$)]$^{2-}$ in similar syntheses. Reactions of the latter directed towards obtaining polynuclear metal compounds, with bonds between different metallic elements, have so far been limited to studies reported by Hawthorne and co-workers[3] using CuCl[3a] or SnPh$_3$Cl[3b] as reagents, and recent results from our laboratory[4] which have led to products with M–Pt[4a] or Mo–W[4b] bonds.

In this paper we describe some trinuclear metal complexes obtained from reactions between the reagents Na$_2$[M(CO)$_3$(η^5-7,8-C$_2$B$_9$H$_9$R'$_2$)], generated *in situ* from [M(CO)$_3$(NCMe)$_3$] and Na$_2$[7,8-C$_2$B$_9$H$_9$R'$_2$], and the rhodium salt [Rh(NCMe)$_3$(η-C$_5$Me$_5$)][BF$_4$]$_2$. The PF$_6{}^-$ salts of the dications [Rh(S)$_3$(η-C$_5$Me$_5$)]$^{2+}$ (S = NCMe, Me$_2$CO, Me$_2$SO, CH$_2$Cl$_2$, *etc.*) have been extensively studied by Maitlis and co-workers.[5]

Results and Discussion

When thf (tetrahydrofuran) solutions of the salts Na$_2$[M(CO)$_3$(η^5-7,8-C$_2$B$_9$H$_9$R'$_2$)] (M = Mo or W, R' = H or Me) are treated with one equivalent of the rhodium(III) complex [Rh(NCMe)$_3$(η-C$_5$Me$_5$)][BF$_4$]$_2$ in the same solvent an immediate colour change from orange to brown occurs. Examination of the products revealed that they were formed in poor yield and consisted of a mixture of the mononuclear rhodium(I) compound [Rh(CO)$_2$(η-C$_5$Me$_5$)], identified by IR and ^{1}H NMR spectroscopy,[6] and molybdenum- and tungsten-dirhodium complexes, the formulations of which are discussed below.

Formation of the products is explicable if it is assumed that a redox reaction initially occurs between [M(CO)$_3$(η^5-7,8-C$_2$B$_9$H$_9$R'$_2$)]$^{2-}$ and [Rh(NCMe)$_3$(η-C$_5$Me$_5$)]$^{2+}$, thereby generating as intermediates [M(CO)$_3$(η^5-7,8-C$_2$B$_9$H$_9$R'$_2$)] and [Rh(NCMe)$_2$(η-C$_5$Me$_5$)]. The acetonitrile groups in the latter would be readily displaced by CO molecules scavenged from molybdenum carbonyl species present, thereby giving [Rh(CO)$_2$(η-C$_5$Me$_5$)]. Alternatively, sequential addition of Rh(η-C$_5$Me$_5$) to the species [M(CO)$_3$(η^5-7,8-C$_2$B$_9$H$_9$R'$_2$)] would yield the trimetal compounds. As soon as the redox nature ($\mathrm{M}^0 \longrightarrow \mathrm{M}^{\mathrm{II}}$, $\mathrm{Rh}^{\mathrm{III}} \longrightarrow \mathrm{Rh}^{\mathrm{I}}$) and stoichiometry of the reaction was appreciated, the reactants were combined in a M : Rh ratio of 1 : 2. Examination of the mixtures of products thus obtained revealed that *ca.* 80–90% of the products consisted of [Rh(CO)$_2$(η-C$_5$Me$_5$)] and the trimetal carbaborane species. It is noteworthy that a redox reaction is also observed[4a] when Tl$_2$[Mo(CO)$_3$(η^5-7,8-C$_2$B$_9$H$_9$Me$_2$)] is treated with AgBF$_4$ in the presence of [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)]. The resultant Mo(CO)$_3$(η^5-7,8-C$_2$B$_9$H$_9$Me$_2$) fragment is captured by the alkylidynetungsten complex to give the dimetal compound [MoW(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η^5-7,8-C$_2$B$_9$H$_9$Me$_2$)].

The new molybdenum- and tungsten-dirhodium compounds were characterised by microanalysis, and by IR and NMR spectroscopy (Tables 1–3). From these data the complexes could be formulated as [MRh$_2$(μ-H)(μ-CO)(μ-σ:η^5-7,8-C$_2$B$_9$H$_8$R'$_2$)(CO)$_2$(η-C$_5$Me$_5$)$_2$] (M = Mo, R' = H **1** or Me **2**; M = W, R' = H **3** or Me **4**). However, the NMR spectra

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† In this paper molybdenum or tungsten atoms form with [*nido*-7,8-C$_2$B$_9$H$_9$R'$_2$]$^{2-}$ (R' = H or Me) dianions *closo*-1,2-dicarba-3-metalladodecaborane icosahedral fragments. However, in the formulae the carbaborane groups are designated as η^5-7,8-C$_2$B$_9$H$_9$R'$_2$ ligands in order to emphasise their pentahapto properties in which they formally act as four-electron donors.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical[a] and physical data for the new compounds

