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(Carbaborane)rhodium–copper and –manganese complexes: crystal structure of [RhCu(PPh_3)(cod)(η^5-7,8-$C_2B_9H_9Me_2$)] *

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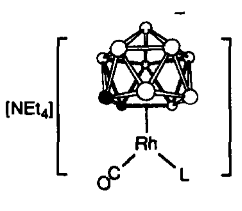
Abstract

Treatment of [CuCl(PPh_3)] with [NEt_4][Rh(cod)(η^5-7,8-$C_2B_9H_9Me_2$)] (cod = cyclo-octa-1,5-diene) in CH_2Cl_2 in the presence of $TlBF_4$ affords the dimetal compound [RhCu(PPh_3)(cod)(η^5-7,8-$C_2B_9H_9Me_2$)], the structure of which has been established by X-ray diffraction (Rh–Cu 2.633(2) Å, Rh–Cu–P 153.3(1)°). Reactions between [$MnBr(CO)_5$] and the tetraethylammonium salts of the complexes [Rh(CO)(PPh_3)(η^5-7,8-$C_2B_9H_9Me_2$)]$^-$ and [Rh(cod)(η^5-7,8-$C_2B_9H_9Me_2$)]$^-$ yield the dimetal compounds [$MnRh(CO)_5$(L)(η^5-7,8-$C_2B_9H_9Me_2$)] (L = PPh_3 or CO) respectively. Treatment of [$Mn(CO)_2$(NO)(η^5-C_5H_4Me)][BF_4] with [NEt_4][Rh(CO)(PPh_3)(η^5-7,8-$C_2B_9H_9Me_2$)] affords [Rh(NO)(PPh_3)(η^5-7,8-$C_2B_9H_9Me_2$)], in an unusual reaction involving transfer of the NO ligand from manganese to rhodium.

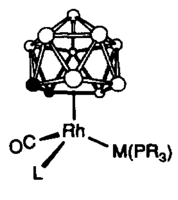
1. Introduction

In earlier papers we described several heteropolynuclear metal complexes in which rhodium is bonded to rhenium [1a], cobalt [1b], iridium [1b], platinum [1c,d], copper [1e] and gold [1e–g]. These compounds were obtained by employing the (carbaborane)rhodium salts [NEt_4][Rh(CO)(L)(η^5-7,8-$C_2B_9H_9R_2$)] (**Ia**, L = PPh_3, R = H; **Ib**, L = CO, R = Me; **Ic**, L = PPh_3, R = Me) or [NEt_4][Rh(CO)(PPh_3)(η^5-7,9-$C_2B_9H_{11}$)] **Id** as precursors. Products with Rh–Au bonds were particularly well studied. They include not only the dimetal compounds [RhAu(CO)(L)(PPh_3)(η^5-7,8-$C_2B_9H_9R_2'$)] (**IIa**, L = PPh_3, R′ = H; **IIb**, L = PPh_3, R′ = Me; **IIc**, L = CO, R′ = Me) obtained by treating the reagents **I** with [AuCl(PPh_3)] [1e,f], but also more complex molecules such as the species [Rh_2Au_2{μ-$Ph_2P(CH_2)_nPPh_2$}$(CO)_2(PPh_3)_2$(η^5-7,9-$C_2B_9H_{11})_2$] (**III**, n = 2–6) [1g] and [WRh_2Au_2(μ_3-CC_6H_4Me-4)$(CO)_6$(η-C_5H_5)(η^5-7,8-$C_2B_9H_9Me_2)_2$] (**IV**) [1f], prepared from the salt **Id** and [Au_2Cl_2{μ-$Ph_2P(CH_2)_nPPh_2$}] (n = 2–6), and from **Ib** and [WAuCl(μ-CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)] respectively.

Related to the rhodium–gold compounds **IIa–IIc**, are the rhodium–copper complexes **IId–IIf**, prepared by treating [CuCl(PR_3)] (R = Ph or Me) with the salts **Ib** or **Ic** [1e]. In this paper we report the synthesis and crystal structure of the complex [RhCu(PPh_3)(cod)(η^5-7,8-$C_2B_9H_9Me_2$)] (**V**), as well as the preparation of the manganese-rhodium complexes [$MnRh(CO)_5$(L)(η^5-7,8-$C_2B_9H_9Me_2$)] (**VIa**, L = PPh_3; **VIb**, L = CO) and



