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Studies on the complex

[Rh(σ, η^5 -7,9-C₂B₉H₁₀[C(H)C₆H₄Me-4]-10)(CO)(PPh₃)];

crystal structure of the compound

[Rh(CO)(PPh₃){ η^5 -7,9-C₂B₉H₁₀[C(H)(C₆H₄Me-4)(PEt₃)]-10}] *

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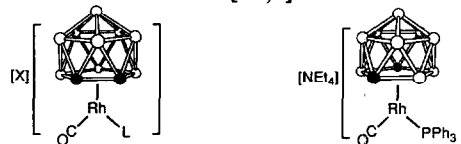
Abstract

Treatment of CO-saturated CH₂Cl₂ solutions of [NEt₄][Rh(CO)(PPh₃)(η^5 -7,9-C₂B₉H₁₁)] with [Mn($\equiv$ C₆H₄Me-4)(CO)₂(η^5 -C₅H₄Me)][BCl₄] affords the complex [Rh(σ, η^5 -7,9-C₂B₉H₁₀[C(H)C₆H₄Me-4]-10)(CO)(PPh₃)]. The latter reacts with K[BH(CHMeEt)₃] in the presence of [NEt₄]Cl to yield [NEt₄][Rh(CO)(PPh₃)(η^5 -7,9-C₂B₉H₁₀(CH₂C₆H₄Me-4)-10)], and with tertiary phosphines (L = PMe₃, PEt₃, or PMe₂Ph) to give the zwitterionic complexes [Rh(CO)(PPh₃)(η^5 -7,9-C₂B₉H₁₀[C(H)C₆H₄Me-4](L)-10)]. The crystal structure of the product with L = PEt₃ has been determined, thereby firmly establishing the structure of this class of complex. The reaction between [AuCl(PPh₃)] and the species with L = PMe₃ in the presence of TIBF₄ affords the dimetal compound [RhAu(CO)(PPh₃)₂(η^5 -7,9-C₂B₉H₁₀[C(H)C₆H₄Me-4](PMe₃)-10)][BF₄]. The NMR spectra of the new compounds are reported, and discussed in relation to their structures.

1. Introduction

The salts [X][Rh(CO)(L)(η^5 -7,9-C₂B₉H₉R'₂)] (I, X = NEt₄, or N(PPh₃)₂; n = 8, L = CO or PPh₃, R' = H or Me; X = NEt₄, n = 9, L = PPh₃, R' = H) [1**] react with a variety of metal complexes to yield products in which a carborane rhodium fragment is σ bonded to another metal atom (Mn, Re, Co, Rh, Ir, Pt, Cu, or Au) with its attendant ligands [2]. However, reactions between the reagents [X][Rh(CO)(L)(η^5 -7,8-C₂B₉H₉R'₂)] (Ia–d) and the manganese compounds [Mn($\equiv$ CR)(CO)₂(η^5 -C₅H₄Me)][BCl₄] (R = C₆H₄Me-4 or C₆H₃Me₂-2,6) followed an unexpected course, affording the mononuclear rhodium complexes [Rh(σ, η^5 -7,8-C₂B₉H₈[C(H)R]-10-R'₂-7,8)(CO)(L)] (R = C₆H₄Me-

4, R' = H, L = PPh₃ (IIa); or CO (IIb); R = C₆H₃Me₂-2,6, R' = H, L = PPh₃ (IIc); R = C₆H₄Me-4, R' = Me, L = PPh₃ (IIId); or CO (IIE)) [2e, 3], instead of the expected dimetal species in which an alkylidyne group bridges a Mn–Rh bond. The formation of the compounds IIa–e probably proceeds via intermediates with metal–metal bonds which facilitate transfer of the alkylidyne group from manganese to rhodium, a process which is evidently followed by insertion of the alkylidyne into the B(10)–H bond. The manganese fragment is released as [Mn(CO)₃(η^5 -C₅H₄Me)], as discussed elsewhere [2e,3].



OBH

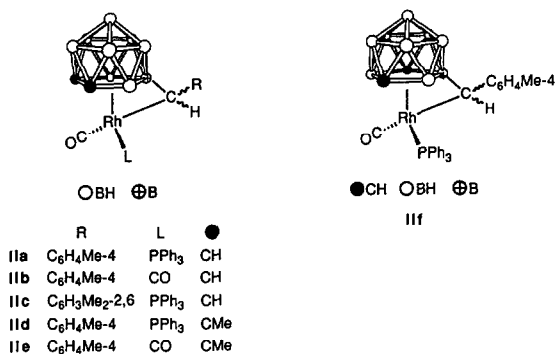
	X	L	●
Ia	NEt ₄	CO	CH
Ib	N(PPh ₃) ₂	PPh ₃	CH
Ic	NEt ₄	CO	CMe
Id	NEt ₄	PPh ₃	CMe

Ie ● CH

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* This paper is dedicated to Professor M.F. Lappert on the occasion of his 65th birthday, and in gratitude for his long-standing friendship.

** Reference with asterisk indicates a note in the list of references.



In this paper we report the reaction between [NEt₄][Rh(CO)(PPh₃)(η^5 -7,9-C₂B₉H₁₁)] (**Ie**) and [Mn($\equiv$ CC₆H₄Me-4)(CO)₂(η^5 -C₅H₄Me)][BCl₄], as well as some reactions of the product [Rh(σ , η^5 -7,9-C₂B₉H₁₀[C(H)C₆H₄Me-4]-10)(CO)(PPh₃)] (**III**). The latter complex is a polytopal isomer of **IIa**, having a 2,1,7-RhC₂B₉ icosahedral core structure, as opposed to the 3,1,2-RhC₂B₉ cage frameworks in the species **IIa-e**.

2. Results and discussion

Treatment of CO-saturated CH₂Cl₂ solutions of **Ie** with [Mn($\equiv$ CC₆H₄Me-4)(CO)₂(η^5 -C₅H₄Me)][BCl₄] gave, after column chromatography on alumina, orange crystals of [Rh(σ , η^5 -7,9-C₂B₉H₁₀[C(H)C₆H₄Me-4]-10)(CO)(PPh₃)] (**III**). As observed previously [2e, 3], the Mn(CO)₂(η^5 -C₅H₄Me) fragment is eliminated as [Mn(CO)₃(η^5 -C₅H₄Me)]. Hence the reaction is carried out in the presence of CO to increase the yield of **III**.

Compound **III** was characterised by the data given in Tables 1–3. The spectroscopic properties are similar to those of **IIa** and are entirely consistent with the structure shown. Thus the presence of the BC(H)-C₆H₄Me-4 group is revealed in the ¹¹B-¹H NMR spectrum (Table 3), in which a diagnostic resonance corresponding in intensity to one boron atom is seen at δ 8.8, a value almost identical with that (δ 8.7) found in the spectrum of [NEt₄][Mo(σ , η^5 -7,8-C₂B₉H₈[C(H)C₆H₄Me-4]-10-Me₂-7,8)(CO)₃], the anion of which also has a C(H)C₆H₄Me-4 moiety bridging the metal atom and the cage [4]. Interestingly, the ¹¹B-¹H NMR resonance for the BC(H)C₆H₄Me-4 group in **IIa** at δ 17.4 [3], is appreciably more deshielded than in **III**.

TABLE 1. Analytical ^a and physical data for the rhodium complexes

Compound	Colour	Yield (%)	$\nu_{\max}(\text{CO})^b$ cm ⁻¹	Analysis (%)	
				C	H
III [Rh(σ , η^5 -7,9-C ₂ B ₉ H ₁₀ [C(H)C ₆ H ₄ Me-4]-10)(CO)(PPh ₃)]	orange	83	2022vs	55.9 (55.4)	5.4 (5.3)
IId [NEt ₄][Rh(CO)(PPh ₃)(η^5 -7,9-C ₂ B ₉ H ₁₀ (CH ₂ C ₆ H ₄ Me-4)-10)] ^c	dark green	97	1923vs	57.6 (58.5)	7.4 (7.2)
IIIe [NEt ₄][Rh(CO)(PPh ₃)(η^5 -7,9-C ₂ B ₉ H ₁₀ [C(H)Me(C ₆ H ₄ Me-4)-10)] ^{c,d}	red	98 (39)	1921s	59.0 (59.0)	7.3 (7.3)
IVa [Rh(CO)(PPh ₃)(η^5 -7,9-C ₂ B ₉ H ₁₀ [C(H)C ₆ H ₄ Me-4](PMe ₃)-10)]	green-yellow	92	1927vs	54.5 (54.5)	6.0 (6.0)
IVb [Rh(CO)(PPh ₃)(η^5 -7,9-C ₂ B ₉ H ₁₀ [C(H)C ₆ H ₄ Me-4](PEt ₃)-10)]	yellow	84	1923vs	55.6 (56.3)	6.5 (6.5)
IVc [Rh(CO)(PPh ₃)(η^5 -7,9-C ₂ B ₉ H ₁₀ [C(H)C ₆ H ₄ Me-4](PMe ₂ Ph)-10)]	yellow	78	1924vs	57.1 (58.0)	6.0 (5.8)
V [NEt ₄][Rh(COMe)(σ , η^5 -7,9-C ₂ B ₉ H ₁₀ [C(H)C ₆ H ₄ Me-4]-10)(PPh ₃)] ^{c,e}	red	98 (59)	1600m br	59.0 (59.0)	7.3 (7.3)
VI [RhAu(CO)(PPh ₃) ₂ (η^5 -7,9-C ₂ B ₉ H ₁₀ [C(H)C ₆ H ₄ Me-4](PMe ₃)-10)][BF ₄]	pale green	98	1972vs	47.9 (48.0)	4.7 (4.6)

^a Calculated values are given in parentheses.

