Inorg. Chem. **1982**, *21*, 4027–4036

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Reactions at the Metal Vertex of a Monometal Metallacarborane Cluster. Chemistry of [*closo*-3,3-(PPh$_3$)$_2$-3-HSO$_4$-3,1,2-RhC$_2$B$_9$H$_{11}$] and [*closo*-3-PPh$_3$-3,3-NO$_3$-3,1,2-RhC$_2$B$_9$H$_{11}$]

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Received March 10, 1982

Reaction of [*closo*-3,3-(PPh$_3$)$_2$-3-H-3,1,2-RhC$_2$B$_9$H$_{11}$] (**1**) with sulfuric or nitric acid affords [*closo*-3,3-(PPh$_3$)$_2$-3-HSO$_4$-3,1,2-RhC$_2$B$_9$H$_{11}$] (**2**) or [*closo*-3-PPh$_3$-3,3-NO$_3$-3,1,2-RhC$_2$B$_9$H$_{11}$] (**3**), respectively. Compound **3** can also be prepared from nitric acid and the dimeric metallacarborane [{*closo*-Rh(PPh$_3$)(C$_2$B$_9$H$_{11}$)}$_2$] or from NO$_2$/N$_2$O$_4$ and **1**. Complexes **2** and **3** have been used to prepare other new metallacarboranes, namely, [*closo*-3-PPh$_3$-3,3-{C(Ph)–C(PPh$_3$)–C(H)–C(Ph)}-3,1,2-RhC$_2$B$_9$H$_{11}$] (**5**), [{*closo*-3-PPh$_3$-3-(μ-CN)-3,1,2-RhC$_2$B$_9$H$_{11}$}$_4$] (**7**), [*closo*-3-PPh$_3$-3-L-3-NO$_3$-3,1,2-RhC$_2$B$_9$H$_{11}$] (L = CO (**8**); L = PPh$_3$ (**9**)), [*closo*-3,3-(PMe$_2$Ph)$_2$-3-NO$_3$-3,1,2-RhC$_2$B$_9$H$_{11}$] (**10**), and [*closo*-3-PPh$_3$-3-CO-3-Cl-3,1,2-RhC$_2$B$_9$H$_{11}$] (**11**). Complexes **5** and **7** have been characterized by X-ray crystallography. The reactions of these new metallacarboranes described herein are representative of interconversions carried out at a discrete transition-metal vertex of a cluster species. Complex **5** crystallizes in space group $P\bar{1}$ with 2 formula units in a cell of dimensions $a = 12.763$ (6) Å, $b = 13.348$ (5) Å, $c = 14.561$ (7) Å, $\alpha = 91.58$ (3)°, $\beta = 93.72$ (3)°, and $\gamma = 74.64$ (3)°. Data were collected at −154 °C on a Picker FACS-1 diffractometer with the θ–2θ scan method. Least-squares refinement, including anisotropic vibration parameters for Rh and P and isotropic vibration parameters for other non-hydrogen atoms, with each phenyl group described as a rigid group having a single isotropic vibration parameter, led to final conventional agreement indices (on F) of $R = 0.048$ and $R_w = 0.051$, based on 4493 unique reflections having $I > 3\sigma(I)$. The molecule consists of a [C$_2$B$_9$H$_{11}$]$^{2-}$ cage and a triphenylphosphine ligand bound to the metal atom of the trisubstituted metallapentacycle Rh–C(Ph)–C(PPh$_3$)–C(H)–C(Ph). Rh–C, Rh–B, B–B, B–C, and C–C distances are normal for a 3,1,2-RhC$_2$B$_9$ closo rhodacarborane fragment, and the pattern of short–long–short C–C bond lengths in the RhC$_4$ ring is reminiscent of a pentasubstituted *cis*-butadiene. The complex **7**·5C$_6$H$_6$ crystallizes in space group $P2/a$ with 4 formula units in a cell of dimensions $a = 26.046$ (8) Å, $b = 15.626$ (3) Å, $c = 30.355$ (8) Å, and $\beta = 106.71$ (2)°. Data were collected at −154 °C on a Syntex $P\bar{1}$ diffractometer with the θ–2θ scan method. Least-squares refinement, including vibration parameters and rigid-group assignments as described above, led to final conventional agreement indices (on F) of $R = 0.063$ and $R_w = 0.078$, based on 9732 unique reflections having $I > 3\sigma(I)$. The molecules consist of four discrete closo phosphinorhodacarborane moieties joined together through their respective metal vertices by cyano ligand bridges. Each tetramer possesses a crystallographic 2-fold axis; the two noncrystallographically equivalent tetramers are very similar. The Rh–Rh separation is approximately 5 Å. Bond distances within each icosahedral fragment are normal for such a closo Rh(III) metallacarborane.

Introduction

One of the more interesting challenges of the contemporary chemistry of metallacarboranes derived from transition metals is the development of new reactions and species that make use of the unique reactivity of the transition-metal vertex. One approach that we have employed utilizes closo metallacarboranes that bear dissociable ligands such as phosphines and carbon monoxide on their transition-metal vertices. The several reports[1] of metallacarboranes of this type that have appeared were mainly concerned with molecular structure and dynamics. In this paper we report the synthesis and reactions of two rhodacarborane species, a bisulfate complex [*closo*-3,3-(PPh$_3$)$_2$-3-HSO$_4$-3,1,2-RhC$_2$B$_9$H$_{11}$] (**2**)[2] and a bidentate nitrate [*closo*-3-PPh$_3$-3,3-NO$_3$-3,1,2-RhC$_2$B$_9$H$_{11}$] (**3**).[3] The molecular structures of **2** and **3** have been reported elsewhere.[2,3]

Results and Discussion

The reaction of [*closo*-3,3-(PPh$_3$)$_2$-3-H-3,1,2-RhC$_2$B$_9$H$_{11}$] (**1**) with either sulfuric or nitric acid in dichloromethane proceeds to give the bisulfate (**2**) or the nitrate (**3**), respectively. Compound **2** precipitates directly from the reaction mixture and can be isolated as orange crystals by vigorous trituration with diethyl ether, and **3** can be purified by column chromatography and obtained as red microcrystals. The nitrate (**3**) can be prepared more conveniently by the reaction of nitric acid with the dimeric metallacarborane [{*closo*-Rh(PPh$_3$)(C$_2$B$_9$H$_{11}$)}$_2$],[4] also in dichloromethane. Attempts to prepare the corresponding complex [*closo*-3-PPh$_3$-3,3-HSO$_4$-3,1,2-RhC$_2$B$_9$H$_{11}$] (**4**) from [{*closo*-Rh(PPh$_3$)(C$_2$B$_9$H$_{11}$)}$_2$] and sulfuric acid, under similar conditions, were unsuccessful. We also note that **3** may be prepared by the reaction of an NO$_2$/N$_2$O$_4$ gas mixture with **1**.

Closo complexes **2** and **3** are formally Rh(III) metallacarboranes, and it is noteworthy that they represent the first reported examples of metallacarboranes that contain metal–

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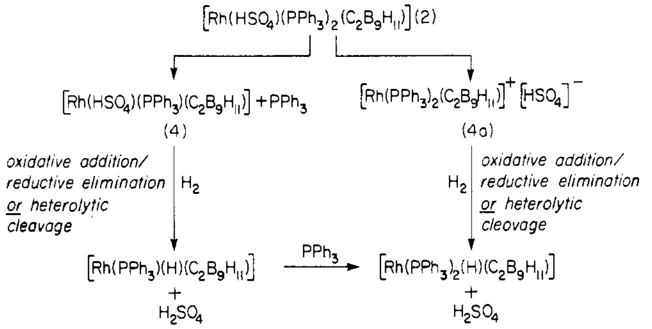
Scheme I



oxygen bonds. In addition, **3** constitutes a rare example of a complex in which a bidentate nitrato ligand and a strong π acceptor, such as triphenylphosphine, share the same coordination sphere. A small number of stable platinum nitrato complexes containing π-acceptor ligands have been reported.[5]

As expected, the reactivities of the monodentate bisulfate **2** and the bidentate nitrate **3** differ. We have found that **2** reacts with hydrogen gas at room temperature to yield **1** and sulfuric acid. Substitution of deuterium gas for hydrogen results in the formation of virtually pure [*closo*-3,3-$(PPh_3)_2$-3-D-3,1,2-$RhC_2B_9H_{11}$] provided that 1 equiv of triphenylphosphine is initially present in the reaction mixture to suppress carborane terminal B–H/B–D exchange.[6] In contrast, the reaction of **3** with hydrogen gives [{*closo*-Rh-$(PPh_3)(C_2B_9H_{11})\}_2$],[4] [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (**1**) and another, as yet uncharacterized, product, all identified by ^1H, ^{31}P, and ^{11}B NMR spectroscopy.[7]

Several mechanisms can be proposed for the reaction of **2** with hydrogen. Four possibilities are shown in Scheme I. The reaction may proceed through the neutral species [*closo*-3-PPh_3-3,3-HSO_4-3,1,2-$RhC_2B_9H_{11}$] (**4**) produced by dissociation of PPh_3 from **2** or through an ionic species such as [*closo*-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{11}]^+[HSO_4]^-$ (**4a**). Secondly, the hypothetical intermediates **4** and **4a** may each react with hydrogen by one of two pathways: heterolytic cleavage to give **1** and sulfuric acid or oxidative addition of hydrogen to generate unprecedented formal Rh(V) seven-coordinate dihydrides, which reductively eliminate H_2SO_4 or lose a proton to give the observed products. Oddly enough, a similar and isoelectronic Ru(IV) dihydride [*closo*-3,3-$(PPh_3)_2$-3,3-H_2-3,1,2-$RuC_2B_9H_{11}$] has been characterized.[8] For an evaluation of the mode of reactivity of (**2**) with hydrogen, the solution behavior of **2** in acetonitrile was examined by ^{31}P FT NMR and conductivity measurements. The $^{31}P\{^1H\}$ FT NMR spectrum of **2** in acetonitrile at 230 K revealed two doublets at +46.9 ppm and +36.1 ppm plus a singlet at −1.5 ppm, which corresponded to free triphenylphosphine. The lower field doublet was found to be characteristic of a mono(triphenylphosphine) rhodacarborane (J_{Rh-P} = 144 Hz), and the higher field doublet is due to a bis(triphenylphosphine) species (J_{Rh-P} = 124 Hz). The nature of the mono(triphenylphosphine) compound was determined directly. This compound was isolated from acetonitrile as a yellow solid, characterized, and found to contain a bis(acetonitrile) triphenylphosphine rhodacarborane cation, [*closo*-3,3-$(NCCH_3)_2$-3-PPh_3-3,1,2-$RhC_2B_9H_{11}]^+[HSO_4]^-$ (**2a**). The $(PPh_3)_2$ complex was not isolable. However, conductivity measurements performed on the acetonitrile solution at 25 °C tentatively indicated that the nature of this $(PPh_3)_2$ species was also cationic. A plot of molar conductivity vs. $(\text{concentration})^{1/2}$ was linear over a concentration range of 1.1–6.4 mM and is indicative of a solution of strong 1:1 electrolytes. Confirmation of the cationic nature of the $(PPh_3)_2$ species (and that of **2a** as well) was obtained by the addition of a bisulfate anion source, μ-nitrido-bis(triphenylphosphorus)(1+) bisulfate, $(PPN)^+(HSO_4)^-$, to the acetonitrile solution of **2**. Addition of 6 equiv of $(PPN)^+(HSO_4)^-$ caused the appearance of a new doublet in the ^{31}P NMR spectrum at +32.4 ppm (J_{Rh-P} = 127 Hz) with a corresponding reduction in all of the signals observed prior to the addition of the excess bisulfate. These results imply that the following equilibria exist in solution:

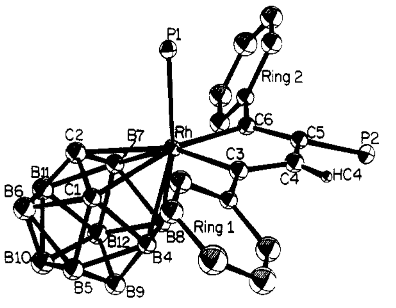


Figure 1. Structure of [*closo*-3-PPh_3-3,3-{$\overline{C(Ph)-C(PPh_3)-C(H)-C(Ph)}$}-3,1,2-$RhC_2B_9H_{11}$] (**5**). The phenyl rings and carborane hydrogens have been omitted for clarity. The thermal ellipsoids represent 50% probability.

$$\mathbf{2} \xrightleftharpoons{CH_3CN} [(PPh_3)_2 \text{ species}]^+[HSO_4]^- \qquad (1)$$

$$[(PPh_3)_2 \text{ species}]^+ \xrightleftharpoons{CH_3CN} \mathbf{2a} + PPh_3 \qquad (2)$$

In the absence of excess bisulfate ion, no detectable amounts of **2** exist in solution. However, addition of $(PPN)^+(HSO_4)^-$ displaces the position of the equilibrium in step 1 in favor of the neutral compound **2** (which appears as the new doublet in the ^{31}P NMR spectrum) and this consequently causes a reduction in the amounts of **2a**, the $(PPh_3)_2$ species, and free PPh_3. The most likely formation for the $(PPh_3)_2$ species is [*closo*-3,3-$(PPh_3)_2$-3-$NCCH_3$-3,1,2-$RhC_2B_9H_{11}]^+[HSO_4]^-$. Support for a solvent-containing $(PPh_3)_2$ compound was provided by the observation that a solution of **2** in acetonitrile at 25 °C does not react with hydrogen gas; however, the reaction does proceed rapidly at elevated temperatures to give **1** in quantitative yields. Thus, it was postulated that, although the species in solution are cationic, strongly bound acetonitrile ligand is present, coordinatively saturating the metal center. This ligand must be thermally labilized in order to allow a hydrogen molecule to attack. Since a simple doublet was observed in the $^{31}P\{^1H\}$ NMR spectrum of the $(PPh_3)_2$ species, both triphenylphosphines are in identical environments. This is probably due to rapid rotation of the metal vertex with respect to the carborane ligand in the cationic bis(triphenylphosphine) acetonitrile complex.

Since these observations prove that in solution compound **2** exists as a mixture of solvent-containing cations, the mechanism for the reaction of **2** with hydrogen gas probably resembles the case outlined in Scheme I in which the formation of a coordinatively unsaturated rhodacarborane cation was the necessary initial step. In the mechanistic scheme for the reaction of **2** with hydrogen gas we intuitively favor the heterolytic cleavage of dihydrogen.

Having found that a cation derived from **2** reacts with hydrogen, we explored the possibility that a reaction would occur between **2** and a reactive organic substrate such as a terminal acetylene. A solution of **2** in tetrahydrofuran reacts

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Table I. Some Distances (Å) and Angles (Deg) in [*closo*-3-PPh$_3$-3,3-{C(Ph)–C(PPh$_3$)–C(H)–C(Ph)}-3,1,2-RhC$_2$B$_9$H$_{11}$] (5)[a]

	A. Distances		
Rh–C(1)	2.279	Rh–B(8)	2.270
Rh–C(2)	2.284	Rh–C(3)	2.058
Rh–B(4)	2.251	Rh–C(6)	2.069
Rh–B(7)	2.328	Rh–P(1)	2.338
P(1)–group 3	1.878	P(2)–group 6	1.806
P(1)–group 4	1.851	P(2)–group 7	1.816
P(1)–group 5	1.854	P(2)–group 8	1.813
C(3)–group 1	1.509	C(3)–C(4)	1.351
C(4)–HC4	0.98	C(4)–C(5)	1.454
C(5)–P(2)	1.795	C(5)–C(6)	1.363
C(6)–group 2	1.513		
C(1)–C(2)	1.606	B(8)–B(9)	1.820
C(1)–B(4)	1.700	B(8)–B(12)	1.797
C(1)–B(5)	1.698	B(9)–B(10)	1.781
C(1)–B(6)	1.727	B(9)–B(12)	1.783
C(2)–B(6)	1.748	B(10)–B(11)	1.772
C(2)–B(7)	1.674	B(10)–B(12)	1.789
C(2)–B(11)	1.722	B(11)–B(12)	1.768
B(4)–B(5)	1.791	C(1)–H(1)	0.94
B(4)–B(8)	1.787	C(2)–H(2)	1.03
B(4)–B(9)	1.767	B(4)–H(4)	1.00
B(5)–B(6)	1.765	B(5)–H(5)	1.14
B(5)–B(9)	1.765	B(6)–H(6)	1.02
B(5)–B(10)	1.766	B(7)–H(7)	1.02
B(6)–B(10)	1.760	B(8)–H(8)	1.04
B(6)–B(11)	1.757	B(9)–H(9)	1.08
B(7)–B(8)	1.816	B(10)–H(10)	1.13
B(7)–B(11)	1.792	B(11)–H(11)	1.15
B(7)–B(12)	1.761	B(12)–H(12)	1.08
	B. Angles		
P(1)–Rh–C(3)	90.0	Cn[b]–Rh–C(3)	124.4
P(1)–Rh–C(6)	90.1	Cn[b]–Rh–C(6)	127.1
C(3)–Rh–C(6)	80.1	Cn[b]–Rh–P(1)	130.1
Rh–C(3)–C(4)	113.8	Rh–C(6)–C(5)	113.4
Rh–C(3)–group 1	124.8	Rh–C(6)–group 2	125.7
C(4)–C(3)–group 1	121.9	C(5)–C(6)–group 2	121.2
C(3)–C(4)–C(5)	116.7	C(6)–C(5)–C(4)	115.8
C(3)–C(4)–HC4	121 (3)	C(6)–C(5)–P(2)	128.2
C(5)–C(4)–HC4	121 (3)	C(4)–C(5)–P(2)	113.4

[a] Estimated standard deviations are as follows. Bond lengths (Å): Rh–P, 0.001; Rh–C, 0.006; Rh–B, 0.007; P–C, 0.006; C–C, 0.008; C–B, 0.009; C–H, 0.04; B–H, 0.06. Angles (deg): Rh–C–C, 0.4; P–Rh–C, 0.2; P–Rh–Cn, 0.2; C–Rh–C, 0.2; C–C–C, 0.3; C–C–P, 0.4. [b] Centroid of the C$_2$B$_3$ face of carborane.

rapidly with an excess of phenylacetylene at 45 °C to afford a yellow complex **5** in excellent yield. Compound **5** can also be obtained from **3** and excess phenylacetylene in the presence of an equimolar portion of triphenylphosphine. Compound **5** was characterized by spectroscopy and an X-ray crystallographic study. The structure of **5** is illustrated in Figure 1, and some selected distances and angles are reported in Table I. The molecule consists of a [C$_2$B$_9$H$_{11}$]$^{2-}$ cage and a triphenylphosphine ligand bound to the metal atom of the trisubstituted metallapentacycle Rh–C(Ph)–C(PPh$_3$)–C(H)–C(Ph). The molecular formula of **5** can thus be written as [*closo*-3-PPh$_3$-3,3-{C(Ph)–C(PPh$_3$)–C(H)–C(Ph)}-3,1,2-RhC$_2$B$_9$H$_{11}$]. The Rh–C, Rh–B, C–C, C–B, and B–B distances are normal for a 3,1,2-RhC$_2$B$_9$ closo rhodacarborane fragment. The metallacycle is best represented as shown in Figure 2, with double bonds localized as indicated. This description is supported by the following structural observations: (a) The angles between the plane of the flat RhC$_4$ ring and the respective planes of the two phenyl substituents (42 and 63°) rule out the significant pπ–pπ overlap. (b) The C(3)–phenyl and C(6)–phenyl bond lengths (1.509 (8) and 1.513 (8) Å, respectively) show no double-bond character. (c) The Rh–C(3) and Rh–C(6) bond distances (2.058 (6) and 2.069 (6) Å, respectively) are within the range found for Rh(III)–C single bonds.[9-12] (d) The four P–C bonds of the C(5)-bonded triphenylphosphonium group are virtually identical. (e) The pattern of the short–long–short C–C bond lengths in the RhC$_4$ ring (1.351 (8), 1.454 (8), and 1.363 (8) Å, respectively) is reminiscent of a pentasubstituted *cis*-butadiene.[13]

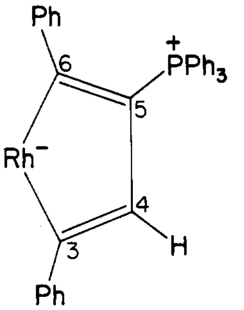
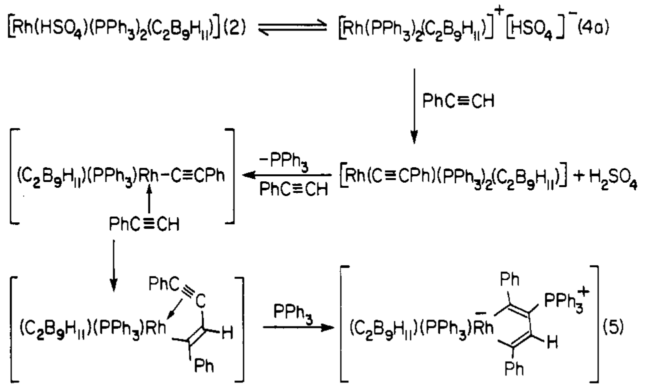


Figure 2. Proposed bonding for metallacycle **5**.

Scheme II



The ^{1}H NMR spectrum of **5** contained two carborane C–H resonances and a signal at δ 6.86 assigned as a vinylic proton. The ^{31}P{^{1}H} NMR spectrum showed two inequivalent phosphorus nuclei, P(1) and P(2), coupled to each other ($J_{P(1)-P(2)}$ = 7 Hz). P(1) (a doublet of doublets) appeared at +30.9 ppm, which is typical of a triphenylphosphine ligand bound directly to the metal vertex of a rhodacarborane fragment ($J_{Rh-P(1)}$ = 129 Hz). On the other hand, P(2), which is not directly coordinated to the metal vertex (also a doublet of doublets), appeared at much higher field (+3.6 ppm) and exhibited a $J_{Rh-P(2)}$ value of 12 Hz. The sharp nature of the signal observed for P(2) also is consistent with its location on a vinylic carbon.