	L	●
Ia	PPh_3	CH
Ib	CO	CMe
Ic	PPh_3	CMe



	M	L	R	●
IIa	Au	PPh_3	Ph	CH
IIb	Au	PPh_3	Ph	CMe
IIc	Au	CO	Ph	CMe
IId	Cu	PPh_3	Ph	CMe
IIe	Cu	CO	Ph	CMe
IIf	Cu	PPh_3	Me	CMe

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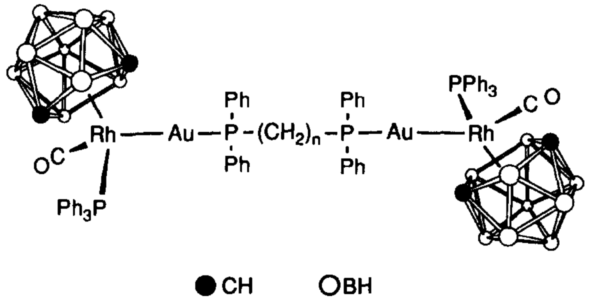
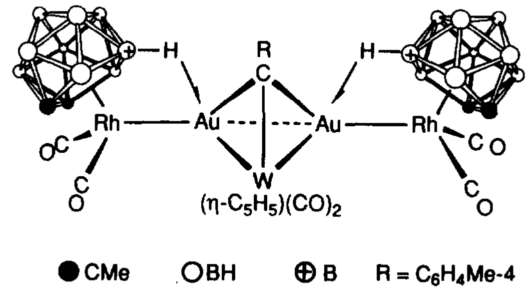


III n = 2 - 6



IV

the nitrosyl(carbaborane)rhodium species $[Rh(NO)(PPh_3)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (**VII**).

2. Results and discussion

Treatment of the reagent $[NEt_4][Rh(cod)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (cod = cycloocta-1,5-diene) [2] with $[CuCl(PPh_3)]$ in CH_2Cl_2, in the presence of $TlBF_4$ to remove chloride as insoluble TlCl, affords the yellow complex **V**, data for which are given in Tables 1–3. Discussion of the spectroscopic properties is deferred until the results of the X-ray diffraction study are given.

The molecular structure is shown in Fig. 1, and selected structural parameters are listed in Table 4. As expected, there is a Rh–Cu bond [2.633(2) Å], and the rhodium atom is ligated by the cod group and by the *nido*-$7,8\text{-}C_2B_9H_9Me_2$ cage in the usual pentahapto manner. The crystal diffracted poorly, and consequently the cage hydrogen atoms were not located. However, there is indirect evidence that in the crystal the H atom bonded to B(4) forms a three-centre two-electron B–H ⇀ Cu bond. Thus the B(4)–Cu separation [2.107(12) Å] is shorter than the B(4)–Rh [2.277(9) Å] distance, which in turn is longer than the B(3)–Rh [2.215(11) Å] or B(5)–Rh [2.262(10) Å] connectivities. Moreover the short B(4)–Cu separation may be compared with the data obtained by X-ray crystallography for $[NEt_4][W_2Cu(\mu\text{-}CC{\equiv}C^tBu)_2(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)_2]$. In the latter, one cage ligand forms an exopolyhedral B–H ⇀ Cu bond, while the other does not [3]. In this ditungsten–copper species the B–Cu separation in the B–H ⇀ Cu unit is 2.33(1) Å, to be compared with the appreciably shorter distance of 2.107(12) Å in **V**. It is also noteworthy that in **V** the Rh–Cu–P angle [153.3(1)°] deviates very appreciably from 180°, the value to be expected if there were no B–H ⇀ Cu interaction. Thus **V** has formulation **Va** in the crystal, rather than **Vb** in which the cage adopts a spectator role. The atom B(4) (Fig. 1) in the open pentagonal C_2B_3 face of the *nido*-C_2B_9 cage ligating the rhodium, is in the β site with respect to the two carbons. Dimetal complexes in which one metal centre carries an $\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2$ ligand frequently display slippage of the cage resulting from formation of an exopolyhedral B–H ⇀ M bond to the second metal atom [4]. This linkage generally involves the boron atom β to the two carbons in the C_2B_3 face unless this site carries an alkyl substituent.