^b Measured in CH₂Cl₂. All spectra show a broad band at ca. 2550 cm⁻¹ due to B-H absorptions.

^c Compound also contains nitrogen. For: **IId** 1.9 (1.8%); **IIIe** and **V** 1.8 (1.8%).

^d Compound formed as an inseparable 2:3 mixture with **V**. Yield quoted is overall value for mixture; figure in parentheses calculated yield for **IIIe**. Microanalytical data is for the isomer mixture. See text.

^e Compound formed as a 3:2 mixture with **IIIe**, see footnote d.

TABLE 2. (footnotes)

^a Chemical shifts δ in ppm, coupling constants in Hz, measurements at ambient temperatures in CD₂Cl₂, R = C₆H₄Me-4.

^b Signals due to BH groups appear as broad unresolved resonances in the range δ ca. -2 to +3.

^c Hydrogen-1 decoupled, chemical shifts are positive to high frequency of SiMe₄ (δ 0.0).

^d Spectrum measured in CDCl₃.

^e Compound formed as an inseparable 2:3 mixture with **V**; peaks assigned on basis of integration of ¹H and ³¹P-¹H NMR spectra and intensities and shifts of the resonances in the ¹³C-¹H NMR spectrum. See text.

^f Measured in CDCl₃ on a sample with [N(PPh₃)₂]⁺ as the counter-ion.

^g Peaks marked with an asterisk due to minor isomer.

^h Formed as an inseparable 3:2 mixture with **IIIe**. See footnote e.

TABLE 2. ¹H and ¹³C NMR data ^a for the complexes

Compound	¹ H ^b (δ)	¹³ C ^c (δ)
III ^f	0.71 [s, 1H, CH(C ₂ B ₉ H ₁₀)], 2.17 (s, 3H, Me-4), 2.88 [s, 1H, CH(C ₂ B ₉ H ₁₀)], 6.37 [br s, 1H, BC(H)R], 6.80–7.90 (m, 19H, Ph and C ₆ H ₄)	^d 191.1 [d of d, CO, J(RhC) 73, J(PC) 22], 141.9 [C ¹ (C ₆ H ₄)], 137.3 [C ⁴ (C ₆ H ₄)], 133.6–128.5 (Ph and C ₆ H ₄), 80.4 [br, BC(H)R], 54.1, 53.0 (C ₂ B ₉ H ₁₀), 21.5 (Me-4)
III ^d	1.03 [s, 1H, CH(C ₂ B ₉ H ₁₀)], 1.23 [t of t, 12H, NCH ₂ Me, J(HH) 7, J(NH) 2], 2.17 [s, 1H, CH(C ₂ B ₉ H ₁₀)], 2.30 (s, 3H, Me-4), 2.45, 2.54 [(AB), 2H, BCH ₂ , J(AB) 12], 3.15 [q, 8H, NCH ₂ Me, J(HH) 7], 6.90, 7.10 [(AB) ₂ , 4H, C ₆ H ₄ , J(AB) 8], 7.27–7.39 (m, 15H, Ph)	198.3 [d of d, CO, J(RhC) 93, J(PC) 21], 145.0 [C ¹ (C ₆ H ₄)], 137.5 [d, C ¹ (Ph), J(PC) 38], 134.1 [d, C ² (Ph), J(PC) 12], 132.1 [C ⁴ (C ₆ H ₄)], 129.4 [C ² (C ₆ H ₄)], 129.2 [d, C ⁴ (Ph), J(PC) 2], 128.2 [C ³ (C ₆ H ₄)], 127.9 [d, C ³ (Ph), J(PC) 9], 53.0 [t, NCH ₂ Me, J(NC) 3], 45.6, 41.7 (C ₂ B ₉ H ₁₀), 33.7 (vbr, BCH ₂ R), 21.1 (Me-4), 7.8 (NCH ₂ Me)
III ^e	0.43 [s, 1H, CH(C ₂ B ₉ H ₁₀)], 1.23 [t of t, 12H, NCH ₂ Me, J(HH) 7, J(NH) 2], ^f 1.25 [d, 3H, BCH Me, J(HH) 7], 2.00 (s, 3H, Me-4), 2.21 [s, 1H, CH(C ₂ B ₉ H ₁₀)], ^f 3.06 [q, br, 1H, BCH Me, J(HH) 7], 3.11 [q, 8H, NCH ₂ Me, J(HH) 7], 6.92, 7.10 [(AB) ₂ , 4H, C ₆ H ₄ , J(AB) 8], 7.20–7.38 (m, 15H, Ph)	198.2 [d of d, CO, J(RhC) 92, J(PC) 21], 150.8 [C ¹ (C ₆ H ₄)], 137.4 [d, C ¹ (Ph), J(PC) 37], 134.3 [d, C ² (Ph), J(PC) 12], 132.1 [C ⁴ (C ₆ H ₄)], 129.2 [C ² or C ³ (C ₆ H ₄)], 129.1 [d, C ⁴ (Ph), J(PC) 2], 128.3 [C ² or C ³ (C ₆ H ₄)], 128.0 [d, C ³ (Ph), J(PC) 10], 52.9 (NCH ₂ Me), 46.2, 41.8 (C ₂ B ₉ H ₁₀), 33.7 [vbr, BC(H)(Me)R], 23.4, 21.0 (Me), 7.7 (NCH ₂ Me)
IV ^a	0.76 [s, 1H, CH(C ₂ B ₉ H ₁₀)], 1.67, * 1.72 [d, 9H, PMe, J(PH) 13], 2.42 [d, 3H, Me-4, J(PH) 2], 2.51, * 2.76 [s, 1H, CH(C ₂ B ₉ H ₁₀)], 4.06 [d, 1H, BC(H)R, J(PH) 18], 7.04–7.63 (m, 19H, Ph and C ₆ H ₄)	196.9 [d of d of d, CO, J(RhC) 92, J(PC) 21 and 4], 136.9 [d, C ¹ (C ₆ H ₄)], J(PC) 4], 136.5 [d, C ¹ (Ph), J(PC) 40], 134.4 [d, C ² (C ₆ H ₄)], J(PC) 7], 134.0 [d, C ² (Ph), J(PC) 12], 132.7 [d, br, C ² (C ₆ H ₄)], J(PC) 7], 130.3, 130.0 [br, C ³ (C ₆ H ₄)], 129.6 [d, C ⁴ (Ph), J(PC) 2], 128.1 [d, C ³ (Ph), J(PC) 10], 127.2 [br, C ⁴ (C ₆ H ₄)], 45.3 (vbr, C ₂ B ₉ H ₁₀), 44.7 (C ₂ B ₉ H ₁₀), 33.7 [vbr, BC(H)R], 21.2, * 19.7 (Me-4), 11.3, * 10.6 [d, PMe, J(PC) 54]
IV ^b	0.75 [s, 1H, CH(C ₂ B ₉ H ₁₀)], 1.10 [d of d of d, 9H, PCH ₂ Me, J(PH) 17, J(HH) 8 and 8], * 1.71 (m, 3H, PCH ₂ Me), 1.97 [d of d of q, 3H, PCH _A H _B Me, J(H _A H _B) 20, J(H _{Me} H) 8, J(PH) 8], * 2.14 (m, 3H, PCH ₂ Me), 2.24 [d of d of q, 3H, PCH _A H _B Me, J(H _A H _B) 20, J(H _{Me} H) 8, J(PH) 8], 2.49, * 2.59 [s, 1H, CH(C ₂ B ₉ H ₁₀)], 4.32 [d, br, 1H, BC(H)R, J(PH) 21], 6.99–7.58 (m, 19H, Ph and C ₆ H ₄)	197.0 [d of d of d, CO, J(RhC) 92, J(PC) 22 and 4], 136.8 [d, C ¹ (C ₆ H ₄)], J(PC) 3], 136.5 [d, C ¹ (Ph), J(PC) 40], 134.1 [d, C ² (C ₆ H ₄)], J(PC) 8], 134.0 [d, C ² (Ph), J(PC) 12], 133.0 [d, C ² (C ₆ H ₄)], J(PC) 8], 130.2 [C ⁴ (C ₆ H ₄)], 129.7 [d, C ³ (C ₆ H ₄)], J(PC) 2], 129.5 [d, C ⁴ (Ph), J(PC) 2], 128.5 [d, C ³ (C ₆ H ₄)], J(PC) 5], 128.1 [d, C ³ (Ph), J(PC) 10], 45.6 (vbr, C ₂ B ₉ H ₁₀), 44.7 (C ₂ B ₉ H ₁₀), 33.9 [vbr, BC(H)R], 21.2, * 19.7 (Me-4), 13.8, * 12.2 [d, PCH ₂ Me, J(PC) 47], * 8.5, 6.6 [d, PCH ₂ Me, J(PC) 5]
IV ^c	* 0.71, 0.78 [s, 1H, CH(C ₂ B ₉ H ₁₀)], 1.85, * 2.13 [d, 3H, PMe, J(PH) 13], * 2.16 [d, 3H, Me-4, J(PH) 3], 2.24, * 2.26 [d, 3H, PMe, J(PH) 13], 2.35 [d, 3H, Me-4, J(PH) 3], 2.45 [s, 1H, CH(C ₂ B ₉ H ₁₀)], * 3.80, 4.52 [d, br, 1H, BC(H)R, J(PH) 21], 6.91–7.71 (m, 24H, Ph and C ₆ H ₄)	197.1 [d of m, CO, J(RhC) 95], 136.7–123.7 (Ph and C ₆ H ₄), 45.9, 44.7 (C ₂ B ₉ H ₁₀), 38.5 [vbr, BC(H)R], 21.2 (Me-4), 10.1, 9.9 [d x 2, PMe, J(PC) 54]
V ^h	0.90 [s, 1H, CH(C ₂ B ₉ H ₁₀)], 1.23 [t of t, 12H, NCH ₂ Me, J(HH) 7, J(NH) 2], 1.86 [s, 1H, CH(C ₂ B ₉ H ₁₀)], 2.10, 2.29 (s x 2, 6H, COMe and Me-4), 3.11 [q, 8H, NCH ₂ Me, J(HH) 7], 4.35 [d, br, 1H, BC(H)R, J(PH) 3], 6.61, 6.84 [(AB) ₂ , 4H, C ₆ H ₄ , J(AB) 8], 7.20–7.38 (m, 15H, Ph)	243.3 [d of d, C(O)Me, J(RhC) 32, J(PC) 13], 150.3 [d of d, C ¹ (C ₆ H ₄)], J(RhC) 4, J(PC) 4], 136.6 [d, C ¹ (Ph), J(PC) 35], 134.0 [d, C ² (Ph), J(PC) 13], 131.4 [C ⁴ (C ₆ H ₄)], 128.9 [C ⁴ (Ph)], 128.1 [C ² or C ³ (C ₆ H ₄)], 127.7 [d, C ³ (Ph), J(PC) 9], 126.9 [C ² or C ³ (C ₆ H ₄)], 57.6 [vbr, BC(H)R], 52.9 (NCH ₂ Me), 41.3 [d, C(O)Me, J(PC) 3], 39.4, 34.5 (C ₂ B ₉ H ₁₀), 21.2 (Me-4), 7.7 (NCH ₂ Me)
VI	1.07 [s, 1H, CH(C ₂ B ₉ H ₁₀)], 1.75 [d, 9H, PMe, J(PH) 13], 2.53 (s, 3H, Me-4), 3.44 [s, 1H, CH(C ₂ B ₉ H ₁₀)], 3.67 [d, 1H, BC(H)R, J(PH) 22], 7.13–7.57 (m, 34H, Ph and C ₆ H ₄)	194.1 [d of m, CO, J(RhC) 76], 138.3 [d, C ¹ (C ₆ H ₄)], J(PC) 4], 134.6–127.7 (Ph and C ₆ H ₄), 57.9, 51.4 (C ₂ B ₉ H ₁₀), 37.2 [vbr, BC(H)R], 21.3 (Me-4), 10.6 [d, PMe, J(PC) 54]