Compound[b]	Colour	$\nu_{max}(CO)$[c]/ cm^{-1}	Analysis (%) C	Analysis (%) H
1 $[MoRh_2(\mu\text{-H})(\mu\text{-CO})(\mu\text{-}\sigma:\eta^5\text{-}7,8\text{-}C_2B_9H_{10})(CO)_2(\eta\text{-}C_5Me_5)_2]$	Brown	1958s, 1897m, 1722w (br)	39.4 (38.1)	5.4 (5.2)
2 $[MoRh_2(\mu\text{-H})(\mu\text{-CO})(\mu\text{-}\sigma:\eta^5\text{-}7,8\text{-}C_2B_9H_8Me_2)(CO)_2(\eta\text{-}C_5Me_5)_2]$	Brown	1958s, 1897m, 1723w (br)	39.7 (39.9)	5.7 (5.6)
3 $[WRh_2(\mu\text{-H})(\mu\text{-CO})(\mu\text{-}\sigma:\eta^5\text{-}7,8\text{-}C_2B_9H_{10})(CO)_2(\eta\text{-}C_5Me_5)_2]$	Brown	1958s, 1891m, 1726w (br)	35.9 (34.3)	5.3 (4.7)
4 $[WRh_2(\mu\text{-H})(\mu\text{-CO})(\mu\text{-}\sigma:\eta^5\text{-}7,8\text{-}C_2B_9H_8Me_2)(CO)_2(\eta\text{-}C_5Me_5)_2]$	Olive green	1956s, 1889m, 1725m (br)	36.3 (35.9)	5.0 (5.0)

[a] Calculated values are given in parentheses. [b] Yields of crude complex are *ca.* 40–50% (see text). Isolation of spectroscopically pure products lowers yields to *ca.* 15%. [c] Measured in CH_2Cl_2. For all carbaborane compounds there is a broad band at 2550 cm^{-1} due to B–H absorptions.

Table 2 Hydrogen-1 NMR data[a] for the new compounds

	δ(¹H)	
Compound	25 °C	−60 °C[b,c]
1	−18.46 (br s, 1 H, RhH), −15.10 (br s, 1 H, RhH), 1.83, 1.84 (s × 2, 30 H, C_5Me_5), 1.97 (s, 2 H, CH)	−19.82 [d of d, 1 H, RhH, *J*(RhH) 20], −13.65 (br d, 1 H, BHRh)
2	−18.59 (br s, 1 H, RhH), −15.16 (br s, 1 H, RhH), 1.83 (s, 30 H, C_5Me_5), 1.98 (s, 6 H, CMe)	−19.79 [d of d, 1 H, RhH, *J*(RhH) 21], −13.65 (br d, 1 H, BHRh)
3	−18.81 [d of d, 1 H, Rh(μ-H)Rh, *J*(RhH) 21, 21], −12.85 [d of q, 1 H, BHRh, *J*(RhH) 29, *J*(BH) 74], 1.77, 1.82 (s × 2, 30 H, C_5Me_5), 2.90, 3.03 (s × 2, 2 H, CH)	−18.74 [d of d, 1 H, RhH, *J*(RhH) 21], −12.80 (br d, 1 H, BHRh)
4	−18.62 [br s, 1 H, Rh(μ-H)Rh], −13.76 [br s, 1 H, W(μ-H)Rh], 1.79, 1.80 (s × 2, 30 H, C_5Me_5), 2.02, 2.18 (s × 2, 6 H, CMe)	−19.21 [d of d, 1 H, RhH, *J*(RhH) 21], −13.18 (br d, 1 H, BHRh)

[a] Chemical shifts (δ) in ppm, coupling constants (*J*) in Hz, measurements in CD_2Cl_2. Proton resonances for terminal B–H groups occur as broad unresolved peaks in the range δ *ca.* −2 to +3. [b] Only chemical shifts negative to high frequency of $SiMe_4$ are included. [c] ^{103}Rh–^1H coupling constants unresolved due to broad peak profiles as a result of quadrupolar effect of boron nuclei.

Table 3 Carbon-13 and boron-11 NMR data[a] for the new compounds

		δ(¹¹B)[c]	
Compound	δ(¹³C)[b]	25 °C	−60 °C[d]
1	247.8 (br s, μ-CO), 232.5, 229.1 (s × 2, CO), 101.9, 101.3 [d × 2, *C*₅Me₅, *J*(RhC) 9], 33.4, 31.7 (s × 2, CH), 10.1, 9.7 (s × 2, C₅*Me*₅)	34.5 (br, 1 B, BRh), 29.6 (br, 1 B, BRh), −4.9 (1 B), −6.5 (1 B), −8.4 (1 B), −10.2 (1 B), −11.9 (2 B), −14.8 (1 B)	43.9 (br, 1 B, BRh), 24.2 [d, 1 B, BHRh, *J*(HB) 66]
2	248.2 (br s, μ-CO), 232.3, 228.5 (s × 2, CO), 101.8, 101.3 [d × 2, *C*₅Me₅, *J*(RhC) 6], 66.7, 65.5 (s × 2, *C*Me), 33.4, 31.7 (s × 2, C*Me*), 10.1, 9.7 (s × 2, C₅*Me*₅)	35.0 (br, 1 B, BRh), 29.8 (br, 1 B, BRh), −4.8 (1 B), −6.5 (1 B), −8.2 (1 B), −11.8 (3 B), −14.8 (1 B)	43.8 (br, 1 B, BRh), 24.0 [d, 1 B, BHRh, *J*(HB) 66]
3	243.4 (br s, μ-CO), 221.8, 219.5 (s × 2, CO), 102.0, 101.1 [d × 2, *C*₅Me₅, *J*(RhC) 6], 35.0, 31.2 (s × 2, CH), 10.0, 9.8 (s × 2, C₅*Me*₅)	35.4 (br, 1 B, BRh), 21.5 [d, 1 B, *J*(HB) 68], −4.3 (1 B), −5.5 (1 B), −9.3 (1 B), −12.6 (1 B), −17.6 (2 B), −21.6 (1 B)	35.6 (br, 1 B, BRh), 21.2 [d, 1 B, BHRh, *J*(HB) 70]
4	242.2 (br s, μ-CO), 223.7, 223.0 (s × 2, CO), 102.1, 101.3 [d × 2, *C*₅Me₅, *J*(RhC) 6], 63.0, 62.4 (s × 2, *C*Me), 35.1, 32.7 (s × 2, C*Me*), 10.2, 9.8 (s × 2, C₅*Me*₅)	36.4 (br, 1 B, BRh), 24.2 (br, 1 B, BRh), −4.4 (1 B), −7.1 (1 B), −10.8 (4 B), −15.2 (1 B)	41.1 (br, 1 B, BRh), 21.6 [d, 1 B, BHRh, *J*(HB) 74]

