# Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 102.<sup>1</sup> Alkylidyne Ligand Migration from Manganese to a Rhodacarbaborane Cluster; Crystal Structure of $[Rh{\sigma,\eta^5}-CH(C_6H_4Me-4)-C_2B_9H_{10}}(CO)(PPh_3)]^*$

# Massimino U. Pilotti and F. Gordon A. Stone

Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Treatment of CO-saturated CH<sub>2</sub>Cl<sub>2</sub> solutions of the salts [X][Rh(CO)L( $\eta^{5}$ -C<sub>2</sub>B<sub>4</sub>H<sub>3</sub>R'<sub>2</sub>)][X = NEt<sub>4</sub>, L = PPh<sub>a</sub>, R' = H; L = CO, R' = Me; X = N(PPh<sub>3</sub>)<sub>2</sub>, L = CO, R' = H] with the reagents [Mn( $\equiv$ CR)- $(CO)_2(\eta - C_5H_4Me)][BCI_4]$  (R = C<sub>6</sub>H<sub>4</sub>Me-4 or C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6) affords the rhodium complexes [Rh{σ,η⁵-CH(R)C₂B₀H₄R′₂}(CO)L] (R = C₅H₄Me-4, R′ = H, L = PPh₃ or CO; R = C₅H₄Me-4, R' = Me, L = CO;  $R = C_{e}H_{3}Me_{2}$ -2,6, R' = H,  $L = PPh_{3}$ ). The structure of the compound  $[Rh{\sigma,\eta^{5}-CH(C_{6}H_{4}Me-4)C_{2}B_{9}H_{10}}(CO)(PPh_{3})]$  was established by X-ray diffraction. The rhodium atom is ligated by the CO and PPh<sub>3</sub> groups [Rh-CO 1.854(3), Rh-P 2.302(1)], and by the  $CH(C_6H_4Me-4)C_2B_9H_{10}$  fragment. In the latter the  $CH(C_6H_4Me-4)$  moiety forms a bridge between the rhodium [Rh-C 2.374(3) Å] and a boron atom [B-C 1.501(4) Å] in the pentagonal face of the cage. This boron atom is in the  $\beta$  site (BBBCC) with respect to the carbon atoms, and all the atoms of the ring are bonded to the rhodium, but the connectivities are somewhat asymmetric [Rh–C 2.373(3) and 2.341(3) Å, Rh–B 2.205(3), 2.165(3), and 2.237(3) Å]. In the molecule the PPh<sub>3</sub> and C<sub>6</sub>H<sub>4</sub>Me-4 groups are transoid to one another about the Rh–CH(C<sub>6</sub>H<sub>4</sub>Me-4)  $\sigma$  bond, but n.m.r. studies on solutions reveal the presence of a second isomer with a cisoid configuration for the PPh<sub>2</sub> and  $C_{e}H_{e}Me$ -4 groups. Reactions of the rhodium compounds with K[BH(CHMeEt)<sub>2</sub>] in tetrahydrofuran led to rupture of the Rh–C(H)R  $\sigma$  bonds and formation, in the presence of NEt<sub>4</sub>Cl, of the salts [NEt<sub>4</sub>][Rh(CO)L{ $\eta^5$ -C<sub>2</sub>B<sub>9</sub>H<sub>8</sub>(CH<sub>2</sub>R)R'<sub>2</sub>}] (L = PPh<sub>2</sub>, R = C<sub>6</sub>H<sub>4</sub>Me-4 or C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6, R' = H;  $L = CO, R = C_{4}H_{4}Me-4, R' = Me$ ). The n.m.r. data (<sup>1</sup>H, <sup>13</sup>C-{<sup>1</sup>H}, <sup>31</sup>P-{<sup>1</sup>H}, and <sup>11</sup>B-{<sup>1</sup>H}) for the new complexes are reported and discussed.

We have recently reported <sup>2</sup> the synthesis of several complexes containing Rh-Co, Rh-Rh, Rh-Ir, and Rh-Au bonds using the salts [NEt<sub>4</sub>][Rh(CO)L( $\eta^5$ -C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>R'<sub>2</sub>)] (1a; L = PPh<sub>3</sub>, R' = H) and (1b; L = CO, R' = Me) as precursors. In this paper we report reactions of the salts (1) with the complexes [Mn(=CR)(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>4</sub>Me)][BCl<sub>4</sub>] (R = C<sub>6</sub>H<sub>4</sub>Me-4 or C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6).

The motive for the present work arose in the following manner. The anions present in the compounds (1) can be isolobally mapped with the well known species  $[M(CO)_5]^{-1}$ (M = Mn or Re). Several years ago, we<sup>3</sup> and others<sup>4</sup> showed that the latter reagents react with the cationic alkylidyne complexes  $[M'(\equiv CR)(CO)_2(\eta - C_5H_5)]^+$  (M' = Mn or Re,  $R = Ph \text{ or } C_6H_4Me-4$ ) to yield dimetal  $\mu$ -ketenyl compounds  $[MM'{\mu-C(CO)R}(CO)_6(\eta-C_5H_5)]$  $(\mathbf{M} = \mathbf{M}' = \mathbf{M}\mathbf{n},$  $R = C_6H_4Me-4$ ; M = Re, M' = Mn, R = Ph; M = Mn,  $M' = Re, R = C_6H_4Me-4$ ). It seemed probable, therefore, that reactions between the salts (1) and the compounds  $[Mn(\equiv CR)(CO)_2(\eta-C_5H_4Me)][BCl_4]$  would afford stable products containing Mn-Rh bonds. However, based on recent work in this laboratory,5 it seemed likely that if dimetal species were formed the carbaborane ligands would adopt a non-spectator role, forming exopolyhedral B-H ----Mn bonds. Thus, for example, this type of three-centre twoelectron bonding is observed in the products  $[MW(\mu-CC_6H_4-$ Me-4)(CO)<sub>3</sub>( $\eta^{5}$ -C<sub>9</sub>H<sub>7</sub>)( $\eta^{5}$ -C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>R'<sub>2</sub>)][ $\eta^{5}$ -C<sub>9</sub>H<sub>7</sub> = indenyl; (2a; M = Mo, R' = Me), (2b; M = W, R' = Me), and (2c; M = Mo, R' = H] obtained by treating the salts [N(PPh<sub>3</sub>)<sub>2</sub>]- $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta^5-C_2B_9H_9R'_2)]$  with  $[M(CO)_2-M(CO)_2+M(CO)_2]$  $(NCMe)_2(\eta^5-C_9H_7)][BF_4]$  (M = Mo or W).<sup>6</sup> In practice, the salts (1) and the species  $[Mn(\equiv CR)(CO)_2(\eta - C_5H_4Me)][BCl_4]$  underwent an unprecedented reaction involving transfer of the alkylidyne ligands from the manganese to the rhodium, accompanied by an insertion of these groups into a B-H bond in the pentagonal BBBCC face of the *nido*-icosahedral  $\eta^{5}$ -C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>R'<sub>2</sub> fragment.

