Carbaboranerhodium Complexes with Rh–Rh, Rh–Cu and Rh–Au Bonds; Crystal Structure of $[NEt_4][Rh_2(\mu\text{-}\sigma:\eta^5\text{-}C_2B_9H_8Me_2)(CO)_3(\eta^5\text{-}C_2B_9H_9Me_2)]$ ‡

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The compound $[NEt_4][Rh(CO)(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ has been prepared and used to synthesise the dimetal complexes $[RhM(CO)(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (M = Cu or Au) and $[RhCu(CO)(PMe_3)(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$. Protonation of $[NEt_4][Rh(CO)(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ gives an unstable hydride $[RhH(CO)(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$. In contrast, treatment of $[NEt_4][Rh(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ with $HBF_4\cdot Et_2O$ affords a dirhodium complex $[Rh_2(CO)_3(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ in which one carbaborane fragment bridges the Rh–Rh bond *via* an exopolyhedral B–H⇀Rh bond. This species can be deprotonated to give an anionic complex $[Rh_2(\mu\text{-}\sigma:\eta^5\text{-}C_2B_9H_8Me_2)(CO)_3(\eta^5\text{-}C_2B_9H_9Me_2)]^-$, the $[NEt_4]^+$ salt of which may be obtained directly from $[NEt_4][Rh(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ by treatment of the latter with $[NHMe_3]Cl$. An X-ray crystallographic study established the structure of the anion. One rhodium centre is ligated by a CO molecule and by a $C_2B_9H_9Me_2$ cage in the normal η^5 bonding mode, the other carries two CO groups and an $\eta^5\text{-}C_2B_9$ cage. However, a boron atom β to the carbons in the pentagonal open $\overline{\mathrm{CCB}\mathit{B}\mathrm{B}}$ face of this cage forms a σ bond to the other rhodium atom [B–Rh 2.05(3) Å], so that this $C_2B_9H_8Me_2$ group bridges the Rh–Rh bond [2.876(3) Å]. The NMR data for the new compounds are reported and discussed.

We are currently investigating the chemistry of the salts $[X][M(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9R'_2)]$ [X = NEt_4, PPh_4 or $N(PPh_3)_2$; M = Mo or W; R = alkyl, alkynyl or aryl; R′ = Me or H] in which the metal atoms occupy the open pentagonal face of a *nido*-icosahedral cage, and are also ligated by an alkylidyne group. These species are becoming important precursors for the synthesis of compounds containing bonds between W or Mo and other metallic elements, *via* reactions with halogeno- or cationic-metal complexes.[1] This aspect of their chemistry drew our attention to the possibility of employing anionic carbaboranerhodium complexes as reagents for the preparation of compounds with metal–metal bonds. The anion of the salt $[NEt_4][Rh(CO)(PPh_3)(\eta^5\text{-}C_2B_9H_{11})]$ **1a**[2] is isolobal with the species $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$, and the latter has long been known as a useful synthon for preparing mixed-metal compounds containing iron.[3] We have recently prepared the compound $[NEt_4][Rh(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **1b**,[4a] and have shown that the latter and the salt **1a** upon treatment with the appropriate reagents afford the complexes $[CoRh(CO)_2(PPh_3)(\eta\text{-}C_4Me_4)(\eta^5\text{-}C_2B_9H_{11})]$ **2**, $[Rh_2(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})]$ **3**, $[RhIrH(\mu\text{-}\sigma:\eta^5\text{-}C_2B_9H_{10})(CO)_3(PPh_3)_2]$ **4**, $[RhAu(CO)L(PPh_3)(\eta^5\text{-}C_2B_9H_9R'_2)]$ **5a** (L = PPh_3, R′ = H), **5b** and **5c** (two isomers) (L = CO, R′ = Me) and $[RhPt(\mu\text{-}H)(\mu\text{-}CO)(PPh_3)(PEt_3)_2(\eta^5\text{-}C_2B_9H_{11})]$ **6**.[4] Moreover, we have established the structure of the compounds **2**–**4** and **6** by X-ray diffraction, and have thereby unambiguously demonstrated three different bonding modes for the carbaborane cage. Thus in complex **6** the cage adopts a spectator role, whereas in **2** and **3** B–H⇀M (M = Co or Rh) bonds exist, while in the product **4** a B–Ir σ bond is present. Many other examples of these different bonding modes are known, and have been reviewed elsewhere.[1] These studies have revealed a delicate balance between structures with and without B–H⇀M bridge bonds, as illustrated by the probable existence in solution of an equilibrium mixture of the two isomers of $[RhAu(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **5b** and **5c**.[4a]

In this paper we report the synthesis of the salt $[NEt_4][Rh(CO)(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **1c**, and its use in the preparation of dimetal species with Rh–Cu or Rh–Au bonds. We also describe further studies with the reagent **1b**, including the formation of two structurally interesting dirhodium compounds.

