Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 112.[1] Synthesis of Rhenium–Rhodium Complexes; Crystal Structure of $[\mathrm{ReRh}\{\mu\text{-}\sigma,\eta^5\text{-}\mathrm{C_2B_9H_7(CH_2C_6H_4Me\text{-}4)Me_2}\}(\mathrm{CO})_4(\eta\text{-}\mathrm{C_5H_4Me})]$ ‡

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Treatment of $[\mathrm{NEt_4}][\mathrm{Rh(CO)_2}(\eta^5\text{-}\mathrm{C_2B_9H_9Me_2})]$ in $\mathrm{CH_2Cl_2}$ with $[\mathrm{Re}(\equiv\mathrm{CC_6H_4Me\text{-}4})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_4Me\text{-}4})][\mathrm{BCl_4}]$ affords the dimetal complex $[\mathrm{ReRh}\{\mu\text{-}\sigma,\eta^5\text{-}\mathrm{C_2B_9H_7(CH_2C_6H_4Me\text{-}4)Me_2}\}(\mathrm{CO})_4(\eta\text{-}\mathrm{C_5H_4Me})]$. The structure was established by X-ray diffraction. The Re–Rh bond [2.888(1) Å] is spanned by the $\mathrm{C_2B_9H_7(CH_2C_6H_4Me\text{-}4)Me_2}$ fragment. The open pentagonal face of the $\mathrm{C_2B_9}$ cage is η^5 co-ordinated to the rhodium, and there is an exopolyhedral B–Re [2.17(2) Å] σ bond involving a boron atom in the α site with respect to the carbon atoms in the $\overline{\mathrm{CC}\mathit{B}\mathrm{BB}}$ ring; the boron atom in the β site $\overline{\mathrm{CCB}\mathit{B}\mathrm{B}}$ carries the $\mathrm{CH_2C_6H_4Me\text{-}4}$ substituent. The rhenium and rhodium atoms are each ligated by two terminally bound CO molecules, and the rhenium is also co-ordinated by the $\eta\text{-}\mathrm{C_5H_4Me}$ group. The related complexes $[\mathrm{ReRh}\{\mu\text{-}\sigma,\eta^5\text{-}\mathrm{C_2B_9H_7(CH_2C_6H_4Me\text{-}4)Me_2}\}(\mathrm{CO})_3\mathrm{L}(\eta\text{-}\mathrm{C_5H_5})]$ (L = CO or $\mathrm{PMe_2Ph}$) have also been prepared. In contrast with the aforementioned results the complex $[\mathrm{Mn}(\equiv\mathrm{CC_6H_4Me\text{-}4})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_4Me})][\mathrm{BCl_4}]$ reacts with $[\mathrm{NEt_4}][\mathrm{Rh(CO)(PPh_3)}(\eta^5\text{-}\mathrm{C_2B_9H_9Me_2})]$ and $[\mathrm{NEt_4}][\mathrm{Rh(cod)}(\eta^5\text{-}\mathrm{C_2B_9H_9Me_2})]$ (cod = cycloocta-1,5-diene) to give the mononuclear rhodium species $[\mathrm{Rh}\{\sigma,\eta^5\text{-}\mathrm{CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2}\}(\mathrm{CO})(\mathrm{PPh_3})]$ and $[\mathrm{Rh}\{\sigma,\eta^5\text{-}\mathrm{CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2}\}(\mathrm{cod})]$, respectively. The NMR data (^{1}H, ^{13}C-{^{1}H}, ^{11}B-{^{1}H}) for the new complexes are reported and discussed.

We have recently employed the rhodium salts $[\mathrm{X}][\mathrm{Rh(CO)L}(\eta^5\text{-}\mathrm{C_2B_9H_9R'_2})]$ **1** [X = $\mathrm{N(PPh_3)_2}$, L = CO, R′ = H; X = $\mathrm{NEt_4}$, L = $\mathrm{PPh_3}$, R′ = H; L = CO or $\mathrm{PPh_3}$, R′ = Me] as reagents for the preparation of several dirhodium compounds and for the synthesis of complexes with bonds between rhodium and other metals.[2] During the course of these studies we discovered an unusual reaction between the salts **1a**–**1c** and the complexes $[\mathrm{Mn}(\equiv\mathrm{CR})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_4Me})][\mathrm{BCl_4}]$ (R = $\mathrm{C_6H_4Me\text{-}4}$ or $\mathrm{C_6H_3Me_2\text{-}2,6}$).[2c] Instead of isolating mixed-metal complexes with manganese–rhodium bonds, as anticipated, the mononuclear rhodium compounds $[\mathrm{Rh}\{\sigma,\eta^5\text{-}\mathrm{CH(R)C_2B_9H_{10}}\}(\mathrm{CO})\mathrm{L}]$ **2a** (R = $\mathrm{C_6H_4Me\text{-}4}$, L = $\mathrm{PPh_3}$), **2b** (R = $\mathrm{C_6H_3Me_2\text{-}2,6}$, L = $\mathrm{PPh_3}$), **2c** (R = $\mathrm{C_6H_4Me\text{-}4}$, L = CO) and $[\mathrm{Rh}\{\sigma,\eta^5\text{-}\mathrm{CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2}\}(\mathrm{CO})_2]$ **2d** were formed. These species result from insertion of an alkylidyne group into a B–H bond of the carbaborane cage and formation of a rhodium–carbon σ bond with the C(H)R fragment.

It is probable that the compounds **2a**–**2d** are formed *via* dimetal intermediates with manganese–rhodium bonds and bridging alkylidyne groups. Loss of a molecule of $[\mathrm{Mn(CO)_3}(\eta\text{-}\mathrm{C_5H_4Me})]$ could occur during the final stages of the reaction pathway. If dimetal species with μ-CR groups are involved in these processes, it seemed worthwhile to study reactions between one or other of the salts **1** and the compound $[\mathrm{Re}(\equiv\mathrm{CC_6H_4Me\text{-}4})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_4Me})]$. It was anticipated reactions of this type would yield stable products with rhenium–rhodium bonds, and such species if isolated might shed light on the pathway leading to the products **2a**–**2d**. It is well known that metal–metal bonds are more robust if they involve elements of the third transition series.