This difference must be associated with the different core structures in the two compounds, *viz.*, 2,1,7-RhC₂B₉ versus 3,1,2-RhC₂B₉. That the peak in the ¹¹B-{¹H} NMR spectrum of **II**f at δ 8.8 is due to the boron nucleus of the BC(H)C₆H₄Me-4 fragment was confirmed by the observation that the signal remained a singlet in a fully coupled ¹¹B spectrum, whereas all the other resonances in the range δ 0.5 to -17.9 became doublets [$J(\text{HB})$ *ca.* 140 Hz] in accord with these signals being due to cage BH groups.

The formula of **II**f is depicted with the C(H)C₆H₄Me-4 group attached to B(10) rather than to the unique B(8) atom which separates the two carbons in the open pentagonal face of the cage ligating the rhodium. Although there is no firm NMR evidence for this assignment, the substantial difference in chemical shifts (δ 0.71 and 2.88) in the ¹H NMR spectrum (Table 2) of the two inequivalent cage CH vertices does suggest the less symmetrical arrangement with one CH vertex adjacent to the BC(H)C₆H₄Me-4 group and the other separated from it by a BH group. That this structural assignment for **II**f is correct is strongly supported by the results of the X-ray diffraction study of a derivative, described below.

The ¹H and ¹³C-{¹H} NMR spectrum of **II**f also confirmed the presence of the BC(H)C₆H₄Me-4 group with a broad singlet at δ 6.37 in the former spectrum for the BC(H) proton, and a broad resonance in the latter spectrum at δ 80.4 for the BC(H) carbon nucleus. The broadness of both peaks is attributed to unresolved ¹¹B-¹H and ¹¹B-¹³C coupling, respectively. In the ¹³C-{¹H} NMR spectrum the resonance for the CO ligand occurs as the anticipated doublet of doublets at δ 191.1 [$J(\text{RhC})$ 73, $J(\text{PC})$ 22 Hz], and the signals for the two inequivalent cage CH vertices are seen (measured in CDCl₃ rather than CD₂Cl₂) at δ 54.1 and 53.0.

The ³¹P-{¹H} NMR spectrum of **II**f shows a single broad doublet [δ 32.0, $J(\text{RhP})$ 145 Hz] at room temperature. This same pattern persists in the spectrum measured at -70°C, indicating the presence of only one species in solution and the absence of fluxionality. This is in marked contrast with compounds **II**a and **II**d which show a duplication of NMR peaks in accord with an equilibrium between two diastereoisomers. This behaviour is attributed to the chiral C(H)R fragments being able to adopt two orientations relative to the Rh(CO)(PPh₃) moiety, with the PPh₃ and R groups

TABLE 3. ¹¹B and ³¹P NMR data ^a for the complexes

Compound	¹¹ B ^b (δ)	³¹ P ^c (δ)
II f	8.8 (s, 1B, BCHR), 0.5 (1B), -10.4 (2B), -13.8 (2B), -17.9 (3B)	32.0 [d, br, PRh, $J(\text{RhP})$ 145]
III d	-0.1 (s, 1B, BCHR), -11.9 (1B), -12.9 (1B), -14.9 (2B), -21.1 (1B), -25.2 (2B), -28.8 (1B)	35.7 [d, PRh, $J(\text{RhP})$ 164]
III e ^d	3.0 [s, 1B, BC(H)(Me)R], -11.6 to -28.4 (vbr, 8B)	36.1 [d, PRh, $J(\text{RhP})$ 166]
IV a ^e	* -4.1, -5.2 (s, 1B, BCHR), -13.1 (1B), -14.5 (2B), -16.8 (1B), -22.9 (1B), -23.7 (1B), -25.9 (1B), -26.8 (1B)	36.5 [d, br, PRh, $J(\text{RhP})$ 168], * 26.6, 25.6 (s, PMe ₃)
IV b ^e	-5.0, * -6.8 (s, 1B, BCHR), -13.1 (1B), -14.4 (2B), -16.9 (1B), -22.8 (1B), -23.7 (1B), -25.8 (1B), -26.6 (1B)	38.5, * 38.4 (s, PEt ₃), 36.4 [d, vbr, PRh, $J(\text{RhP})$ 164]
IV c ^e	* -3.7, -5.1 (s, 1B, BCHR), -13.1 (1B), -14.6 (2B), -16.8 (1B), -22.9 (1B), -23.7 (1B), -25.9 (1B), -26.8 (1B)	36.3 [d, br, PRh, $J(\text{RhP})$ 164], * 25.9, 24.4 (s, PMe ₂ Ph)
V ^f	3.0 (s, 1B, BCHR), -11.6 to -28.4 (vbr, 8B)	30.2 [d, PRh, $J(\text{RhP})$ 198]
VI	0.4 (s, 1B, BCHR), -1.2 (1B, BF ₄), -2.8 to -24.1 (vbr, 8B)	34.1 [d, br, PRh, $J(\text{RhP})$ 126], 33.7 (s, PMe ₃), 30.7 [d, PAu, $J(\text{RhP})$ 4]

^a Chemical shifts (δ) in ppm, coupling constants in Hz, measurements in CD₂Cl₂ at ambient temperatures.