Results and Discussion

Treatment of a thf (tetrahydrofuran) solution of $[RhCl(CO)(PPh_3)_2]$ with $Tl_2[7,8\text{-}C_2B_9H_9Me_2]$[5] followed by $[NEt_4]Cl$ affords the salt $[NEt_4][Rh(CO)(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **1c**, characterised by the data given in Tables 1 and 2. As expected, the IR spectrum shows a strong CO stretching band at 1924 cm^{-1}, which may be compared with that observed[2] in the spectrum of **1a** at 1910 cm^{-1}. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of the salt **1c** consists of a doublet [*J*(RhP) 184 Hz] at δ 45.3. The corresponding data for **1a** are δ 34.1 [*J*(RhP) 156 Hz].[2] The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of complex **1c** show the expected resonances, including in the latter spectrum a signal for the CO ligand at δ 192.1, displaying both $^{103}Rh\text{-}^{13}C$ (79 Hz) and $^{31}P\text{-}^{13}C$ (24 Hz) coupling.

The reaction between the salt **1b** and $[CuCl(PPh_3)]$ in CH_2Cl_2, in the presence of the chloride-abstracting reagent $TlBF_4$, gives the dimetal compound $[RhCu(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **5d**. A similar synthesis employing the reagent **1c** yields $[RhCu(CO)(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **5e**. Data characterising these two products are given in Tables 1 and 2. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **5d** shows a broad singlet resonance for the $Cu(PPh_3)$ group at δ 5.9, whereas the spectrum of **5e** shows the expected two signals, a broad singlet at δ 3.9 for the $Cu(PPh_3)$ group and a doublet at δ 45.2 [*J*(RhP) 166 Hz] for the $Rh(PPh_3)$ fragment. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **5e** the resonance for the CO ligand is a doublet of doublets at δ 188.5 [*J*(RhC) 72, *J*(PC) 21 Hz], while the CO groups in **5d** give rise to a doublet signal at δ 184.2 [*J*(RhC) 73 Hz].

The rhodium–copper compound $[RhCu(CO)(PMe_3)(PPh_3)$-

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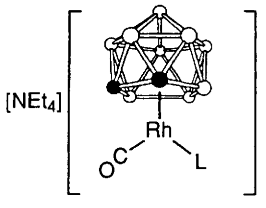
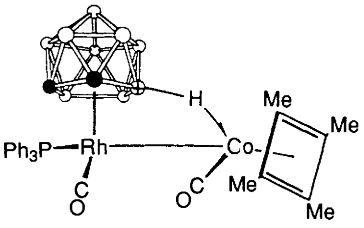
‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

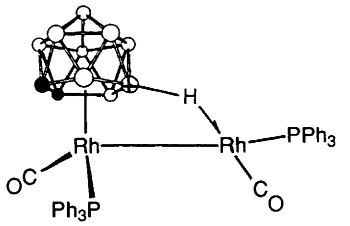


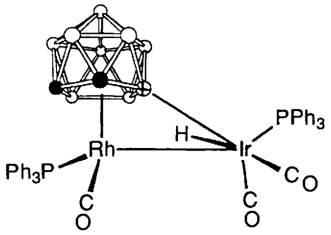
	●	L
1a	CH	PPh$_3$
1b	CMe	CO
1c	CMe	PPh$_3$



● CH ○ BH ⊕ B

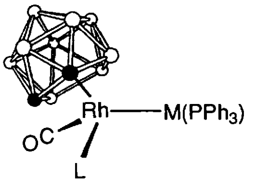
2



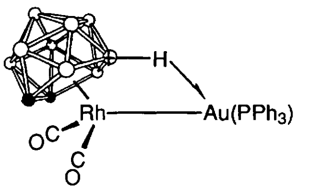


● CH ○ BH ⊕ B

3 **4**

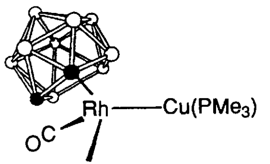


	●	M	L
5a	CH	Au	PPh$_3$
5b	CMe	Au	CO
5d	CMe	Cu	CO
5e	CMe	Cu	PPh$_3$
5g	CMe	Au	PPh$_3$



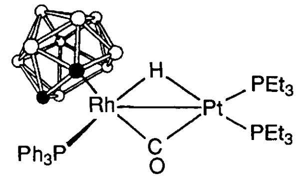
● CMe ○ BH ⊕ B

5c



5f

● CMe ○ BH



6

● CH ○ BH

(η^5-$C_2B_9H_9Me_2$)] **5f** was obtained from the reagent **1c** in CH_2Cl_2 and [CuCl(PMe$_3$)], in the presence of $TlBF_4$. The ^{31}P-{^1H} NMR data (Table 2) show the expected two resonances. However, the complex decomposes in solution, probably *via* dissociation of the PMe$_3$ group since the signals for this fragment in the ^1H and ^{13}C-{^1H} NMR spectra were very broad.

Treatment of compound **1c** with [AuCl(PPh$_3$)] and $TlBF_4$ in CH_2Cl_2 affords [RhAu(CO)(PPh$_3$)$_2$(η^5-$C_2B_9H_9Me_2$)] **5g**. In the IR spectrum of the latter the CO stretching band is at 1983 cm^{-1}, to be compared with that observed at 1998 cm^{-1} for the closely related compound **5a**.[4a] Unlike the species **5b**, which appears to exist in solution in equilibrium with an isomer **5c**,[4a] compound **5g** is present in solution as a single isomer. This is revealed by the nature of the ^{31}P-{^1H} NMR spectrum which displays the expected doublet resonance for the Rh(PPh$_3$) group at δ 43.9 [*J*(RhP) 150 Hz] and a singlet signal for the Au(PPh$_3$) fragment at δ 5.9. In contrast, the spectrum of [RhAu(CO)$_2$(PPh$_3$)(η^5-$C_2B_9H_9Me_2$)] **5b** displays two ^{31}P-{^1H} NMR signals for Au(PPh$_3$) groups in different environments, and the ^{11}B-{^1H} NMR spectrum showed a peak indicating the presence of a B–H→Au group, as required for structure **5c**. The ^{11}B-{^1H} NMR spectrum of compound **5g**, however, showed no such signal, only broad unresolved resonances in the range δ −4.6 to −15.0, which are typical for a complex in which the carbaborane cage does not form an exopolyhedral B–H→M bond.