During the course of the work we have also prepared two other mononuclear rhodium compounds structurally akin to the species **2a**–**2d**: *viz* $[\mathrm{Rh}\{\sigma,\eta^5\text{-}\mathrm{CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2}\}(\mathrm{CO})(\mathrm{PPh_3})]$ **2e** and $[\mathrm{Rh}\{\sigma,\eta^5\text{-}\mathrm{CH(C_6H_4Me\text{-}4)C_2B_9H_8Me_2}\}(\mathrm{cod})]$ **2f** (cod = cycloocta-1,5-diene).

Results and Discussion

Treatment of a $\mathrm{CH_2Cl_2}$ solution of the reagent **1c** with 1 equivalent of the salt $[\mathrm{Re}(\equiv\mathrm{CC_6H_4Me\text{-}4})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_4Me})][\mathrm{BCl_4}]$ gave the dimetal compound $[\mathrm{ReRh}\{\mu\text{-}\sigma,\eta^5\text{-}\mathrm{C_2B_9H_7(CH_2C_6H_4Me\text{-}4)Me_2}\}(\mathrm{CO})_4(\eta\text{-}\mathrm{C_5H_4Me})]$ **3a**. The closely related complex $[\mathrm{ReRh}\{\mu\text{-}\sigma,\eta^5\text{-}\mathrm{C_2B_9H_7(CH_2C_6H_4Me\text{-}4)Me_2}\}(\mathrm{CO})_4(\eta\text{-}\mathrm{C_5H_5})]$ **3b** was obtained from the reaction between **1c** and $[\mathrm{Re}(\equiv\mathrm{CC_6H_4Me\text{-}4})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})][\mathrm{BCl_4}]$. Treatment of compound **3b** with $\mathrm{PMe_2Ph}$ in $\mathrm{CH_2Cl_2}$ affords $[\mathrm{ReRh}\{\mu\text{-}\sigma,\eta^5\text{-}\mathrm{C_2B_9H_7(CH_2C_6H_4Me\text{-}4)Me_2}\}(\mathrm{CO})_3(\mathrm{PMe_2Ph})(\eta\text{-}\mathrm{C_5H_5})]$ **3c**. Data characterising the compounds **3a**–**3c** are given in Tables 1 and 2, but discussion of the spectroscopic properties is deferred until the results of an X-ray diffraction study on complex **3a** are described.

Two views of the molecule are shown in Fig. 1, and the important structural parameters are listed in Table 3. As expected, there is a Re–Rh bond [2.888(1) Å], but the most important structural feature is the bonding of the carbaborane cage. While the latter is η^5 co-ordinated to the rhodium *via* its open pentagonal face, it also forms a boron–rhenium σ bond *via* B(3). Moreover, the latter atom symmetrically bridges the metal–metal bond [B(3)–Re and B(3)–Rh 2.17(2) Å]. This results in the C(2)–B(3) [1.93(2) Å] and B(3)–B(4) [1.88(2) Å] connectivities being relatively long compared with the corresponding distances in other structures in which a $\mathrm{C_2B_9}$ cage ligates rhodium.[2] The atom B(4) in the open pentagonal face of

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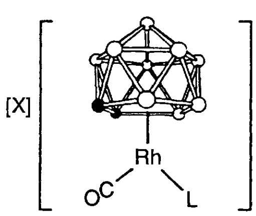
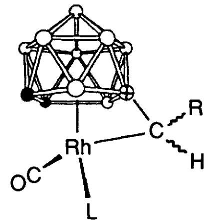
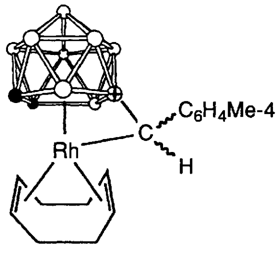


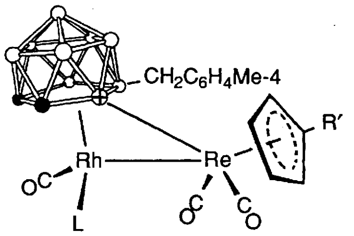
	X	L	●
1a	$N(PPh_3)_2$	CO	CH
1b	NEt_4	PPh_3	CH
1c	NEt_4	CO	CMe
1d	NEt_4	PPh_3	CMe



	L	R	●
2a	PPh_3	C_6H_4Me-4	CH
2b	PPh_3	$C_6H_3Me_2$-2,6	CH
2c	CO	C_6H_4Me-4	CH
2d	CO	C_6H_4Me-4	CMe
2e	PPh_3	C_6H_4Me-4	CMe



2f



	L	R′
3a	CO	Me
3b	CO	H
3c	PMe_2Ph	H

●CMe ○BH ⊕B

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

Compound[b]	Yield (%)	ν(CO)[c]/cm^{-1}			Analysis (%) C	Analysis (%) H
2e $[Rh\{\sigma,\eta^5\text{-}CH(R)C_2B_9H_8Me_2\}(CO)(PPh_3)]$	52	2007vs			52.2[d] (51.7)	5.5 (5.3)
2f $[Rh\{\sigma,\eta^5\text{-}CH(R)C_2B_9H_8Me_2\}(cod)]$	41				50.8 (50.5)	6.9 (7.3)
3a $[ReRh\{\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_7(CH_2R)Me_2\}(CO)_4(\eta\text{-}C_5H_4Me)]$	37	2072vs 1909s	2032s	1972s	34.6 (35.5)	4.2 (3.9)
3b $[ReRh\{\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_7(CH_2R)Me_2\}(CO)_4(\eta\text{-}C_5H_5)]$	41	2073s 1918s	2031vs	1972s	33.1 (34.1)	4.0 (4.0)
3c $[ReRh\{\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_7(CH_2R)Me_2\}(CO)_3(PMe_2Ph)(\eta\text{-}C_5H_5)]$	49	1981w	1957vs	1895s	40.5 (39.8)	4.8 (4.7)