Although there is persuasive evidence that in the solid state the rhodium-copper complex **V** has a B–H ⇀ Cu linkage, in solution neither the ^1H nor the $^{11}B\text{-}\{^1H\}$ NMR spectra indicate the presence of such a bond. In the ^1H NMR spectrum (Table 2) there is no high field quartet signal in the range *ca.* δ −4.0 to −10.0, diagnostic for a B–H ⇀ metal linkage [1f]. Similarly, the $^{11}B\text{-}\{^1H\}$ NMR spectrum did not display a resonance for a single boron nucleus at *ca.* δ 10–30, a

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

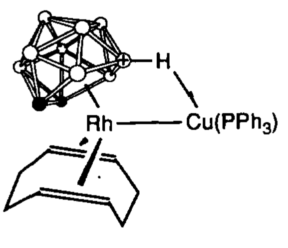
Compound		Colour	Yield (%)	$\nu_{max}(CO)$ [b] (cm^{-1})	Analysis (%)	
					C	H
V	$[RhCu(PPh_3)(cod)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$	Yellow	52		52.0 (51.6)	6.4 (6.0)
VIa	$[MnRh(CO)_5(PPh_3)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$	Red	47	2099s, 2060s, 2035vs, 2010vs, 1974m	44.0 (44.9)	4.7 (4.1)
VIb	$[MnRh(CO)_6(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$	Red	38	2098s, 2060s, 2036vs, 2010vs, 1974m	23.9 (24.6)	2.8 (3.0)
VII	$[Rh(NO)(PPh_3)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$	Yellow	59	1767s [c]	47.5 (47.5)	6.2 (5.4)

[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] $\nu_{max}(NO)$.

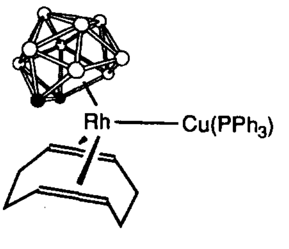
TABLE 2. ^{1}H and ^{13}C NMR data [a] for the complexes

Compound	^{1}H	^{13}C [b]
V	2.08 (s, 6 H, CMe), 2.30 (s, 8 H, CH_2 (cod)), 4.28 (s, 4 H, CH (cod)), 7.40–7.60 (m, 15 H, Ph)	133.5–128.2 (Ph), 80.6 (d, CH (cod), *J*(RhC) 10), 70.2 (*C*Me), 32.2 (CH_2 (cod)), 27.6 (C*Me*)
VIa [c]	−13.1 (q, 1 H, BHMn, *J*(BH) 80), −12.4* (br, 1 H, BHMn), 2.43 (s, 6 H, CMe), 2.14* (s, 6 H, CMe), 7.11–7.68 (m, 30 H, Ph)	217.1 (br, Mn(CO)), 191.7 (d of d, Rh(CO), *J*(PC) 26, *J*(RhC) 68), 135.7–128.2 (Ph), 69.5, 65.7*, 62.5* (*C*Me), 31.0*, 29.4, 28.1* (C*Me*)
VIb	−13.3 (q, 1 H, BHMn, *J*(BH) 85), 2.32 (s, 6 H, CMe)	184.9 (d, CO, *J*(RhC) 66), 71.7 (*C*Me), 30.9 (C*Me*)
VII	2.22 (s, 6 H, CMe), 7.20–7.60 (m, 15 H, Ph)	135.2–128.3 (Ph), 75.1 (*C*Me), 30.5 (C*Me*)

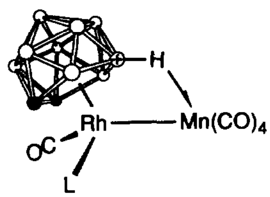
[a] Chemical shifts (δ) in ppm, coupling constants in hertz, measurements in CD_2Cl_2 at ambient temperatures. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$. [c] Peaks due to minor isomer asterisked (see text).



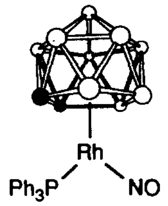
Va



Vb



	L
VIa	PPh3
VIb	CO



VII

feature also characteristic for a B–H → M group. Only the usual broad overlapping peaks for 9 B nuclei were seen in the range δ −11.5 to −17.6 (Table 3). There are two explanations for these observations. Either in solution the molecules of **V** do not possess an exo-polyhedral B–H → Cu bond, or the ^{1}H and ^{11}B-{^{1}H} NMR signals for the B–H → Cu linkages were too broad and weak to be observed. As mentioned above, the structure of $[NEt_4][W_2Cu(\mu\text{-}CC{\equiv}C^tBu)_2(CO)_4(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)_2]$ has been established by X-ray crystallography and the μ-H atom of the B–H → Cu bond located. Nevertheless, neither the ^{1}H nor the ^{11}B-{^{1}H} NMR spectra of the ditungsten–copper species reveals resonances for the B–H → Cu moiety [3]. The situation is further complicated by the distinct possibility that in solution **V** exhibits dynamic behaviour between the two isomers **Va** and **Vb**. There is some NMR evidence that the complex **IIc** in solution exists in equilibrium with an isomer with a B–H → Au bond of the kind identified by X-ray crystallography in **IV** [1f]. The ^{31}P-{^{1}H} NMR spectrum of **V** shows a singlet resonance (δ 5.3) for the $Cu(PPh_3)$ group as expected. In the spectrum of **IIe** the corresponding signal is seen at δ 5.9.