Hawthorne and co-workers[6] have reported the synthesis of

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

Compound		Colour	Yield (%)	ν_{max}(CO)[b]/cm^{-1}	Analysis (%)	
					C	H
1c	$[NEt_4][Rh(CO)(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Orange	60	1924vs,	50.0 (49.9)[c,d]	7.0 (6.8)
5d	$[RhCu(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Yellow	40	2049vs, 1995vs	43.6 (44.5)	3.3 (4.2)
5e	$[RhCu(CO)(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$	Yellow	55	1970vs	55.5 (55.9)	5.3 (5.2)
5f	$[RhCu(CO)(PMe_3)(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Yellow	34	1965vs	45.3 (45.1)	6.9 (5.9)
5g	$[RhAu(CO)(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$	Yellow	69	1983vs	48.0 (48.9)	4.5 (4.4)
7	$[RhH(CO)(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$	Yellow	72	2047vs	51.3 (52.7)	7.0 (6.0)
8	$[Rh_2(CO)_3(\eta^5\text{-}C_2B_9H_9Me_2)_2]$	Purple	37	2072vs, 2051s	21.0 (21.6)	6.0 (5.1)
9	$[NEt_4][Rh_2(\mu\text{-}\sigma{:}\eta^5\text{-}C_2B_9H_8Me_2)(CO)_3(\eta^5\text{-}C_2B_9H_9Me_2)]$	Red	41	2046vs, 2004vs	29.0 (30.0)[e]	5.6 (6.6)

[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2; medium to weak broad bands observed at *ca.* 2560 cm^{-1} are due to B–H absorptions. [c] Crystallises with one molecule of CH_2Cl_2. [d] N 1.7 (1.8%). [e] N 2.1 (1.9%).

Table 2 Hydrogen-1, carbon-13 and phosphorus-31 NMR data[a] for the complexes

Compound	^{1}H(δ)	^{13}C[b](δ)	^{31}P[c](δ)
1c	1.24 [t, 12 H, CH$_2$*Me*, *J*(HH) 7], 1.96 (s, 6 H, CMe), 3.16 [q, 8 H, C*H*$_2$Me, *J*(HH) 7], 7.32–7.77 (m, 15 H, Ph)	192.1 [d of d, CO, *J*(RhC) 79, *J*(PC) 24], 138.8–126.8 (Ph), 75.3 (*C*Me), 54.6 (*C*H$_2$Me), 28.9 (C*Me*), 7.1 (CH$_2$*Me*)	45.3 [d, *J*(RhP) 184]
5d	2.30 (s, 6 H, CMe), 7.43–7.48 (m, 15 H, Ph)	184.2 [d, CO, *J*(RhC) 73], 132.0–126.2 (Ph), 88.7 (*C*Me), 29.1 (C*Me*)	5.9 (s, PCu)
5e	2.29 (s, 6 H, CMe), 7.00–7.30 (m, 30 H, Ph)	188.5 [d of d, CO, *J*(RhC) 72, *J*(PC) 21], 135.4–127.6 (Ph), 67.5 (*C*Me), 25.3 (C*Me*)	45.2 [d, PRh, *J*(RhP) 166], 3.9 (s, PCu)
5f	1.10–2.30 (m, br, 15 H, CMe and MeP), 7.11–7.63 (m, 15 H, Ph)	189.0 [d of d, CO, *J*(RhC) 73, *J*(PC) 19], 134.8–128.2 (Ph), 61.9 (*C*Me), 33.0–30.0 (vbr, MeP and C*Me*)	45.2 [d, PRh, *J*(RhP) 166], 3.9 (s, PCu)
5g	2.00 (s, 6 H, CMe), 7.40–7.56 (m, 30 H, Ph)	[d] 138.1–131.7 (Ph), 71.0 (*C*Me), 29.2 (C*Me*)	43.9 [d, PRh, *J*(RhP) 150], 5.9 (s, PAu)
7	−7.60 [d of d, 1 H, RhH, *J*(RhH) 24, *J*(PH) 24], 1.92, 2.18 (s × 2, 6 H, CMe), 7.36–7.59 (m, 15 H, Ph)	[d] 133.6–127.8 (Ph), 62.6, 62.2 (*C*Me), 27.8, 26.7 (C*Me*)	44.7 [d, PRh, *J*(RhP) 121]
8	−7.01 [q, 1 H, BHRh, *J*(BH) 70], 2.41, 2.55 (s × 2, 12 H, CMe)	[e] 183.8 [d, CO, *J*(RhC) 65] 72.8, 72.4, 70.2, 67.9 (*C*Me), 31.3, 29.8, 24.7, 24.1 (C*Me*)	
9	1.28 [t, 12 H, CH$_2$*Me*, *J*(HH) 7], 2.33, 2.48, 2.49, 2.60 (C*Me*)	189.8 [d, CO, *J*(RhC) 72], 67.0, 65.2, 63.7, 62.7 (*C*Me), 52.9 (*C*H$_2$Me), 30.4, 29.9, 28.9, 28.8 (C*Me*), 6.7 (CH$_2$*Me*)	