# **Results and Discussion**

At room temperature in  $CH_2Cl_2$ , the reaction between the salts (1a) and  $[Mn(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_4Me)][BCl_4]$  affords the orange crystalline complex  $[Rh\{\sigma,\eta^5-CH(C_6H_4Me-4)C_2B_9H_{10}\}(CO)(PPh_3)]$  (3a), data for which are given in Tables 1—3. Subsequently, the synthesis of (3a), and related species described below, was carried out using CO-saturated solutions of  $CH_2Cl_2$ . This procedure was adopted to increase yields, after it became apparent that an  $Mn(\eta-C_5H_4Me)$  fragment was being eliminated in the reaction, presumably as  $[Mn(CO)_3(\eta-C_5H_4Me)]$ .

Examination of the spectroscopic data for (3a) made it immediately apparent that it was not an MnRh species. Thus there was only one CO stretching band in the i.r. spectrum, and the <sup>1</sup>H n.m.r. spectrum revealed the absence of an  $\eta$ -C<sub>5</sub>H<sub>4</sub>Me group. It was also evident from the <sup>11</sup>B-{<sup>1</sup>H} n.m.r. data that the  $\eta$ -C<sub>2</sub>B<sub>9</sub>H<sub>11</sub> ligand present in the precursor (1a) had become modified as a result of this reaction. Fortunately, good-quality

<sup>\*</sup> Carbonyl[(7,8,9,10,11-η)-7,8-dicarba-*nido*-undecaboran-10-yl(*p*-tolyl)methyl](triphenylphosphine)rhodium.

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single crystals of (3a) were available for an X-ray diffraction study, the results of which are summarised in Table 4. The structure of the compound is shown in the Figure.

Compound (3a) is thus a mononuclear rhodium complex ligated, as expected, by a PPh<sub>3</sub> group [Rh–P 2.302(1) Å] and a CO molecule, the latter being bound in an essentially linear manner [Rh–C–O 174.4(3)°]. Unexpectedly, although the carbaborane cage is  $\eta^5$  co-ordinated to the rhodium, as it is in the precursor (1a), this ligand now carries a C(H)C<sub>6</sub>H<sub>4</sub>Me-4 substituent at B(4) [C(4)–B(4) 1.501(4) Å]. Moreover, C(4) is linked to the Rh atom [Rh–C(4) 2.374(3) Å], so that there is a BCH(C<sub>6</sub>H<sub>4</sub>Me-4)Rh bridge system. The Rh-C(4) distance,



Figure. Molecular structure of  $[Rh{\sigma,\eta^5-CH(C_6H_4Me-4)C_2B_9H_{10}}-(CO)(PPh_3)]$  (3a), showing the atom labelling scheme

however, is relatively long for a Rh–C  $\sigma$  bond (normal range 2.036-2.192 Å).<sup>7</sup> This is perhaps not surprising since appreciable strain would be expected in the molecule to accommodate the three-membered RhB(4)C(4) ring. Indeed this strain may be responsible for the somewhat asymmetric way in which the pentagonal BBBCC face ligates the metal centre [Rh-C(1) 2.373(3), Rh-C(2) 2.341(3), Rh-B(5) 2.237(3), Rh-B(3) 2.205(3), and Rh-B(4) 2.165(3) Å]. Slippage of the carbaborane cage carries B(4) closer to the rhodium atom. This slippage may be quantified in terms of three parameters: (i) a slip distance ( $\Delta$ ) from the perpendicular through the centroid of the non-bonded pentagonal B(6)-B(10) girdle to the metal atom, and (ii) two fold angles  $\theta$  and  $\phi$  representing the angles between the perpendicular through the centroid of the B(6)B(7)B(8)B(9)B(10) ring and the planes defined by B(5)C(1)-C(2)B(3) and B(3)B(4)B(5), respectively.<sup>8</sup> For compound (3a) these parameters are  $\Delta = 0.31$  Å,  $\theta = 1.3^{\circ}$ , and  $\varphi = 2.3^{\circ}$ . As discussed below, the n.m.r. data for (3a) reveal that the complex exists as a mixture of two isomers. The crystal structure corresponds to what we believe to be the major isomer, with the PPh<sub>3</sub> and C<sub>6</sub>H<sub>4</sub>Me-4 groups in a transoid configuration with respect to the Rh-C(4) bond.

Having established the crystal structure of (3a), the n.m.r. data (Tables 2 and 3) can be evaluated. The <sup>11</sup>B-{<sup>1</sup>H} n.m.r. spectrum showed a diagnostic signal at  $\delta$  17.4 p.p.m. for an exopolyhedral B-C linkage. Moreover, this resonance remained a singlet in a <sup>11</sup>B n.m.r. spectrum, while the other resonances became doublets due to <sup>1</sup>H-<sup>11</sup>B coupling. For the compounds [NEt<sub>4</sub>][Mo{ $\sigma,\eta^5$ -CH(C<sub>6</sub>H<sub>4</sub>Me-4)C<sub>2</sub>B<sub>9</sub>H<sub>8</sub>Me<sub>2</sub>}-(CO)<sub>3</sub>] (4),<sup>9</sup> [MoW{ $\mu-\sigma,\eta^5$ -CH(C<sub>6</sub>H<sub>4</sub>Me-4)C<sub>2</sub>B<sub>9</sub>H<sub>8</sub>Me<sub>2</sub>}-(CO)<sub>3</sub>( $\eta$ -EtC<sub>2</sub>Et)( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)] (5),<sup>10</sup> and [WRu{ $\mu-\sigma,\eta^5$ -CH-(C<sub>6</sub>H<sub>4</sub>Me-4)C<sub>2</sub>B<sub>9</sub>H<sub>8</sub>Me<sub>2</sub>})-(CO)<sub>3</sub>( $\eta$ -EtC<sub>2</sub>Et)( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)] (5),<sup>10</sup> and [WRu{ $\mu-\sigma,\eta^5$ -CH-(C<sub>6</sub>H<sub>4</sub>Me-4)C<sub>2</sub>B<sub>9</sub>H<sub>8</sub>Me<sub>2</sub>)-(CO)<sub>3</sub>(PMe<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] (6)<sup>11</sup> the <sup>11</sup>B-{<sup>11</sup>H} n.m.r. signals for the BCH(C<sub>6</sub>H<sub>4</sub>Me-4) nuclei occur at  $\delta$  8.7, 34.0, and 65.4 p.p.m., respectively.