A possible mechanism for the formation of **5** from **2** is shown in Scheme II. The first step involves the dissociation of the bisulfate anion from **2**, giving **4a**. Next, a σ-acetylido complex is formed with the elimination of sulfuric acid, and the subsequent loss of triphenylphosphine is followed by complexation of a second phenylacetylene molecule. Insertion of the coordinated phenylacetylene molecule into the Rh–C bond of the σ-phenylacetylido ligand may then take place. Coordination of an additional acetylene molecule and subsequent insertion into a metal–carbon bond have been observed in the linear oligomerization of acetylene catalyzed by [Ni-

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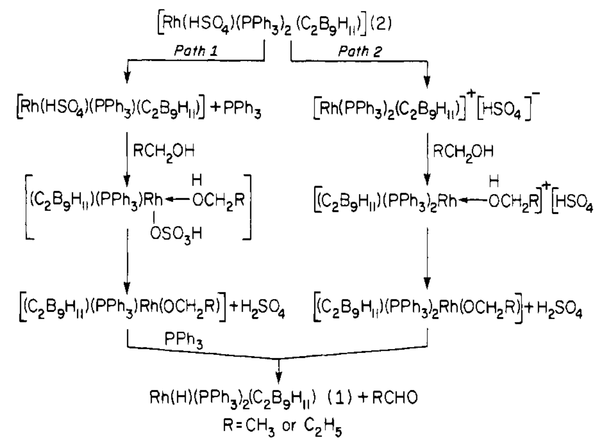
Scheme III



$(CO)_2(PPh_3)_2]$.[14] It is noteworthy that in the present case the insertion step occurs in such a fashion that the phenyl substituent is in a position α to the rhodium atom and that only one isomer is formed in the reaction. A similar mode of addition has been noted in the reaction of $[Ni(CH_3)(PPh_3)(acac)]$ with phenylacetylene;[15] the vinyl complex formed by the addition of the $Ni-CH_3$ moiety to the phenylacetylene triple bond bears the phenyl substituent on the carbon atom immediately adjacent to the nickel center. In the final step, nucleophilic attack of triphenylphosphine on the coordinated organic ligand occurs, producing **5**. An example of such an attack on a coordinated unsaturated molecule is the reaction of $[Os_3(H)(CO)_{10}(CH{=}CH_2)]$ with dimethylphenylphosphine to give $[Os_3(H)(CO)_{10}(^-CHCH_2P^+Me_2Ph)]$.[16] The reaction of phenylacetylene with either **2** or **3**, the latter in the presence of triphenylphosphine, to give **5** constitutes the first example of metallacycle construction at a metal vertex of a metallacarborane cluster.

Not surprisingly, it was found that [*closo*-3,3-$(PPh_3)_2$-3-HSO_4-3,1,2-$RhC_2B_9H_{11}$] (**2**) formally dehydrogenates simple alcohols to give the corresponding aldehydes. As examples one finds that **2** reacts with ethanol or 1-propanol at slightly elevated temperatures to produce acetaldehyde or propionaldehyde, respectively. Complex **1** and sulfuric acid are also produced. This reaction occurs heterogeneously since both the reactant (**2**) and product (**1**) are insoluble in ethanol and 1-propanol. Two possible mechanisms for this facile reaction are shown in Scheme III.

In path 1, loss of triphenylphosphine from **2** is followed by coordination of alcohol, and in path 2, loss of the bisulfate anion occurs before the alcohol becomes bound. Hydrogen transfer subsequent to this results in the elimination of the aldehyde from the alkoxyrhodacarborane species; formation of complex **1** in path 1 requires the presence of triphenylphosphine.

In order to confirm that the hydroxy proton on the alcohol is indeed lost to form sulfuric acid and that an α-hydrogen from the alcohol becomes the rhodium-bound hydride in complex **1** upon elimination of aldehyde, we reacted **2** with ethanol-d_1 and with ethanol-d_5. The rhodacarborane products formed from these two reactions were examined by ^1H NMR and IR spectroscopy to determine the amounts of Rh–H and Rh–D present. Compound **1** produced in the reaction of **2** with ethanol-d_5 exhibited no Rh–H resonances in the ^1H NMR and no Rh–H peaks in the infrared spectra. A weak band at 1520 cm^{-1}, corresponding to a Rh–D stretch, was observed. The product (**1**) formed in the reaction of **2** with ethanol-d_1 revealed a strong six-line pattern in the hydride region of the ^1H NMR (−8.3 ppm). A weak band was observed for the Rh–H stretch at 2065 cm^{-1} in the infrared spectrum as well whereas no IR bonds due to Rh–D could be detected. These results indicate that the fate of deuterium in O–D and C–D bonds is consistent with the two mechanisms presented. A mechanism similar to the one depicted in path 1 of Scheme III has been proposed to account for the catalytic dehydrogenation of alcohols by nitrato– and perfluorocarboxylato–ruthenium complexes.[17] In contrast, the reaction reported here proceeds stoichiometrically, and attempts to make it catalytic by the addition of sulfuric acid have been unsuccessful.

Table II. Some Distances (Å) and Angles (Deg) in [{*closo*-3-PPh_3-3-(μ-CN)-3,1,2-$RhC_2B_9H_{11}$}$_4$] (**7**)[a]

	monomer 1	monomer 2	monomer 3	monomer 4
		A. Distances		
Rh–P	2.307 (3)	2.322 (3)	2.307 (3)	2.298 (3)
Rh–CN	2.031 (9)	2.049 (8)	2.057 (8)	2.047 (8)
	2.046 (9)	2.054 (8)	2.046 (8)	2.060 (9)
CN–CN[b]	1.162 (16)	1.149 (16)	1.119 (12)	1.147 (13)
CN–CN[c]	1.149 (11)		1.136 (12)	
Rh–C(carborane)	2.217 (12)	2.260 (11)	2.209 (12)	2.242 (11)
	2.219 (11)	2.204 (12)	2.245 (12)	2.244 (11)
Rh–B(carborane)	2.207 (14)	2.238 (12)	2.226 (12)	2.217 (11)
	2.222 (12)	2.201 (11)	2.243 (12)	2.219 (11)
	2.204 (11)	2.197 (12)	2.211 (12)	2.199 (11)
P-phenyl 1[d]	1.840	1.827	1.841	1.819
P-phenyl 2	1.819	1.813	1.802	1.819
P-phenyl 3	1.826	1.822	1.823	1.834
C–C(carborane)	1.655 (15)	1.680 (15)	1.625 (15)	1.644 (15)
C–B(carborane)	1.735 (12)	1.730 (31)	1.729 (24)	1.741 (15)
B–B(carborane)	1.780 (4)	1.785 (6)	1.793 (4)	1.783 (7)
		B. Angles		
P–Rh–CN	90.5 (3)	89.0 (3)	94.6 (3)	86.9 (3)
	87.5 (3)	95.9 (3)	87.2 (3)	91.9 (3)
CN–Rh–CN	90.3 (3)	86.9 (3)	87.1 (3)	89.2 (3)
Rh–CN–CN	174.3 (9)	170.5 (9)	173.4 (10)	175.1 (10)
	172.5 (8)	173.7 (11)	169.8 (10)	176.4 (10)

[a] Estimated standard deviations in the least significant figures are given in parentheses. Phenyl groups were refined as rigid groups with C–C as 1.39 Å and C–H as 1.00 Å. [b] See caption to Figure 3. These distances are for CN–CN linking monomers 1–1, 2–2, etc. [c] These distances are for CN–CN linking monomers 1–2 and 3–4. [d] Because the phenyl rings were refined as rigid groups, errors in distances involving them are not available.

[*closo*-3,3-$(PPh_3)_2$-3-HSO_4-3,1,2-$RhC_2B_9H_{11}$] (**2**) reacts with sodium bromide (in benzene/water at reflux) or with hydrochloric acid (in tetrahydrofuran at room temperature) to afford, in good yield, [*closo*-3,3-$(PPh_3)_2$-3-X-3,1,2-$RhC_2B_9H_{11}$] (**6**) (X = Br or Cl[18]). The bisulfate (**2**) also reacts with sodium cyanide to afford a yellow compound (**7**) initially formulated as [*closo*-3,3-$(PPh_3)_2$-3-CN-3,1,2-$RhC_2B_9H_{11}$]. The infrared spectrum of **7** contained bands typical of coordinated triphenylphosphine and carborane ligands. A strong, sharp peak at 2146 cm^{-1} was also observed. This was attributed to ν(CN) and seemed characteristic of a terminal cyano ligand coordinated to a Rh(III) center.[19] In addition, the $^{31}P\{^1H\}$ NMR spectrum of **7** showed one doublet at +40.9 ppm (J_{Rh-P} = 117 Hz). However, elemental analyses and molecular weight studies were consistent with the for-

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(14) Meriwether, L. S.; Leto, M. F.; Colthup, E. C.; Kennerly, G. W. *J. Org. Chem.* **1962**, *27*, 3930.

(15) Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 4410.

(16) Churchill, M. R.; Shapley, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 2357.

(17) Critchlow, P. B.; Robinson, S. D. *Inorg. Chem.* **1978**, *17*, 1902 and references therein.

(18) (a) Siedle, A. R. *J. Organomet. Chem.* **1975**, *90*, 249. (b) Grey, R.; Hawthorne, M. F., unpublished results.

(19) For comparison: $[RhH_2(CN)(PPh_3)_2]$, ν(CN) at 2110 cm^{-1} (Favero, G.; Rigo, P. *Gazz. Chim. Ital.* **1972**, *102*, 597); $[\{RhCl(CN)_2(PPh_3)_2\}_2(\mu\text{-NCCN})]$, terminal ν(CN) at 2145 and 2135 cm^{-1} (Favero, G.; Corain, B.; Rigo, P.; Turco, A. *Ibid.* **1973**, *103*, 297).

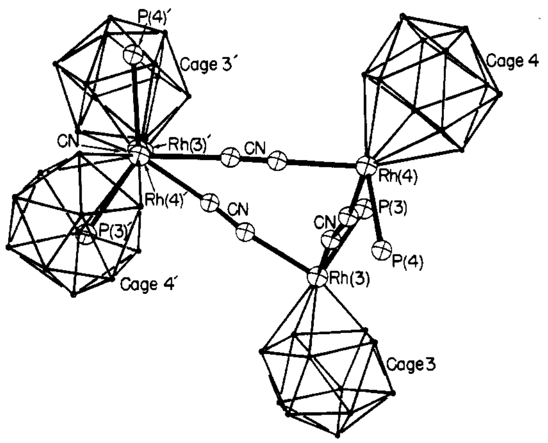

Figure 3. One of the two crystallographically unique molecules of [{*closo*-3-PPh_3-3-(μ-CN)-3,1,2-$RhC_2B_9H_{11}$}$_4$] (**7**), with the phenyl rings and hydrogen atoms omitted for clarity and the atoms of the C_2B_9 cages drawn with an artificially small radius. The asymmetric unit of the crystal unit cell consists of two distinct half-tetramers. The other half of each tetramer is generated by a twofold rotation axis passing through the center of two opposing C≡N bonds. The consequent 50%–50% disorder in these CN linkages indicates the other CN ligands suffer from 50%–50% disorder also, with the assumption that each Rh is bound to one N and one C atom of two bridging CN^- ligands.

mulation of **7** as [{Rh(CN)(PPh_3)($C_2B_9H_{11}$)}$_4$]. In order to determine the exact nature of **7** an X-ray crystallographic study was carried out. One of the two crystallographically unique molecules of **7** is illustrated in Figure 3, and some distances and angles are shown in Table II.