[a] Chemical shifts (δ) in ppm, coupling constants (*J*) in Hz, measurements in CD_2Cl_2. [b] Hydrogen-1 decoupled, chemical shifts are to high frequency of $SiMe_4$ (δ 0.0). [c] Hydrogen-1 decoupled, measured at 115.53 MHz, chemical shifts are positive to high frequency of $BF_3{\cdot}Et_2O$ (external). Signals ascribed to more than one nucleus may result from overlapping peaks, and do not necessarily indicate symmetry equivalence. [d] Only resonances due to BRh and B–H→Rh groups listed for this temperature. The *J*(HB) values were obtained from fully coupled ¹¹B spectra.

indicated that in solution three of the compounds adopted a different isomeric form at low temperatures than at ambient temperatures. This feature and the spectroscopic properties are discussed after the results of an X-ray diffraction study of compound **4** are described.

The molecule is shown in Fig. 1, and selected structural parameters are listed in Table 4. The core of the molecule consists of a triangle of metal atoms [Rh(1)–Rh(2) 2.859(1), W–Rh(1) 2.736(1), W–Rh(2) 2.822(1) Å]. A similar triangle exists[7] in the complexes $[WRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-CO})(CO)_2(\eta^5\text{-}C_9H_7)\{HB(pz)_3\}]$ [C_9H_7 = indenyl, $HB(pz)_3$ = hydrotris(pyrazol-1-yl)borate] [Rh–Rh 2.646(2), av. W–Rh 2.848(2) Å][7a] and $[WRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-CO})(acac)_2(CO)_2(\eta\text{-}C_5H_5)]$ (acac = acetylacetonate) [Rh–Rh 2.613(2), av. W–Rh 2.786(2) Å].[7b] The appreciably shorter Rh–Rh separations in these molecules, compared with **4**, is due to the presence in the latter of the bridging hydrido ligand [H(1)] discussed below. It is well established that metal–metal bonds are lengthened by 0.10–0.45 Å by the presence of μ-H groups.[8]

The rhodium atoms carry C_5Me_5 rings, as expected, and for each of these ligands three of the rhodium to ring-carbon distances are perceptibly shorter [Rh(1)–C(13) 2.20(1), Rh(1)–C(14) 2.23(1), Rh(1)–C(15) 2.27(1); Rh(2)–C(22) 2.19(1), Rh(2)–C(23) 2.19(1), Rh(2)–C(24) 2.17(1) Å] than the other two [Rh(1)–C(11) 2.30(1), Rh(1)–C(12) 2.29(1); Rh(2)–C(21) 2.26(1), Rh(2)–C(25) 2.22(1) Å]. This reflects a small degree of ring slippage to the η³-bonding mode, a well established feature of cyclopentadienylrhodium chemistry, allowing the metal centres to have 16 rather than 18 electron valence shells.[9]

The three CO groups ligate the tungsten atom, but whereas

Table 4 Selected internuclear distances (Å) and angles (°) for the complex [$WRh_2(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}\sigma:\eta^5\text{-}7,8\text{-}C_2B_9H_8Me_2)(CO)_2(\eta\text{-}C_5Me_5)_2$] **4**

Rh(1)–Rh(2)	2.859(1)	Rh(1)–W	2.736(1)	Rh(1)–B(5)	2.11(2)	Rh(1)–C(6)	2.20(1)
Rh(1)–H(1)	1.78	Rh(2)–W	2.822(1)	Rh(2)–B(4)	2.39(2)	Rh(2)–H(4d)	1.73
Rh(2)–H(1)	1.78	W–C(1)	2.29(1)	W–C(2)	2.41(1)	W–B(3)	2.40(1)
W–B(4)	2.08(1)	W–B(5)	2.20(1)	W–C(5)	1.96(1)	W–C(6)	2.08(1)
W–C(7)	1.99(1)	C(1)–C(2)	1.65(2)	C(1)–C(3)	1.53(2)	C(1)–B(5)	1.75(2)
C(1)–B(6)	1.70(2)	C(1)–B(7)	1.72(2)	C(2)–C(4)	1.52(2)	C(2)–B(3)	1.75(2)
C(2)–B(6)	1.72(2)	C(2)–B(10)	1.72(2)	B(3)–B(4)	1.78(1)	B(3)–B(9)	1.75(2)
B(3)–B(10)	1.77(2)	B(4)–B(5)	1.52(1)	B(4)–B(8)	1.71(1)	B(4)–B(9)	1.83(1)
B(4)–H(4d)	1.14	B(5)–B(7)	1.79(2)	B(5)–B(8)	1.75(2)	B(6)–B(7)	1.71(2)
B(6)–B(10)	1.72(2)	B(6)–B(11)	1.70(2)	B(7)–B(8)	1.73(2)	B(7)–B(11)	1.72(2)
B(8)–B(9)	1.75(2)	B(8)–B(11)	1.74(2)	B(9)–B(10)	1.79(2)	B(9)–B(11)	1.84(2)
B(10)–B(11)	1.80(2)	C(5)–O(5)	1.23(2)	C(6)–O(6)	1.20(2)	C(7)–O(7)	1.19(2)
W–Rh(1)–Rh(2)	60.5(1)	W–Rh(1)–B(5)	52.1(3)	W–Rh(1)–C(6)	48.3(3)	W–Rh(1)–H(1)	93.3(1)
Rh(2)–Rh(1)–B(5)	76.6(3)	Rh(2)–Rh(1)–C(6)	61.6(3)	Rh(2)–Rh(1)–H(1)	36.5(1)	B(5)–Rh(1)–C(6)	100.1(5)
W–Rh(2)–Rh(1)	57.6(1)	W–Rh(2)–B(4)	46.0(1)	W–Rh(2)–H(4d)	70.7(1)	W–Rh(2)–H(1)	90.5(1)
Rh(1)–Rh(2)–H(1)	36.6(1)	B(4)–Rh(2)–H(4d)	26.1(1)	B(4)–Rh(2)–Rh(1)	68.7(1)	B(4)–Rh(2)–H(1)	78.8(1)
H(4d)–Rh(2)–H(1)	84.4(1)	Rh(1)–W–Rh(2)	61.9(1)	Rh(1)–W–C(5)	101.0(4)	Rh(1)–W–C(6)	52.2(3)
Rh(1)–W–C(7)	136.5(4)	Rh(2)–W–C(5)	139.6(4)	Rh(2)–W–C(6)	63.5(3)	Rh(2)–W–C(7)	86.5(4)
C(5)–W–C(6)	77.1(5)	C(5)–W–C(7)	83.7(5)	C(6)–W–C(7)	88.0(5)	Rh(1)–B(5)–W	78.7(4)
Rh(1)–C(6)–W	79.5(4)	Rh(1)–C(6)–O(6)	124.1(9)	Rh(2)–B(4)–W	77.9(1)	B(4)–H(4d)–Rh(2)	112.0(1)
W–C(5)–O(5)	177.5(12)	W–C(6)–O(6)	154.7(9)	W–C(7)–O(7)	177.2(11)	Rh(1)–H(1)–Rh(2)	106.9(1)