In an attempt to isolate species with Mn–Rh bonds, reactions between $[MnBr(CO)_5]$ and the reagents **Ic**

TABLE 3. ^{11}B and ^{31}P NMR data [a] for the complexes

Compound	^{11}B [b]	^{31}P [c]
V	−11.5 to −17.6 (br, 9 B)	5.3 (s)
VIa [d]	28.3, 28.6* (1 B, B-H-Mn), −3.2 to −17.4 (br, 8 B)	28.6 (d, *J*(RhP) 115), 28.2* (d, *J*(RhP) 135)
VIb	29.5 (1 B, B-H-Mn), −2.5 to −18.0 (br, 8 B)	
VII	−1.3 to −11.3 (br, 9 B)	39.4 (d, *J*(RhP) 172)

[a] Chemical shifts (δ) in ppm, coupling constants in hertz, measurements in CD_2Cl_2 at ambient temperatures. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $BF_3 \cdot Et_2O$ (external). [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of 85% H_3PO_4 (external). [d] Peaks asterisked are due to minor isomer (see text).

and $[NEt_4][Rh(cod)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$, in the presence of $TlBF_4$, were next investigated. Treatment of $[MnBr(CO)_5]$ with **Ic** in CH_2Cl_2 afforded $[MnRh(CO)_5(PPh_3)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (**VIa**), and the corresponding reaction of the manganese compound with $[NEt_4][Rh(cod)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ yielded $[MnRh(CO)_6(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (**VIb**). Data characterizing complexes **VIa** and **VIb** are given in Tables 1-3. Examination of the NMR spectra of **VIa** revealed that in solution it exists as a mixture of two isomers in the ratio 2:1, based on the observed relative peak intensities in the $^{31}P\text{-}\{^1H\}$ spectrum. The major isomer is assigned the structure shown with the carbaborane cage bridging the metal-metal linkage via an exo-polyhedral $B_\beta\text{-}H \rightharpoonup Mn$ bond. The minor isomer (not shown) is likely to involve bridge bonding involving a BH vertex α to the CMe groups in the open C_2B_3 face of the *nido*-icosahedral C_2B_9 cage. A similar equilibration between isomers with $B_\beta\text{-}H \rightharpoonup M$ and $B_\alpha\text{-}H \rightharpoonup M$ groups has been observed with (carbaborane)tungsten-iridium and -platinum compounds [5].

In agreement with the formulation of **VIa** as a mixture of two isomers, in the $^{31}P\text{-}\{^1H\}$ NMR spectrum (Table 3) there are two doublet resonances at δ 28.6 [J(RhP) 115] and 28.2 [J(RhP) 135] respectively, the former resonance having *ca.* twice the intensity of the latter. The $^{11}B\text{-}\{^1H\}$ NMR spectrum was also revealing, displaying a diagnostic peak for the $B\text{-}H \rightharpoonup Mn$ group of the major isomer at δ 28.3, and a signal for the minor isomer at δ 28.6. In the ^1H NMR spectrum (Table 2) characteristic peaks for the $B\text{-}H \rightharpoonup Mn$ groups occur for the major isomer as a quartet at δ -13.1 [J(BH) 80] and for the minor as a broad unresolved signal at δ -12.4.

TABLE 4. Selected internuclear distances (Å) and angles (deg) for $[RhCu(PPh_3)(cod)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (V)