^b Hydrogen-1 decoupled, chemical shifts are positive to high frequency of BF₃·Et₂O (external). R = C₆H₄Me-4.

^c Hydrogen-1 decoupled, chemical shifts are positive to high frequency of 85% H₃PO₄ (external).

^d Formed as a mixture with **V**; peak assignments based on rel. int. (see text).

^e Peaks marked with asterisk are due to minor isomer.

^f Formed as a mixture with **III**e. See footnote d and text.

having either a *cisoid* or *transoid* relationship with each other. However, in the crystalline state the latter arrangement occurs in **IIa** [3], and we assume that this *transoid* structure exists for **IIc** also. As a consequence of the dynamic behaviour of **IIa**, the ³¹P-{¹H} NMR spectrum at -50°C shows two resonances at δ 35.1 [d, *J*(RhP) 147 Hz] and 34.0 [d, *J*(RhP) 143 Hz] with relative intensity 3:2. These signals almost coalesce in the room temperature spectrum. The dynamic behaviour was also revealed in the ¹H NMR spectrum, since at -40°C there were two sets of resonances. Those for the C(H)C₆H₄Me-4 protons of the two diastereoisomers of **IIa** are seen at δ 6.13 and 6.16, to be compared with the single peak observed at δ 6.37 for **IIc**.

The interconversion of the diastereoisomers of **IIa**, so as to allow the PPh₃ and C₆H₄Me-4 groups to be either *transoid* or *cisoid* to one another, is attributed to a low energy pathway involving breaking of the weak Rh-C(H)C₆H₄Me-4 bond [3]. This process would allow rotation of the B-C(H)C₆H₄Me-4 linkage, which, when followed by reformation of the Rh-C(H)C₆H₄Me-4 bond, would transform the PPh₃ and C₆H₄Me-4 groups between *cisoid* and *transoid* configurations. Compound **IIc** has a greater potential for forming diastereoisomers than **IIa** since in addition to the chiral BC(H)C₆H₄Me-4

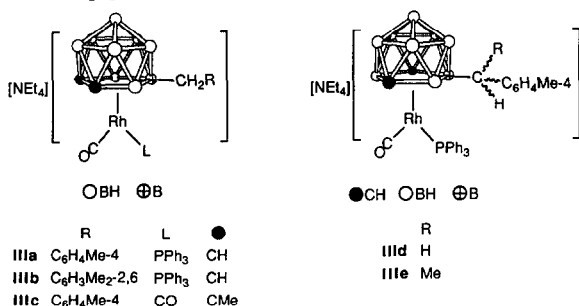
and rhodium centres, the boron atom of the former group is also chiral. However, for steric reasons it is reasonable to consider that only one diastereoisomer of **IIc** might exist.

Treatment of the complexes **IIa**, **IIc**, and **Ile** with K[BH(CHMeEt)₃], followed by addition of [NEt₄]Cl, gave the salts **IIIa**, **IIIb**, and **IIIc**, respectively, demonstrating the electrophilic character of the exopolyhedral carbon atoms of the C(H)R groups in the complexes **II** [3]. Similarly, the reaction between **IIc** and the reagent K[BH(CHMeEt)₃], followed by addition of [NEt₄]Cl, afforded the related compound [NEt₄][Rh(CO)(PPh₃)(η^5 -7,9-C₂B₉H₁₀(CH₂C₆H₄Me-4)-10)] (**IIId**). Data fully characterising this product are given in Tables 1-3, and are similar to those of its isomer **IIIa**, after allowing for variations arising because of the different 2,1,7- and 3,1,2-RhC₂B₉ icosahedral core structures of the two species. The ³¹P-{¹H} NMR spectrum of **IIId** shows a doublet resonance at δ 35.7 [*J*(RhP) 164 Hz] to be compared with the corresponding doublet in the spectrum of **IIIa** at δ 33.7 [*J*(RhP) 154 Hz] [3]. The linkage of the CH₂C₆H₄Me-4 group to a chiral boron atom in **IIId** results in non-equivalence of the methylene protons in the ¹H NMR spectrum, due to their being diastereotopic. Thus an AB quartet, integrating for two protons, is observed at δ

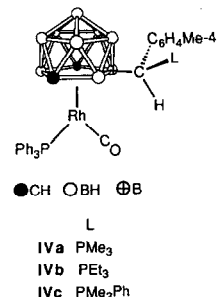
TABLE 4. Selected internuclear distances (Å) and angles (°) in the complex [Rh(CO)(PPh₃)(η^5 -7,9-C₂B₉H₁₀[C(H)C₆H₄Me-4(PEt₃)]-10)] · CH₂Cl₂ (**IVb**)

Rh-P(1)	2.286(2)	Rh-B(1)	2.275(6)	Rh-C(2)	2.331(5)	Rh-B(3)	2.261(7)
Rh-C(4)	2.357(6)	Rh-B(5)	2.210(7)	Rh-C(5)	1.804(6)	P(2)-C(10)	1.818(6)
B(1)-C(2)	1.688(8)	B(1)-B(5)	1.863(9)	B(1)-B(6)	1.801(9)	B(1)-B(10)	1.784(9)
B(1)-C(10)	1.650(7)	C(2)-B(3)	1.721(8)	C(2)-B(6)	1.711(9)	C(2)-B(7)	1.686(8)
B(3)-C(4)	1.668(10)	B(3)-B(7)	1.810(10)	B(3)-B(8)	1.808(10)	C(4)-B(5)	1.700(9)
C(4)-B(8)	1.677(10)	C(4)-B(9)	1.679(10)	B(5)-B(9)	1.801(10)	B(5)-B(10)	1.811(10)
B(6)-B(7)	1.765(9)	B(6)-B(10)	1.741(10)	B(6)-B(11)	1.741(9)	B(7)-B(8)	1.776(11)
B(7)-B(11)	1.790(11)	B(8)-B(9)	1.767(11)	B(8)-B(11)	1.785(11)	B(9)-B(10)	1.769(9)
B(9)-B(11)	1.763(11)	B(10)-B(11)	1.790(10)	C(5)-O(5)	1.145(9)	C(10)-C(11)	1.527(7)
P(1)-Rh-B(1)	144.1(2)	P(1)-Rh-C(2)	109.0(1)	B(1)-Rh-C(2)	43.0(2)		
P(1)-Rh-B(3)	95.6(2)	B(1)-Rh-B(3)	77.0(2)	C(2)-Rh-B(3)	44.0(2)		
P(1)-Rh-C(4)	121.3(2)	B(1)-Rh-C(4)	76.2(2)	C(2)-Rh-C(4)	71.0(2)		
B(3)-Rh-C(4)	42.3(2)	P(1)-Rh-B(5)	163.2(2)	B(1)-Rh-B(5)	49.1(2)		
C(2)-Rh-B(5)	75.4(2)	B(3)-Rh-B(5)	76.1(3)	C(4)-Rh-B(5)	43.6(2)		
P(1)-Rh-C(5)	89.9(2)	B(1)-Rh-C(5)	105.0(3)	C(2)-Rh-C(5)	143.9(3)		
B(3)-Rh-C(5)	167.0(3)	C(4)-Rh-C(5)	125.2(3)	B(5)-Rh-C(5)	95.4(3)		
Rh-B(1)-C(2)	70.3(3)	Rh-B(1)-B(5)	63.7(3)	C(2)-B(1)-B(5)	102.8(4)		
Rh-B(1)-C(10)	106.4(4)	C(2)-B(1)-C(10)	122.0(4)	B(5)-B(1)-C(10)	128.4(5)		
B(10)-B(1)-C(10)	124.3(5)	Rh-C(2)-B(1)	66.7(3)	Rh-C(2)-B(3)	65.9(3)		
B(1)-C(2)-B(3)	111.9(4)	Rh-B(3)-C(2)	70.1(3)	Rh-B(3)-C(4)	71.9(3)		
C(2)-B(3)-C(4)	106.9(5)	Rh-C(4)-B(3)	65.8(3)	Rh-C(4)-B(5)	63.6(3)		
B(3)-C(4)-B(5)	109.8(4)	Rh-B(5)-B(1)	67.3(3)	Rh-B(5)-C(4)	72.8(3)		
B(1)-B(5)-C(4)	106.6(4)	B(8)-B(9)-B(10)	108.5(5)	B(6)-B(10)-B(9)	107.6(5)		
B(7)-B(8)-B(9)	107.2(5)	B(6)-B(7)-B(8)	107.6(5)	B(7)-B(6)-B(10)	108.9(5)		
Rh-C(5)-O(5)	176.8(6)	P(2)-C(10)-B(1)	119.9(4)	P(2)-C(10)-C(11)	109.6(4)		
B(1)-C(10)-C(11)	114.5(4)						