[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 $SiMe_4$. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of 85% H_3PO_4 (external). [d] CO signal not observed due to insolubility of complex. [e] Measured at −70 °C.

several hydridorhodium complexes of formulation $[RhH(PR_3)_2(\eta^5\text{-}C_2B_9H_{10}R')]$ (R = alkyl or aryl; R′ = H, alkyl or aryl). These species were prepared by treating $[RhCl(PPh_3)_3]$ with salts of the *nido*-anions $[C_2B_9H_{11}R']^-$ in refluxing ethanol. We attempted to prepare the related hydrido-complexes $[RhH(CO)L(\eta^5\text{-}C_2B_9H_9Me_2)]$ (L = CO or PPh$_3$) by protonating the salts **1b** and **1c**. Treatment of the latter with $HBF_4{\cdot}Et_2O$ gave the relatively unstable complex $[RhH(CO)(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **7**, the IR spectrum of which showed a single CO stretch at 2047 cm^{-1}. The ^{31}P-{^{1}H} NMR spectrum showed the expected doublet [*J*(RhP) 121 Hz] at δ 44.7. The ^{1}H NMR spectrum showed a high-field HRh signal at δ −7.6 [d of d, *J*(RhH) 24, *J*(PH) 24 Hz], and two resonances for the CMe groups (δ 1.92 and 2.18), as expected since the rhodium atom is a chiral centre.

An unexpected product was isolated on protonation of compound **1b**. Treatment of the latter in CH_2Cl_2 with $HBF_4{\cdot}Et_2O$ afforded a purple dirhodium compound $[Rh_2(CO)_3(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **8**, data for which are given in Tables 1 and 2. The structure proposed is strongly supported by the ^{1}H, ^{13}C-{^{1}H} and ^{11}B-{^{1}H} NMR spectra. The ^{1}H NMR spectrum measured at ambient temperatures shows a diagnostic high-field quartet resonance for a B–H$\rightharpoonup$Rh group at δ −7.01 [*J*(BH) 70 Hz]. Compound **3** shows in its ^{1}H NMR spectrum a similar signal at δ −5.8 [*J*(BH) 80 Hz].[4b] The presence of the B–H$\rightharpoonup$Rh group in **8** was confirmed by the appearance in the ^{11}B-{^{1}H} NMR spectrum of a peak at δ 22.6, with the remaining boron atoms of the cage displaying characteristic broad bands in the range δ −1.0 to −16.7. In a fully coupled ^{11}B NMR spectrum the B–H$\rightharpoonup$Rh resonance was a doublet [*J*(BH) 70 Hz], as expected. The ^{11}B NMR resonance for the B–H$\rightharpoonup$Rh group in the spectrum of compound **3** is seen at δ 18.7.

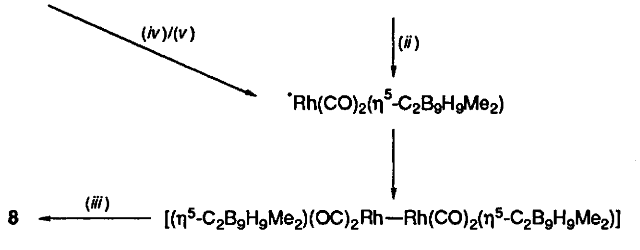
The ^{1}H and ^{13}C-{^{1}H} NMR data for compound **8** revealed that it underwent dynamic behaviour in solution. Thus the ^{13}C-{^{1}H} NMR spectrum measured at −70 °C showed only one doublet CO resonance at δ 183.8 [*J*(RhC) 65 Hz], indicating that the CO groups must undergo site exchange on the NMR time-scale even at −70 °C. Presumably this involves transient species with μ-CO groups. However, at −70 °C the expected four cage *C*Me resonances (δ 72.8, 72.4, 70.2 and 67.9) and four peaks for the C*Me* groups (δ 31.3, 29.8, 24.7 and 24.1) are observed. In the low-temperature (−70 °C) ^{1}H NMR spectrum only two CMe peaks are seen, rather than the four anticipated, but these signals are significantly broader than those seen in the room-temperature spectrum and probably represent overlap of near-coincident resonances.

The formation of complex **8** rather than the mononuclear rhodium compound $[RhH(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ is of interest. It seems likely that the hydrido species is formed initially, but is oxidised with loss of hydrogen, leading to dimerisation and subsequent release of a CO molecule upon formation of the B–H$\rightharpoonup$Rh bond (see Scheme 1). The hydrido species $[RhH(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ would be expected to be appreciably less stable than the bis(phosphine) species $[RhH(PR_3)_2(\eta^5\text{-}$

$C_2B_9H_{10}R')$],[6] mentioned above, in line with the general trend that CO ligands stabilise metal–hydrogen bonds in complexes less effectively than do PR_3 groups. It is interesting that [$RhH(CO)_2(\eta^5-C_2B_9H_9Me_2)$] is isolobally mapped with [$FeH(CO)_2(\eta-C_5H_5)$] which is also unstable.