Rh-Cu	2.633(2)	Rh-C(1)	2.319(8)	Rh-C(2)	2.342(9)	Rh-B(3)	2.215(11)
Rh-B(4)	2.277(9)	Rh-B(5)	2.262(10)	Rh-C(11)	2.166(11)	Rh-C(12)	2.208(11)
Rh-C(15)	2.151(9)	Rh-C(16)	2.169(10)	Cu-P	2.182(3)	Cu-B(4)	2.107(12)
Cu ··· B(5)	2.395(10)	C(1)-C(2)	1.602(13)	C(1)-C(3)	1.532(14)	C(1)-B(5)	1.761(15)
C(1)-B(6)	1.716(15)	C(1)-B(7)	1.783(15)	C(2)-C(4)	1.567(15)	C(2)-B(3)	1.724(15)
C(2)-B(7)	1.744(13)	C(2)-B(8)	1.671(16)	B(3)-B(4)	1.814(16)	B(3)-B(8)	1.782(16)
B(3)-B(9)	1.817(17)	B(4)-B(5)	1.796(15)	B(4)-B(9)	1.804(17)	B(4)-B(10)	1.807(15)
B(5)-B(6)	1.816(14)	B(5)-B(10)	1.820(17)	B(6)-B(7)	1.729(19)	B(6)-B(10)	1.752(18)
B(6)-B(11)	1.783(20)	B(7)-B(8)	1.758(17)	B(7)-B(11)	1.781(20)	B(8)-B(9)	1.797(17)
B(8)-B(11)	1.806(17)	B(9)-B(10)	1.774(17)	B(9)-B(11)	1.772(18)	B(10)-B(11)	1.734(17)
C(11)-C(12)	1.416(16)	C(11)-C(18)	1.533(18)	C(12)-C(13)	1.517(15)	C(13)-C(14)	1.535(17)
C(14)-C(15)	1.522(15)	C(15)-C(16)	1.394(16)	C(16)-C(17)	1.544(18)	C(17)-C(18)	1.525(19)

Cu-Rh-C(1)	103.1(2)	Cu-Rh-C(2)	123.9(2)	C(1)-Rh-C(2)	40.2(3)
Cu-Rh-B(3)	95.7(3)	C(1)-Rh-B(3)	74.0(4)	C(2)-Rh-B(3)	44.3(4)
Cu-Rh-B(4)	50.2(3)	C(1)-Rh-B(4)	76.6(3)	C(2)-Rh-B(4)	76.4(4)
B(3)-Rh-B(4)	47.6(4)	Cu-Rh-B(5)	58.0(3)	C(1)-Rh-B(5)	45.2(4)
C(2)-Rh-B(5)	74.1(3)	B(3)-Rh-B(5)	78.7(4)	B(4)-Rh-B(5)	46.6(4)
Cu-Rh-C(11)	106.6(3)	C(1)-Rh-C(11)	96.9(4)	C(2)-Rh-C(11)	116.4(4)
B(3)-Rh-C(11)	157.4(4)	B(4)-Rh-C(11)	151.6(4)	B(5)-Rh-C(11)	109.9(4)
Cu-Rh-C(12)	71.0(3)	C(1)-Rh-C(12)	116.7(4)	C(2)-Rh-C(12)	151.0(4)
B(3)-Rh-C(12)	164.0(4)	B(4)-Rh-C(12)	120.9(4)	B(5)-Rh-C(12)	100.3(4)
C(11)-Rh-C(12)	37.7(4)	Cu-Rh-C(15)	85.1(3)	C(1)-Rh-C(15)	162.6(4)
C(2)-Rh-C(15)	122.6(3)	B(3)-Rh-C(15)	90.1(4)	B(4)-Rh-C(15)	98.1(4)
B(5)-Rh-C(15)	139.5(4)	C(11)-Rh-C(15)	95.3(4)	C(12)-Rh-C(15)	80.4(4)
Cu-Rh-C(16)	122.3(3)	C(1)-Rh-C(16)	133.6(4)	C(2)-Rh-C(16)	100.0(4)
B(3)-Rh-C(16)	91.5(4)	B(4)-Rh-C(16)	124.8(4)	B(5)-Rh-C(16)	170.1(4)
C(11)-Rh-C(16)	79.8(5)	C(12)-Rh-C(16)	88.6(4)	C(15)-Rh-C(16)	37.7(4)
Rh-Cu-P	153.3(1)	Rh-Cu-B(4)	56.1(3)	P-Cu-B(4)	149.8(3)
Rh-Cu-B(5)	53.2(3)	P-Cu-B(5)	131.7(3)	B(4)-Cu-B(5)	46.5(4)
Cu-P-C(21)	116.3(3)	Cu-P-C(31)	111.3(2)	C(21)-P-C(31)	106.2(3)
Cu-P-C(41)	114.0(2)	C(21)-P-C(41)	105.7(3)	C(31)-P-C(41)	102.1(3)
Rh-B(4)-Cu	73.7(3)	Cu-B(4)-B(3)	133.5(6)	Cu-B(4)-B(5)	75.3(5)
Cu-B(4)-B(9)	165.6(7)	Cu-B(4)-B(10)	113.5(7)	Rh-B(5)-Cu	68.8(3)
Cu-B(5)-C(1)	137.8(6)	Cu-B(5)-B(4)	58.3(5)	Cu-B(5)-B(6)	158.6(8)
Cu-B(5)-B(10)	101.1(7)	C(12)-C(11)-C(18)	126.1(10)	C(11)-C(12)-C(13)	123.0(10)
C(12)-C(13)-C(14)	112.7(9)	C(13)-C(14)-C(15)	114.3(9)	C(14)-C(15)-C(16)	123.7(10)
C(15)-C(16)-C(17)	123.1(10)	C(16)-C(17)-C(18)	113.2(10)	C(11)-C(18)-C(17)	111.2(9)