An interesting feature of the <sup>11</sup>B-{<sup>1</sup>H} n.m.r. spectrum of compound (**3a**) was the appearance of 10 signals, some of which corresponded in intensity to two boron nuclei. Clearly more than one species is present in solution. This was confirmed by the <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum which when measured at -50 °C showed two doublet resonances (Table 3) of relative intensity *ca.* 3:2, corresponding to two Rh(PPh<sub>3</sub>) environments. Moreover, examination of the <sup>1</sup>H and <sup>13</sup>C-{<sup>1</sup>H} n.m.r. spectrum (Table 2) peaks corresponding to a C(H)C<sub>6</sub>H<sub>4</sub>Me-4 group with two different configurations. We

# Table 1. Analytical<sup>a</sup> and physical data for the rhodium complexes

				Analysis (%)		
Compound	Colour	Yield (%)	$v_{max.}(CO)^{b}/cm^{-1}$	С	Н	N
(3a) $[Rh{\sigma,\eta^{5}-CH(C_{6}H_{4}Me-4)C_{2}B_{9}H_{10}}(CO)(PPh_{3})]$	Orange	52	2 013vs	54.5 (55.3)	5.3 (5.3)	
( <b>3b</b> ) [Rh{ $\sigma,\eta^{5}$ -CH(C <sub>6</sub> H <sub>3</sub> Me <sub>2</sub> -2,6)C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> }(CO)(PPh <sub>3</sub> )]	Orange	53	2 011vs	55.2 (56.0)	6.1 (5.5)	
(3c) $[Rh{\sigma,\eta^{5}-CH(C_{6}H_{4}Me-4)C_{2}B_{9}H_{10}](CO)_{2}]$	Red	50	2 080vs, 2 041s	36.6 (36.5)	5.3 (4.6)	
(3d) $[Rh{\sigma,\eta^{5}-CH(C_{6}H_{4}Me-4)C_{2}B_{9}H_{8}Me_{2}](CO)_{2}]$	Yellow	52	2 074vs, 2 034s	40.3 (39.8)	5.4 (5.2)	
(7a) [NEt <sub>4</sub> ][Rh(CO)(PPh <sub>3</sub> ){ $\eta^{5}$ -C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> (CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> - Me-4)}]	Orange	98	1 923vs	57.5 (58.5)	7.0 (7.2)	2.0 (1.8)
(7b) [NEt <sub>4</sub> ][Rh(CO)(PPh <sub>3</sub> ){ $\eta^{5}$ -C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> (CH <sub>2</sub> C <sub>6</sub> H <sub>3</sub> - Me <sub>2</sub> -2,6)}]	Orange	98	1 923vs	57.9 (58.9)	7.8 (7.3)	2.1 (1.8)
$(7c) [NEt_4] [Rh(CO)_2 {\eta^{5}-C_2B_9H_8(CH_2C_6H_4Me-4)-Me_2}]$	Yellow	98	2 009vs, 1 940s	46.8 (47.7)	7.8 (7.8)	2.1 (2.5)

<sup>a</sup> Calculated values are given in parentheses. <sup>b</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub>; medium to weak bands at ca. 2 560 cm<sup>-1</sup> are due to B-H absorptions.