[a] Calculated values are given in parentheses. [b] R = C_6H_4Me-4. All complexes are orange. [c] Measured in CH_2Cl_2. All complexes show a broad band at *ca.* 2550 cm^{-1} due to B–H. [d] Crystallises with 1 molecule of CH_2Cl_2.

the cage carries a $CH_2C_6H_4Me$-4 substituent [B(4)–C(40) 1.63(2) Å]. Interestingly, the cage ligand μ-σ,η^5-$C_2B_9H_7(CH_2C_6H_4Me\text{-}4)Me_2$ has been previously structurally identified by X-ray crystallography in the complex $[WPt(\mu\text{-}H)\{\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_7(CH_2C_6H_4Me\text{-}4)Me_2\}(CO)_2(PMe_3)(PEt_3)_2]$.[3] In the latter, and in the product **3a**, the $CH_2C_6H_4Me$-4 group is attached to a boron atom in the β site with respect to the carbons in the pentagonal $\overline{CCB\mathit{B}B}$ face of the cage, while the exopolyhedral B–M (Pt or Re) σ bond involves a boron atom in the α site of the $\overline{CC\mathit{B}BB}$ ring.

The rhodium atom is co-ordinated by two CO molecules in a linear manner. The rhenium atom is also ligated by two terminal CO groups, and carries the C_5H_4Me ring.

Having established the molecular structure of compound **3a** the spectroscopic data for all three species **3** may be interpreted. The IR spectra of complexes **3a** and **3b** display four CO stretching bands. That of compound **3c** shows the expected three CO absorptions. The presence of the PMe_2Ph group on rhodium in the latter complex revealed itself by a doublet resonance in the ^{31}P-$\{^1H\}$ NMR spectrum at δ −2.73 [*J*(RhP) 148 Hz].

The ^{11}B-$\{^1H\}$ NMR data for the complexes **3** were definitive in revealing the presence of both B–Re and $BCH_2C_6H_4Me$-4 groups in these compounds. In the spectra there are two deshielded resonances each of relative intensity corresponding to one boron atom. The most deshielded signal at δ 62.0 for **3a**, 61.8 for **3b** and 56.7 for **3c** may be ascribed to the BRe group. In the ^{11}B-$\{^1H\}$ NMR spectrum of the above mentioned compound $[WPt(\mu\text{-}H)\{\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_7(CH_2C_6H_4Me\text{-}4)Me_2\}(CO)_2(PMe_3)(PEt_3)_2]$ the corresponding resonance is at δ 36.2,[3] while in the spectrum of $[N(PPh_3)_2][WRu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_8Me_2)(CO)_3(\eta\text{-}C_5H_5)]$ the peak for the BRu group is more deshielded at δ 45.9.[4] The signals in the spectra of the complexes **3** at δ 12.7 (**3a**), 12.8 (**3b**) and 13.8 (**3c**) may be assigned to the $BCH_2C_6H_4Me$-4 groups. In the spectrum of $[WPt(\mu\text{-}H)\{\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_7(CH_2C_6H_4Me\text{-}4)Me_2\}(CO)_2(PMe_3)(PEt_3)_2]$ the corresponding resonance is at δ 10.6,[3] and

Table 2 Hydrogen-1, carbon-13 and boron-11 NMR data[a] for the complexes

Compound	^{1}H(δ)	^{13}C[b](δ)	^{11}B[c](δ)
2e[d]	2.19, *2.20, *2.22, 2.26, *2.28, 2.29 (s × 6, 9 H, CMe and Me-4), 6.51, *6.67 [d × 2, 1 H, BC(*H*)C_6H_4Me-4, *J*(RhH) 6], 7.00–7.40 (m, 19 H, C_6H_4 and Ph)	187.4 [d of d, CO, *J*(RhC) 74, *J*(PC) 24], 144.0 [$C^1(C_6H_4)$], 137.8–128.5 (C_6H_4 and Ph), 98.1 [vbr, B*C*(H)C_6H_4Me-4], 72.1, *71.9, 70.6, *70.5 (*C*Me), 29.4, *28.2, *27.1, 26.3 (C*Me*), 21.5, *21.4 (Me-4)	17.1 [1 B, BC(H)C_6H_4Me-4], −9.2 to −15.9 (br m, 8 B)
2f	1.58–1.80 [m, 8 H, CH_2(cod)], 2.14 (s, 6 H, CMe and/or Me-4), 2.17 (s, 3 H, CMe or Me-4), 4.60–5.30 [m, 4 H, CH(cod)], 6.71 [br s, 1 H, BC(*H*)C_6H_4Me-4], 7.01, 7.29 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 7]	[e] 141.2 [$C^1(C_6H_4)$], 137.8, 129.8, 129.2 (C_6H_4), 96.3, 96.2, 95.8, 95.0 [d × 4, CH(cod), *J*(RhC) 8], 70.0, 69.7 (*C*Me), 31.8, 31.5 (C*Me*), 27.8, 27.0, 26.8, 25.9 [CH_2(cod)], 20.6 (Me-4)	24.0 [1 B, BC(H)C_6H_4Me-4], −2.4 to −19.4 (br m, 8 B)
3a	1.96 (m, C*H_2*C_6H_4Me-4, 2 H), 2.18, 2.22, 2.26 (s × 3, 12 H, Me-4, CMe and C_5H_4*Me*), 5.18–5.52 (br m, 4 H, C_5*H_4*Me), 6.82, 6.89 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	202.9, 200.6 (ReCO), 189.7 [d, RhCO, *J*(RhC) 68], 186.7 [d, RhCO, *J*(RhC) 66], 142.6 [$C^1(C_6H_4)$], 133.3, 129.3, 129.0 (C_6H_4), 103.1 [*C*Me(C_5H_4Me)], 90.1, 90.0, 86.2, 85.8 [*C*H(C_5H_4Me)], 71.8, 67.9 (*C*Me), 34.0 (C*Me*), 32.6 (br, B*C*$H_2C_6H_4$Me-4), 30.6 (C*Me*), 20.8 (Me-4), 20.2 (C_5H_4*Me*)	62.0 (1 B, BRe), 12.7 (1 B, $BCH_2C_6H_4$Me-4), 2.8 to −20.0 (br m, 7 B)
3b	[f] 2.17 (s, 3 H, Me-4), 2.23, 2.26 (s × 2, 6 H, CMe), 5.51 (s, 5 H, C_5H_5), 6.82, 6.88 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8]	[g] 200.8, 197.9 (ReCO), 187.5 [d, RhCO, *J*(RhC) 68], 183.8 [d, RhCO, *J*(RhC) 56], 141.6 [$C^1(C_6H_4)$], 132.6, 128.2, 127.2 (C_6H_4), 86.5 (C_5H_5), 78.2, 70.6 (*C*Me), 32.9 (C*Me*), 31.8 (br, B*C*$H_2C_6H_4$Me-4), 29.7 (C*Me*), 20.1 (Me-4)	61.8 (1 B, BRe), 12.8 (1 B, $BCH_2C_6H_4$Me-4), −0.8 to −39.3 (br m, 7 B)
3c	[f] 1.92 [d, 3 H, MeP, *J*(PH) 10], 1.97 [d, 3 H, MeP, *J*(PH) 10], 2.16, 2.19, 2.20 (s × 3, 9 H, Me-4 and CMe), 5.42 (s, 5 H, C_5H_5), 6.75, 6.85 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) 8], 7.39–7.62 (m, 15 H, Ph)	[g] 203.7, 199.1 (ReCO), 191.4 [d of d, RhCO, *J*(RhC) 72, *J*(PC) 19], 144.5 [$C^1(C_6H_4)$], 131.9–127.3 (C_6H_4 and Ph), 86.6 (C_5H_5), 71.8, 70.2 (*C*Me), 32.9, 27.8 (C*Me*), 20.4 (Me-4), 17.9 [d, MeP, *J*(PC) 33], 31.0 (br, B*C*$H_2C_6H_4$Me-4), 15.2 [d, MeP, *J*(PC) 34]	56.7 (1 B, BRe), 13.8 (1 B, $BCH_2C_6H_4$Me-4), 0.9 to −37.5 (m, 7 B)