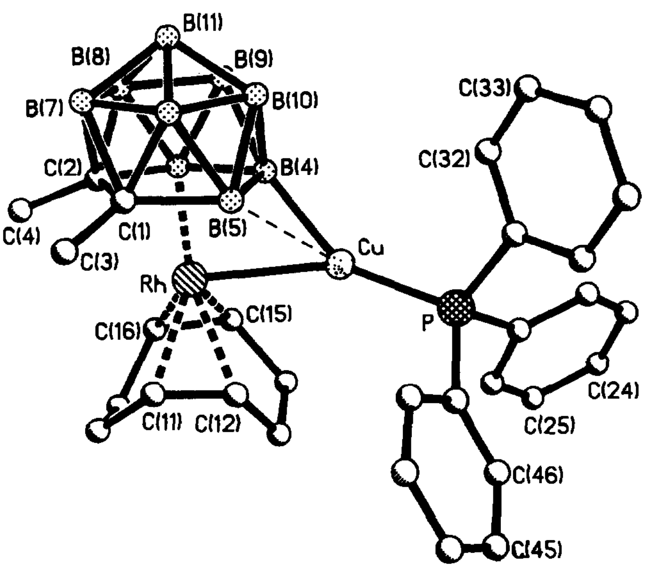


Fig. 1. Molecular structure of $[RhCu(PPh_3)(cod)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (V) showing the crystallographic numbering scheme.

The $^{13}C\text{-}\{^1H\}$ NMR spectrum was also informative (Table 2). A broad resonance for the $Mn(CO)_4$ group was observed at δ 217.1, indicating site-exchange among the four carbonyl groups at this metal centre at room temperature. The Rh(CO) group gives rise to a doublet-of-doublets at δ 191.7 [*J*(PC) 26, *J*(RhC) 68]. Evidently the CO peaks for the major and minor isomers overlap. In contrast, the signals for the cage CMe groups of both isomers are seen. The major isomer has resonances at δ 69.5 (*C*Me) and 29.4 (C*Me*), and the minor at δ 65.7 and 62.5 (*C*Me) and 31.0 and 28.1 (C*Me*). In principle the two CMe groups in both isomers should be chemically and magnetically inequivalent. The observation of only a single set of *C*Me and C*Me* resonances for the major isomer presumably results from fortuitous chemical shift equivalence.

Complex **VIb** was formed as a single isomer, as revealed by the absence of duplicate signals in the NMR spectra. Both the ^1H NMR spectrum, with a quartet signal at δ -13.3 [*J*(BH) 85], and the $^{11}B\text{-}\{^1H\}$ NMR spectrum, with a deshielded resonance for a single boron nucleus at δ 29.5, unequivocally establish the presence of the $B\text{-}H \rightarrow Mn$ bond. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum the resonance for the $Rh(CO)_2$ group was a doublet at δ 184.9 [*J*(RhC) 66]. No peak for the $Mn(CO)_4$ moiety was observed, and we attribute this to exchange of these CO groups on the NMR time-scale, and the broadening of carbonyl resonances when ligating manganese due to the quadrupolar effect of ^{55}Mn ($I = 5/2$). Diagnostic peaks due to the CMe groups were observed at δ 71.7 (*C*Me) and 30.9 (C*Me*). As expected, based on the formulation proposed for **VIb**, neither the ^1H nor the $^{13}C\text{-}\{^1H\}$ NMR spectra showed resonances attributable to a cod ligand. Evidently in the synthesis the cod group is displaced by two CO molecules scavenged presumably from $[MnBr(CO)_5]$.