We also observed that compound **8** is formed if the salt **1b** in CH_2Cl_2 is treated with either $AgBF_4$ or CF_3SO_3Me. The latter reagent was used in an attempt to isolate a methyl complex [$RhMe(CO)_2(\eta^5-C_2B_9H_9Me_2)$], but this species is evidently unstable also. If it decomposed oxidatively, or *via* homolytic fission of the Rh–Me bond, the formation of **8** is understandable, although other pathways could also lead to the dirhodium compound. Formation of the latter upon treatment of **1b** with $AgBF_4$ is readily understood as a process involving oxidation of the anion, metallic silver being observed as a product.

Treatment of compound **1b** in CH_2Cl_2 with [$NHMe_3$]Cl yields the salt [NEt_4][$Rh_2(\mu-\sigma:\eta^5-C_2B_9H_8Me_2)(CO)_3(\eta^5-C_2B_9H_9Me_2)$] **9**. This reaction occurs slowly over a period of *ca.* 1–2 d at ambient temperatures, proceeding through the intermediacy of compound **8**. The latter on treatment with NMe_3 affords the anion of **9** as the [$NHMe_3$]$^+$ salt, in a reaction which is complete in *ca.* 30 min at room temperature. Evidently in the synthesis of the salt **9** from the reagents **1b** and [$NHMe_3$]Cl the latter acts as a source of HCl for protonation, and once complex **8** is formed the NMe_3 present deprotonates the B–H⇀Rh bridge, a process which has precedent in a tungsten–ruthenium system.[7] Interestingly, treatment of complex **9** with $HBF_4 \cdot Et_2O$ at −78 °C, followed by slowly warming to room temperature, yields compound **8**, showing that deprotonation of the latter is readily reversed.



Scheme 1 (*i*) + HBF_4; (*ii*) $-H_2$; (*iii*) −CO; (*iv*) $AgBF_4$; (*v*) −Ag, −[NEt_4][BF_4]

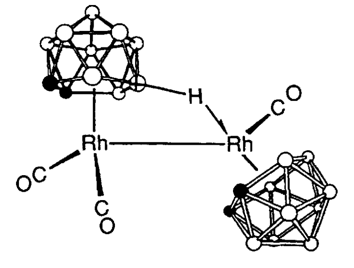
Formation of the salt **9** was observed in several reactions of the reagent **1b**, and it is evidently a thermodynamically favoured product. Thus in attempts to obtain mixed-metal complexes from compound **1b** we treated the latter with [$CuCl(PMe_3)$], [$MBr(CO)_5$] (M = Mn or Re) and [$RuCl(PPh_3)_2(\eta-C_5H_5)$], respectively, in the presence of $TlBF_4$. In all these reactions no metal–metal bonded species were produced although compound **9** was formed. Evidently, the anion [$Rh(CO)_2(\eta^5-C_2B_9H_9Me_2)$]$^-$ is readily oxidised (see Scheme 1) giving complex **8**, which is then deprotonated under basic conditions, yielding **9**.

The structure of the salt **9** was unambiguously established by an X-ray diffraction study, even though the crystal diffracted poorly. The structure of the anion is shown in Fig. 1, and important parameters are listed in Table 3. The Rh(1)–Rh(2) distance [2.876(3) Å] is appreciably longer than the metal–metal bond in complex **3** [2.692(3) Å], but is comparable with that in [$Rh_2(PPh_3)_2(\eta^5-C_2B_9H_{11})_2$] **10** [2.763(1) Å].[8] The latter species contains two B–H⇀Rh bridge bonds, and is formed in a variety of reactions including oxidation of the hydrido complex [$RhH(PPh_3)_2(\eta^5-C_2B_9H_{11})$]. This is analogous to the formation of compound **8** by oxidising the salt **1b** with $AgBF_4$, mentioned above.

In compound **9** the B(4) atom bridges the Rh–Rh bond [Rh(1)–B(4) 2.15(3), Rh(2)–B(4) 2.05(3) Å]. This boron atom is in the β site with respect to the carbon atoms in the open pentagonal face of the cage η^5 co-ordinated to Rh(1). Exo-polyhedral B–H⇀M or B–M bridge bonds may involve boron atoms in either the α or the β sites with respect to the carbons in the $\overline{CCBBB}$ open face of the C_2B_9 cages, as demonstrated by the structure of compounds **2**–**4**[4b] and many other dimetal species.[1] Interestingly, in complex **10** the isomer identified crystallographically has one B^{α}–H⇀Rh linkage and one B^{β}–H⇀Rh bond.[8]

In the anion of **9**, Rh(1) carries two terminal carbonyl groups and Rh(2) has one such ligand. The atom Rh(2) is also ligated by a $C_2B_9H_9Me_2$ cage which is co-ordinated in the usual η^5 manner.