# Table 2. Hydrogen-1 and carbon-13 n.m.r. data " for the rhodium complexes

Compound	<sup>1</sup> Η(δ)	$^{13}C^{b}(\delta)$
( <b>3a</b> )°	<sup>4</sup> 2.23* (s, 3 H, Me-4), 2.31 (s, 3 H, Me-4), 2.84, 2.93*, 3.77*, 3.82 [s × 4, br, 4 H, CH( $C_2B_9H_{11}$ )], 6.13, 6.16 [d × 2, BC(H) $C_6H_4$ Me-4 (both isomers), J(RhH) 4], 6.76—7.59 (m, 38 H, $C_6H_4$ , Ph, both isomers)	189.1, 186.9 [d of d $\times$ 2, CO (both isomers), J(RhC) 75, J(PC) 24], 143.5 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> )], 141.8—128.8 (C <sub>6</sub> H <sub>4</sub> and Ph), 95.9 [br, BC(H)C <sub>6</sub> H <sub>4</sub> Me-4], 94.4* [br, BC(H)C <sub>6</sub> H <sub>4</sub> Me-4], 50.2, 49.2, 46.7 (2C) [CH(C <sub>2</sub> B <sub>9</sub> H <sub>11</sub> ) both isomers], 21.8 (Me-4, both isomers)
( <b>3b</b> )	2.13 (s, 6 H, $Me_2$ -2,6), 2.75, 3.84 [s x 2, br, $CH(C_2B_9H_{11})$ ], 6.48 [s, br, 1 H, $BC(H)C_6H_3Me_2$ -2,6], 7.01–7.45 (m, 18 H, $C_6H_3$ and Ph)	189.0 [d of d, CO, $J(RhC)$ 75, $J(PC)$ 25], 141.0—126.9 (m, C <sub>6</sub> H <sub>3</sub> and Ph), 95.0 [br, BC(H)C <sub>6</sub> H <sub>3</sub> Me <sub>2</sub> -2,6], 46.5 [CH(C <sub>2</sub> B <sub>9</sub> H <sub>11</sub> )], 22.5 (Me <sub>2</sub> -2,6)
( <b>3c</b> ) <sup><i>e</i></sup>		184.4, 183.1 [d × 2, CO, $J(RhC)$ 72 and 69], 141.5 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> )], 140.2, 130.8, 130.0 (C <sub>6</sub> H <sub>4</sub> ), 110.2 [br, BC(H)C <sub>6</sub> H <sub>4</sub> Me-4], 51.6, 51.2 [CH(C <sub>2</sub> B <sub>9</sub> H <sub>11</sub> )], 21.7 (Me-4)
( <b>3d</b> )	2.18 (s, 3 H, Me-4), 2.32 (s, 6 H, CMe), 6.87 [d, 1 H, $BC(H)C_6H_4Me$ -4, $J(RhC)$ 3], 7.0, 7.4 [(AB) <sub>2</sub> , 4 H, $C_6H_4$ , $J(AB)$ 8]	183.7, 180.4 [d × 2, CO, J(RhC) 70], 140.9 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> )], 138.8, 129.4, 128.9 (C <sub>6</sub> H <sub>4</sub> ), 77.6, 76.8 (CMe), 29.1, 28.5 (CMe), 20.6 (Me-4)
(7 <b>a</b> )	<sup>f</sup> 1.16 [t, 12 H, $CH_2Me$ , $J(HH)$ 7], 2.28 (s, 3 H, Me-4), 2.48 (s, br, 2 H, $BCH_2C_6H_4Me$ -4), 3.02 [q, 8 H, $CH_2$ - Me, $J(HH)$ 7], 6.93, 7.16 [(AB) <sub>2</sub> , 4 H, $C_6H_4$ , $J(AB)$ 8], 7.33—7.66 (m, 15 H, Ph)	201.1 [d of d, CO, $J(RhC)$ 86, $J(PC)$ 22], 147.5—127.9 (C <sub>6</sub> H <sub>4</sub> and Ph), 52.9 (CH <sub>2</sub> Me), 34.2 (br, BCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Me-4), 29.9 [CH(C <sub>2</sub> B <sub>9</sub> H <sub>11</sub> )], 21.2 (Me-4), 7.7 (CH <sub>2</sub> Me)
( <b>7b</b> )	<sup>f</sup> 1.13 [t, 12 H, CH <sub>2</sub> Me, J(HH) 7], 2.30 (s, 6 H, Me <sub>2</sub> -2,6), 2.69 (s, br, 2 H, BCH <sub>2</sub> C <sub>6</sub> H <sub>3</sub> Me <sub>2</sub> -2,6), 2.95 [q, 8 H, CH <sub>2</sub> Me, J(HH) 7], 6.70–7.70 (m, 18 H, C <sub>6</sub> H <sub>3</sub> and Ph)	200.6 [d of d, CO, $J(RhC)$ 85, $J(PC)$ 24], 148.8—122.2 (C <sub>6</sub> H <sub>3</sub> and Ph), 52.9 (CH <sub>2</sub> Me), 29.6 [CH(C <sub>2</sub> B <sub>9</sub> H <sub>11</sub> )], 27.0 (br, BCH <sub>2</sub> C <sub>6</sub> H <sub>3</sub> Me <sub>2</sub> -2,6), 21.7 (Me <sub>2</sub> -2,6), 7.8 (CH <sub>2</sub> Me)
(7c)	1.27 [t, 12 H, $CH_2Me$ , $J(HH)$ 7], 2.25 (s, 3 H, Me-4), 2.26 (s, 6 H, CMe), 2.41 (s, br, 2 H, $BCH_2C_6H_4$ Me-4), 3.11 [q, 8 H, $CH_2$ Me, $J(HH)$ 7], 6.93, 7.01 [(AB) <sub>2</sub> , 4 H, $C_6H_4$ , $J(AB)$ 8]	191.5 [d, CO, $J$ (RhC) 76], 147.5 [C <sup>1</sup> (C <sub>6</sub> H <sub>4</sub> )] 131.5, 129.4, 128.0 (C <sub>6</sub> H <sub>4</sub> ), 59.4 (CMe), 53.9 (CH <sub>2</sub> Me), 34.0 (br, BCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Me-4), 31.3 (CMe), 21.1 (Me-4), 7.8 (CH <sub>2</sub> Me)
Chemical shifts	s are in p.p.m., coupling constants are in Hz, measurements in CE	$P_{2}Cl_{2}$ at ambient temperatures, unless otherwise stated <sup>b</sup> Hydrogen-1

<sup>*a*</sup> Chemical shifts are in p.p.m., coupling constants are in Hz, measurements in  $CD_2Cl_2$  at ambient temperatures, unless otherwise stated. <sup>*b*</sup> Hydrogen-1 decoupled, chemical shifts are positive to high frequency of SiMe<sub>4</sub>. <sup>*c*</sup> Peaks for minor isomer (see text) are asterisked. Spectra measured at -40 °C. <sup>*d*</sup> Measured in  $CDCl_3$ . <sup>*e*</sup> Proton n.m.r. spectrum not measured. <sup>*f*</sup> Signal due to  $CH(C_2B_9H_{11})$  masked by peaks due to  $CH_2Me$  of  $NEt_4^+$ .

 Table 3. Boron-11 and phosphorus-31 n.m.r. data " for the complexes

Compound	$^{11}\mathrm{B}^{b}(\delta)$	$^{31}P^{c}(\delta)$
( <b>3a</b> ) <sup>d</sup>	17.4 [1 B, BC(H)C <sub>6</sub> H <sub>4</sub> Me-4], -2.8 (1 B), $-3.4^*$ (1 B), $-7.0^*$ (1 B), $-8.7$ (1 B), $-10.8$ (2 B), $-12.9^*$ (2 B), $-14.9$ (2 B), $-18.9$ (1 B), $-21.9$ (1 B)	<sup>e</sup> 35.1 [d, J(RhP) 147], 34.0* [d, J(RhP) 143]
( <b>3b</b> )	18.7 [1 $\hat{B}$ , $\hat{BC}(H)C_6H_3Me_2-2,6]$ , -14.2 (vbr, 9 $\hat{B}$ )	30.7 [d, J(RhP) 146]
(3c)	18.2 [1 B, BC(H)C <sub>6</sub> H <sub>4</sub> Me-4], 1.9 (1 B), $-9.0$ (1 B), $-10.2$ (1 B), $-12.0$ (1 B), $-12.4$ (1 B), $-12.8$ (1 B), $-17.3$ (1 B), $-21.8$ (1 B)	
( <b>3d</b> )	17.6 [1 B, BC(H)C <sub>6</sub> H <sub>4</sub> Me-4], 0.4 (1 B), -6.0 (1 B), -6.4 (1 B), -8.1 (1 B), -9.8 (2 B), -11.1 (1 B), -12.6 (1 B)	
(7a)	3.5 (1 B), BCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Me-4), $-14.9$ to $-17.4$ (5 B), $-26.7$ (2 B), $-30.8$ (1 B)	33.7 [d. J(RhP) 154]
(7b)	3.3 (1 B, BCH <sub>2</sub> C <sub>6</sub> H <sub>3</sub> Me <sub>2</sub> -2.6), $-16.0$ to $-17.2$ (5 B), $-26.4$ (2 B), $-30.9$ (1 B)	33.9 [d. J(RhP) 155]
(7c)	12.9 (1 B, BCH <sub>2</sub> Č <sub>6</sub> H <sub>4</sub> Me-4), -12.5 (2 B), -14.1 (1 B), -15.5 (1 B), -16.4 (2 B), -19.2 (1 B)	···· [····· (····· ) ····]

<sup>*a*</sup> Chemical shifts in p.p.m., coupling constants in Hz, measurements in  $CD_2Cl_2-CH_2Cl_2$  at ambient temperatures, unless otherwise stated. <sup>*b*</sup> Hydrogen-1 decoupled, chemical shifts are positive to high frequency of BF<sub>3</sub>-Et<sub>2</sub>O (external). <sup>*c*</sup> Hydrogen-1 decoupled, chemical shifts are positive to high frequency of 85% H<sub>3</sub>PO<sub>4</sub> (external). <sup>*d*</sup> Peaks for minor isomer (see text) are asterisked. <sup>*e*</sup> Spectrum measured at -50 °C.