2.45 and 2.54 [$J(AB)$ 12 Hz] (Table 2). This contrasts with the 1H NMR spectrum of **IIIa** where only a broad signal is seen at δ 2.48 [3], because the CH_2 protons are equivalent since the boron atom CCB $\bar{B}$ B to which the $CH_2C_6H_4Me$ -4 fragment is attached is not chiral. In the ^{13}C - $\{^1H\}$ NMR spectrum of **III**d resonances for the cage CH vertices occur at δ 45.6 and 41.7, with the signal for the BCH_2 nucleus appearing as a very broad peak at δ 33.7, the broadness presumably due to unresolved ^{11}B - ^{13}C coupling. In the ^{13}C - $\{^1H\}$ NMR spectrum of **IIIa** the resonance for the BCH_2 nucleus is at δ 34.2 [3].



Having established that the exopolyhedral carbon atom in **II**f was susceptible to nucleophilic attack by H^- , it was decided to investigate whether the carbon atom would add tertiary phosphines to form ylide type structures. Treatment of **II**f in THF with PMe_3 , PEt_3 , or PMe_2Ph gave, respectively, the zwitterionic complexes [Rh(CO)(PPh₃)(η^5 -7,9- $C_2B_9H_{10}$)[C(H)(R)(L)]-10] (R = C₆H₄Me-4, L = PMe_3 (**IVa**), PEt_3 (**IVb**), or PMe_2Ph (**IVc**)), characterised by the data given in Tables 1–3. Duplication of some resonances in the NMR spectra of these products revealed that they were each formed as a mixture of two diastereoisomers, one of which was present in solution in very minor amount, typically 10% or less based on peak intensities. Discussion of the NMR data is deferred, however, until the results of an X-ray diffraction study on **IVb** are described.



Selected bond distances and angles are given in Table 4, and the molecule **IVb** is shown in Fig. 1. The exopolyhedral carbon atom C(10) is chiral, so that in one of the two diastereoisomers the H, PEt_3 , and C_6H_4Me -4 groups will be arranged in this clockwise

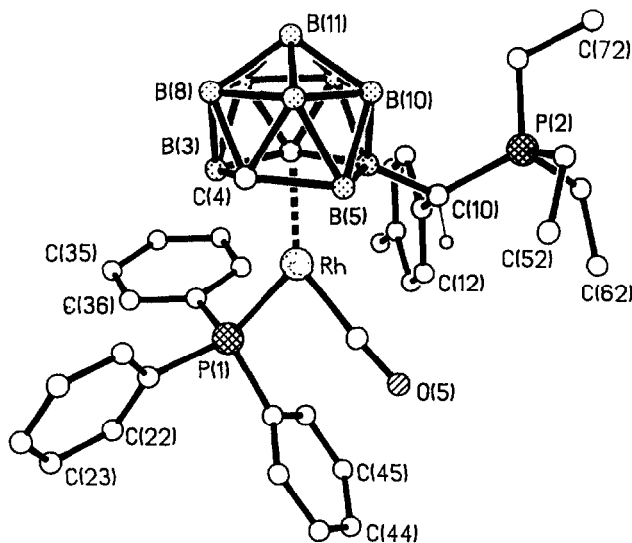


Fig. 1. The molecular structure of [Rh(CO)(PPh₃)(η^5 -7,9- $C_2B_9H_{10}$)[C(H)(C₆H₄Me-4)(PEt_3)]-10] (**IVb**), showing the crystallographic numbering scheme.

order when viewed along the C(10)–B bond towards the boron atom in the CBCBB face of the cage, while the other diastereoisomer will have an H, C_6H_4Me -4, PEt_3 orientation. It is seen from Fig. 1 that the former configuration is the one revealed by the X-ray diffraction study. Moreover, NMR measurements on solutions of the crystals employed in the X-ray work revealed that they were those of the major isomer. The molecular structure also clearly shows that the PPh_3 , PEt_3 and C_6H_4Me -4 groups are oriented so that they point away from each other, an arrangement one would anticipate based on steric considerations. Significantly also, the PPh_3 ligand is orientated such that it is as far away from C(10) as possible. One may postulate that as the PEt_3 molecule attacks the exopolyhedral C atom in **II**f, rupture of the Rh–C σ bond is accompanied by rotation of the Rh(CO)(PPh₃) unit, so as to move the bulky PPh_3 ligand away from the sterically demanding C(H)(C₆H₄Me-4)(PEt_3) fragment. Furthermore, the orientation of the Rh(CO)(PPh₃) moiety in the precursor **II**f, assuming it has a *transoid* P–Rh–C structure similar to that established for **IIa** [3], would clearly make it very unlikely for the PEt_3 molecule to attack the carbon atom in the former species from below the plane of the C(H)C₆H₄Me-4 fragment. This accounts for the predominance of the diastereoisomer identified in the X-ray diffraction study which is the isomer which would result from approach of the PEt_3 molecule from above and to the right of the μ -C(H)C₆H₄Me-4 group in **II**f, as depicted in the structural formula of **IVb**.

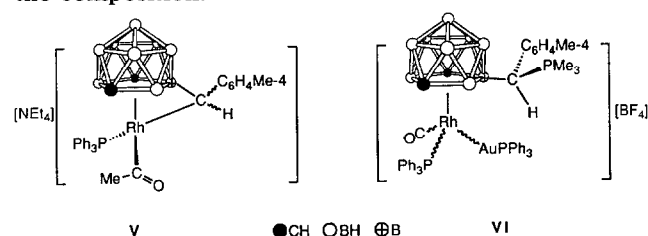
The crystal structure of **IVb** having been established, the NMR data (Tables 2 and 3) are readily interpreted. In the ^{31}P - $\{^1H\}$ NMR spectrum the resonance for the

PPh₃ ligand occurs as a very broad doublet at δ 36.4 [$J(\text{RhP})$ 164 Hz]. No signal for the PPh₃ group of the minor isomer was detected due either to the weakness or broadness of the resonance, or because it was hidden by the broad doublet of the major isomer. The resonance for the PEt₃ group of the major isomer occurs at δ 38.5, and for the minor isomer at δ 38.4. The relative intensity of these peaks was *ca.* 18:1, and as expected there was no ¹⁰³Rh-³¹P coupling on either signal, both signals being sharp singlets. The chemical shifts for the PEt₃ groups in the two isomers are similar to that observed (δ 35.5) in the spectrum of the zwitterionic complex [Cr(CO)₃{ η^5 -C₅H₄(CH₂PEt₃)}] [5]. In the ¹¹B-{¹H} NMR spectrum of **IVb** the resonances for the BC(H)(C₆H₄Me-4)(PEt₃) nuclei of the major and minor isomers occur at δ -5.0 and -6.8, respectively. These shifts are appreciably more shielded than those customarily observed for cage boron atoms bonded to exopolyhedral carbons which generally occur in the range δ *ca.* 1 to 12 [6]. However, the C(H)(C₆H₄Me-4)(L) groups in the compounds **IV**, with their tertiary phosphine substituents, are without precedent, and there is no doubt about the assignment of the peaks at δ -5.0 and -6.8 because in a fully coupled ¹¹B NMR spectrum of **IVb** they remain as singlets whereas all the resonances for the BH groups (δ -13.1 to -26.6) become doublets.