Cyclopentadienyl rings

	Mean	Range		Mean	Range
Rh(1)–C	2.26(4)	2.20–2.30	Rh(2)–C	2.21(3)	2.17–2.26
C(11)–C(15)	1.42(2)	1.39–1.46	C(21)–C(25)	1.42(3)	1.38–1.46
C(11–15)–C(16–20)	1.50(3)	1.46–1.55	C(21–25)–C(26–30)	1.49(2)	1.47–1.52

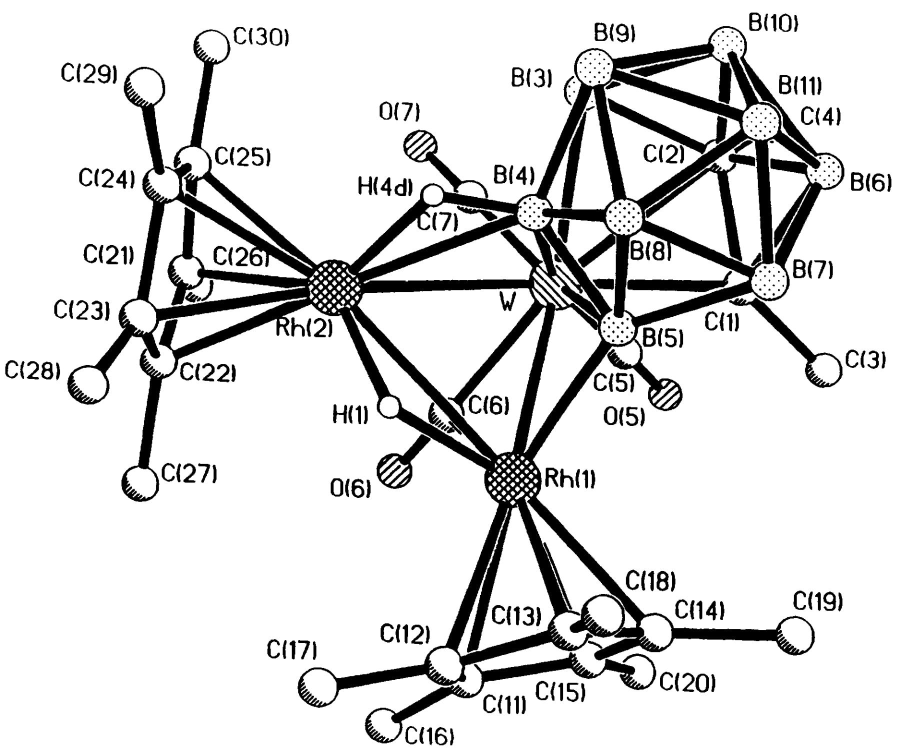
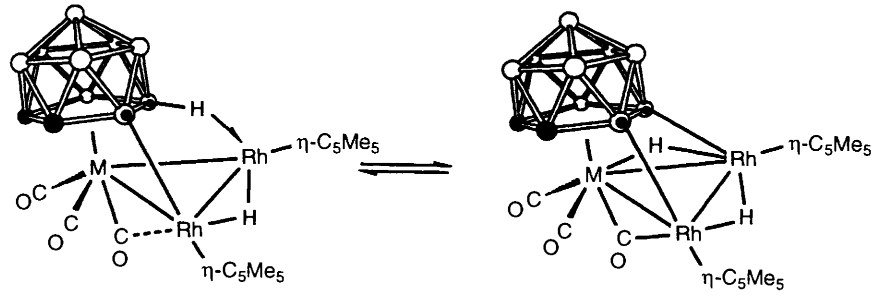


Fig. 1 Molecular structure of [$WRh_2(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}\sigma:\eta^5\text{-}7,8\text{-}C_2B_9H_8Me_2)(CO)_2(\eta\text{-}C_5Me_5)_2$] **4**, showing the crystallographic labelling scheme

two are essentially terminally bound [W–C(5)–O(5) and W–C(7)–O(7) 177(1)°], one carbonyl [C(6)O(6)] semi-bridges the W–Rh(1) bond [W–C(6)–O(6) 154(1)°, W–C(6) 2.08(1), Rh(1)–C(6) 2.20(1) Å]. The presence of a bridging CO ligand in the trimetal complexes is indicated by a band at *ca.* 1723 cm^{-1} in their solution IR spectra. The two terminally bound CO groups give rise to absorptions at *ca.* 1958 and 1893 cm^{-1}.