Rh-P	2.302(1)	Rh-C(1)	2.373(3)	RhC(2)	2.341(3)	Rh-C(3)	1.854(3)
Rh-C(4)	2.374(3)	Rh-B(3)	2.205(3)	Rh-B(4)	2.165(3)	Rh-B(5)	2.237(3)
C(1) - C(2)	1.558(4)	C(1) - B(5)	1.683(4)	C(1)-B(8)	1.677(4)	C(1)-B(9)	1.716(5)
C(2) - B(3)	1.687(4)	C(2) - B(9)	1.717(4)	C(2) - B(10)	1.679(5)	C(3)-O(3)	1.135(4)
C(4) - C(41)	1.468(4)	C(4) - B(4)	1.501(4)	B(3) - B(4)	1.833(4)	B(3)-B(6)	1.773(5)
B(3) - B(10)	1.771(5)	B(4) - B(5)	1.834(4)	B(4) - B(6)	1.767(5)	B(4)-B(7)	1.761(4)
B(5) - B(7)	1.771(5)	B(5) - B(8)	1.771(5)	B(6) - B(7)	1.790(4)	B(6)-B(10)	1.774(5)
B(6) - B(11)	1.771(4)	B(7) - B(8)	1.771(4)	B(7) - B(11)	1.764(5)	B(8)-B(9)	1.749(5)
B(8) - B(11)	1.763(5)	B(9) - B(10)	1.746(5)	B(9) - B(11)	1.763(5)	B(10) - B(11)	1.777(5)
C(4)-H(40)	0.98(3)						
	P-Rh-C(3)	89.0(1)	P-Rh-C(4)	102.1(1)	C(3)-Rh- $C(4)$	109.9(1)	
	Rh-C(3)-O(3)	174.4(3)	Rh-C(4)-H(40)	102(1)	Rh-C(4)-C(41)	116.7(2)	
	H(40)-Ć(4)-Ć(41)	110(1)	Rh-C(4)-B(4)	63.3(1)	H(40)-C(4)-B(4)	119(2)	
	C(41) - C(4) - B(4)	129.0(2)	Rh-B(4)-C(4)	78.4(2)	B(3)-B(4)-C(4)	114.9(2)	
	B(5)-B(4)-C(4)	111.1(2)	B(6)-B(4)-C(4)	142.3(2)	B(7)-B(4)-C(4)	138.6(2)	











propose that in solution (3a) exists as a mixture of two diastereoisomers, (A) and (C) of Scheme 1. As mentioned above, the structure established by X-ray diffraction is (A), with the  $C_6H_4$ Me-4 and PPh<sub>3</sub> groups transoid to one another.

Detailed variable-temperature n.m.r. studies on compound (3a) were not possible due to its low solubility in solvents other than  $CH_2Cl_2$ . Nevertheless, changes in the spectra with temperature, including a near coalescence of the two <sup>31</sup>P-{<sup>1</sup>H} resonances at room temperature, indicated that the isomers interconvert on the n.m.r. time-scale. The close similarity of the

structures (A) and (C) and the broadness of some peaks, however, results in overlapping of some of the signals for each isomer. We propose that the pathway for interconversion involves rotation of the B(4)-C(4) bond (Figure), which could occur via the intermediacy of the zwitterionic structure (B) (Scheme 1). Indeed, structure (B) may be an important canonical form in the ground-state structure of (3a) and related complexes described below. It is noteworthy that the X-ray diffraction study showed that the hybridisation around C(4) was more akin to  $sp^2$  than  $sp^3$  [H(40)–C(4)–B(4) 119(2), B(4)-C(4)-C(41) 129.0(2), and H(40)-C(4)-C(41) 110(1)°]. Moreover, as mentioned above, the Rh-C(4) distance is long. The bonding of the  $\sigma$ ,  $\eta^5$ -CH(C<sub>6</sub>H<sub>4</sub>Me-4)C<sub>2</sub>B<sub>9</sub>H<sub>10</sub> group to the rhodium has similarities to that invoked for the attachment of fulvene ligands to metal centres in certain complexes. Thus in the salt  $[RhL(cod)][PF_6]$  (L =  $\eta$ -1,3,6-tri-t-butylfulvene, cod = cyclo-octa-1,5-diene) the co-ordination of the fulvene group is best described <sup>12</sup> by two resonance forms:



A contribution from a canonical form having a zwitterionic structure akin to (**B**) (Scheme 1) has also been proposed to account for the bonding of fulvene to chromium in tricarbonyl- $(\eta$ -fulvene)chromium.<sup>13</sup>

Treatment of compound (1a) with  $[Mn(=CC_6H_3Me_2 2,6)(CO)_2(\eta-C_5H_4Me)][BCl_4]$  in  $CH_2Cl_2$  afforded the complex  $[Rh{\sigma,\eta^{5}-CH(C_{6}H_{3}Me_{2}-2,6)C_{2}B_{9}H_{10}}(CO)(PPh_{3})]$ (3b). Similarly, reactions between  $[Mn(\equiv CC_6H_4Me-4)(CO)_2 (\eta-C_5H_4Me)$  [BCl<sub>4</sub>] and (1c) and (1b) gave, respectively, the compounds  $[Rh{\sigma,\eta^5}-CH(C_6H_4Me-4)C_2B_9H_8R'_2](CO)_2]$  (3c; R' = H) and (3d; R' = Me). Data characterising the species (3b)-(3d) are given in Tables 1-3. The n.m.r. data revealed that for complex (3b) only a single species existed in solution. This can be explained by the bulkiness of the C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6 group,14 which on steric grounds could lead to the cisoid  $Ph_3P-Rh-CC_6H_3Me_2-2,6$  structure [Scheme 1, (C)] being unfavoured. Compounds (3c) and (3d) contain Rh(CO)<sub>2</sub> groups, and the resulting symmetry in the molecules would not give rise to diastereoisomers of the kind invoked for (3a), and hence only one set of peaks would be observed in an n.m.r.