The NMR data for compound **9** are in accord with the structure established by X-ray diffraction, apart from evidence of site exchange of the CO ligands in solution. The ^1H NMR



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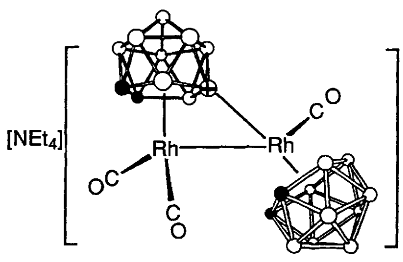
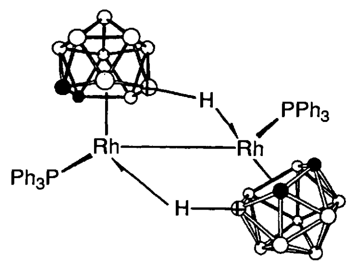


9

● CMe ○ BH ⊕ B



10

● CH ○ BH ⊕ B

Table 3 Selected internuclear distances (Å) and angles (°) for $[NEt_4][Rh_2(\mu\text{-}\sigma:\eta^5\text{-}C_2B_9H_8Me_2)(CO)_3(\eta^5\text{-}C_2B_9H_9Me_2)]$ **9**

Rh(1)–Rh(2)	2.876(3)	Rh(1)–C(3)	1.89(3)	Rh(1)–C(4)	1.87(3)	Rh(1)–C(1)	2.44(2)
Rh(1)–C(2)	2.34(3)	Rh(1)–B(3)	2.21(3)	Rh(1)–B(4)	2.15(3)	Rh(1)–B(5)	2.23(3)
Rh(2)–C(5)	1.81(3)	Rh(2)–B(4)	2.05(3)	Rh(2)–C(1′)	2.35(3)	Rh(2)–C(2′)	2.21(4)
Rh(2)–B(3′)	2.23(4)	Rh(2)–B(4′)	2.20(4)	Rh(2)–B(5′)	2.27(4)	C(3)–O(3)	1.15(4)
C(4)–O(4)	1.12(3)	C(5)–O(5)	1.16(3)	C(1)–C(2)	1.59(3)	C(1)–B(5)	1.80(4)
C(2)–B(3)	1.74(4)	B(3)–B(4)	1.80(4)	B(4)–B(5)	1.84(4)	C(1′)–C(2′)	1.56(5)
C(1′)–B(5′)	1.65(5)	C(2′)–B(3′)	1.72(6)	B(3′)–B(4′)	1.79(5)	B(4′)–B(5′)	1.81(5)
Rh(2)–Rh(1)–C(3)	107(1)	Rh(2)–Rh(1)–C(4)	89(1)	C(3)–Rh(1)–C(4)	89(1)	Rh(2)–Rh(1)–B(4)	45.3(7)
Rh(1)–Rh(2)–C(5)	95(1)	Rh(1)–Rh(2)–B(4)	48.2(7)	Rh(1)–C(3)–O(3)	175(3)	Rh(1)–C(4)–O(4)	172(3)
Rh(2)–C(5)–O(5)	175(3)						

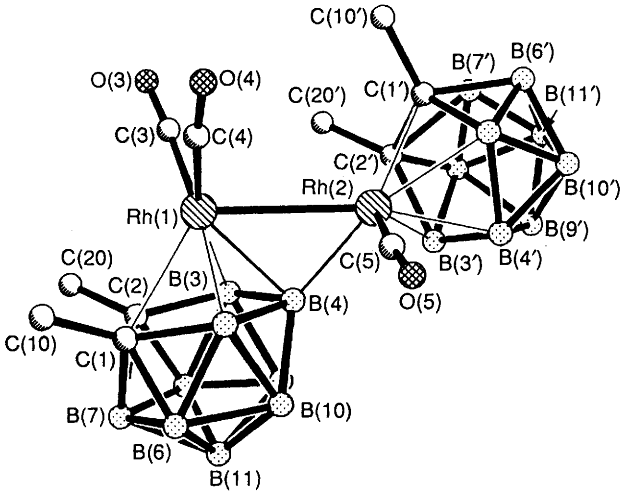


Fig. 1 The structure of the anion $[Rh_2(\mu\text{-}\sigma:\eta^5\text{-}C_2B_9H_8Me_2)(CO)_3(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ of complex **9** showing the crystallographic labelling scheme

spectrum shows peaks at δ 2.33, 2.48, 2.49 and 2.60, relative intensity 1:1:1:1, in accord with the presence of four non-equivalent cage CMe groups. In agreement, the $^{13}C\text{-}\{^1H\}$ NMR spectrum displays four *C*Me and four C*Me* resonances (Table 2). Only one CO signal at δ 189.8 [*J*(RhC) 72 Hz] is seen, and so the three CO ligands must exchange rapidly as they do for complex **8** in solution. The presence of the B(4)–Rh exopolyhedral σ bond is unequivocally established by the appearance of a highly deshielded singlet resonance for one boron nucleus at δ 45.5 in the ^{11}B NMR spectrum. The remaining borons giving rise to broad peaks in the range δ −0.3 to −18.0. The B–Ir exopolyhedral σ bond in complex **4** gives rise to a $^{11}B\text{-}\{^1H\}$ resonance at δ 35.6,[4b] and for $[N(PPh_3)_2][WRu(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}\sigma:\eta^5\text{-}C_2B_9H_8Me_2)(CO)_3(\eta\text{-}C_5H_5)]$, which has a Ru–B bond, the corresponding signal is at δ 45.9.[7]

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 atmosphere. Alumina (Brockman activity II) was used for chromatography (2 × 15 cm columns). The reagents **1b**,[4a] $Tl_2[7,8\text{-}C_2B_9H_9Me_2]$[5] and $[RhCl(CO)(PPh_3)_2]$[9] were prepared as described previously. The reagent $HBF_4\cdot Et_2O$ consisted of a 54% solution of HBF_4 in Et_2O. The instrumentation used for the spectroscopic measurements was reported earlier.[4] The $^{11}B\text{-}\{^1H\}$ NMR spectra were measured in CD_2Cl_2, and chemical shifts are positive to high frequency of $BF_3\cdot Et_2O$ (external). Analytical and other data for new compounds are listed in Table 1.