Although neither of the two bridging hydrido ligands [H(1) and H(4d)] was located in the electron-density-difference maps, they were assigned to their respective sites on the basis of potential-energy minimisation calculations.[10] Moreover, the presence of these μ-H ligands was unambiguously shown by NMR spectroscopy as discussed below. The hydride H(1) spans the Rh(1)–Rh(2) bond and the Rh(1)–H(1) and Rh(2)–H(1) distances (*ca.* 1.78 Å) are in good agreement with studies on other compounds with Rh(μ-H)Rh bonds.[8] The hydride H(4d) is part of a three-centre two-electron B(4)–H(4d)⟶Rh(2) bridge system. As is usual in structures with an η^5-7,8-$C_2B_9H_9Me_2$ framework and an exopolyhedral B–H⟶M bond, the boron atom forming the bridge is in the β site relative to the two



A **B**

○ BH ◉ B

	M	●
1	Mo	CH
2	Mo	CMe
3	W	CH
4	W	CMe

carbons in the CC*B*BB ring ligating the tungsten.[11] The presence of the B(4)–H(4d)→Rh(2) linkage leads to slippage of the tungsten atom towards B(4), and this results in the W–B(4) connectivity [2.08(1) Å] being appreciably shorter than those between tungsten and the other atoms in the pentagonal C_2B_3 ring [W–C(1) 2.29(1), W–C(2) 2.41(1), W–B(3) 2.40(1), W–B(5) 2.20(1) Å]. The Rh(2)–B(4) distance [2.39(2) Å] in **4** may be compared with that [2.22(1) Å] in $[Rh_2(CO)_2(PPh_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ a molecule which also has an exopolyhedral B–H→Rh bond.[12a] These separations are appreciably longer than the exopolyhedral B–Rh σ bond [2.05(3) Å] in $[NEt_4][Rh_2(\mu\text{-}\sigma{:}\eta^5\text{-}7,8\text{-}C_2B_9H_8Me_2)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$.[12b]

The NMR spectra (^1H, $^{13}C\text{-}\{^1H\}$, $^{11}B\text{-}\{^1H\}$ and ^{11}B) of the trimetal complexes were measured at room temperature, and the proton and boron spectra were also recorded at intervals down to −60 °C (Tables 2 and 3). This revealed that, with the exception of **3**, two different isomeric forms (**A** and **B**) of these species existed at the two temperature extremes. Molecular structure **A** is that found in the crystal structure of **4**, and is the only form present for complex **3** at ambient and at low temperatures. Thus in the ^1H NMR spectrum of **3** there is a diagnostic[13] resonance for the Rh(μ-H)Rh group at δ −18.81, which occurs as a doublet-of-doublets due to proton coupling with rhodium atoms in different environments. There is also a characteristic[11b] signal for the B–H→Rh group at δ −12.85, and this appears as a doublet-of-quartets (Table 2) as a result of $^{103}Rh\text{-}^1H$ and $^{11}B\text{-}^1H$ couplings. In the ^1H NMR spectrum recorded at −60 °C the signals for the protons of the Rh(μ-H)-Rh and B–H→Rh moieties are again seen, although at this temperature the $^{11}B\text{-}^1H$ coupling is unresolved on the latter resonance as a result of quadrupolar relaxation effect of the boron nuclei, a common feature of such spectra at low temperatures.

The $^{11}B\text{-}\{^1H\}$ NMR spectrum of compound **3** is also in agreement with it existing as isomer **A**. At both room temperature and at −60 °C a broad peak at δ *ca.* 35.5, corresponding in intensity to one boron nucleus, is characteristic for the presence of a B–Rh σ bond.[11b] Moreover, in a fully coupled ^{11}B spectrum this signal did not become a doublet, indicating that it was not due to a BH group. There was also a relatively deshielded peak corresponding to one boron nucleus at δ *ca.* 21.4 which in a fully coupled ^{11}B spectrum became a doublet [*J*(HB) *ca.* 69 Hz]. This resonance is diagnostic for the B–H→Rh group present in **3**.[11b]

The $^{13}C\text{-}\{^1H\}$ NMR spectrum shows the expected resonances. The broad peak at δ 243.4 may be ascribed to the semi-bridging CO ligand on the basis of its chemical shift, while the signals at δ 221.8 and 219.5 are due to the terminally bound CO groups. The ligated carbon atoms of the non-equivalent C_5Me_5 ligands are responsible for the resonances at δ 102.0 and 101.1. The non-equivalent cage CH groups give rise to peaks (δ 35.0 and 31.2) at the edge of the chemical shift range (δ 35–50) previously observed for such nuclei.[11b]

In contrast with **3**, the complexes **1**, **2** and **4** all display dynamic behaviour in solution as revealed by their NMR spectra. At −60 °C limiting low-temperature spectra were observed, which corresponded to the presence of one isomer **A**. As the temperature is raised, however, changes in the ^1H and $^{11}B\text{-}\{^1H\}$ NMR spectra indicate conversion into the isomer with structure **B**, resulting from the B–H→Rh group in **A** undergoing an oxidative addition at its rhodium atom to generate a second B–Rh σ bond and a M(μ-H)Rh group. It has been previously observed that exopolyhedral B–H→Ir linkages in some (carbaborane)tungsten–iridium complexes will also undergo an oxidative addition process to yield B–Ir and Ir–H bonds,[14] but a similar process with a B–H→Rh group has not been observed previously.