●СН ОВН ӨРВ

Scheme 1.  $R = C_6H_4$  Me-4. Proposed pathway for the interconversion of the two isomers (A) and (C) of (3a)

spectrum. However, a contribution to the bonding of a dipolar structure, similar to (B) (Scheme 1), is possible for all the compounds (3). The electrophilic character of the exopolyhedral carbon atoms would then favour addition of  $H^-$  to these centres leading to rupture of the Rh–C  $\sigma$  bonds in these species.

In order to substantiate this hypothesis the compounds (3a), (3b), and (3d) were treated with K[BH(CHMeEt)] in thf (tetrahydrofuran), and in this manner the salts [NEt<sub>4</sub>][Rh- $(CO)L\{\eta^{5}-C_{2}B_{9}H_{8}(CH_{2}R)R'_{2}\}\]$  [(7a; L = PPh<sub>3</sub>, R = C<sub>6</sub>H<sub>4</sub>-Me-4, R' = H), (7b; L = PPh<sub>3</sub>, R = C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6, R' = H), and (7c; L = CO,  $R = C_6H_4Me-4$ , R' = Me)] were obtained, after addition of NEt<sub>4</sub>Cl to the mixtures. Data characterising the compounds are given in Tables 1-3. The presence of the  $BCH_2R(R = C_6H_4Me-4 \text{ or } C_6H_3Me_2-2,6)$  groups was clearly revealed by the n.m.r. data. In the <sup>11</sup>B-{<sup>1</sup>H} n.m.r. spectra of the three compounds there are diagnostic peaks for the  $BCH_2R$ nuclei at δ 3.5 [(7a)], 3.3 [(7b)], and 12.9 p.p.m. [(7c)] (Table 3). These chemical shifts may be compared with those for the corresponding boron nuclei in the spectra of the complexes  $[Mo(CO)_4 \{\eta^5 - C_2 B_9 H_8 (CH_2 C_6 H_4 Me-4) Me_2\}]$  (8)  $(\delta 13.4 \text{ p.p.m.})^9$  and  $[WPt(\mu-H)]{\mu-\sigma:\eta^5-C_2B_9H_7(CH_2C_6H_4-$ Me-4)Me<sub>2</sub>{(CO)<sub>2</sub>L(PEt<sub>3</sub>)<sub>2</sub>] (9a;  $L = PMe_3$ ) ( $\delta$  10.4 p.p.m.) and (9b; L = CO) ( $\delta$  13.7 p.p.m.).<sup>15</sup> In the <sup>13</sup>C-{<sup>1</sup>H} n.m.r. spectra of the complexes (7) there are characteristic peaks for the BCH<sub>2</sub>R nuclei at  $\delta$  34.2 [(7a)], 27.0 [(7b)], and 34.0 p.p.m. [(7c)]. These signals, which are broad due to unresolved <sup>13</sup>C-<sup>11</sup>B coupling, may be compared with the resonances for the  $BCH_2C_6H_4$ Me-4 nuclei in compounds (8) ( $\delta$  32.6),<sup>9</sup> (9a) ( $\delta$  31.8), and (9b) ( $\delta$  33.3 p.p.m.).<sup>15</sup> Similarly, in the <sup>1</sup>H n.m.r. spectra of the species (7) broad peaks for the BCH<sub>2</sub>R nuclei occur at δ 2.48 [(7a)], 2.69 [(7b)], and 2.41 [(7c)] (Table 2). The <sup>1</sup>H n.m.r. resonance for the  $BCH_2C_6H_4Me-4$  group in (8) occurs at  $\delta$  2.18.<sup>9</sup> These resonances for this group in the spectra of (9a) and (9b) occur at  $\delta$  1.96 and 2.07, respectively, but are overlapped by signals for the  $P(CH_2Me)_3$  protons.<sup>15</sup> Interestingly, the neutral complex (8) is obtained by protonation of the salt (4) with  $HBF_4 \cdot Et_2O$  in the presence of CO.<sup>9</sup> This synthesis may be compared with those for the salts (7), involving treatment of the neutral complexes (3a), (3b), or (3d) with  $H^-$ , derived from K[BH(CHMeEt)\_3]. In both reactions M-C (M = Mo or Rh)  $\sigma$  bonds are broken, as a result of electrophilic and nucleophilic attack, respectively, at the bridging carbon atom.

The X-ray diffraction study on compounds (3a) establishes that in this species the CHR group is attached to the boron atom in the pentagonal face of the cage which is in the  $\beta$  position with respect to the CH groups. A <sup>11</sup>B-<sup>11</sup>B correlation spectroscopy (COSY) n.m.r. spectrum of complex (3c) was in agreement with attachment of the CH(C<sub>6</sub>H<sub>4</sub>Me-4) substituent to the  $\beta$  boron atom. Unfortunately, the two-dimensional <sup>11</sup>B boron n.m.r. spectra of the other complexes were not resolvable



due to the broadness of the peaks. However, the <sup>1</sup>H and <sup>13</sup>C- $\{^{1}H\}$  n.m.r. spectra for (7c) (Table 2) show that the cage CMe groups are equivalent, suggesting the presence of a plane of symmetry in this molecule. This can only be achieved if the CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-4 substituent on the cage is linked to the  $\beta$  boron

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Scheme 2.  $L = PPh_3 \text{ or } CO; R' = H \text{ or } Me; R = C_6H_4Me-4 \text{ or } C_6H_3Me_2-2,6; mcp = \eta-C_5H_4Me.$  (*i*) + [Mn(=CR)(CO)<sub>2</sub>(mcp)][BCl<sub>4</sub>]; (*ii*) - CO; (*iii*) + CO; (*iv*) - [Mn(CO)<sub>3</sub>(mcp)]

atom ( $\dot{B}BBC\dot{C}$ ). We can infer, therefore, that the organic group is similarly attached in the precursor (3d), and in the other rhodium complexes also.