The reaction between **Ic** and $[Mn(CO)_2(NO)(\eta\text{-}C_5H_4Me)][BF_4]$ was studied in the expectation that a dimetal compound $[MnRh(CO)(NO)(PPh_3)(\eta\text{-}C_5H_4Me)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ might be formed. Surprisingly, the mononuclear rhodium complex $[Rh(NO)(PPh_3)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (**VII**) was the product of this reaction, and data characterizing this species are given in Tables 1–3. Formation of **VII** involves transfer of the NO ligand from manganese to rhodium, probably via a dimetal complex with bridging NO and CO groups. The other product of this reaction would be $[Mn(CO)_3(\eta\text{-}C_5H_4Me)]$. Interestingly, a similar ligand transfer from manganese to rhodium occurs in the reaction between **Ia** and $[Mn(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_4Me)][BCl_4]$ which yields $[Rh\{\sigma,\eta^5\text{-}CH(C_6H_4Me\text{-}4)C_2B_9H_{10}\}(CO)(PPh_3)]$ [6]. In this process the alkylidyne group in the manganese precursor transfers to the rhodium with insertion into the $B_\beta H$ vertex in the C_2B_3 pentagonal ring of the carbaborane ligand, while also forming a σ bond with the rhodium.

3. Experimental details

All experiments were carried out under nitrogen by use of Schlenk tube techniques. Light petroleum refers to the fraction of b.p. 40–60°C. Products were separated by column chromatography on alumina (Brockmann activity II). Celite pads, used to remove TlCl or TlBr by filtration, were *ca.* 3 cm thick. IR measurements were made with a Perkin–Elmer 1600 Series FT instrument, and NMR spectra were recorded with JEOL GX270 and GX400 spectrometers. All NMR chemical shifts (δ) are in ppm and coupling constants are given in hertz. The reagents $[NEt_4][Rh(cod)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ [1a] and **Ic** [1e] were prepared by methods previously described. The complex $[Mn(CO)_2(NO)(\eta^5\text{-}C_5H_4Me)][BF_4]$ was obtained by procedures used to prepare the $\eta\text{-}C_5H_5$ analogue [7].

3.1. Synthesis of the complex $[RhCu(PPh_3)(cod)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$

A mixture of the reagents $[NEt_4][Rh(cod)(\eta^5\text{-}7,8\text{-}C_2B_9H_9Me_2)]$ (0.20 g, 0.39 mmol), $[CuCl(PPh_3)]$ (0.14 g, 0.39 mmol), and $TlBF_4$ (0.18 g, 0.62 mmol) in CH_2Cl_2 (20 cm^3) was stirred for 2 h. The resulting suspension was filtered through Celite, and solvent removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (*ca.* 3 cm^3) and chromatographed. Elution with CH_2Cl_2 + light petroleum (1:1) gave a yellow fraction which, following removal of solvent *in vacuo*, gave yellow microcrystals of [RhCu(PPh$_3$)(cod)(η^5-7,8-$C_2B_9H_9$-Me_2)] (**V**) (0.14 g).

3.2. Synthesis of complexes with Mn–Rh bonds

(i) The salt **1c** (0.20 g, 0.29 mmol) in CH_2Cl_2 (20 cm^3) was treated with [MnBr(CO)$_5$] (0.08 g, 0.29 mmol) in the presence of $TlBF_4$ (0.21 g, 0.72 mmol). After stirring the mixture for 1 h, it was filtered through Celite. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (*ca.* 4 cm^3) and chromatographed. Elution with CH_2Cl_2 + light petroleum (1:3), followed by removal of solvent *in vacuo*, gave red microcrystals of [MnRh(CO)$_5$(PPh$_3$)(η^5-7,8-$C_2B_9H_9Me_2$)] (**VIa**) (0.09 g).

(ii) A mixture of the reagents [NEt$_4$][Rh(cod)(η^5-7,8-$C_2B_9H_9Me_2$)] (0.20 g, 0.39 mmol), [MnBr(CO)$_5$] (0.11 g, 0.39 mmol), and $TlBF_4$ (0.21 g, 0.72 mmol) in CH_2Cl_2 (20 cm^3) was stirred for *ca.* 1 h. After filtration through Celite, and removal of solvent from the filtrate *in vacuo*, the residue was dissolved in CH_2Cl_2 (*ca.* 5 cm^3) and chromatographed. Elution with CH_2Cl_2 + light petroleum (1:4) gave a yellow fraction, from which [MnRh(CO)$_6$(η^5-7,8-$C_2B_9H_9Me_2$)] (**VIb**) (0.07 g) was isolated as red microcrystals, after removal of solvent *in vacuo*.