In the ^1H NMR spectrum of **1** at −60 °C there is a doublet-of-doublets at δ −19.82 and a very broad doublet at δ −13.65 (Table 2 and Fig. 2). Based on the above discussion of the ^1H NMR spectrum of **3**, these signals may be assigned to the Rh(μ-H)Rh and B–H→Rh hydrido ligands, respectively. Failure to observe $^{11}B\text{-}^1H$ coupling and to measure the $^{103}Rh\text{-}^1H$ coupling from the B–H→Rh resonance may again be ascribed to the longer relaxation time of the boron nuclei at the lower temperature. As the temperature is raised the peak pattern changes (Fig. 2) until at 20 °C only broad peaks are observed at δ −18.46 and −15.10, and these are assigned to the Rh(μ-H)Rh and W(μ-H)Rh groups, respectively, on the basis of their chemical shifts. Nevertheless, it appears a further dynamic process is occurring involving exchange of the bridging hydrides between sites.

The conclusions reached from the ^1H NMR spectra of **1** are supported by the data from the $^{11}B\text{-}\{^1H\}$ and ^{11}B NMR spectra (Table 3). At −60 °C, diagnostic signals for B–Rh and B–H→Rh groups are seen at δ 43.9 and 24.2, respectively.[11b] These assignments are supported by the fully coupled ^{11}B spectra when the former signal remains a singlet and the latter becomes a doublet [*J*(HB) 66 Hz]. Upon warming to 20 °C (Fig. 3), the pattern changes to two very broad peaks at δ 34.5 and 29.6, assignable to cage-boron atoms exopolyhedrally bound to a transition metal.[11b] These resonances in a ^{11}B spectrum remained as broad singlets, indicating that they were not due to BH groups.

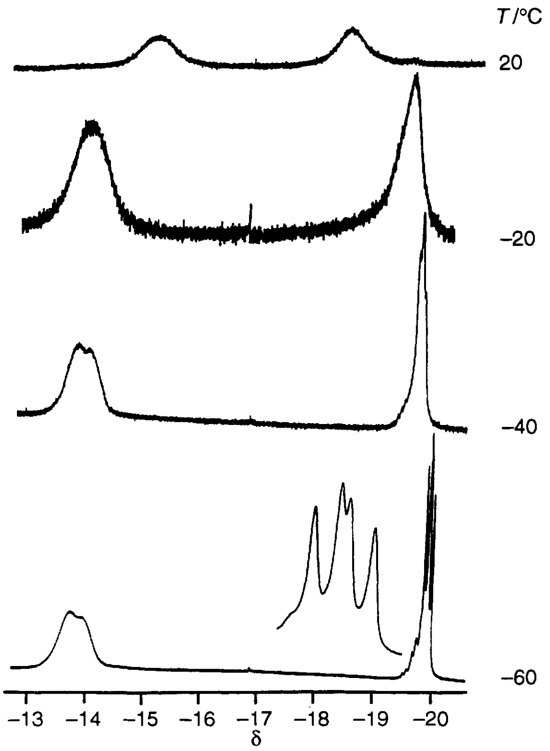


Fig. 2 The temperature dependence of the ^{1}H NMR spectrum of $[MoRh_2(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}\sigma:\eta^5\text{-}7,8\text{-}C_2B_9H_{10})(CO)_2(\eta\text{-}C_5Me_5)_2]$ **1**

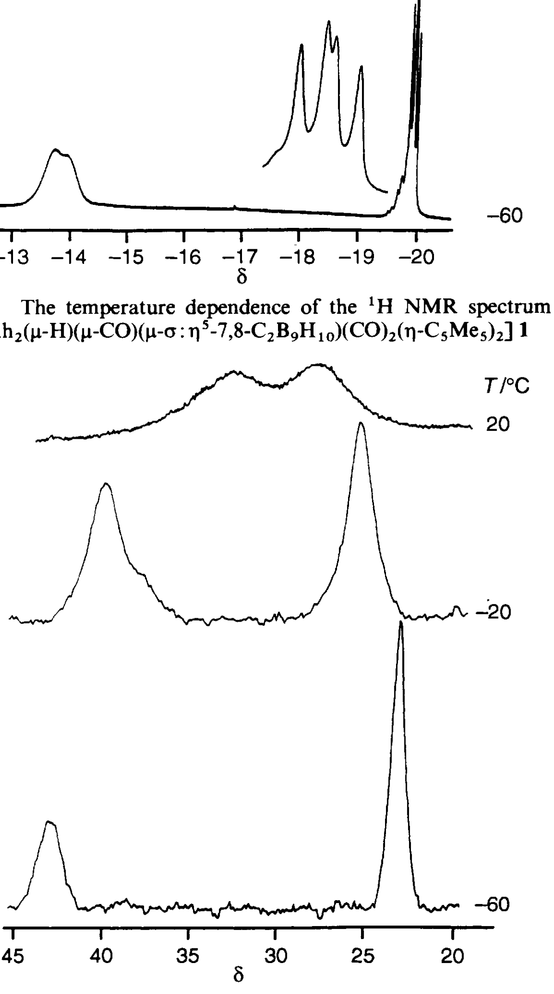


Fig. 3 The temperature dependence of the ^{11}B-{^{1}H} NMR spectrum of $[MoRh_2(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}\sigma:\eta^5\text{-}7,8\text{-}C_2B_9H_{10})(CO)_2(\eta\text{-}C_5Me_5)_2]$ **1**

The NMR signals of the nuclei assigned to the B–H⟶M and B–M groups in the ^{1}H and ^{11}B-{^{1}H} spectra of **2** at room temperature and at −60 °C are virtually identical with those of **1** at these respective temperatures. The signals corresponding to the B–H⟶M and B–M groups in the room temperature ^{1}H and ^{11}B-{^{1}H} spectra of complex **4**, on the other hand, are very similar to those of **1** at −20 °C (see Figs. 2 and 3), indicating the presence of an equilibrium mixture of the two isomers of **4** at this temperature. The ^{1}H and ^{11}B-{^{1}H} NMR resonances of these groups at −60 °C, however, are virtually identical with those of **1** at −60 °C, indicating that at this temperature isomer **A** of **4** is the sole species present in solution.