Formation of the complexes (3) effectively involves a 'hydroboration' of the alkylidyne ligands present in the precursors  $[Mn(\equiv CR)(CO)_2(\eta - C_5H_4Me)][BCl_4]$ . The pathway by which this novel process occurs must remain a matter of speculation in the absence of kinetic or other data, but a possible route is indicated in Scheme 2. The first step is likely to be nucleophilic attack of the anions of the salts (1) on the alkylidyne carbon atoms of the species  $[Mn(\equiv CR)(CO)_2(\eta - C_5H_4Me)]^+$ , based on previous studies on reactions of the manganese reagents.<sup>16</sup> The substituted-alkylidene complex (D) is structurally related to the alkylidene compound  $[Mn{=C(Ph)Co(CO)_4}(CO)_2(\eta-C_5H_4$ obtained by treating  $[Mn(\equiv CPh)(CO)_2(\eta-C_5-$ Me)].  $H_4Me$ )][BCl<sub>4</sub>] with Na[Co(CO)<sub>4</sub>]<sup>16c</sup> Intermediate (E), with its exopolyhedral B-H $\rightarrow$  Mn bond and  $\mu$ -CR group, has ample precedent in the compounds (2) and related species.<sup>5</sup> The suggested transformation of (E) into (F) is similar to the proposed route to compound (5), which is prepared by treating (2a) with EtC=CEt.<sup>10</sup> The final step in the suggested pathway, the conversion of the intermediate (F) into one or other of the compounds (3) with release of  $[Mn(CO)_3(\eta - C_5H_4Me)]$ , may be related to the formation of compound (4) in the reaction between [NEt<sub>4</sub>][Mo(= $CC_6H_4Me-4$ )(CO){P(OMe)<sub>3</sub>}( $\eta^5-C_2$ - $B_9H_9Me_2$ ] and  $[Fe_2(CO)_9]$ .<sup>9</sup> The latter reaction probably involves the intermediacy of a dimetal complex which decomposes by loss of an iron carbonyl fragment.

The results described in this paper further demonstrate the variety of new species which may be obtained *via* the salts (1).<sup>2,17</sup> Further studies using these reagents are underway.

## 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  $(2 \times 15 \text{ cm columns})$ . The complexes [Mn( $\equiv$ CR)(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>4</sub>Me)][BCl<sub>4</sub>] (R = C<sub>6</sub>-

H<sub>4</sub>Me-4 or C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6) were prepared from  $[Mn(CO)_3(\eta-C_5H_4Me)]$  using procedures described previously.<sup>16</sup> The salts (1) were obtained by methods reported earlier.<sup>2b,18</sup> The reagent K[BH(CHMeEt)<sub>3</sub>] (1.0 mol dm<sup>-3</sup> solution in thf) was obtained from Aldrich Chemicals. The instrumentation used for the spectroscopic studies has been listed previously.<sup>2b</sup> Analytical and other data for the new compounds are given in Table 1.

Synthesis of the Rhodium Complexes.—(i) The compounds (1a) (0.50 g, 0.76 mmol) and  $[Mn(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_4Me)][BCl_4]$  (0.34 g, 0.76 mmol) were dissolved in  $CH_2Cl_2$ (30 cm<sup>3</sup>) saturated with carbon monoxide, and the mixture was stirred for 30 min. Solvent was removed *in vacuo*, and the residue was dissolved in  $CH_2Cl_2$ -light petroleum (4 cm<sup>3</sup>, 3:2) and chromatographed using a water-cooled jacketed column. Elution with the same solvent mixture removed an orange fraction. Solvent was removed *in vacuo* and the residue was recrystallised twice from  $CH_2Cl_2$ -light petroleum (*ca.* 50 cm<sup>3</sup>, 1:10) at -78 °C affording orange *microcrystals* of  $[Rh{\sigma,\eta^5}-CH(C_6H_4Me-4)C_2B_9H_{10}](CO)(PPh_3)]$  (3a) (0.25 g).

(*ii*) In a similar experiment, the salt (1a) (0.50 g, 0.76 mmol) and  $[Mn(\equiv CC_6H_3Me_2-2,6)(CO)_2(\eta-C_5H_4Me)][BCl_4]$  (0.35 g, 0.76 mmol) yielded orange *microcrystals* of  $[Rh{\sigma,\eta^5-CH(C_6H_3-Me_2-2,6)C_2B_9H_{10}](CO)(PPh_3)]$  (3b) (0.26 g), crystallised from CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (*ca.* 50 cm<sup>3</sup>, 1:10) at -78 °C.

(*iii*) As in the synthesis of (**3a**), the reagents (**1c**) (0.50 g, 1.20 mmol) and  $[Mn(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_4Me)]$  (0.54 g, 1.2 mmol) afforded  $[Rh{\sigma,\eta^5}-CH(C_6H_4Me-4)C_2B_9H_{10}](CO)_2]$  (**3c**) (0.24 g), as red *microcrystals* from  $CH_2Cl_2$ -light petroleum (*ca.* 50 cm<sup>3</sup>, 1:10) at -78 °C.

(*iv*) In a similar procedure, compound (**1b**) (0.40 g, 0.89 mmol) and  $[Mn(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_4Me)]$  (0.40 g, 0.89 mmol) gave, after crystallisation from  $CH_2Cl_2$ -hexane (*ca.* 50 cm<sup>3</sup>, 1:10) at -78 °C, yellow *microcrystals* of  $[Rh{\sigma,\eta^{5}-CH(C_6H_4Me-4)C_2B_9H_8Me_2}(CO)_2]$  (**3d**) (0.20 g).

Synthesis of the Rhodium Salts [NEt<sub>4</sub>][Rh(CO)L{ $\eta^{5}$ -C<sub>2</sub>B<sub>9</sub>-H<sub>8</sub>(CH<sub>2</sub>R)R'<sub>2</sub>}](L = PPh<sub>3</sub>, R = C<sub>6</sub>H<sub>4</sub>Me-4 or C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6, R' = H; L = CO, R = C<sub>6</sub>H<sub>4</sub>Me-4, R' = Me).--(i) Complex

Table 5. Atomic positional parameters (fractional co-ordinates  $\times 10^4$ ) for compound (3a) with estimated standard deviations in parentheses