Synthesis of the Salt $[NEt_4][Rh(CO)(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$.—A thf (40 cm^3) solution of $[RhCl(CO)(PPh_3)_2]$ (2.0 g, 2.9 mmol) was treated with $Tl_2[7,8\text{-}C_2B_9H_9Me_2]$ (1.65 g, 2.9 mmol), and the mixture was stirred for 20 min at room temperature. The salt $[NEt_4]Cl$ (0.58 g, 3.50 mmol) was added, and stirring was continued for 30 min, after which the mixture was filtered through a Celite pad (*ca.* 4 cm). Solvent was removed *in vacuo*, and the residue was crystallised from $CH_2Cl_2\text{–}Et_2O$ (10 cm^3, 1:4) to give orange *microcrystals* of $[NEt_4][Rh(CO)(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **1c** (1.18 g).

Synthesis of the Complex $[RhH(CO)(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$.—A CH_2Cl_2 (20 cm^3) solution of compound **1c** (0.20 g, 0.29 mmol) was treated with $HBF_4\cdot Et_2O$ (*ca.* 0.58 mmol) at −78 °C, and the mixture was stirred for 15 min, before warming slowly to room temperature. Stirring was continued for 10 min, after which solvent was removed *in vacuo*. The residue was washed (5 × 5 cm^3) with light petroleum and recrystallised from CH_2Cl_2–light petroleum (1:4) to afford $[RhH(CO)(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **7** (0.11 g).

Preparation of the Complexes with Rhodium–Copper and –Gold Bonds.—(*i*) A mixture of compound **1b** (0.20 g, 0.41 mmol), $[CuCl(PPh_3)]$ (0.15 g, 0.42 mmol) and $TlBF_4$ (0.18 g, 0.62 mmol) was stirred in CH_2Cl_2 (20 cm^3) for 1 h. The resulting suspension was filtered through a Celite pad (*ca.* 3 cm), and solvent was removed *in vacuo* from the filtrate. The residue was dissolved in CH_2Cl_2 (3 cm^3), and chromatographed on alumina. Elution with CH_2Cl_2–light petroleum (1:1) gave a yellow fraction, which after removal of solvent *in vacuo* gave yellow *microcrystals* of $[RhCu(CO)_2(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **5d** (0.11 g).

(*ii*) A mixture of compound **1c** (0.20 g, 0.29 mmol), $[CuCl(PPh_3)]$ (0.10 g, 0.28 mmol) and $TlBF_4$ (0.18 g, 0.62 mmol) in CH_2Cl_2 (20 cm^3) was stirred for 45 min. The mixture was then worked up as described for complex **5d** to afford yellow *microcrystals* of $[RhCu(CO)(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **5e** (0.19 g).

(*iii*) Using a similar procedure, the reagents **1c** (0.20 g, 0.29 mmol), $[CuCl(PMe_3)]$ (0.05 g, 0.28 mmol) and $TlBF_4$ (0.18 g, 0.62 mmol) gave yellow *microcrystals* of $[RhCu(CO)(PMe_3)(PPh_3)(\eta^5\text{-}C_2B_9H_9Me_2)]$ **5f** (0.067 g).

(*iv*) The salt **1c** (0.20 g, 0.29 mmol) in CH_2Cl_2 (20 cm^3) was treated with $[AuCl(PPh_3)]$ (0.14 g, 0.28 mmol) and $TlBF_4$ (0.18 g, 0.62 mmol). After stirring the mixture for 1 h it was filtered through a Celite pad (*ca.* 3 cm). Solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2 (3 cm^3) and chromatographed. Elution with CH_2Cl_2–light petroleum (1:2) followed by removal of solvent *in vacuo* from the yellow eluate yielded *microcrystals* of $[RhAu(CO)(PPh_3)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **5g** (0.14 g).

Synthesis of the Dirhodium Complexes.—(*i*) A CH_2Cl_2 (20 cm^3) solution of the salt **1b** (0.20 g, 0.41 mmol) was treated with $HBF_4\cdot Et_2O$ (0.82 mmol) at −78 °C. After warming the solution to room temperature, stirring was continued until an IR spectrum showed that the reaction was complete. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (5

Table 4 Atomic positional parameters (fractional coordinates, × 10^4) with estimated standard deviations in parentheses for complex **9**