Table 5 Data for crystal structure analysis of compound **4**

Molecular formula	$C_{27}H_{45}B_9O_3Rh_2W$
M	904.6
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	11.770(2)
b/Å	15.089(3)
c/Å	18.949(2)
β/°	98.39(1)
U/Å^3	3329.3(1)
Z	4
D_c/Mg m^{-3}	1.81
F(000)	1760
μ(Mo-Kα)/cm^{-1}	45.20
T/K	292
Scan speed/° min^{-1}	0.43–3.44
Scan range, ω/°	1.15 + 0.34 tanθ
2θ Range/°	3.0–40.0
Radiation	Mo-Kα ($\bar{\lambda}$ = 0.710 73 Å)
Data-to-parameter ratio	7.3:1
R, R' (R_{all})	0.050, 0.060 (0.056)
R_{int}	0.029
S (goodness-of-fit)	1.17
Max., min. residual density/e Å^{-3}	2.66, −1.33

We have reported several triangulated trimetal complexes with a *nido*-7,8-C_2B_9 ligand, and have found that the carbaborane cage can adopt several different bonding modes.[15] Thus in $[PPh_4][WCo_2(\mu_3\text{-}CPh)(CO)_8(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ the carbaborane group is η^5 co-ordinated to the tungsten atom,[15a] adopting a spectator role as does the cyclopentadienyl ligand in $[WCo_2(\mu_3\text{-}CPh)(CO)_8(\eta\text{-}C_5H_5)]$. However, in solution the carbaborane-containing tungstendicobalt cluster releases two molecules of CO to afford $[PPh_4][WCo_2(\mu_3\text{-}CPh)(CO)_6(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$, a species with a B–H⟶Co exopolyhedral bond to each cobalt atom. Similarly, in the complex $[NEt_4][Mo_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_7(PMe_3)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ the metal triangle is triply bridged on one side by the alkylidyne group and on the other by two B–H⟶M bonds, in this case with M = Mo.[15b] In contrast, in the compounds $[NEt_4][MFe_2(\mu_3\text{-}CR)(\mu\text{-}\sigma:\sigma'\text{-}\eta^5\text{-}7,8\text{-}C_2B_9H_7Me_2)(CO)_8]$ (M = Mo or W; R = Ph, C_6H_4Me-4 or C_6H_4Me-2) there are two B–Fe σ bonds bridging one face of the metal triangle with the carbaborane cage η^5 co-ordinated to molybdenum or tungsten in the usual manner.[15c] It is noteworthy that the isomeric form **A** of the compounds **1**–**4**, established by X-ray diffraction for **4** in the crystal and indicated by NMR spectroscopy for all four species at low temperatures, is of a new type, since it combines in one structure both an exopolyhedral B–H⟶M three-centre bond and an exopolyhedral B–M σ bond.

Experimental

Light petroleum refers to that fraction of b.p. 40–60 °C. All solvents were dried over appropriate drying agents before use. Chromatography columns *ca.* 15 cm long and 3 cm in diameter were packed with alumina (Brockmann activity II). All experiments were carried out under nitrogen using Schlenk-tube techniques. Spectroscopic equipment used has been described previously.[4a] The compounds $[M(CO)_3(NCMe)_3]$ (M = Mo or W)[16] and $[NHMe_3][7,8\text{-}C_2B_9H_{10}R'_2]$[1] were obtained as described earlier. The salt $[Rh(NCMe)_3(\eta\text{-}C_5Me_5)][BF_4]_2$ was prepared by the procedure employed to prepare the PF_6^- analogue.[17]

Synthesis of the Complexes $[MRh_2(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}\sigma:\eta^5\text{-}7,8\text{-}C_2B_9H_8R'_2)(CO)_2(\eta\text{-}C_5Me_5)_2]$ (M = Mo *or* W, R′ = H *or* Me).—The complexes were all prepared using a similar procedure and so only a representative synthesis is described.