Atom	x	у	z	Atom	x	у	z
Rh	2 529(1)	903(1)	2 240(1)	C(62)	128(2)	866(2)	2 161(2)
Р	1 532(1)	1 286(1)	2 880(1)	C(63)	-404(1)	250(3)	1 632(3)
C(1)	2 248(1)	886(2)	333(2)	C(64)	-285(2)	-717(3)	1 149(3)
C(2)	2 844(1)	69(2)	719(2)	C(65)	375(2)	-1060(3)	1 151(3)
C(3)	2 694(2)	-237(3)	3 227(3)	C(66)	909(1)	-447(3)	1 660(2)
O(3)	2 832(2)	-968(2)	3 781(2)	C(71)	1 261(1)	2 719(2)	2 815(2)
C(4)	3 223(1)	2 444(2)	2 858(2)	C(72)	1 484(2)	3 414(3)	3 668(3)
C(41)	3 735(1)	2 283(2)	3 831(2)	C(73)	1 305(2)	4 505(3)	3 633(3)
C(42)	3 648(2)	2 763(3)	4 802(2)	C(74)	903(2)	4 923(3)	2 740(3)
C(43)	4 143(2)	2 677(3)	5 711(2)	C(75)	671(2)	4 246(3)	1 885(3)
C(44)	4 739(2)	2 118(3)	5 695(3)	C(76)	854(1)	3 147(3)	1 914(2)
C(45)	4 831(2)	1 649(3)	4 728(3)	<b>B</b> (3)	3 487(2)	624(3)	1 604(2)
C(46)	4 346(2)	1 737(3)	3 821(2)	<b>B</b> (4)	3 240(2)	2 066(2)	1 728(2)
C(441)	5 288(2)	2 017(4)	6 668(3)	<b>B</b> (5)	2 387(2)	2 137(3)	903(2)
C(51)	1 549(1)	972(2)	4 302(2)	<b>B</b> (6)	3 807(2)	1 679(3)	850(3)
C(52)	2 146(2)	1 121(3)	5 021(3)	B(7)	3 122(2)	2 621(3)	418(2)
C(53)	2 157(2)	973(3)	6 111(3)	<b>B</b> (8)	2 482(2)	1 886(3)	-450(3)
C(54)	1 590(2)	661(3)	6 489(3)	B(9)	2 764(2)	537(3)	-583(3)
C(55)	994(2)	490(4)	5 780(3)	<b>B</b> (10)	3 560(2)	392(3)	239(3)
C(56)	974(2)	652(3)	4 697(2)	<b>B</b> (11)	3 354(2)	1 635(3)	-486(3)
C(61)	800(1)	528(2)	2 172(2)				. ,

(3a) (0.15 g, 0.24 mmol) in thf (20 cm<sup>3</sup>) was treated with K[BH(CHMeEt)<sub>3</sub>] (0.6 cm<sup>3</sup>, 0.60 mmol) and the mixture stirred for 30 min; then NEt<sub>4</sub>Cl (0.10 g, 0.55 mmol) was added. Stirring was continued for 1 h, after which the mixture was filtered through a Celite pad ( $3 \times 5$  cm). Solvent was removed *in vacuo*, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 cm<sup>3</sup>), and Et<sub>2</sub>O was added (*ca.* 50 cm<sup>3</sup>) dropwise, with vigorous stirring. The orange solid thus obtained was washed with Et<sub>2</sub>O (10 cm<sup>3</sup>) and dried *in vacuo* to give orange *microcrystals* of [NEt<sub>4</sub>][Rh-(CO)(PPh<sub>3</sub>){ $\eta^{5}$ -C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-4)}] (7a) (0.18 g).

(*ii*) Using a similar procedure, compound (**3b**) (0.15 g, 0.23 mmol) and K[BH(CHMeEt)<sub>3</sub>] (0.60 mmol) in thf (20 cm<sup>3</sup>), after addition of NEt<sub>4</sub>Cl (0.10 g, 0.55 mmol), gave orange *microcrystals* of [NEt<sub>4</sub>][Rh(CO)(PPh<sub>3</sub>){ $\eta^{5}$ -C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>(CH<sub>2</sub>C<sub>6</sub>-H<sub>3</sub>Me<sub>2</sub>-2,6)}] (**7b**) (0.17 g).

(*iii*) The salt  $[NEt_4][Rh(CO)_2{\eta^5-C_2B_9H_8(CH_2C_6H_4Me-4)Me_2}]$  (7c) (0.13 g) was similarly obtained from (3d) (0.10 g, 0.23 mmol), K[BH(CHMeEt)\_3] (0.60 mmol), and NEt\_4Cl (0.10 g, 0.55 mmol).

Crystal Structure Determination.—Crystals of compound (3a) grow as orange prisms by diffusion of light petroleum into a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex. That chosen for study (dimensions *ca.*  $0.35 \times 0.20 \times 0.75$  mm) was sealed in a Lindemann tube under nitrogen, and diffracted intensities ( $\theta$ — 2 $\theta$  scans) were collected at 298 K on a Nicolet P2<sub>1</sub> four-circle diffractometer. Of 5 408 unique data ( $2.9 \le 2\theta \le 50^{\circ}$ ), 4 963 had  $F \ge 2\sigma(F)$ , where  $\sigma(F)$  is the standard deviation in F based on counting statistics. Only these data were used in the solution and refinement of the structure, after corrections for Lorentz, polarisation, and X-ray absorption effects, the latter by an empirical method based on azimuthal scan data.<sup>19</sup>

Crystal data. C<sub>29</sub>H<sub>33</sub>B<sub>9</sub>OPRh, M = 628.8, monoclinic, a = 19.819(11), b = 12.146(2), c = 12.591(3) Å,  $\beta = 99.56(3)^{\circ}$ , U = 2.989(2) Å<sup>3</sup>, Z = 4,  $D_c = 1.40$  g cm<sup>-3</sup>, F(000) = 1.280, space group  $P2_1/a$  (no. 14), Mo- $K_{\alpha}$  X-radiation (graphite monochromator),  $\bar{\lambda} = 0.710.69$  Å,  $\mu$ (Mo- $K_{\alpha}$ ) = 6.37 cm<sup>-1</sup>.

The structure was solved by Patterson methods and successive Fourier difference syntheses were used to locate all the light atoms, including the hydrogen atoms which were not in the Ph,  $C_6H_4$ , and Me-4 groups. The hydrogen atoms in these groups were included in calculated positions (C-H, 0.96 Å) with fixed isotropic thermal parameters (*ca.* 1.2 $U_{equiv}$ , of the

parent carbon atom). All atoms, except hydrogens, were refined with anisotropic thermal parameters. Refinement by blockedcascade least squares led to R = 0.027 (R' = 0.029) with a weighting scheme of the form  $w^{-1} = [\sigma^2(F) + 0.000 \ 2|F|^2]$ . The final electron-density difference synthesis showed no residual peaks > 0.9 or < -0.5 eÅ<sup>-3</sup>.

In order to distinguish carbon from boron atoms, initially all cage atoms were treated as boron until sufficient data became available to allow a distinction to be made on the basis of the thermal parameters and the bond lengths. In general, C-C separations are ca. 1.65 Å or less, and B-B distances are ca. 1.70 Å or more. The data collected were of excellent quality and thus we are confident of our assignment.

Calculations were performed on a Data General S230 'Eclipse' computer with the SHELXTL system of programs.<sup>19</sup> Scattering factors with corrections for anomalous dispersion were taken from ref. 20. Atomic co-ordinates are listed in Table 5.

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

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