In the ¹³C-{¹H} NMR spectrum of **IVb** only the resonance for the BC(H)(C₆H₄Me-4)(PEt₃) nucleus of the major isomer is seen (δ 33.9). Six peaks are observed for the carbon nuclei of the C₆H₄ ring, a feature diagnostic for hindered rotation about the C(10)-C(11) bond (Fig. 1) [7]. The large PEt₃ group evidently prevents free rotation. The cage CH vertices of **IVb** are clearly inequivalent with two resonances being seen at δ 45.6 and 44.7. Signals for the cage CH and CO groups of the minor diastereoisomer are not observed, but the resonance for the CO ligand of the major isomer occurs as a doublet of doublets of doublets at δ 197.0 [$J(\text{RhC})$ 92, $J(\text{PC})$ 22 and 4 Hz]. The ¹H NMR spectrum is as expected, allowing for the fact that few peaks for the minor isomer are revealed due to its low concentration. A diagnostic resonance [6] for the BC(H)(C₆H₄Me-4)(PEt₃) proton occurs at δ 4.32 as a broad doublet [$J(\text{PH})$ 21 Hz]. The CH₂ protons of the PEt₃ moiety give rise to a complex pattern (Table 2) as a consequence of their being diastereotopic. The spectroscopic data for **IVa** and **IVc** may be interpreted in a similar manner to those of **IVb**, leaving no doubt that all three compounds have similar structures. Although the ¹³C-{¹H} NMR spectra of **IVa** and **IVc** were insufficiently resolved in the aromatic region to allow all resonances to be identified, it was evident that for these species also the C₆H₄ fragment displays more

than four signals, in accord with restricted rotation about the C-C¹(C₆H₄Me-4) bond.

The reaction between compound **IIb** and MeLi was also investigated and found to give a chromatographically inseparable mixture (*ca.* 2:3) of [NEt₄][Rh(CO)(PPh₃){ η^5 -7,9-C₂B₉H₁₀[C(H)(Me)(C₆H₄Me-4)]-10}] (**IIIe**) and [NEt₄][Rh(COMe){ σ,η^5 -7,9-C₂B₉H₁₀[C(H)-C₆H₄Me-4]-10}(PPh₃)] (**V**). The NMR signals recorded on mixtures of these two products were well resolved, allowing the resonances for both to be assigned on the basis of the observed chemical shifts, coupling constants, and peak intensities. Moreover, the NMR data revealed that both **IIIe** and **V** exist as single diastereoisomers. Since the two complexes are isomers, microanalysis of the mixture (Table 1) was indicative of the composition.



Clearly **IIIe** arises from nucleophilic attack of Me⁻ on the exopolyhedral bridging carbon atom of **IIb**, whereas **V** results from attack on the carbonyl ligand. Since the two compounds are so disparate, and there is no interconversion between them, it is reasonable for their spectroscopic properties to be discussed separately. In the ¹¹B-{¹H} NMR spectrum of **IIIe** there is a diagnostic resonance for the BC(H)(Me)(C₆H₄Me-4) nucleus at δ 3.0, and correspondingly in the ¹³C-{¹H} NMR spectrum there is a very broad peak for the BC(H)(Me)(C₆H₄Me-4) carbon atom at δ 33.7. In the latter spectrum the CO resonance occurs as a doublet of doublets at δ 198.2 [$J(\text{RhC})$ 92, $J(\text{PC})$ 21 Hz]. This observation clarifies the somewhat unexpected pattern seen for the CO resonance in the spectrum of **IVb** which, as mentioned above, occurs as a doublet of doublets of doublets (J 92, 22, and 4 Hz). Clearly the small 4 Hz coupling must be a ⁴ $J(\text{PC})$ coupling with the PEt₃ group. Interestingly, the C₆H₄ group in the ¹³C-{¹H} NMR spectrum of **IIIe** gives rise to the customary four peaks, indicating free rotation about the C-C¹(C₆H₄Me-4) bond. This is in contrast with the six signals for the C₆H₄ group seen in the spectrum of **IVb**, mentioned earlier. Since the Me group in **IIIb** is appreciably less sterically demanding than the tertiary phosphine molecules present in the complexes **IV** it is not surprising that rotation about the C-C¹(C₆H₄Me-4) bond can take place in **IIIe**.

Owing to the presence of the peaks from the NEt₄⁺ counter ion in **IIIe**, in the ¹H NMR spectrum it was

initially impossible to detect the resonances due to the BC(H)(Me)(C₆H₄Me-4) protons. Accordingly the synthesis was repeated using [N(PPh₃)₂]⁺ as the counter ion. This allowed the signal for the BC(H)Me group to be measured as a doublet [*J*(HH) 7 Hz] at δ 1.25, and the BC(H)Me proton to be seen as a quartet [*J*(HH) 7 Hz] at δ 3.06. The C₆H₄Me-4 protons resonated as a singlet at δ 2.00.

The IR spectrum of **V** displays a broad band at 1600 cm⁻¹, typical for an acyl group. In the ¹³C-{¹H} NMR spectrum the signal for this group is seen at δ 243.3 [*J*(RhC) 32, *J*(PC) 13 Hz]. A very broad resonance at δ 57.6 must be assigned to the C(H)C₆H₄Me-4 nucleus, although it is considerably less deshielded than those observed in the neutral complex **III** (δ 80.4) and the other species of type **II** [2e, 3]. In the ¹¹B-{¹H} NMR spectrum the presence of the BC(H)C₆H₄Me-4 nucleus is revealed by a resonance at δ 3.0, the remaining boron atoms giving broad overlapping signals in the range δ -11.6 to -28.4.

For all the complexes **III** and **IV** the CO stretches in the IR spectra (Table 1) are at very similar or even the same frequencies as those of the salts **I** (for **Ie**, $\nu_{\max}$ (CO) is at 1915 cm⁻¹ [8]). In contrast, $\nu_{\max}$ (CO) for **III** (2022 cm⁻¹) is *ca.* 100 cm⁻¹ higher in frequency. This suggests that in the species **III** and **IV** negative charge resides to an appreciable degree at the metal centres, leading to the expectation that the rhodium atoms in the latter might show nucleophilic character, reacting with electrophiles in certain circumstances, as does rhodium in the reagents **I**. To test this idea the reaction between **IVa** and [Au(PPh₃)]⁺ was investigated.

Treatment of **IVa** in THF with [AuCl(PPh₃)], in the presence of TIBF₄, afforded the green complex [RhAu(CO)(PPh₃)₂(η^5 -7,9-C₂B₉H₁₀[C(H)C₆H₄Me-4](PMe₃)-10)][BF₄] (**VI**), fully characterised by the data given in Tables 1–3. The salt **VI** is closely related to the neutral complexes [RhAu(CO)(PPh₃)₂(η^5 -7,*n*-C₂B₉H₁₁)] (*n* = 8 [2b] or 9 [2g]) obtained by treating the salts **Ib** or **Ie**, respectively, with [AuCl(PPh₃)] in the presence of TIBF₄ to facilitate removal of chloride as insoluble TiCl₄.

The ³¹P-{¹H} NMR spectrum of **VI** has resonances for the Rh(PPh₃) group at δ 34.1 [*J*(RhP) 126 Hz], the PMe₃ group at δ 33.7, and the Au(PPh₃) group at δ 30.7 [*J*(RhP) 4 Hz]. No other signals were observed, indicating that only one diastereoisomer was formed, probably for steric reasons connected with the bulky Au(PPh₃) group. In the ³¹P-{¹H} NMR spectrum of [RhAu(CO)(PPh₃)₂(η^5 -7,9-C₂B₉H₁₁)] resonances for the Rh(PPh₃) and Au(PPh₃) groups are seen at δ 36.4 [*J*(RhP) 132 Hz] and 33.2, respectively [2g]. In the IR spectrum of this compound the CO stretch is at 1993 cm⁻¹, to be compared with that at 1972 cm⁻¹ for **VI**.

The latter value reflects the different Rh–CO bonding in the two complexes. The CO absorption for **VI** is appreciably lower than one would expect for a cationic carbonyl complex, and must be a consequence of the positive charge being some distance away at the phosphorus atom, thus allowing significant back bonding from the rhodium to the carbonyl ligand. The shift in frequency from 1927 cm⁻¹ in **IVa** to 1972 cm⁻¹ in **VI** is, however, consistent with a transition from an anionic- to a cationic- type rhodium complex, lending credence to the proposal that there is significant separation and localisation of the positive and negative charges in the zwitterionic compounds **IV**. Thus effectively, in the formation of **VI** from **IVa** the rhodium centre has gone from being anionic in character to neutral. In accord with this, the magnitude of the ¹⁰³Rh–¹³C CO coupling in the ¹³C-{¹H} NMR spectrum decreases from 92 Hz in **IVa** to 76 Hz in **VI**, a value very close to that (73 Hz) in [RhAu(CO)(PPh₃)₂(η^5 -7,9-C₂B₉H₁₁)] [2g]. The 92 Hz ¹⁰³Rh–¹³C CO coupling for **IVa** is typical for a rhodium complex in which the metal centre carries a negative charge.