3.3. Synthesis of the compound [Rh(NO)(PPh$_3$)(η^5-7,8-$C_2B_9H_9Me_2$)]

The salt **1c** (0.20 g, 0.29 mmol) in CH_2Cl_2 (20 cm^3) was treated with [Mn(CO)$_2$(NO)(η-C_5H_4Me)][BF$_4$] (0.08 g, 0.29 mmol), and the mixture was stirred for *ca.* 6 h. The resulting suspension was filtered through Celite, and solvent was removed *in vacuo* from the filtrate. The residue was dissolved in CH_2Cl_2 (*ca.* 4 cm^3) and chromatographed. Elution with CH_2Cl_2 + light petroleum (1:2) gave a yellow eluate, which after removal of solvent *in vacuo*, yielded yellow microcrystals of [Rh(NO)(PPh$_3$)(η^5-7,8-$C_2B_9H_9Me_2$)] (**VII**) (0.10 g).

3.4. Crystal structure determination

Crystals of **V** were grown from CH_2Cl_2 + light petroleum as yellow needles and the sample used was cut from a large needle and had dimensions *ca.* 0.62 × 0.51 × 0.55 mm. Diffracted intensities were collected using a Siemens R3m/v four-circle diffractometer at 293 K. Of the 4123 data collected (Wyckoff ω-scan, $2\theta \leq 55°$), 2840 unique data had $F \geq 4\sigma(F)$, and only these were used for structure solution and refinement. The data were corrected for Lorentz, polarization and X-ray absorption effects. An empirical absorption correction was applied for the latter using a method based on azimuthal scan data [8].

Crystal data. $C_{30}H_{42}B_9CuPRh$, $M = 697.4$, orthorhombic, space group $Pna2_1$, $a = 18.082(5)$, $b = 8.316(3)$, $c = 21.129(6)$ Å, $U = 3177.3(1.7)$ Å^3, $Z = 4$, $D_c = 1.46$ g cm^{-3}, $F(000) = 1424$, μ(Mo-Kα) = 12.5 cm^{-1}, Mo-Kα X-radiation (graphite monochromator) $\bar{\lambda} = 0.71073$ Å.

The structure was solved by conventional heavy atom methods and successive difference Fourier syntheses were used to locate all non-hydrogen atoms which were refined with anisotropic thermal parameters. The crystal diffracted comparatively poorly, and because of the limited data the phenyl rings were treated as rigid groups. The poor data did not allow location of hydro-

TABLE 5. Atomic coordinates ($\times 10^4$) for **V** (with estimated standard deviations in parentheses

	x	y	z
Rh	1649(1)	−414(1)	0
Cu	1718(1)	1770(2)	901(1)
P	1985(1)	2588(3)	1855(1)
C(1)	391(4)	−905(11)	−90(5)
C(2)	722(5)	−493(12)	−774(4)
C(3)	194(5)	−2632(14)	97(7)
C(4)	919(6)	−1866(13)	−1253(5)
B(3)	1241(6)	1244(14)	−743(5)
B(4)	1140(5)	2089(11)	44(6)
B(5)	622(5)	591(15)	466(5)
B(6)	−279(5)	484(17)	88(7)
B(7)	−226(6)	−190(16)	−685(5)
B(8)	349(6)	1147(16)	−1100(6)
B(9)	565(7)	2816(14)	−592(6)
B(10)	156(6)	2358(16)	149(5)
B(11)	−320(7)	1910(18)	−541(6)
C(11)	1941(6)	−2688(13)	432(6)
C(12)	2214(6)	−1456(12)	831(6)
C(13)	3027(6)	−1020(14)	872(6)
C(14)	3255(6)	246(15)	381(6)
C(15)	2768(5)	289(13)	−206(5)
C(16)	2601(5)	−1063(16)	−569(6)
C(17)	2913(7)	−2753(16)	−425(7)
C(18)	2406(7)	−3758(13)	−5(9)
C(21)	2828(3)	3792(8)	1938(3)
C(22)	2810	5358	2174
C(23)	3463	6241	2228
C(24)	4134	5558	2045
C(25)	4152	3992	1808
C(26)	3499	3109	1755
C(31)	1240(3)	3790(8)	2187(3)
C(32)	718	4450	1775
C(33)	100	5242	2016
C(34)	2	5375	2669
C(35)	523	4715	3081
C(36)	1142	3923	2840
C(41)	2069(3)	975(7)	2430(3)
C(42)	1462	−54	2473
C(43)	1469	−1324	2905
C(44)	2084	−1565	3292
C(45)	2691	−536	3248
C(46)	2683	734	2817

gen atoms which were not included in the refinement. Final $R = 0.047$ ($R' = 0.045$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0005F^2]$. The final electron density difference synthesis showed no peaks > 0.45 or < -0.66 e Å^{-3}. All calculations were performed on a DEC MicroVax II computer with the SHELXTL PLUS system of programs [8]. Scattering factors with corrections for anomalous dispersion were taken from reference [9]. Atom coordinates are listed in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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