[a] Chemical shifts (δ) in ppm, 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 $SiMe_4$ (0.0 ppm). [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $BF_3{\cdot}Et_2O$ (external). [d] Peaks asterisked are due to minor isomer (see text). [e] Signal for B*C*(H)C_6H_4Me-4 nucleus not observed. [f] Resonance for BC*H_2*C_6H_4Me-4 protons not observed. [g] Measured at −40 °C.

Table 3 Selected internuclear distances (Å) and angles (°) for the complex [ReRh{μ-σ,η^5-$C_2B_9H_7(CH_2C_6H_4Me\text{-}4)Me_2$}$(CO)_4$(η-$C_5H_4$Me)] **3a**

Re–Rh	2.888(1)	Rh–C(1)	2.30(1)	Rh–C(2)	2.19(1)	Rh–B(3)	2.17(2)
Re–B(3)	2.17(2)	Rh–B(4)	2.24(2)	Rh–B(5)	2.24(1)	Rh–C(3)	1.90(1)
Rh–C(4)	1.97(2)	Re–C(5)	1.89(2)	Re–C(6)	1.94(1)	C(1)–C(2)	1.65(2)
C(1)–B(5)	1.72(2)	C(1)–C(10)	1.51(2)	C(2)–B(3)	1.93(2)	B(3)–B(4)	1.88(2)
C(2)–C(20)	1.52(2)	B(4)–B(5)	1.81(2)	B(4)–C(40)	1.63(2)	C(40)–C(41)	1.51(2)
C(3)–O(3)	1.13(2)	C(4)–O(4)	1.12(2)	C(5)–O(5)	1.14(2)	C(6)–O(6)	1.14(2)
Rh–Re–B(3)	48.2(4)	B(3)–Re–C(5)	78.0(6)	B(3)–Re–C(6)	110.0(6)	C(5)–Re–C(6)	82.4(6)
Rh–Re–C(5)	111.2(4)	Rh–Re–C(6)	80.6(4)	Re–Rh–B(3)	48.4(4)	Re–Rh–C(3)	106.6(4)
Re–Rh–C(4)	91.0(5)	C(3)–Rh–C(4)	88.3(7)	Re–B(3)–Rh	83.4(5)	B(4)–C(40)–C(41)	114(1)
Rh–C(3)–O(3)	178(1)	Rh–C(4)–O(4)	177(2)	Re–C(5)–O(5)	175(1)	Re–C(6)–O(6)	176(1)

for the salt [NEt_4][$Rh(CO)_2${η^5-$C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2$}] it is at δ 12.9.[2c] In the ^{11}B-{^{1}H} NMR spectra of the complexes **3** there are also broad peaks in the range δ *ca.* 3 to −40 due to the seven BH vertices of the cages.

The ^{1}H and ^{13}C-{^{1}H} NMR spectra of the compounds **3** were as expected, although peaks due to the CH_2 group of the $BCH_2C_6H_4$Me-4 fragment were not seen in all the spectra. This is not unusual since these resonances are often broad due to the proximity of ^{11}B nuclei and are lost in the baseline unless the complex is very soluble and the solution concentrated. In their ^{13}C-{^{1}H} NMR spectra complexes **3a** and **3b** show four CO resonances (Table 2). The two peaks in each spectrum due to CO molecules ligating the rhodium atom are easily identified as they occur as doublets as a result of ^{103}Rh–^{13}C coupling. As expected, the spectrum of compound **3c** shows only three CO resonances, and these are at δ 203.7 and 199.1 for the $Re(CO)_2$ group and at δ 191.4 for the Rh(CO)(PPh_3) moiety. The latter signal is a doublet of doublets [*J*(RhC) 72, *J*(PC) 19 Hz]. The asymmetry of the compounds **3** results in a non-equivalence of the carbaborane cage CMe fragments. Consequently, the latter give rise to two peaks in the ^{1}H NMR spectrum and four peaks in the ^{13}C-{^{1}H} NMR spectrum of each complex. Lack of a plane of symmetry in the species **3a** leads to the appearance of five signals for the ring carbon nuclei of the C_5H_4Me ligand (Table 2).