The ¹³C-{¹H} NMR spectrum of **VI** shows resonances for the non-equivalent cage CH vertices at δ 57.9 and 51.4, a very broad peak for the BC(H)(C₆H₄Me-4)(PMe₃) atom at δ 37.2, and peaks for the Me-4 and PMe₃ groups at δ 21.3 and 10.6 [*J*(PC) 54 Hz], respectively. In the ¹H NMR spectrum the BC(H)(C₆H₄Me-4)(PMe₃) is a doublet at δ 3.67 [*J*(PH) 22 Hz], and in the ¹¹B-{¹H} NMR spectrum the signal at δ 0.4 is assigned to the BC(H)(C₆H₄Me-4)(PMe₃) nucleus. In agreement this resonance remains a singlet in a proton-coupled ¹¹B spectrum.

The reactions reported in this paper illustrate the reactive nature of the μ -C(H)R groups in the complexes **II** and the nucleophilicity of the rhodium centres in the compounds **IV**. Both observations exemplify the potential of these compounds for further syntheses.

3. Experimental section

Light petroleum refers to the fraction of b.p. 40–60°C. All solvents were distilled over appropriate drying agents prior to use. Chromatography columns, *ca.* 15 cm long and 3 cm wide, were packed with alumina (Brockmann activity II). Celite pads used to remove TiCl₄ by filtration, were *ca.* 3 cm thick. All experiments were carried out under nitrogen by using Schlenk-tube techniques. The NMR measurements were made with a Bruker AMX 360 MHz instrument. Throughout this paper chemical shifts (δ) are expressed in ppm. The IR spectra were recorded with a Bruker IFS 25 spectrometer. The reagents [NEt₄][Rh(CO)(PPh₃)(η^5 -7,9-C₂B₉H₁₁)] (**Ie**) [8], [Mn(=CC₆H₄Me-4)(CO)₂(η^5 -C₅H₄Me)]

[BCl₄] [9], and [AuCl(PPh₃)] [10] were prepared by procedures previously described. The reagent K[BH(CHMeEt)₃] (1.0 mol dm⁻³ solution in THF) was obtained from Aldrich Chemicals. Analytical and other data for the new compounds are given in Table 1.

3.1. Synthesis of [Rh(σ,η^5 -7,9-C₂B₉H₁₀[C(H)C₆H₄Me-4]-10)(CO)(PPh₃)]

A CH₂Cl₂ (25 cm³) solution of **Ie** (0.50 g, 0.76 mmol) was saturated with CO gas, [Mn($\equiv$ CC₆H₄Me-4)(CO)₂(η^5 -C₅H₄Me)] [BCl₄] (0.34 g, 0.76 mmol) was added, and the mixture stirred under CO for ca. 5 min. Solvent was removed *in vacuo* and the residue dissolved in CH₂Cl₂-light petroleum (10 cm³, 3:2) and chromatographed on alumina at -10°C. Elution with the same solvent mixture afforded an orange eluate. Solvent was removed *in vacuo* and the residue crystallised from CH₂Cl₂-light petroleum (50 cm³, 1:20) to give the product as an orange oil due to the presence of [Mn(CO)₃(η^5 -C₅H₄Me)], another product of the reaction. Trituration with light petroleum (50 cm³) for ca. 2 h afforded orange microcrystals of [Rh(σ,η^5 -7,9-C₂B₉H₁₀[C(H)C₆H₄Me-4]-10)(CO)(PPh₃)] (**III**f), and removed the [Mn(CO)₃(η^5 -C₅H₄Me)], which is soluble in light petroleum. The product was washed with light petroleum (2 $\times$ 25 cm³) and dried *in vacuo* (0.40 g).

3.2. Reactions of the complex [Rh(σ,η^5 -7,9-C₂B₉H₁₀[C(H)C₆H₄Me-4]-10)(CO)(PPh₃)]

(i) A THF (20 cm³) solution of **III**f (0.15 g, 0.24 mmol) was treated with K[BH(CHMeEt)₃] (0.27 cm³, 0.27 mmol) and the mixture stirred for ca. 15 min, after which [NEt₄]Cl (0.048 g, 0.27 mmol) was added and the mixture further stirred for 1 h. Solvent was removed *in vacuo* and the yellow-green residue extracted with CH₂Cl₂ (2 $\times$ 20 cm³); the extracts were filtered through a Celite pad to give a green solution, from which the solvent was removed *in vacuo*. The residue was redissolved in the minimum of CH₂Cl₂ (3 cm³) and Et₂O (50 cm³) was added dropwise with vigorous stirring to afford a green oil. This oil was washed with Et₂O (2 $\times$ 20 cm³) and then triturated with light petroleum (50 cm³) for ca. 1 h to give dark green microcrystals of [NEt₄][Rh(CO)(PPh₃)(η^5 -7,9-C₂B₉H₁₀(CH₂C₆H₄Me-4)-10)] (**III**d), which were washed with light petroleum (2 $\times$ 10 cm³) and dried *in vacuo* (0.18 g).

(ii) To a THF (15 cm³) solution of **III**f (0.10 g, 0.16 mmol) was added PMe₃ (0.30 cm³ of a 0.5 mol dm⁻³ solution in THF, 0.16 mmol). The mixture lightened immediately and was stirred for ca. 15 min, after which the solvent was removed *in vacuo*. The orange residue was dissolved in CH₂Cl₂-light petroleum (5 cm³, 3:2) and chromatographed on alumina at -10°C. Elution

with the same solvent mixture afforded initially an orange fraction, followed by a yellow band. The orange band was collected and subsequently shown by IR and NMR spectroscopy to be a trace of unreacted **III**f. The yellow band was eluted with pure CH₂Cl₂, affording a green-yellow solution. Removal of solvent *in vacuo*, followed by crystallisation from CH₂Cl₂-light petroleum (30 cm³, 1:10) gave green-yellow microcrystals of [Rh(CO)(PPh₃)(η^5 -7,9-C₂B₉H₁₀[C(H)C₆H₄Me-4](PMe₃)-10)] (**IV**a), which were washed with light petroleum (2 $\times$ 10 cm³) and dried *in vacuo* (0.11 g).

(iii) Similarly a THF (15 cm³) solution of **III**f (0.10 g, 0.16 mmol) was treated with PEt₃ (0.024 cm³, 0.16 mmol), causing the solution to lighten in colour immediately from dark orange to golden yellow. After ca. 5 min stirring the solvent was removed *in vacuo*. The resulting residue was dissolved in CH₂Cl₂-light petroleum (5 cm³, 3:2) and chromatographed on alumina at -10°C. Elution with the same solvent mixture afforded a yellow eluate. Removal of solvent *in vacuo*, followed by crystallisation from CH₂Cl₂-light petroleum (20 cm³, 1:10) gave yellow microcrystals of [Rh(CO)(PPh₃)(η^5 -7,9-C₂B₉H₁₀[C(H)C₆H₄Me-4](PEt₃)-10)] (**IV**b), which were washed with light petroleum (2 $\times$ 10 cm³) and dried *in vacuo* (0.10 g).

(iv) In a similar experiment, involving stirring of **III**f in THF (15 cm³) with PMe₂Ph (0.32 cm³ of a 0.5 mol dm⁻³ solution in THF, 0.16 mmol) for ca. 10 min, chromatographing as above, and crystallising the yellow eluate from CH₂Cl₂-light petroleum (20 cm³, 1:4), afforded yellow microcrystals of [Rh(CO)(PPh₃)(η^5 -7,9-C₂B₉H₁₀[C(H)C₆H₄Me-4](PMe₂Ph)-10)] (**IV**c), (0.10 g).