The molecule has a cyclic structure consisting of four discrete closo phosphinorhodacarborane moieties joined together through their respective metal vertices by essentially linear cyano ligand bridges. The formula of **7** can thus be written as [{*closo*-3-PPh_3-3-(μ-CN)-3,1,2-$RhC_2B_9H_{11}$}$_4$]. Metal–metal bonds are absent in **7**, and the Rh–Rh separation is approximately 5 Å, the structure being held together entirely by the cyano groups. The bond distances within each $RhC_2B_9H_{11}$ fragment are normal for such a closo Rh(III) metallacarborane and, with the assumption that each carborane cage occupies three coordination sites, the geometry about the rhodium centers can be classified as octahedral. The triphenylphosphine ligands are unexceptional and are staggered with respect to one another, probably for steric reasons. Although the Rh–cyano group angles are all nearly linear, 170–176°, the torsion angles Rh–C–N–Rh range from 16 to 78°; the $(RhCN)_4$ moiety is not planar. At first, this may appear to be due to packing forces, but the fact that the two unique tetrameric molecules exhibit nearly identical angles of twist indicates that this distortion from planarity is due to electronic or intramolecular steric effects. Although dimeric and polymeric transition-metal complexes containing bridging cyano ligands are well-known,[20] we believe that **7** represents the first example of a discrete tetramer with such linkages. Finally we note that, contrary to our expectation, the reaction of **3** with sodium cyanide under analogous conditions gave only an intractable mixture of products.

It is well-known that the nitrato ligand may be either a bidentate four-electron donor or a monodentate two-electron donor toward a transition-metal center.[21] Accordingly, we have studied the reaction of **3** with donor ligands L (L = CO, PPh_3, or PMe_2Ph) in the hope that a complex of the type [*closo*-3-PPh_3-3-L-3-NO_3-3,1,2-$RhC_2B_9H_{11}$], containing the relatively uncommon monodentate nitrato group, would be formed.

The reaction of **3** with carbon monoxide or triphenylphosphine in diethyl ether gave good yields of [*closo*-3-PPh_3-3-CO-3-NO_3-3,1,2-$RhC_2B_9H_{11}$] (**8**) or [*closo*-3,3-$(PPh_3)_2$-3-NO_3-3,1,2-$RhC_2B_9H_{11}$] (**9**), respectively. However, reaction of **3** with excess dimethylphenylphosphine resulted in the displacement of triphenylphosphine with the formation of [*closo*-3,3-$(PMe_2Ph)_2$-3-NO_3-3,1,2-$RhC_2B_9H_{11}$] (**10**) in excellent yield. Complexes **8–10**, formally Rh(III) metallacarboranes containing monodentate NO_3 ligands, were characterized by elemental analyses and infrared and NMR spectroscopy.

As previously reported[3] solutions of **9** exhibit $^{31}P\{^1H\}$ NMR spectra that confirm the presence of uncoordinated triphenylphosphine. This observation is consistent with the equilibrium

$$\mathbf{9} \rightleftharpoons \mathbf{3} + PPh_3$$

We have also observed that **8** slowly loses its carbonyl ligand in solution. Thus the $^{31}P\{^1H\}$ NMR spectrum of **8** initially contains an intense doublet at +41.2 ppm (J_{Rh-P} = 107 Hz) together with a weak resonance due to **3**. Over a period of weeks the signal due to **8** disappears and is replaced by a strong resonance characteristic of **3**. The $^{31}P\{^1H\}$ NMR spectrum of **10** consists of only one doublet at +11.2 ppm (J_{Rh-P} = 132 Hz), and no uncoordinated dimethylphenylphosphine is apparent. Thus, in contrast to **2**, **8**, and **9**, the species **10** shows no apparent tendency to dissociate its ligands in solution.

Like **2**, [*closo*-3,3-$(PPh_3)_2$-3-NO_3-3,1,2-$RhC_2B_9H_{11}$] (**9**) reacts with hydrogen to afford [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (**1**). In contrast, **10** does not react with hydrogen in benzene under similar conditions. Finally, **10** reacts with hydrochloric acid to give the known compound [*closo*-3,3-$(PMe_2Ph)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$][22] in quantitative yield.

The synthesis of the nitrato rhodacarboranes **3**, **8**, **9**, and **10** offered a possible opportunity for distinguishing between mono- and bidentate nitrato ligands on the basis of their infrared absorption bands. However, on comparison of the infrared spectra of **3**, **8**, **9**, and **10** (as Nujol mulls), it became apparent that no simple distinction could be made with confidence. All four complexes exhibited a strong bond in the regions 1515–1450 and 1282–1220 cm^{-1}, no other obvious distinguishing features being observed. The presence of phosphine and carborane ligands also hampered the identification of any other lower frequency nitrato ligand vibrations that may have been present. In this context we note that in **3** the $\nu(NO_3)$ band in the region 1282–1220 cm^{-1} often appeared as two absorptions, closely spaced and nearly equal in intensity, apparently as a result of solid-state splitting.

The synthesis of [*closo*-3,3-$(PPh_3)_2$-3-X-3,1,2-$RhC_2B_9H_{11}$] (X = H, Br, or Cl[18]) can be achieved easily and conveniently from **3** by direct reaction with triphenylphosphine and either hydrogen, tetraethylammonium bromide, or hydrochloric acid. Similarly the complex [*closo*-3-PPh_3-3-CO-3-Cl-3,1,2-$RhC_2B_9H_{11}$] (**11**) can be prepared directly from **3** by reaction with carbon monoxide followed by addition of hydrochloric acid. Compound **11** was characterized by elemental analyses and infrared and NMR spectroscopy. Previous attempts to prepare **11** by displacement of triphenylphosphine from **6** (X = Cl) with carbon monoxide had been unsuccessful.[23] In contrast to **8**, **11** does not appear to lose its carbonyl ligand in solution. Some further facile reactions involving **6**, **8**, **9**, and **11** are illustrated in Scheme IV.

Finally, we note that the complexes [*closo*-3-PPh_3-3,3-

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[20] Sharpe, A. G. "The Chemistry of Cyano Complexes of the Transition Metals"; Academic Press: New York, 1976.

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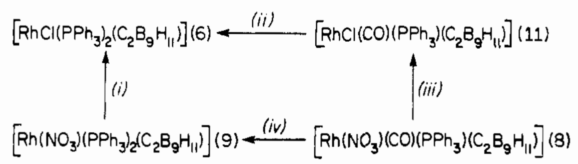
[22] Baker, R. T. Ph.D. Thesis, UCLA, 1980.

[23] Grey, R.; Hawthorne, M. F., unpublished results.

Scheme IV



(i) Hydrochloric acid, THF.

(ii) Triphenylphosphine, THF.

(iii) Hydrochloric acid, Et_2O.

(iv) Triphenylphosphine, Et_2O.

Reactions (i) through (iv) proceed at room temperature.

{C(Ph)–C(PPh_3)–C(H)–C(Ph)}-3,1,2-$RhC_2B_9H_{11}$] (**5**), [*closo*-3-PPh_3-3-CO-3-NO_3-3,1,2-$RhC_2B_9H_{11}$] (**8**), and [*closo*-3-PPh_3-3-CO-3-Cl-3,1,2-$RhC_2B_9H_{11}$] (**11**) are racemic and chiral at their metal vertices.

Experimental Section

In general, manipulations were carried out in an inert-atmosphere with standard Schlenk techniques or on a high-vacuum line. Unless otherwise specified all solvents were purified by standard procedures and distilled under argon before use. Ethanol (absolute or 95%) was used without further treatment. The reagents employed were obtained commercially and were at least of reagent grade quality. The NO_2/N_2O_4 mixture, hydrogen, deuterium (99.5 atom % D), and carbon monoxide were obtained from Liquid Carbonic and used without further treatment. Phenylacetylene (Aldrich) was distilled under vacuum before use and 1-propanol (Aldrich) was distilled from anhydrous potassium carbonate. [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (**1**)[1a] and [{*closo*-Rh(PPh_3)($C_2B_9H_{11}$)}$_2$][4] were prepared by literature methods.

Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer 137 or 521 spectrometer and were calibrated against the 1601-cm^{-1} band of polystyrene. ^{31}P, ^{11}B, and ^1H NMR spectra were obtained on a Bruker WP200 FT spectrometer. Additional ^1H NMR spectra were measured on a Varian Associates A-60 instrument, and other ^{11}B NMR spectra were recorded on a spectrometer built by Professor F. Anet of the Department of Chemistry, University of California, Los Angeles, CA. ^1H NMR spectra are with reference to internal tetramethylsilane, ^{31}P NMR spectra are calibrated against an external D_3PO_4 standard, and ^{11}B NMR spectra are with reference to external $BF_3 \cdot OEt_2$. All chemical shifts (reported in ppm) are quoted as positive downfield. Conductometric measurements were performed with use of a Beckman Conductivity Bridge, Model RC-19, and platinum electrodes.

Analyses and molecular weight determinations were by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Preparation of [*closo*-3,3-$(PPh_3)_2$-3-HSO_4-3,1,2-$RhC_2B_9H_{11}$] (2). Sulfuric acid (95–98%, 3.0 mL, 50 mmol) was added to a solution of **1** (2.0 g, 2.62 mmol) in dichloromethane (100 mL) in the air, and the mixture was stirred rapidly for 15 min. The resulting gelatinous precipitate was filtered off, washed with dichloromethane (3 × 20 mL), and then vigorously triturated with diethyl ether to give air-stable crystals of **2** (1.3 g, 56%). An analytical sample, as a tetrahydrofuran (THF) solvate, was obtained by recrystallization from THF/heptane.

Anal. Calcd for $C_{42}H_{50}B_9O_5P_2SRh$: C, 54.30; H, 5.42; B, 10.47; Rh, 11.08; P,6.67; S, 3.45. Found: C, 54.51; H, 5.71; B, 10.66; Rh, 11.29; P, 6.47; S, 3.42.

Infrared spectrum:[24] 3065 (w), 2600 (vs), 2545 (vs), 2530 (vs), 1595 (w), 1575 (w), 1480 (vs), 1435 (vs), 1300 (w), 1240 (w), 1160 (vs), 1090 (m), 1050 (vs), 1025 (w), 1005 (w), 880 (m), 745 (vs), 700 (vs) cm^{-1}.

NMR spectra (ppm):[25] $^{31}P\{^1H\}$ (81.02 MHz, THF/Me_2SO, room temperature): +33.4 (J_{Rh-P} = 152 Hz) and a singlet due to uncoordinated triphenylphosphine. Cooling to −32 °C gives the following: +36.2 (d, J_{Rh-P} = 166 Hz), +33.0 (d, J_{Rh-P} = 157 Hz), +26.8 (d, J_{Rh-P} = 132 Hz), and a signal due to uncoordinated triphenylphosphine. $^{11}B\{^1H\}$ (80.5 MHz, Me_2SO, room temperature): −9.0 (s, br), +5.0 (s, br).

Preparation of [*closo*-3,3-$(NCCH_3)_2$-3-PPh_3-3,1,2-$RhC_2B_9H_{11}$]$^+$[HSO_4]$^-$ (2a). A solution of **2** (1.35 g, 1.45 mmol) in acetonitrile (80 mL) was stirred for 10 min, the volume was reduced to 20 mL in vacuo, and 80 mL of diethyl ether was added with stirring. The resultant yellow precipitate was isolated, washed with 2 × 50 mL of diethyl ether, and dried in vacuo to give **2a** (0.54 g, 55%).

Anal. Calcd for $C_{24}B_9H_{33}RhN_2PSO_4$: C, 42.59; H, 4.92; B, 14.38; Rh, 15.21; N, 4.14; P, 4.58; S, 4.74. Found: C, 42.43; H, 5.04; B, 13.90; Rh, 14.88; N, 4.23; P, 4.59; S, 4.89.