As previously mentioned, reactions between the salts [Mn(≡CR)$(CO)_2$(η-C_5H_4Me)][BCl_4] (R = C_6H_4Me-4 or C_6H_3-Me_2-2,6) and **1a**, **1b** or **1c** give the mononuclear rhodium compounds **2a**–**2d**, respectively.[2c] However, experience has shown that in reactions involving carbaborane metal complexes minor changes in the nature of the other ligands present, or replacement of CH by CMe groups in the cage, can lead to different structures for the products isolated. For this reason reactions between [Mn(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_4Me)]-[BCl_4] and the salts **1d** and [NEt_4][Rh(cod)(η^5-$C_2B_9H_9$-Me_2)][5] **1e** were investigated.

The reaction between **1d** and [Mn(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_4Me)][BCl_4] in CH_2Cl_2 yielded the complex [Rh{σ,η^5-CH(C_6H_4Me-4)$C_2B_9H_8Me_2$}(CO)(PPh_3)] **2e**. Similarly, the manganese reagent with **1e** gave the compound [Rh{σ,η^5-CH(C_6H_4Me-4)$C_2B_9H_8Me_2$}(cod)] **2f**. Data for these species are listed in Tables 1 and 2, and it is evident that they are similar in structure to the compounds **2a**–**2d** isolated previously.[2c]

Compound **2e** was formed as a mixture of two isomers, as revealed by the appearance of several peaks in duplicate in the

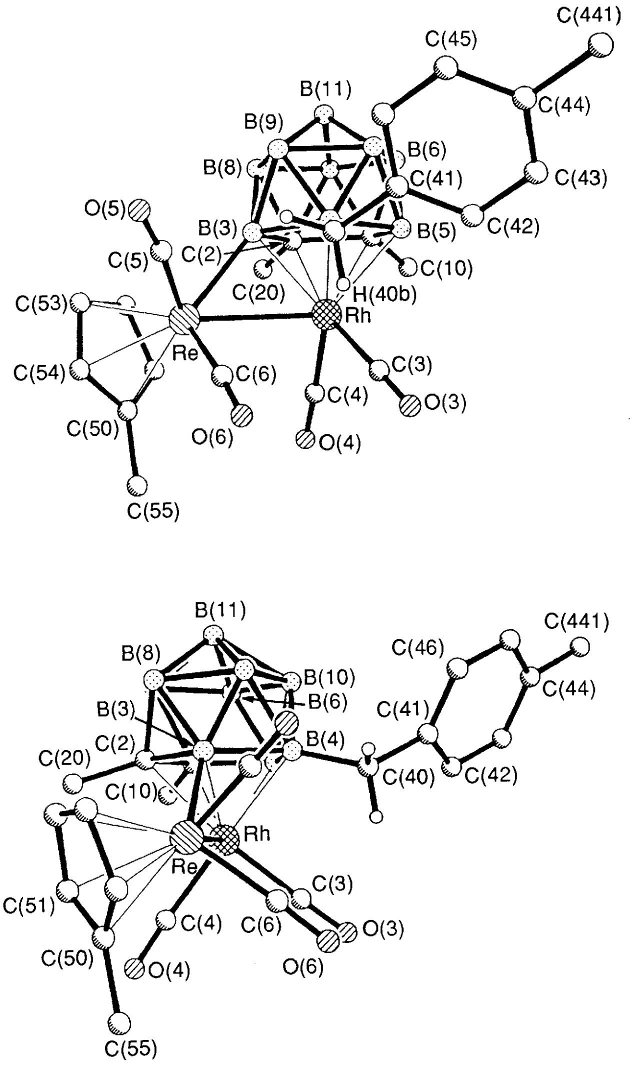


Fig. 1 Molecular structure of the complex [ReRh{μ-σ,η^5-$C_2B_9H_7(CH_2C_6H_4Me\text{-}4)Me_2$}(CO)$_4$(η-$C_5H_4Me$)] **3a**, showing the atomic labelling scheme

^{1}H and ^{13}C-{^{1}H} NMR spectra. The presence of two isomers was most clearly revealed in the ^{13}P-{^{1}H} NMR spectrum which displayed two resonances, each a doublet at δ 35.6 [*J*(RhP) 144] and 33.1 [*J*(RhP) 146 Hz], respectively. These signals were of relative intensity 2:1, and peaks for the major and minor isomers in the ^{1}H and ^{13}C-{^{1}H} NMR spectra were of similar relative intensity, in accord with an isomer ratio of *ca.* 2:1. It was observed previously that complex **2a** also existed in solution as a mixture of two isomers, and this was attributed to the possibility that the PPh_3 ligand could be either cisoid or transoid to the C_6H_4Me-4 group.[2c] Only one isomer was observed for complex **2b** and this was ascribed to the bulkiness of the $C_6H_3Me_2$-2,6 group leading to the cisoid Ph_3P–Rh–C–$C_6H_3Me_2$-2,6 arrangement being unfavoured. The presence of two CO groups in **2c** and **2d** leads to the absence of diastereoisomers, as invoked for complexes **2a** and **2e**. Similarly, as expected, compound **2f** shows NMR signals corresponding to the presence of one isomer.