Table 6 Atomic positional parameters (fractional coordinates, × 10^4) for compound **4** with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
W	4964(1)	2199(1)	1728(1)
C(1)	6871(8)	1943(7)	1685(6)
C(2)	6237(10)	2006(8)	853(6)
B(3)	5468(10)	3002(8)	725(7)
B(4)	5796(10)	3393(8)	1616(6)
B(5)	6568(11)	2872(8)	2178(7)
B(6)	7683(11)	2234(8)	1049(7)
B(7)	7916(10)	2742(8)	1863(7)
B(8)	7193(10)	3741(8)	1761(7)
B(9)	6483(10)	3855(8)	890(7)
B(10)	6819(12)	2870(8)	438(8)
B(11)	7909(10)	3343(9)	1089(7)
C(3)	7235(11)	1025(7)	1981(6)
C(4)	5934(11)	1195(8)	389(7)
C(5)	4726(10)	929(8)	1866(7)
O(5)	4604(9)	138(7)	1977(7)
C(6)	4099(10)	2170(7)	2608(7)
O(6)	3364(6)	1929(6)	2941(4)
C(7)	3448(11)	2126(8)	1115(7)
O(7)	2548(8)	2117(7)	736(6)
Rh(1)	5763(1)	2717(1)	3095(1)
Rh(2)	4219(1)	3845(1)	2199(1)
C(11)	5518(9)	2346(7)	4242(6)
C(12)	6119(10)	3156(7)	4261(6)
C(13)	7175(10)	2985(8)	3965(6)
C(14)	7207(9)	2088(7)	3812(5)
C(15)	6185(8)	1690(7)	3965(5)
C(16)	4450(12)	2109(10)	4566(9)
C(17)	5732(13)	3985(9)	4550(8)
C(18)	8113(11)	3621(10)	3948(7)
C(19)	8243(9)	1593(9)	3683(7)
C(20)	5833(11)	701(8)	3891(7)
C(21)	2281(8)	3889(7)	2107(7)
C(22)	2795(9)	4218(7)	2768(5)
C(23)	3432(9)	4963(7)	2678(6)
C(24)	3370(9)	5096(7)	1908(6)
C(25)	2668(8)	4422(7)	1558(5)
C(26)	1429(10)	3174(9)	2001(8)
C(27)	2538(10)	3839(8)	3469(7)
C(28)	4007(10)	5571(8)	3234(7)
C(29)	3892(10)	5864(8)	1570(6)
C(30)	2284(10)	4356(8)	768(6)

A solution of $Na_2[7,8\text{-}C_2B_9H_{11}]$ was generated by refluxing $[NHMe_3][7,8\text{-}C_2B_9H_{12}]$ (0.20 g, 1.0 mmol) in thf (30 cm^3) with NaH [0.20 g, 5.0 mmol from a 60% dispersion in mineral oil, washed with thf (2 × 20 cm^3)] for 12 h. The solution was added to $[Mo(CO)_3(NCMe)_3]$ (0.30 g, 1.0 mmol). After stirring the mixture for 0.5 h, two molar equivalents of $[Rh(NCMe)_3(\eta\text{-}C_5Me_5)][BF_4]_2$ (1.07 g, 2.0 mmol) were added, and stirring was continued for a further 2 h, after which solvent was removed *in vacuo*. The residue was extracted with CH_2Cl_2 (3 cm^3) and the extract chromatographed. Elution with light petroleum–CH_2Cl_2 (3:1) gave an orange eluate identified as $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$.[6] Further elution with the same solvent mixture gave a brown eluate. After removal of solvent *in vacuo*, the product (*ca.* 0.20 g) was recrystallised from CH_2Cl_2–light petroleum (5 cm^3, 1:5) and dried *in vacuo* to give brown *microcrystals* of $[MoRh_2(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}\sigma{:}\eta^5\text{-}7,8\text{-}C_2B_9H_{10})(CO)_2(\eta\text{-}C_5Me_5)_2]$ **1** (0.14 g, 18%).

Crystal Structure Determination and Refinement.—Crystals of complex **4** were grown by diffusion of light petroleum into CH_2Cl_2 solutions. A conoscopic examination of **4**, using crystal rotation between two crossed polarizers on a Zeiss Photomicroscope (II), verified the biaxial (birefringent) nature and optical quality of the system. Data were obtained from a dark purple crystal (0.20 × 0.26 × 0.26 mm) on an Enraf-Nonius CAD4-F automated diffractometer equipped with a dense graphite monochromator (take-off angle 5.8°). Data were collected in the ω–2θ mode in the 2θ range 3.0–40.0° (*h* 0–11, *k* 0–14, *l* −18 to 18). Final unit-cell parameters and standard deviations were obtained from high-angle reflections ($28 < 2\theta < 40°$). No significant variations were observed in the intensities of the monitored standard reflections (every 2 h, < 1.2%). Hence, electronic reliability and the stability of the studied crystal were confirmed. All intensity data were corrected for Lorentz and polarisation effects after which an empirical absorption correction, based on high-angle ψ scans, was made (max., min. transmission factors = 0.9977, 0.8952). Of the 3462 measured intensities, 3091 were independent. After averaging the data (R_{int} = 0.029), 2793 reflections fitted $F_i \geqslant 4.0\ \sigma(F_i)$. Space-group assignment was based on systematic absences ($0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$). Crystal data, experimental and statistical summaries, and pertinent refinement parameters are presented in Table 5.

The heavy-atom Patterson method was employed to locate the rhodium and tungsten atoms. Fourier-difference mapping located all other non-hydrogen atoms. The blocked full-matrix least-squares method was employed to refine the model.[18] After applying a secondary extinction correction [$g = 7(3) \times 10^{-5}$ e^{-2}] and anisotropic refinement of all non-hydrogen atoms, final reliability factors were established, $R = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|] = 0.050$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.060$ with a mean shift/error value of 3.4×10^{-2} and 'goodness-of-fit' value (*S*) of 1.17. Hydrogen atoms H(1) and H(4d) were located by using the program XHYDEX.[10] All other H-atom positions were idealised (C–H 0.96 and B–H 1.10 Å) and allowed to ride on their respective bonding atoms with fixed isotropic displacement coefficients (80 and 60 × 10^{-3} Å^2, respectively). There were 380 parameters refined where $\Sigma w||F_o| - |F_c||^2$ was minimised, $w^{-1} = \sigma^2(F) + 0.0043F^2$. A final Fourier-difference map revealed some electron density in the vicinity of the heavy metal atoms which is quite normal. Elsewhere, the density map was virtually featureless. Atomic scattering factors and associated anomalous dispersion correction factors were taken from ref. 19. Final atomic positional parameters for non-hydrogen atoms are given in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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