Atom	x	y	z	Atom	x	y	z
Rh(1)	375(1)	3840(1)	3188(1)	C(10′)	−250(29)	1883(20)	2361(11)
Rh(2)	639(1)	2378(1)	3389(1)	C(2′)	−892(27)	1973(21)	3345(15)
C(3)	−791(22)	3917(20)	2810(12)	C(20′)	−1669(10)	2483(19)	3136(15)
O(3)	−1458(16)	4000(18)	2558(11)	B(3′)	−344(29)	1797(20)	3896(14)
C(4)	1097(17)	3719(17)	2615(9)	B(4′)	759(26)	1340(19)	3729(13)
O(4)	1479(15)	3577(15)	2268(8)	B(5′)	720(25)	1285(19)	3073(13)
C(5)	1980(20)	2416(15)	3392(10)	B(6′)	−266(40)	745(28)	2954(19)
O(5)	2840(14)	2389(12)	3410(9)	B(7′)	−1218(38)	1097(20)	3092(20)
C(1)	1142(16)	4714(13)	3713(9)	B(8′)	−1392(33)	1318(21)	3639(16)
C(10)	1521(18)	5310(14)	3378(9)	B(9′)	−319(27)	875(18)	3943(12)
C(2)	−7(16)	4607(14)	3823(10)	B(10′)	396(28)	585(21)	3454(14)
C(20)	−761(19)	5147(15)	3656(10)	B(11′)	−945(25)	524(19)	3463(14)
B(3)	−375(18)	3745(14)	3898(10)	N	3747(13)	8365(10)	508(7)
B(4)	745(18)	3244(14)	3822(10)	C(30)	3285(21)	9073(14)	578(10)
B(5)	1717(18)	3870(16)	3657(10)	C(40)	3353(23)	9569(17)	209(11)
B(6)	1864(19)	4473(15)	4167(10)	C(50)	4839(18)	8419(15)	393(9)
B(7)	784(18)	4949(17)	4279(10)	C(60)	5448(26)	8733(18)	789(13)
B(8)	−174(20)	4341(16)	4407(10)	C(70)	3323(19)	8005(15)	72(10)
B(9)	345(19)	3489(14)	4419(9)	C(80)	2204(22)	7982(17)	40(12)
B(10)	1619(19)	3576(17)	4261(10)	C(90)	3551(22)	7956(15)	929(10)
B(11)	1064(19)	4192(13)	4621(8)	C(100)	4022(30)	7252(21)	914(15)
C(1′)	−339(26)	1645(18)	2904(11)				

cm^3) and chromatographed at −40 °C. Elution with CH_2Cl_2–light petroleum (1:2) gave a purple fraction. Removal of solvent *in vacuo* and crystallisation from CH_2Cl_2–light petroleum (1:4) afforded purple *microcrystals* of $[Rh_2(CO)_3(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ **8** (0.092 g).

(*ii*) A CH_2Cl_2 (20 cm^3) solution of compound **1b** (0.20 g, 0.41 mmol) was treated with $[NHMe_3]Cl$ (0.02 g, 0.20 mmol), and the mixture was stirred for 36 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (4 cm^3) and chromatographed, eluting with the same solvent. Removal of solvent *in vacuo* and crystallisation of the residue from CH_2Cl_2–light petroleum (1:4) gave red *microcrystals* of $[NEt_4][Rh_2(\mu\text{-}\sigma:\eta^5\text{-}C_2B_9H_8Me_2)(CO)_3(\eta^5\text{-}C_2B_9H_9Me_2)]$ **9** (0.12 g).

Crystal-structure Determination.—Crystals of compound **9** were grown from CH_2Cl_2–light petroleum as dark red prisms. A crystal of dimensions *ca.* 0.25 × 0.20 × 0.20 mm was sealed under nitrogen in a glass capillary tube. Diffracted intensities were measured (θ–2θ scans) at 298 K in the range $3 \leqslant 2\theta \leqslant 50°$ on a Siemens R3m/V four-circle diffractometer. Of 5776 unique data, measured at 298 K, 2103 had $F \geqslant 4\sigma(F)$, and only these were used in the solution and refinement of the structure, after corrections for Lorentz, polarisation and X-ray absorption effects. The latter was by an empirical method using azimuthal scan data.[10]

Crystal data. $C_{19}H_{49}B_{18}NO_3Rh_2$, $M = 740.0$, orthorhombic, space group *Pbca*, $a = 13.502(2)$, $b = 19.148(4)$, $c = 27.588(5)$ Å, $U = 7133(3)$ Å^3, $Z = 8$, $D_c = 1.38$ g cm^{-3}, $F(000) = 2736$, Mo-Kα X-radiation, graphite monochromator, $\bar{\lambda} = 0.710\ 73$ Å, μ(Mo-Kα) = 9.3 cm^{-1}.

The structure was solved by heavy-atom methods and successive Fourier difference syntheses were used to locate all non-hydrogen atoms. Because of the poor quality and weak data only the metal, CO, C(1) to B(11), C(10) and C(20) atoms were refined anisotropically. The hydrogen atoms were included in calculated positions (C–H 0.96, B–H 1.10 Å) using BHGEN[11] with fixed isotropic parameters [C*H*, $U_{iso} = 0.08$ Å^2; B*H*, $U_{iso} = 1.2\ U_{iso}$(B)]. Refinement was by full-matrix least-squares techniques on a DEC micro-Vax II computer with the SHELXTL PLUS system of programs,[10] and converged at $R = 0.091$ ($R' = 0.088$), with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0015|F|^2]$ giving a satisfactory analysis of variance. The final electron-density difference map showed no peaks $\geqslant 1.19$ or $\leqslant -0.70$ e Å^{-3}.

Scattering factors with corrections for anomalous dispersion were taken from ref. 12. Atomic 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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