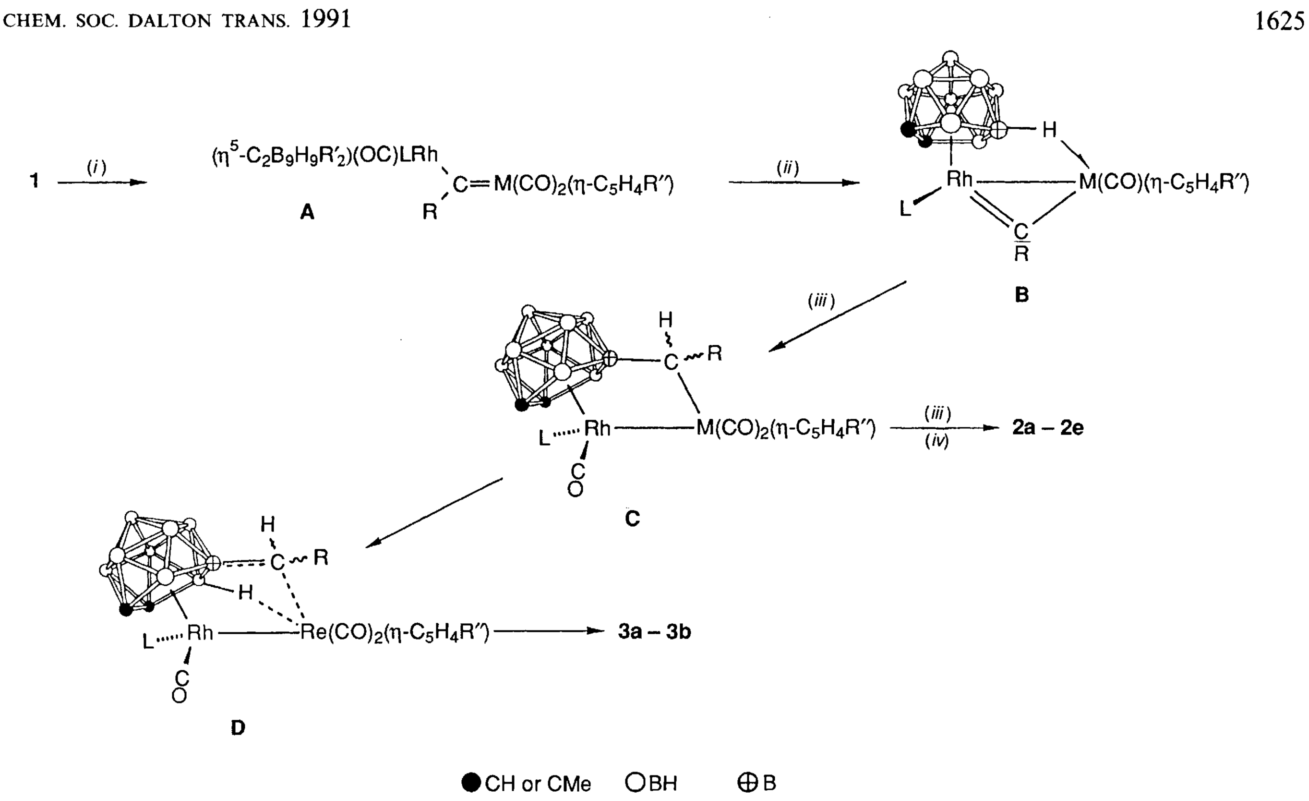
It seems likely, from the work described herein and in our earlier paper,[2c] that the reactions between the salts **1** and the reagents [M(≡CR)(CO)$_2$(C_5H_4R')][BCl_4] (M = Mn or Re, R = C_6H_4Me-4 or $C_6H_3Me_2$-2,6, R′ = H or Me) initially follow the same pathway. However, evidently at some point the pathways diverge, yielding products of either type **2** or type **3**. Moreover, it is by no means certain that all the salts **1** function in the same manner. Thus those containing CO groups can readily release this ligand at an appropriate stage in the reaction profile and recapture a CO molecule later, whereas the isolation of compound **2f** suggests that the cod ligand in the salt **1e** is not released at any stage. In the various intermediates it is also possible that the η^5-C_2B_9 cage can undergo slippage to an η^3 bonding mode and formally contribute two rather than four electrons to the rhodium centre. This would be analogous to the well known slippage of C_5H_5 groups from η^5 to η^3 bonding in complexes containing Rh(η-C_5H_5) groups.

Possible reaction pathways to the compounds **2a**–**2e** or **3a** and **3b** when the reagents **1a**–**1d** are employed are shown in Scheme 1. We have previously mentioned[2c] precedents for an intermediate of type **A**. Earlier work provides numerous examples of dimetal species with structures akin to **B**. Moreover, the bridging BC(H)(R)M group present in **C** has also been identified in several compounds,[6] and in some preparations of compound **3a** formation of a species with ν_{max}(CO) at 2058s, 2022s, 1952vs and 1868m cm^{-1} was observed. This species might be an intermediate of type **C**. However, attempts to isolate it for characterisation yielded only [Re(CO)$_3$(η-C_5H_4Me)] and trace amounts of other products not identified. If **C** were to contain the relatively weaker Mn–Rh bond, formation of the complexes **2a**–**2e** could occur *via* loss of an Mn(CO)$_2$(η-C_5H_4Me) fragment. The latter would scavenge a CO molecule to afford [Mn(CO)$_3$(η-C_5H_4Me)]. If the probable intermediate **C** possessed the more robust Re–Rh bond, there might be the possibility of activation of a B–H bond adjacent to the BC(H)(C_6H_4Me-4)Re fragment giving a transient species like **D**. Transfer of hydrogen from boron to carbon could then afford the compounds **3**. Yields of the complexes **2a**–**2e** and **3a** and **3b** are *ca.* 50% or less, which would accord with processes involving dissociation and scavenging of CO molecules. Clearly Scheme 1 would require modification to account for the observation of the minor and unidentified products observed in some reactions, and also to accommodate the formation of **2f**. The latter might form *via* a step in which the cod molecule adopts an η^2 bonding mode in an intermediate such as **B**, or in a process in which the carbaborane ligand undergoes slippage, as mentioned above, to accommodate an η^4 cod molecule.

Experimental

Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. All solvents were rigorously dried before use. Light petroleum refers to that fraction of b.p. 40–60 °C. Chromatography columns (*ca.* 20 cm in length and 4 cm in diameter) were packed with aluminium oxide (Brockman activity II alumina). The IR spectra were measured with a Perkin-Elmer FT 1600 spectrometer, NMR spectra with JEOL JNM GX 270 and GX 400 spectrometers. The ^{31}P-{^{1}H} NMR chemical shifts were measured in CD_2Cl_2 and are positive to high frequency of 85% H_3PO_4 (external). The salts **1c** and **1d**[2b,c] and the reagents [M(≡CC_6H_4Me-4)(CO)$_2$(η-C_5H_4Me)][BCl_4] (M = Mn or Re), [Re(≡CC_6H_4-Me-4)(CO)$_2$(η-C_5H_5)][BCl_4][7] and [Rh_2(μ-Cl)$_2$(cod)$_2$][8] were obtained by methods previously described.