Infrared spectrum: 3350 (w), 2600 (s, sh), 2545 (vs), 2500 (s, sh), 2300 (vw), 2280 (vw), 1585 (vw), 1565 (vw), 1480 (m), 1435 (vs), 1320 (w), 1240 (vs), 1170 (w), 1160 (vs), 1120 (vw), 1090 (s), 1050 (vs), 1020 (w), 1005 (w), 995 (w), 900 (vw), 855 (m), 845 (s), 750 (vs), 700 (vs) cm^{-1}.

NMR spectra (ppm): $^{31}P\{^1H\}$ (81.02 MHz, CH_3CN/CD_3CN, 230 K) +46.0 (d, J_{Rh-P} = 144 Hz); $^{11}B\{^1H\}$ (126.7 MHz, CH_3CN, room temperature) −23.4 (s, br), −7.6 (s, br), −3.9 (s, br), +11.0 (s, br), +13.1 (s, br).

Preparation of [*closo*-3-PPh_3-3,3-NO_3-3,1,2-$RhC_2B_9H_{11}$] (3). (a) A solution of **1** (2.92 g, 3.83 mmol) in reagent grade (RG) dichloromethane (200 mL) in the air was treated with nitric acid (70%, 0.5 mL, 7.9 mmol) and the resulting red mixture stirred at room temperature for 30 min. The solution was then evaporated to dryness and the residue chromatographed on a silica gel column prepared in dichloromethane (RG). Elution with dichloromethane gave a broad red band turning blue at the front. This was collected and treated with nitric acid (70%, 10 drops from a dropping pipet) with stirring for 10 min. Addition of heptane (200 mL, RG) followed by removal of dichloromethane in vacuo gave a red microcrystalline precipitate of **3** (1.55 g, 72%).

(b) To a solution of [{*closo*-Rh(PPh_3)($C_2B_9H_{11}$)}$_2$][4] (1.0 g, 1.01 mmol) in dichloromethane (200 mL, RG) under argon was added nitric acid (70%, 0.5 mL, 7.9 mmol), and the mixture was stirred for 10 min at room temperature. Addition of heptane (100 mL, RG) to the bright red solution followed by removal of dichloromethane in vacuo gave air-stable red microcrystalline **3** (1.08 g, 96%).

(c) A gentle stream of an NO_2/N_2O_4 mixture was bubbled through a stirred yellow suspension of **1** (0.51 g, 0.67 mmol) in benzene (130 mL) under argon at room temperature. After 15 min the gas mixture source was removed, and stirring was continued for a further 5 min, after which the dark red solution was evaporated to dryness in vacuo. The residue was chromatographed on a silica gel column prepared in hexane (RG) under argon. Elution with dichloromethane (RG) gave a red band, which was collected and treated with hexane (10 mL, RG). Evaporation and further hexane addition (10 mL) gave, on overnight standing, red needle crystals of **3** (0.13 g, 34%).

Infrared spectrum: 3040 (s), 2604 (s, sh), 2571 (s, sh) 2538 (vs), 1590 (vw), 1565 (m), 1506 (vs), 1473 (s), 1431 (s), 1326 (w), 1309 (w), 1252 (s), 1236 (s), 1221 (m), 1192 (w), 1164 (w), 1144 (w), 1094 (s), 1076 (w), 1065 (vw), 1032 (w), 1011 (s), 1001 (m), 981 (m), 936 (vw), 923 (vw), 902 (w), 870 (vw), 859 (vw), 848 (vw), 801 (vw), 791 (w), 755 (s), 750 (s, sh), 728 (m, sh), 712 (s), 697 (vs) cm^{-1}.

NMR spectra (ppm): $^{31}P\{^1H\}$ (81.02 MHz, $CDCl_3$, room temperature) +36.1 (d, J_{Rh-P} = 169 Hz); $^{11}B\{^1H\}$ (64.15 MHz, $CDCl_3$, room temperature) −25.7 (s, br), −9.2 (s, br), −3.1 (s, br), +11.8 (s, br).

Reaction of 2 with Hydrogen or Deuterium. A stirred solution of **2** (0.2 g, 0.22 mmol) in THF (100 mL) was treated with hydrogen gas (1 atm) for 10 min at room temperature. Addition of water (100 mL) followed by removal of THF in vacuo gave yellow microcrystalline **1** (0.15 g, 82%). A similar reaction of **2** with deuterium in the presence of 1 equiv of triphenylphosphine gave [*closo*-3,3-$(PPh_3)_2$-3-D-3,1,2-$RhC_2B_9H_{11}$] in 88% yield (infrared spectrum shows ν(Rh–D) at 1520 cm^{-1}, Nujol mull).

Preparation of [*closo*-3-PPh_3-3,3-{C(Ph)–C(PPh_3)–C(H)–C(Ph)}-3,1,2-$RhC_2B_9H_{11}$] (5). (a) To a slurry of **2** (0.41 g, 0.44 mmol) in THF (20 mL) under nitrogen was added phenylacetylene (2.0 mL, 20 mmol) with stirring. The mixture was then warmed to 45 °C, and after 2 min a yellow precipitate had formed. After 20 min the mixture was cooled to room temperature, and the precipitate was isolated, washed with hexane (3 × 10 mL), and dried in vacuo, giving **5** (0.41

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[24] Intensities of the absorption bands are designated (in parentheses) as follows: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

[25] NMR abbreviations: s, singlet; d, doublet; m, multiplet; br, broad.

g, 97%). An analytical sample was obtained by recrystallization from dichloromethane/ethanol.

Anal. Calcd for $C_{54}H_{52}B_9P_2Rh$: C, 66.37; H, 5.44; B, 10.10; Rh, 10.68; P, 6.43. Found: C, 66.47; H, 5.52; B, 9.32; Rh, 10.02; P, 6.30.

Infrared spectrum: 3050 (w), 2560 (vs), 2520 (vs), 1590 (m), 1575 (w), 1460 (vs), 1435 (vs), 1375 (vs), 1315 (w), 1195 (w), 1160 (w), 1105 (vs), 1090 (vs), 1030 (w), 1005 (m), 990 (w), 791 (w), 760 (vs), 720 (vs), 700 (vs) cm^{-1}.

NMR spectra (ppm): ^1H (200.12 MHz, CD_2Cl_2, room temperature) +7.7–7.0 (m, 40, Ph), +6.86 (s, 1, vinyl CH), +2.4 (s, 1, carborane CH), +2.1 (s, 1, carborane CH); $^{31}P\{^1H\}$ (81.02 MHz, pyridine-d_5, room temperature) +30.9 (d of d, $J_{Rh-P(1)}$ = 129 Hz, $J_{P(1)-P(2)}$ = 7 Hz), +3.6 (d of d, $J_{Rh-P(2)}$ = 12 Hz, $J_{P(2)-P(1)}$ = 7 Hz).

(b) Triphenylphosphine (0.15 g, 0.57 mmol) was added at room temperature to a stirred solution of **3** (0.3 g, 0.54 mmol) in THF (150 mL) under argon. After 15 min phenylacetylene 1.0 mL, 10 mmol) was added to the stirred solution. After 20 h heptane (100 mL) was added to the now yellow-orange solution; removal of THF in vacuo gave a yellow precipitate, which was filtered off in air, washed with petroleum ether (bp 35–60 °C, RG), and dried, giving **5** (0.51 g, 98%) as air-stable yellow microcrystals identified by infrared and ^{31}P NMR spectroscopy.

Reaction of 2 with Alcohols. (a) With Ethanol. Complex **2** (0.08 g, 0.09 mmol) was suspended in absolute ethanol (3.0 mL) and the mixture heated to 50 °C in a water bath with shaking. After 5 min a bright yellow crystalline precipitate had formed. After cooling, the yellow product was filtered off, washed with ethanol (3 × 1 mL) and diethyl ether (2 × 1 mL), and dried by suction, giving **1** (0.58 g, 89%). The reaction of **2** with ethanol-d_1 was performed exactly as above to provide product **1** as well. The reaction of **2** with ethanol-d_5 was carried out as follows: Complex **2** (0.09 g, 0.10 mmol) was suspended in a solution consisting of 1.27 mL (0.02 mol) of ethanol-d_6 and 0.8 mL (0.04 mol) of distilled water. The mixture was heated as discussed above, and the yellow product [*closo*-3,3-$(PPh_3)_2$-3-D-3,1,2-$RhC_2B_9H_{11}$] was isolated by filtration, rinsed with 3 mL of diethyl ether, and dried in vacuo. The production of acetaldehyde in the reaction was verified in a separate experiment as follows: Complex **2** (0.28 g, 0.30 mmol) was dissolved in *o*-dichlorobenzene (15 mL) under nitrogen. Absolute ethanol (5.0 mL) was then added with stirring. Nitrogen gas was continuously bubbled through the reaction mixture, and the exit stream (with entrained acetaldehyde) was bubbled through a solution of 2,4-dinitrophenylhydrazine in sulfuric acid/ethanol/water. After 18 h the indicator solution was extracted with benzene (4 × 10 mL) and the combined extracts were chromatographed on a basic alumina column prepared in benzene. Elution with dichloromethane gave a yellow band, which was collected and evaporated to dryness in vacuo. This gave bright yellow crystals of acetaldehyde 2,4-dinitrophenylhydrazone (0.021 g, 31%; mp 157 °C; lit.[26] mp 157 °C).

(b) With 1-Propanol. Complex **2** (0.25 g, 0.27 mmol) was suspended in 1-propanol (10 mL) and the suspension heated to 50 °C in a water bath for 10 min. The resulting bright yellow crystalline precipitate was filtered off, washed with ethanol (3 × 4 mL) and diethyl ether (2 × 5 mL), and air-dried, giving **1** (0.193 g, 94%).

The yield of propionaldehyde was determined in a separate experiment as follows: Complex **2** (0.3 g, 0.32 mmol) was charged into a 250-mL round-bottom flask equipped with a seal-off neck, a break-seal, and a magnetic stir-bar. The flask was evacuated to a high vacuum through the seal-off neck. 1-Propanol (10 mL) was then distilled into the flask from anhydrous potassium carbonate (after four "freeze–pump–thaw" cycles to remove dissolved gases). The flask was then sealed under high vacuum and transferred to an oil bath at 75 °C. The suspension was stirred for 3 days. The flask was then cooled, and the volatiles were removed by alembic distillation under high vacuum. The yield of propionaldehyde was determined to be 84% by GLC analysis (4-ft column, 10% Carbowax 20 M on Chromosorb P, acid washed).

Preparation of [*closo*-3,3-$(PPh_3)_2$-3-Br-3,1,2-$RhC_2B_9H_{11}$] (6, X = Br). (a) Sodium bromide (1.2 g, 10 mmol) and complex **2** (0.5 g, 0.54 mmol) were heated together to the reflux temperature in benzene (150 mL) (to which water, 1 mL, had been added) for 30 min under nitrogen. The resulting mixture was cooled and filtered onto silica gel (20-mL dry volume). The resulting slurry was taken to dryness and applied to a silica gel column prepared in hexane. Elution with benzene produced a bright orange fraction, which was collected and evaporated to dryness. Recrystallization of the residue from benzene/heptane gave **6** (X = Br) as air-stable orange crystals (0.29 g, 65%).

Anal. Calcd for $C_{38}H_{41}B_9BrP_2Rh$: C, 54.35; H, 4.92; B, 11.58; Rh, 12.25; P, 7.38; Br, 9.52. Found: C, 54.60; H, 5.21; B, 11.60; Rh, 12.02; P, 7.34; Br, 8.94.