(v) Compound **III**f (0.20 g, 0.32 mmol) in THF (15 cm³) was treated with MeLi (0.23 cm³, 0.32 mmol), the mixture immediately darkening to red. After ca. 15 min stirring [NEt₄]Cl (0.071 g, 0.39 mmol) was added, and the mixture stirred for a further 30 min. The solvent was then removed *in vacuo*, the resulting red residue extracted with CH₂Cl₂ (2 $\times$ 20 cm³) and the extracts were filtered through a Celite pad to afford a dark red filtrate. Solvent was removed *in vacuo*, and the oily residue crystallised from CH₂Cl₂-light petroleum (20 cm³, 1:6) to give a red oil, which was washed with light petroleum (2 $\times$ 10 cm³) and then triturated with Et₂O (ca. 50 cm³) for ca. 1 h to afford a red powder, which was dried *in vacuo*. IR and NMR spectroscopy established that this was an inseparable mixture of the complexes, [NEt₄][Rh(CO)(PPh₃)(η^5 -7,9-C₂B₉H₁₀[C(H)(Me)C₆H₄Me-4]-10)] (**III**e), and [NEt₄][Rh(COMe)(σ,η^5 -7,9-C₂B₉H₁₀[C(H)C₆H₄Me-4]-10)(PPh₃)] (**V**) (0.24 g), formed in ca. 2:3 ratio, based on the relative intensities of the ³¹P and ¹H NMR resonances of the mixture.

TABLE 5. Crystal data for compound **IVb**

Molecular formula	C ₃₅ H ₄₈ B ₉ OP ₂ Rh·CH ₂ Cl ₂
M	831.8
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (non-standard No. 14)
<i>a</i> /Å	13.027(4)
<i>b</i> /Å	17.415(4)
<i>c</i> /Å	18.501(5)
β /°	98.92(2)
<i>U</i> /Å ³	4146(2)
<i>Z</i>	4
<i>D_c</i> /Mg m ⁻³	1.33
<i>F</i> (000)	1712
μ (Mo K α)/cm ⁻¹	6.47
<i>T</i> /K	295
Diffractometer	Siemens R3m/V
Scan type	Wyckoff ω
Scan speed/° min. ⁻¹	2–14.65
Scan range (ω)	1.20
2 θ range (°)	5.0–50.0
Radiation	Mo K α (λ , 0.71073 Å)
Collected data	7917
Unique data	7298
Observed data [<i>F</i> ≥ 5.0 σ (<i>F</i>)]	5133
Data-to-parameter ratio	10.3:1
Weighting scheme	$w^{-1} = [\sigma^2(F) + 0.0005 F ^2]$
<i>R</i> , <i>R_w</i>	0.049, 0.048
Residual density (max., min./eÅ ⁻³)	1.03, –1.01

3.3. Reaction of [AuCl(PPh₃)] with [Rh(CO)(PPh₃)]{ η^5 -7,9-C₂B₉H₁₀[C(H)(C₆H₄Me-4)(PMe₃)]-10}

The compounds **IVa** (0.080 g, 0.11 mmol), [AuCl(PPh₃)] (0.056 g, 0.11 mmol), and TlBF₄ (0.036 g, 0.12 mmol) were stirred in THF (20 cm³) for *ca.* 2 h. The mixture was then filtered through a Celite pad, to remove TlCl, giving a pale yellow-green solution. Solvent was removed *in vacuo*, and the residue crystallised from CH₂Cl₂-light petroleum (20 cm³, 1:6) to afford pale green microcrystals of [RhAu(CO)(PPh₃)₂]{ η^5 -7,9-C₂B₉H₁₀[C(H)(C₆H₄Me-4)(PMe₃)]-10}[BF₄] (**VI**), which were washed with light petroleum (2 × 5 cm³) and dried *in vacuo* (0.13 g).

3.4. Crystal structure determination

Crystals of compound **IVb** were grown from a CH₂Cl₂-light petroleum (6 cm³, 1:5) solution. The X-ray data were obtained from a clear yellow rectangular crystal (0.41 × 0.42 × 0.61 mm). Crystal data and relevant parameters are summarised in Table 5. The collected intensities showed no signs of significant decay. After the intensity data were corrected for Lorentz and polarization effects, an empirical absorption correction was applied.

The structure was solved by Patterson and Fourier methods using the SHELXTL package [11]. The structure was refined by full-matrix least-squares, with anisotrop-

ic thermal parameters for all non-hydrogen atoms. The hydrogen atoms attached to the boron atoms and C(10) were located and refined with fixed isotropic thermal parameters (*U*_{iso} = 0.08 Å²). All remaining hydrogen

TABLE 6. Atomic positional parameters (fractional coordinates × 10⁴) for **IVb**, with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Rh	2201(1)	1994(1)	1409(1)
P(1)	1468(1)	3003(1)	1934(1)
P(2)	2011(1)	925(1)	–1029(1)
B(1)	2910(5)	1623(4)	416(3)
C(2)	3441(4)	2463(3)	739(3)
B(3)	3852(5)	2430(4)	1669(3)
C(4)	3845(5)	1509(4)	1916(3)
B(5)	3157(5)	983(4)	1232(4)
B(6)	4177(5)	1917(4)	247(3)
B(7)	4739(5)	2467(5)	1007(4)
B(8)	5005(6)	1838(5)	1768(4)
B(9)	4549(6)	918(4)	1468(4)
B(10)	3992(5)	982(4)	535(4)
B(11)	5150(5)	1503(5)	878(4)
C(5)	993(5)	1473(4)	1340(4)
O(5)	251(4)	1111(3)	1292(4)
C(10)	1947(4)	1586(3)	–277(3)
C(11)	1568(4)	2369(3)	–579(3)
C(12)	579(4)	2632(3)	–506(3)
C(13)	224(4)	3340(3)	–776(3)
C(14)	831(4)	3813(3)	–1128(3)
C(15)	1817(5)	3562(3)	–1207(3)
C(16)	2169(4)	2846(3)	–936(3)
C(17)	450(5)	4593(3)	–1410(4)
C(21)	1686(4)	3066(3)	2938(3)
C(22)	1131(4)	3580(3)	3312(3)
C(23)	1273(5)	3598(3)	4065(3)
C(24)	1995(5)	3110(4)	4456(3)
C(25)	2565(5)	2606(4)	4096(3)
C(26)	2401(5)	2589(3)	3338(3)
C(31)	1864(4)	3949(3)	1635(3)
C(32)	1840(4)	4066(3)	885(3)
C(33)	2157(5)	4762(4)	633(3)
C(34)	2519(5)	5337(3)	1104(4)
C(35)	2568(5)	5222(3)	1847(4)
C(36)	2246(4)	4535(3)	2108(3)
C(41)	42(4)	3021(3)	1749(3)
C(42)	–508(5)	2564(4)	2172(4)
C(43)	–1577(5)	2476(5)	2007(5)
C(44)	–2116(5)	2859(5)	1405(5)
C(45)	–1594(5)	3310(5)	988(4)
C(46)	–510(4)	3393(4)	1144(3)
C(51)	2017(5)	–49(4)	–716(4)
C(52)	1410(7)	–224(5)	–125(5)
C(61)	877(5)	1097(5)	–1739(4)
C(62)	–155(6)	942(5)	–1519(5)
C(71)	3123(5)	1054(4)	–1484(3)
C(72)	3156(6)	552(5)	–2154(4)
Cl(1)	6156(4)	4748(3)	977(3)
Cl(2)	5424(5)	5704(5)	1867(4)
Cl(3)	5118(6)	6203(6)	887(8)
C	5102(16)	5204(13)	1187(12)

atoms were included in calculated positions ($C-H = 0.96 \text{ \AA}$) with fixed isotropic thermal parameters ($U_{iso} = 0.08 \text{ \AA}^2$). The asymmetric unit contains a badly disordered molecule of CH_2Cl_2 . One of the Cl atoms [Cl(1)] has a reasonably well defined location but it was necessary to refine the second Cl atom as two separate components [Cl(2) and Cl(3)] each having a 50% site occupancy. The final difference Fourier map showed the highest peak to be $1.03 \text{ e \AA}^{-3}$, this being in the vicinity of the disordered solvent molecule. Atomic scattering factors were taken from ref. [12]. Final atomic positional parameters for non-hydrogen atoms are given in Table 6.

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

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References and notes

- 1 In the complexes discussed in this paper rhodium atoms form with $[nido\text{-}7,n\text{-C}_2\text{B}_9\text{H}_9R'_2]^{2-}$ ($n = 8$ or 9) anions *closo*-1,2-dicarba-3-rhodadodecaborane and *closo*-1,7-dicarba-2-rhodadodecaborane structures, respectively. In the formulae the carborane groups are designated as $\eta^5\text{-C}_2\text{B}_9\text{H}_9R'_2$ in order to emphasise their pentahapto ligand properties in which these *nido*-fragments

formally act as four electron donors. We therefore treat the cages in the products as *nido*-11-vertex ligands with the numbering as for an icosahedron from which the twelfth vertex has been removed, in order to avoid a cumbersome labelling system.

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