The precursor to [Re(≡CC_6H_4Me-4)(CO)$_2$(η-C_5H_5)][BCl_4] is [Re(CO)$_3$(η-C_5H_5)], and this complex was prepared in high yield by a new procedure. The complex [ReBr(CO)$_5$] (4.93 g, 12.14 mmol) was dissolved in thf (tetrahydrofuran) (100 cm^3), and the solution was refluxed for 12 h so as to obtain [ReBr(thf)$_2$(CO)$_3$] *in situ*. The reagent Na(C_5H_5) (1.00 g, 11.36 mmol) was then added to the cooled solution, and the mixture was stirred for 1 h. The white precipitate of NaBr which formed was filtered off under nitrogen using a Celite plug (3 × 3 cm). Solvent was removed *in vacuo*, the residue was dissolved in hexane (10 cm^3) and chromatographed (5 × 3 cm column). The eluate was collected, and solvent was reduced in volume to *ca.* 5 cm^3 *in vacuo*. Cooling to −78 °C overnight afforded white *crystals* of [Re(CO)$_3$(η-C_5H_5)] (3.46 g, 85%), identified by IR spectroscopy. The crystals were washed (2 × 5 cm^3) with cold (−20 °C) hexane, and dried *in vacuo*.



Scheme 1 L = PPh_3 or CO; R′ = H or Me; R = C_6H_4Me-4 or $C_6H_3Me_2$-2,6; R″ = H or Me. (*i*) +[M(≡CR)$(CO)_2$(η-C_5H_4R'')][BCl_4]; (*ii*) −CO; (*iii*) +CO; (*iv*) −[M$(CO)_3$(η-C_5H_4R'')]

Analytical and other data for the new compounds are given in Table 1.

Synthesis of the Mononuclear Rhodium Complexes.—(*i*) A mixture of the salts **1d** (0.20 g, 0.29 mmol) and [Mn(≡CC_6H_4-Me-4)$(CO)_2$(η-C_5H_4Me)][BCl_4] (0.13 g, 0.29 mmol) in CH_2Cl_2 (25 cm^3) was stirred for 1 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (4 cm^3) and chromatographed. Elution of an orange band with CH_2Cl_2–light petroleum (1:4), and removal of solvent *in vacuo* gave a residue which was recrystallised twice from CH_2Cl_2–light petroleum (*ca.* 20 cm^3, 1:5) to yield orange *microcrystals* of [Rh{σ,η^5-CH(C_6H_4Me-4)$C_2B_9H_8Me_2$}(CO)(PPh_3)] **2e** (0.10 g).

(*ii*) The reagent [NEt_4][Rh(cod)(η^5-$C_2B_9H_9Me_2$)] (0.39 mmol) was first prepared by treating [Rh_2(μ-$Cl)_2(cod)_2$] with Tl_2[7,8-$C_2B_9H_9Me_2$] in tetrahydrofuran in the presence of NEt_4Cl. The carbaboranerhodium salt in CH_2Cl_2 (25 cm^3) was then treated with [Mn(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_4Me)]-[BCl_4] (0.17 g, 0.39 mmol) and the mixture was stirred for 4 h. Solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (4 cm^3) and chromatographed. Elution with CH_2Cl_2–light petroleum (1:3) removed an orange band. Solvent was evaporated *in vacuo* and the residue was recrystallised from CH_2Cl_2–light petroleum (20 cm^3, 1:4) giving orange *microcrystals* of [Rh{σ,η^5-CH(C_6H_4Me-4)$C_2B_9H_8Me_2$}(cod)] **2f** (0.07 g).

Synthesis of the Rhenium–Rhodium Complexes.—(*i*) The alkylidynerhenium compound [Re(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_4Me)][BCl_4] (0.24 g, 0.41 mmol) was added to a CH_2Cl_2 (15 cm^3) solution of **1c** (0.20 g, 0.41 mmol), and the mixture was stirred for 20 min. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (3 cm^3) and chromatographed at −20 °C. Elution with CH_2Cl_2–light petroleum (1:4) yielded an orange fraction from which solvent was removed *in vacuo*. Recrystallisation of the residue from CH_2Cl_2–light petroleum (10 cm^3, 4:1) gave orange *microcrystals* of [ReRh{μ-σ,η^5-$C_2B_9H_7$($CH_2C_6H_4Me$-4)Me_2}$(CO)_4$(η-C_5H_4Me)] **3a** (0.11 g).

(*ii*) Similarly, [Re(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)][BCl_4] (0.23 g, 0.41 mmol) was added to a CH_2Cl_2 (15 cm^3) solution of **1c** (0.20 g, 0.41 mmol), and the mixture was stirred for 20 min. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (3 cm^3) and chromatographed at −20 °C, eluting with CH_2Cl_2–light petroleum (1:1). Removal of solvent *in vacuo* from an orange eluate and recrystallisation of the residue twice from CH_2Cl_2–light petroleum (1:5) gave orange *microcrystals* of [ReRh{μ-σ,η^5-$C_2B_9H_7$($CH_2C_6H_4Me$-4)Me_2}-$(CO)_4$(η-C_5H_5)] **3b** (0.12 g).

(*iii*) Compound **3b** (0.20 g, 0.27 mmol) in CH_2Cl_2 (20 cm^3) was treated with PMe_2Ph (0.27 mmol) at −78 °C, and the mixture was stirred for *ca.* 1 h. After warming slowly to room temperature, solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (3 cm^3) and chromatographed. Elution with CH_2Cl_2–light petroleum (1:2) removed an orange band. Evaporation of solvent *in vacuo* gave orange *microcrystals* of [ReRh{μ-σ,η^5-$C_2B_9H_7$($CH_2C_6H_4Me$-4)Me_2}$(CO)_3$(PMe_2-Ph)(η-C_5H_5)] **3c** (0.10 g).