Infrared spectrum: 3000 (w), 2540 (vs), 2520 (vs), 1590 (w), 1570 (w), 1480 (vs), 1430 (vs), 1265 (w), 1185 (w), 1160 (w), 1100 (vs), 1090 (vs), 1080 (s), 1025 (w), 1020 (w), 1005 (m), 995 (m), 895 (w), 740 (vs), 695 (vs) cm^{-1}.

NMR spectra (ppm): ^1H (60 MHz, CD_2Cl_2, room temperature) +7.5–7.2 (m, 30, Ph), (s, 2, carborane CH); $^{31}P\{^1H\}$ (81.02 MHz, CD_2Cl_2, room temperature) +27.7 (d, J_{Rh-P} = 134 Hz).

(b) Complex **3** (0.4 g, 0.72 mmol) was dissolved in dichloromethane (100 mL, RG) at room temperature under argon, and triphenylphosphine (0.24 g, 0.92 mmol) was added with stirring. After 5 min tetraethylammonium bromide (0.21 g, 1.0 mmol) was added and the mixture stirred for 45 min. The red solution was then chromatographed on a silica gel column prepared in dichloromethane (RG) in the air. Elution with dichloromethane gave a broad orange band, which, when collected, treated with heptane (200 mL, RG), and evaporated, gave a red precipitate. This was washed with petroleum ether (bp 20–40 °C, RG) and dried by suction, giving **6** (X = Br) (0.59 g, 98%) as a dichloromethane solvate identified by infrared spectroscopy.

Preparation of [{*closo*-3-PPh_3-3-(μ-CN)-3,1,2-$RhC_2B_9H_{11}$}$_4$] (7). A mixture of **2** (1.07 mmol) and sodium cyanide (1.0 g, 20 mmol) in benzene (100 mL) and water (1.0 mL) was heated to reflux temperature with stirring under nitrogen for 20 min, after which the mixture was cooled to room temperature and filtered to remove excess cyanide (*care*!). The bright yellow filtrate was dried over anhydrous magnesium sulfate and filtered onto silica gel (10-mL dry volume), and the resulting slurry was taken to dryness. The mixture was then applied to a silica gel column prepared in hexane. Elution with benzene gave a bright yellow band, which, upon removal of the solvent, gave air-stable **7** (0.46 g, 82%). An analytical sample was obtained by recrystallization from dichloromethane/ethanol.

Anal. Calcd for $C_{84}H_{104}B_{36}N_4P_4Rh_4$: C, 48.17; H, 5.00; B, 18.58; Rh, 19.65; P, 5.91; N, 2.67. Found: C, 48.77; H, 5.38; B, 18.42; Rh, 19.12; P, 5.97; N, 2.55.

Molecular weight: calcd for $C_{84}H_{104}B_{36}N_4P_4Rh_4$, 2092; found, 2043 ($CHCl_3$).

Infrared spectrum: 3048 (w), 2570 (vs), 2146 (vs), 1595 (w), 1580 (w), 1480 (vs), 1435 (vs), 1200 (w), 1170 (w), 1100 (vs), 1025 (w), 1010 (w), 990 (m), 745 (vs), 695 (vs) cm^{-1}.

NMR spectra (ppm): ^1H (200.12 MHz, CD_2Cl_2, room temperature) +7.6–7.3 (m, 15, Ph), +3.2 (s, 1, carborane CH), +2.1 (s, 1, carborane CH); $^{31}P\{^1H\}$ (81.02 MHz, CD_2Cl_2, room temperature) +40.9 (d, J_{Rh-P} = 117 Hz); $^{11}B\{^1H\}$ (111.8 MHz, $CHCl_3$, room temperature) +8.5 (s, br), –1.6 (s, br), –5.3 (s, br), –8.8 (s, br).

Preparation of [*closo*-3-PPh_3-3-CO-3-NO_3-3,1,2-$RhC_2B_9H_{11}$] (8). A solution of **3** (0.174 g, 0.31 mmol) in diethyl ether (50 mL) under argon was treated with carbon monoxide (1 atm) with stirring at room temperature for 1–2 min (until the solution turned yellow from orange-red). Heptane (2 × 200 mL) was then added with rapid stirring. Cooling to 0 °C overnight gave a yellow precipitate, which was filtered off in air, washed with pentane (RG), and dried by suction, giving air-stable **8** (0.13 g, 72%). An analytical sample was obtained by drying in vacuo.

Anal. Calcd for $C_{21}H_{26}B_9NO_4PRh$: C, 42.92; H, 4.46; N, 2.38; P, 5.27; B, 16.56; Rh, 17.51. Found: C, 42.46; H, 4.60; N, 2.59; P, 5.36; B, 16.06; Rh, 16.44.

Molecular weight: calcd for $C_{21}H_{26}B_9NO_4PRh$, 588; found, 602 (toluene).

Infrared spectrum: 2994 (m), 2538 (vs), 2088 (vs), 1656 (vw), 1582 (vw), 1565 (vw), 1529 (w), 1495 (vs), 1473 (m), 1431 (s), 1326 (vw), 1309 (vw), 1260 (vs), 1214 (vw), 1192 (vw), 1164 (w), 1100 (s), 1094 (s, sh), 1076 (vw), 1032 (vw), 1016 (w), 1001 (m), 981 (w), 967 (vs), 940 (vw), 923 (vw), 898 (vw), 859 (vw), 852 (vw), 804 (w), 767 (w, sh), 750 (s), 725 (m), 695 (s) cm^{-1}.

NMR spectrum (ppm): $^{31}P\{^1H\}$ (81.02 MHz, $CDCl_3$, room temperature) +41.2 (d, J_{Rh-P} = 107 Hz).

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[26] "Handbook of Tables for Organic Compound Identification", 3rd ed.; CRC Press, Cleveland, OH, 1967; p 144.

Preparation of [*closo*-3,3-$(PPh_3)_2$-3-NO_3-3,1,2-$RhC_2B_9H_{11}$] (9).[27] Triphenylphosphine (2.25 g, 0.95 mmol) was added to a stirred solution of **3** (0.5 g, 0.9 mmol) in diethyl ether (100 mL) under argon at room temperature and the resulting mixture stirred for 15 min. Addition of heptane (100 mL) and removal of diethyl ether in vacuo afforded an orange precipitate, which was collected in air, washed with heptane, and dried by suction, giving air-stable **9** (0.59 g, 81%). The analytical sample was obtained by drying in vacuo.

Anal. Calcd for $C_{38}H_{41}B_9NO_3P_2Rh$: C, 55.53; H, 5.03; N, 1.70; P, 7.54; B, 11.84; Rh, 12.52. Found: C, 55.62; H, 5.26; N, 1.58; P, 7.39; B, 11.62; Rh, 12.25.

Infrared spectrum: 3040 (w), 2571 (m), 2538 (m), 1590 (vw), 1577 (vw), 1484 (s), 1473 (s, sh), 1431 (s), 1318 (vw), 1267 (vs), 1192 (w), 1164 (w), 1088 (m), 1032 (vw, sh), 1022 (w), 1006 (m, sh), 991 (m), 981 (m, sh), 931 (vw), 898 (vw), 859 (vw), 801 (vw), 753 (s), 700 (s) cm^{-1}.

NMR spectrum (ppm): $^{31}P\{^1H\}$ (81.02 MHz, $CDCl_3$, room temperature) +28.0 (d, J_{Rh-P} = 134 Hz) and signals due to **3** and uncoordinated triphenylphosphine.

Preparation of [*closo*-3,3-$(PMe_2Ph)_2$-3-NO_3-3,1,2-$RhC_2B_9H_{11}$] (10). Dimethylphenylphosphine (approximately 0.15 mL) was added to a stirred red solution of **3** (0.3 g, 0.54 mmol) in diethyl ether (100 mL) at room temperature under argon. The solution turned yellow instantly. After 15 min heptane (50 mL) was added and removal of diethyl ether in vacuo gave a yellow crystalline precipitate. This was filtered off in air, washed with heptane (3 × 30 mL, RG), and dried by suction, giving air-stable **10** (0.29 g, 94%). An analytical sample was obtained by drying in vacuo.

Anal. Calcd for $C_{18}H_{33}B_9NO_3P_2Rh$: C, 37.69; H, 5.80; N, 2.44; P, 10.80; B, 16.96; Rh, 17.94. Found: C, 37.38; H, 5.66; N, 2.50; P, 10.74; B, 16.65; Rh, 17.49.

Molecular weight: calcd for $C_{18}H_{33}B_9NO_3P_2Rh$, 574; found, 567 and 576 (benzene).

Infrared spectrum: 2994 (w), 2538 (vs), 1590 (w), 1577 (w), 1473 (vs), 1462 (m), 1431 (s), 1326 (m), 1318 (m), 1300 (m), 1284 (s), 1260 (vs), 1199 (m), 1171 (w), 1131 (w), 1112 (m, sh), 1100 (s), 1082 (w), 1065 (w), 1022 (s), 1006 (s, sh), 986 (vs), 953 (vs), 927 (vw), 918 (vs), 910 (vs), 886 (w), 874 (w), 859 (m), 852 (m), 804 (m), 750 (vs), 733 (s), 715 (s), 697 (s) cm^{-1}.

NMR spectra (ppm): $^{31}P\{^1H\}$ (81.02 MHz, $CDCl_3$, room temperature) +11.2 (d, J_{Rh-P} = 132 Hz); $^{11}B\{^1H\}$ (127.04 MHz, $CHCl_3$, room temperature) −19.6 (s), −15.5 (s), −5.6 (s), −2.4 (s), +8.0 (s).

Preparation of [*closo*-3-PPh_3-3-CO-3-Cl-3,1,2-$RhC_2B_9H_{11}$] (11). (a) Complex **3** (0.4 g, 0.72 mmol) was dissolved in THF (100 mL under argon at room temperature), and carbon monoxide was passed through the stirred red solution until it turned yellow (about 1–2 min). Hydrochloric acid (37%, 0.2 mL, 2.4 mmol) was then added dropwise and the resulting orange-yellow solution stirred for 15 min. Addition of heptane (100 mL), removal of THF in vacuo, and further addition of heptane (70 mL) gave a golden yellow precipitate. This was filtered off in air, washed with heptane (RG), and dried by suction, giving air-stable **11** (0.34 g, 85%). Drying in vacuo gave an analytical sample.

Anal. Calcd for $C_{21}H_{26}B_9ClOPRh$: C, 44.96; H, 4.67; Cl, 6.32; B, 17.34; P, 5.52; Rh, 18.34. Found: C, 45.81; H, 4.63; Cl, 6.73; B, 17.58; P, 5.57, Rh, 18.20.

Molecular weight: calcd for $C_{21}H_{26}B_9ClOPRh$, 561; found, 552 (benzene).

Infrared spectrum: 2994 (w), 2639 (w), 2571 (m), 2538 (s), 2506 (m), 2088 (vs), 1590 (w), 1577 (w), 1484 (m), 1431 (s), 1318 (w), 1199 (w), 1164 (w), 1125 (vw), 1100 (s), 1076 (w), 1032 (vw), 1016 (w), 1006 (w), 986 (m), 940 (vw), 931 (vw), 923 (vw), 859 (vw), 764 (m), 750 (m), 744 (m, sh), 725 (w), 712 (m), 696 (s) cm^{-1}.