Crystal Structure Determination.—Crystals of compound **3a** grow as orange prisms by diffusion of light petroleum into a CH_2Cl_2 solution of the complex. That chosen for study (dimensions *ca.* 0.15 × 0.15 × 0.20 mm) was sealed in a glass capillary tube under nitrogen, and diffracted intensities (Wyckoff ω scans) were collected at 298 K on a Siemens R3m/V four-circle diffractometer. Of 2711 unique data ($3 \leqslant 2\theta \leqslant 50°$), 2194 had $F \geqslant 4\sigma(F)$, where $\sigma(F)$ is the standard deviation in F based on counting statistics. Only these data were used in the solution and refinement of the structure, after corrections for Lorentz, polarisation and X-ray absorption effects, the latter by an empirical method based on azimuthal scan data.[9]

Crystal data. $C_{22}H_{29}B_9O_4ReRh$, $M = 743.9$, orthorhombic, space group $P2_12_12_1$, $a = 10.726(2)$, $b = 13.531(4)$, $c = 18.574(4)$ Å, $U = 2696(1)$ Å^3, $Z = 4$, $D_c = 1.83$ g cm^{-3}, $F(000) = 1432$, Mo-Kα X-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,73$ Å, μ(Mo-Kα) = 51.79 cm^{-1}.

The structure was solved by Patterson methods, and successive Fourier difference syntheses were used to locate all

Table 4 Atomic positional parameters (fractional coordinates $\times 10^4$) for compound **3a** with estimated standard deviations in parentheses

Atom	x	y	z
Re	10 094(1)	9 457(1)	1 747(1)
Rh	7 891(1)	10 480(1)	1 252(1)
C(1)	6 430(12)	9 888(11)	454(7)
C(10)	6 101(16)	10 640(12)	−113(8)
C(2)	7 789(11)	9 313(9)	437(6)
C(20)	8 621(12)	9 447(12)	−220(6)
B(3)	8 287(16)	8 921(11)	1 391(8)
B(4)	6 941(13)	9 363(14)	1 956(8)
B(5)	5 908(13)	9 973(13)	1 325(8)
B(6)	5 305(14)	9 092(14)	707(8)
B(7)	6 452(16)	8 675(12)	176(8)
B(8)	7 629(14)	8 118(12)	712(8)
B(9)	7 077(14)	8 127(12)	1 610(8)
B(10)	5 594(15)	8 796(15)	1 598(8)
B(11)	6 024(17)	7 951(14)	903(9)
C(3)	7 558(14)	11 489(11)	1 936(7)
O(3)	7 378(13)	12 069(9)	2 361(7)
C(4)	8 918(17)	11 435(13)	718(9)
O(4)	9 540(12)	11 975(9)	432(7)
C(5)	9 697(12)	8 526(12)	2 469(7)
O(5)	9 551(11)	7 951(8)	2 906(6)
C(6)	9 886(12)	10 384(10)	2 537(7)
O(6)	9 839(11)	10 926(8)	3 004(5)
C(40)	6 961(12)	9 528(15)	2 825(6)
C(42)	4 903(8)	10 275(5)	3 173(4)
C(43)	3 731	10 211	3 496
C(44)	3 354	9 331	3 821
C(45)	4 150	8 515	3 824
C(46)	5 322	8 579	3 502
C(41)	5 698	9 459	3 176
C(441)	2 050(13)	9 262(16)	4 136(8)
C(50)	11 962(9)	10 142(6)	1 356(6)
C(51)	11 300	9 855	728
C(52)	11 127	8 816	753
C(53)	11 682	8 459	1 396
C(54)	12 198	9 278	1 769
C(55)	12 458(13)	11 146(11)	1 524(9)

the non-hydrogen atoms which were refined anisotropically. The phenyl ring and the C_5H_4Me group were treated as rigid bodies. The hydrogen atoms were included in calculated positions [C–H 0.96 Å, U_{iso} 0.08 Å^2, B–H 1.1 Å, $U_{iso} = 1.2\ U_{iso}(B)$, using the program BHGEN[10]]. Refinement by full-matrix least squares led to $R = 0.034$ ($R' = 0.032$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0004|F|^2]$. The final electron-density difference synthesis showed no residual peaks $> +1.0$ or < -0.5 e Å^{-3}.

Calculations were performed on a DEC micro-Vax II computer with the SHELXTL PLUS system of programs.[9] Scattering factors and corrections for anomalous dispersion were taken from ref. 11. Atom coordinates are listed in Table 4.

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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References

1 Part 111, S. A. Brew, N. Carr, M. D. Mortimer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1991, 811.

2 (*a*) J. R. Fernandez, G. E. Helm, J. A. K. Howard, M. U. Pilotti and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1990, 1747; (*b*) N. Carr, M. C. Gimeno, J. E. Goldberg, M. U. Pilotti, F. G. A. Stone and I. Topaloğlu, *J. Chem. Soc., Dalton Trans.*, 1990, 2253; (*c*) M. U. Pilotti and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1990, 2625; (*d*) M. U. Pilotti, F. G. A. Stone and I. Topaloğlu, *J. Chem. Soc., Dalton Trans.*, 1991, 1355.

3 M. J. Attfield, J. A. K. Howard, A. N. de M. Jelfs, C. M. Nunn and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 2219.

4 M. Green, J. A. K. Howard, A. N. de M. Jelfs, O. Johnson and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 73.

5 D. M. Speckman, C. B. Knobler and M. F. Hawthorne, *Organometallics*, 1985, **4**, 426.

6 F. G. A. Stone, *Adv. Organomet. Chem.*, 1990, **31**, 53.

7 E. O. Fischer, E. W. Meineke and F. R. Kreissl, *Chem. Ber.*, 1977, **110**, 1140; E. O. Fischer, J. K. R. Wanner, G. Müller and J. Riede, *Chem. Ber.*, 1985, **118**, 3311.

8 G. Giordano and R. H. Crabtree, *Inorg. Synth.*, 1979, **19**, 218.

9 G. M. Sheldrick, SHELXTL PLUS programs used with the Nicolet-Siemens X-ray system.

10 P. Sherwood, BHGEN, a program for the calculation of idealised H positions for *nido*-icosahedral carbaborane fragments, Bristol University, 1986.

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

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