NMR spectrum (ppm): $^{31}P\{^1H\}$ (81.02 MHz, $CDCl_3$, room temperature) +39.6 (d, J_{Rh-P} = 107 Hz).

(b) A solution of **8** (0.14 g, 0.24 mmol) in diethyl ether (100 mL), stirred at room temperature under argon, was treated with hydrochloric acid (37%, 3 drops from a dropping pipet). After 15 min heptane (200 mL) was added and the diethyl ether removed in vacuo. Further addition of heptane (200 mL) completed the precipitation of the product, which was filtered off in air, washed with heptane (RG), and dried by suction, giving **11** (0.05 g, 37%) identified by infrared spectroscopy.

Table III. Crystal Data for 5 and $7{\cdot}5C_6H_6$

	5	$7{\cdot}5C_6H_6$
cryst syst	triclinic, $P\bar{1}$, $Z = 2$	monoclinic, $P2/a$, $Z = 4$
a, Å	12.763 (6)	26.046 (8)
b, Å	13.348 (5)	15.626 (3)
c, Å	14.561 (7)	30.355 (8)
α, deg	91.58 (3)	90
β, deg	93.72 (3)	106.71 (2)
γ, deg	74.64 (3)	90
V, Å^3	2404	11833
calcd density, g/cm^3	1.34 (119 K)	1.35 (119 K)
obsd density, g/cm^3	. . .	1.24
(sin θ)/λ data collection limit, Å^{-1}	0.538	0.538
scan rate, deg/min	2	3
scan range, deg	2.2 + 0.692 tan θ	1.8 + 0.688 tan θ
bkgd	20 s	0.5 × scan time
abs coeff, cm^{-1}	4.56 (Mo Kα)	5.77 (Mo Kα)
no. of reflctns collected	6266 (hemisphere)	15 992 (quadrant)
no. of reflctns used	4493	9732
R	0.048	0.063
R_W	0.051	0.078
goodness-of-fit	1.50	2.03
data-to-parameter ratio	26	20

Formation of [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RC_2B_9H_{11}$] (1)[1a] from 3 or 9 and Hydrogen. (a) A solid mixture of **3** (0.09 g, 0.16 mmol) and triphenylphosphine (0.046 g, 0.18 mmol) was dissolved in THF (30 mL) under argon. Hydrogen gas (1 atm) was then bubbled gently through the orange-red solution with stirring at room temperature for 10 min. The resulting yellow solution was treated with absolute ethanol (100 mL); evaporation in vacuo gave a yellow precipitate, which was filtered off in air, washed with ethanol and diethyl ether, and dried by suction, giving **1** (0.11 g, 90%) identified by infrared spectroscopy.

(b) Hydrogen (1 atm) was bubbled through a stirred orange-red solution of **9** (0.2 g, 0.24 mmol) in THF (50 mL) at room temperature under argon. After 10 min absolute ethanol (150 mL) was added. Evaporation in vacuo gave a yellow precipitate, which was collected in air, washed with ethanol and diethyl ether, and dried by suction, giving **1** (0.15 g, 79%) identified by infrared spectroscopy.

Reaction of [*closo*-3-PPh_3-3-CO-3-NO_3-3,1,2-$RhC_2B_9H_{11}$] (8) with Triphenylphosphine. A solid mixture of **8** (0.063 g, 0.11 mmol) and triphenylphosphine (0.063 g, 0.24 mmol) was dissolved in diethyl ether (70 mL) and the resulting solution stirred under argon at room temperature for 30 min. Heptane (200 mL) was then added and the diethyl ether removed in vacuo. Evaporation to a low volume gave an orange precipitate, which was filtered off in air, washed with pentane (RG), and dried by suction, giving **9** (0.068 g, 77%) identified by infrared spectroscopy.

Preparation of [*closo*-3,3-$(PPh_3)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$][18] (6, X = Cl). (a) A solid mixture of **3** (0.1 g, 0.18 mmol) and triphenylphosphine (0.05 g, 0.19 mmol) was dissolved in THF (30 mL) under argon. To the resulting solution was added, with stirring, hydrochloric acid (37%, 2 drops from a dropping pipet), and the mixture was stirred for 10 min. Ethanol (100 mL) was then added, and the mixture was reduced in volume by evaporation, giving a light-orange precipitate. This was collected in air, washed with ethanol and petroleum ether (bp 35–60 °C, RG), and dried by suction, giving **6** (X = Cl) (0.12 g, 84%) identified by infrared spectroscopy.

(b) Four drops of hydrochloric acid (37%) were added to a stirred orange-red solution of **9** (0.2 g, 0.24 mmol) in THF (50 mL) at room temperature under argon. After 10 min ethanol (150 mL) was added. Evaporation to a low volume gave an orange precipitate, which was filtered off in air, washed with ethanol and petroleum ether (bp 35–60 °C, RG), and dried by suction, giving **6** (X = Cl) (0.17 g, 90%) identified by infrared spectroscopy.

(c) To a solution of **11** (0.3 g, 0.54 mmol) in THF (100 mL) under argon was added triphenylphosphine (0.15 g, 0.57 mmol), and the mixture was stirred at room temperature for 15 min. Addition of heptane (50 mL) followed by evaporation gave an orange precipitate; further addition of heptane (50 mL) gave **6** (X = Cl) (0.35 g, 81%), which was isolated in the air, washed with ethanol and pentane (RG), and dried by suction.

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(27) Difficulties were occasionally encountered in obtaining complex **9** by this method in a pure state, complex **3** appearing frequently as an impurity.

Table IV[a]

A. Positional (in Fractional Coordinates) and Thermal Parameters of the Nongroup Atoms in 5

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Rh	0.15780 (4)	0.15338 (4)	0.28636 (3)	*b*	C(4)	0.3069 (5)	0.2789 (5)	0.3302 (4)	1.4 (1)
P(1)	0.0143 (1)	0.3009 (1)	0.2556 (1)	*b*	C(5)	0.3173 (4)	0.2559 (4)	0.2325 (4)	1.3 (1)
P(2)	0.4413 (1)	0.2716 (1)	0.1911 (1)	*b*	C(6)	0.2492 (5)	0.2016 (4)	0.1929 (4)	1.3 (1)
C(1)	0.0982 (5)	0.0544 (4)	0.3857 (4)	1.5 (1)	H(1)	0.056 (3)	0.101 (3)	0.429 (3)	1.6 (9)
C(2)	0.0479 (5)	0.0430 (5)	0.2832 (4)	1.8 (1)	H(2)	−0.031 (3)	0.084 (3)	0.266 (3)	0.6 (8)
B(4)	0.2362 (5)	0.0269 (5)	0.3874 (4)	1.6 (1)	H(4)	0.280 (3)	0.053 (3)	0.438 (3)	1.6 (8)
B(5)	0.1683 (6)	−0.0622 (5)	0.4300 (5)	2.1 (1)	H(5)	0.168 (4)	−0.071 (3)	0.507 (3)	1.6 (10)
B(6)	0.0449 (6)	−0.0506 (6)	0.3638 (5)	2.0 (1)	H(6)	−0.025 (4)	−0.052 (4)	0.393 (3)	1.3 (10)
B(7)	0.1426 (6)	0.0042 (5)	0.2060 (5)	1.6 (1)	H(7)	0.125 (4)	0.020 (4)	0.137 (4)	2.1 (12)
B(8)	0.2712 (6)	−0.0083 (5)	0.2718 (5)	1.4 (1)	H(8)	0.344 (4)	−0.007 (4)	0.245 (3)	2.0 (11)
B(9)	0.2772 (6)	−0.1065 (6)	0.3576 (5)	2.0 (1)	H(9)	0.357 (4)	−0.149 (4)	0.383 (3)	1.3 (10)
B(10)	0.1592 (6)	−0.1539 (6)	0.3421 (5)	2.0 (1)	H(10)	0.156 (4)	−0.235 (5)	0.358 (3)	1.2 (10)
B(11)	0.0762 (6)	−0.0856 (6)	0.2496 (5)	1.9 (1)	H(11)	0.014 (5)	−0.116 (5)	0.204 (4)	3.3 (15)
B(12)	0.2194 (6)	−0.1189 (6)	0.2444 (5)	1.9 (1)	H(12)	0.254 (5)	−0.176 (5)	0.196 (4)	3.2 (15)
C(3)	0.2348 (5)	0.2403 (4)	0.3721 (4)	1.2 (1)	HC4	0.356 (4)	0.314 (4)	0.366 (3)	1.5 (11)

B. Anisotropic Thermal Parameters for 5[c]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	equiv B, Å^2
Rh	166 (2)	106 (3)	126 (2)	−32 (2)	8 (2)	−9 (2)	1.1
P(1)	173 (8)	142 (8)	154 (9)	−45 (6)	−2 (6)	−19 (8)	1.2
P(2)	163 (8)	195 (9)	212 (9)	−46 (7)	18 (7)	12 (7)	1.5

[a] Estimated standard deviations in the least signficant figures are given in parentheses. [b] Anisotropic thermal parameters. [c] U values have been multiplied by 10 000.0.

Table V[a]

A. Positional (in Fractional Coordinates) and Thermal Parameters for $7 \cdot 5C_6H_6$

nongroup atom	10^4x	10^4y	10^4z	B Å^2	nongroup atom	10^4x	10^4y	10^4z	B Å^2
Rh(1)	1741.3 (3)	−713.3 (5)	4218.3 (3)	*b*	Rh(3)	3050.1 (3)	5805.2 (5)	867.8 (3)	*b*
P(1)	2355 (1)	−1109 (2)	3839 (1)	*b*	P(3)	2366 (1)	6259 (2)	1154 (1)	*b*
CN(1)	1939 (4)	537 (6)	4184 (3)	1.4 (2)	CN(3)	2604 (4)	5898 (6)	189 (3)	1.7 (2)
CN(1)′	2342 (4)	−847 (5)	4820 (3)	1.4 (2)	CN(3)′	2748 (4)	4594 (6)	860 (3)	1.6 (2)
C(11)	1167 (4)	−1063 (7)	4606 (4)	2.3 (3)	C(31)	3864 (4)	5207 (7)	1134 (4)	2.5 (2)
C(12)	964 (5)	−217 (7)	4273 (4)	2.5 (3)	C(32)	3792 (5)	5724 (7)	655 (4)	2.2 (2)
B(14)	1322 (5)	−1902 (7)	4298 (4)	1.2 (2)	B(34)	3690 (5)	5802 (8)	1536 (4)	2.0 (3)
B(15)	719 (5)	−1889 (8)	4456 (4)	1.7 (2)	B(35)	4370 (6)	5579 (10)	1589 (5)	2.6 (3)
B(16)	500 (5)	−813 (8)	4444 (4)	1.8 (2)	B(36)	4435 (6)	5517 (9)	1022 (5)	3.1 (3)
B(17)	968 (6)	−471 (8)	3695 (5)	1.7 (3)	B(37)	3573 (6)	6800 (9)	708 (5)	2.3 (3)
B(18)	1189 (6)	−1568 (8)	3712 (4)	1.5 (3)	B(38)	3518 (5)	6867 (8)	1298 (4)	1.4 (3)
B(19)	714 (6)	−2206 (8)	3895 (4)	1.9 (3)	B(39)	4172 (5)	6631 (8)	1676 (4)	2.4 (2)
B(110)	209 (5)	−1538 (8)	3979 (4)	2.0 (2)	B(310)	4634 (6)	6470 (9)	1350 (5)	2.7 (3)
B(111)	362 (6)	−452 (9)	3861 (5)	1.7 (3)	B(311)	4260 (7)	6540 (10)	755 (4)	2.9 (3)
B(112)	499 (6)	−1316 (8)	3526 (4)	1.9 (3)	B(312)	4104 (6)	7253 (8)	1165 (4)	2.3 (3)
Rh(2)	2251.0 (3)	2490.3 (5)	4098.6 (3)	*b*	Rh(4)	2475.6 (3)	2609.8 (5)	859.2 (3)	*b*
P(2)	1366 (1)	2934 (2)	3948 (1)	*b*	P(4)	3369 (1)	2250 (2)	1074 (1)	*b*
CN(2)	2006 (4)	1259 (5)	4153 (3)	1.3 (2)	CN(4)	2649 (4)	3885 (6)	844 (3)	1.7 (2)
CN(2)′	2429 (4)	2558 (6)	4802 (3)	1.7 (2)	CN(4)′	2500 (4)	2504 (5)	189 (3)	2.0 (2)
C(21)	2796 (4)	1943 (7)	3709 (4)	1.9 (2)	C(41)	1695 (5)	2971 (7)	982 (4)	2.2 (2)
C(22)	2271 (5)	2491 (8)	3378 (4)	1.8 (2)	C(42)	1623 (5)	2152 (7)	629 (4)	2.2 (2)
B(24)	3129 (5)	2501 (8)	4166 (4)	2.0 (3)	B(44)	2216 (5)	2811 (8)	1479 (4)	1.5 (2)
B(25)	3401 (6)	2333 (8)	3709 (4)	2.5 (3)	B(45)	1531 (6)	2729 (8)	1467 (4)	2.2 (3)
B(26)	2861 (5)	2320 (8)	3203 (4)	2.1 (2)	B(46)	1147 (6)	2317 (9)	931 (5)	2.4 (3)
B(27)	2273 (5)	3542 (7)	3622 (4)	1.6 (2)	B(47)	2105 (5)	1339 (8)	885 (4)	1.7 (2)
B(28)	2827 (5)	3539 (7)	4152 (4)	1.8 (2)	B(48)	2472 (6)	1765 (8)	1445 (4)	1.9 (3)
B(29)	3428 (6)	3358 (9)	3974 (4)	2.1 (3)	B(49)	2006 (6)	1947 (9)	1759 (5)	2.2 (3)
B(210)	3245 (6)	3262 (9)	3359 (5)	2.3 (3)	B(410)	1356 (6)	1611 (10)	1418 (5)	2.6 (3)
B(211)	2545 (6)	3350 (9)	3147 (5)	2.3 (3)	B(411)	1418 (5)	1260 (8)	878 (4)	2.2 (3)
B(212)	2899 (5)	4004 (8)	3624 (4)	1.9 (3)	B(412)	1928 (6)	1043 (9)	1387 (5)	2.1 (3)

B. Anisotropic Thermal Parameters for $7 \cdot 5C_6H_6$[c]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	equiv B, Å^2
Rh(1)	110 (6)	126 (5)	154 (4)	−8 (4)	18 (4)	5 (5)	1.1
Rh(2)	158 (6)	132 (5)	137 (4)	−6 (4)	40 (4)	14 (5)	1.1
Rh(3)	195 (6)	147 (5)	197 (4)	−22 (4)	66 (4)	−14 (5)	1.4
Rh(4)	224 (6)	136 (5)	180 (4)	−12 (4)	59 (4)	7 (5)	1.4
P(1)	199 (19)	181 (15)	261 (17)	16 (14)	103 (15)	23 (14)	1.6
P(2)	180 (19)	145 (15)	214 (17)	14 (14)	33 (15)	32 (12)	1.5
P(3)	255 (19)	158 (15)	253 (17)	20 (14)	107 (15)	2 (14)	1.7
P(4)	218 (19)	192 (16)	236 (17)	10 (14)	59 (15)	−12 (12)	1.7

[a] Standard deviations are given in parentheses. [b] Anisotropic thermal parameters. [c] U values have been multiplied by 10 000.0.

(d) A solution of **2** (0.3 g, 0.32 mmol) in THF (100 mL) under argon was treated with hydrochloric acid (37%, 6 drops from a dropping pipet) and the mixture stirred at room temperature for 15 min. Fifty milliliters of heptane was then added and THF removed in vacuo. The resulting light orange precipitate was collected in air, washed with petroleum ether (bp 35–60 °C, RG), and dried by suction, giving **6** (X = Cl) (0.26 g, 93%) identified by infrared spectroscopy.

Reaction of [*closo*-3,3-(PMe$_2$Ph)$_2$-3-NO$_3$-3,1,2-RhC$_2$B$_9$H$_{11}$] (10) with Hydrochloric Acid. A yellow solution of **10** (0.1 g, 0.17 mmol) in THF (100 mL) under argon was treated with hydrochloric acid (37%, 6 drops from a dropping pipet) and the mixture stirred under argon at room temperature. After 15 min 6 further drops of acid were added. After 75 min heptane (100 mL) was added and the THF removed in vacuo. After 75 min heptane (100 mL) was added and the THF removed in vacuo. The yellow precipitate was filtered off in air, washed with pentane (RG), and dried by suction, giving a compound (0.09 g) identified as [*closo*-3,3-(PMe$_2$Ph)$_2$-3-Cl-3,1,2-RhC$_2$B$_9$H$_{11}$][22] (95%) by infrared spectroscopy.

X-ray Crystallographic Study of [*closo*-3-PPh$_3$-3,3-{C(Ph)—C(PPh$_3$)—C(H)—C(Ph)}-3,1,2-RhC$_2$B$_9$H$_{11}$] (5) and [{*closo*-3-PPh$_3$-3-(μ-CN)-3,1,2-RhC$_2$B$_9$H$_{11}$}$_4$]·5C$_6$H$_6$ (7·5C$_6$H$_6$). Crystals of the two compounds chosen for data collection had the dimensions 0.10 mm × 0.12 mm × 0.10 mm (**5**) and 0.20 mm × 0.30 mm × 0.45 mm (**7**·5C$_6$H$_6$). They exhibited the faces ($\bar{1}00$), (100), (015), ($0\bar{1}\bar{5}$), ($0\bar{3}\bar{1}$), and (031) (**5**) and (610), ($\bar{6}\bar{1}0$), ($10\bar{3}$), ($\bar{1}03$), ($0\bar{1}0$), and (010) (**7**·5C$_6$H$_6$), respectively. Data were collected, and preliminary crystallographic experiments were performed on a Picker FACS-I diffractometer (**5**) and on a Syntex P$\bar{1}$ diffractometer (**7**·5C$_6$H$_6$). Both crystals were maintained at −154 °C by a cold nitrogen stream from an apparatus designed by Strouse.[28] Crystals of **7** from several solvent mixtures exhibited rapid deterioration, apparently due to solvent loss. Suitable crystals were finally produced from benzene/ethanol. After the data-collection crystal of **7**·5C$_6$H$_6$ was mounted, it was immediately transferred to the cold nitrogen stream. The orientation of each crystal was determined by indexing reflections found photographically. For **7**·5C$_6$H$_6$ an axial photograph revealed the presence of a mirror plane, which suggested a monoclinic space group. For **5** the absence of symmetry suggested a triclinic cell. Preliminary data were collected to identify the intense high-angle data. Accurate cell constants were obtained by a least-squares fit of 15 (**7**·5C$_6$H$_6$) and 19 (**5**) high-angle reflections, respectively. Data were collected in the θ–2θ scan mode with Zr-filtered Mo Kα radiation for **5** and with graphite-monochromatized Mo Kα radiation for **7**·5C$_6$H$_6$. Three intense reflections were periodically monitored during data collection for each crystal. For **5** the intensities of the standards showed an isotropic decay of 8% and the raw data were corrected for this. Intensities of the standards for **7**·5C$_6$H$_6$ fluctuated only slightly during the course of data collection. Other details of data collection are presented in Table III.

Data were corrected for Lorentz, polarization, and absorption effects.[29] The data for **7**·5C$_6$H$_6$ were corrected by an empirical method based on the fluctuation in intensities of three reflections near χ = 90°. The three reflections (and their 2θ values) are $46\bar{2}$ (17°), $79\bar{2}$ (26°), and $9,11,\bar{3}$ (32°). All three absorption curves exhibited the same shape with maxima and minima coinciding. The systematic absences $h0l$, $h = 2n + 1$, observed for **7**·5C$_6$H$_6$ suggested the space group Pa or $P2/a$. Successful refinement of the structure in the latter space group showed it to be the correct choice. An ignorance factor of 0.04 was used for each complex. For **5** only data satisfying the criteria $I_0 > 3\sigma(I_0)$ were retained for structure solution and refinement. For **7**·5C$_6$H$_6$ only data satisfying the 3σ criterion with $(\sin\theta)/\lambda$ less than 0.40 Å^{-1} were used in the structure analysis, and only in the final cycles of refinement was the entire data set used.

The structure were solved by the heavy-atom/Fourier synthesis method. In subsequent structure refinements the phenyl groups of the triphenylphosphine moieties were treated as rigid groups with C–C and C–H bond distances set at 1.39 and 1.00 Å, respectively. During the least-squares process the positional and rotational parameters and the overall temperature factors of each group were allowed to vary and all the individual temperature factors were set at zero. For the nongroup atoms all positional and thermal parameters (the Rh and P atoms were allowed to vibrate anisotropically; all other atoms isotropically) and the scale factor were varied in the full-matrix least-squares process.

A difference-Fourier synthesis of **5** revealed the 11 cage hydrogen atoms and the vinylic hydrogen of the metallacycle. The positional and thermal parameters of these atoms were also varied in three cycles of least squares, and convergence was realized at $R(F) = 0.048$. A final difference-Fourier synthesis showed no significant peaks.

For **7**·5C$_6$H$_6$ all non-hydrogen atoms of the tetramer were varied in three cycles of least-squares refinement to an agreement factor 0.163. A difference-Fourier synthesis at this point showed peaks attributed to five molecules of benzene. From this point on, the full data set was used in the refinement (9732 observed reflections). Three cycles of full-matrix least-squares refinement converged to an agreement factor 0.063. A final difference-Fourier synthesis revealed peaks attributable to hydrogen atoms on the cage atoms only. These atoms were not included in the model. All cyano group atoms were treated as half-carbon, half-nitrogen; an averaged carbon–nitrogen scattering factor was applied.

Final atomic parameters for **5** and **7**·5C$_6$H$_6$ can be found in Tables IV and V.

Acknowledgment. We thank C. A. O'Con, Dr. D. Busby, and R. T. Baker for assistance in obtaining NMR spectra and Dr. R. Grey for preliminary experiments. Financial support of this work by the National Science Foundation (Grant CHE78-05679) and the Office of Naval Research is gratefully acknowledged.

Registry No. **1**, 53687-46-0; **2**, 82807-94-1; **2a**, 82807-96-3; **3**, 82807-97-4; **4**, 82807-98-5; **5**, 82807-99-6; **6**, X = Br, 82808-00-2; **6**, X = Cl, 56465-0-77; **7**, 82823-03-8; **8**, 82808-02-4; **9**, 72930-70-2; **10**, 82808-03-5; **11**, 72920-94-6; *closo*-3,3-(PPh$_3$)$_2$-3-D-3,1,2-RhC$_2$B$_9$H$_{11}$, 82808-04-6; Rh, 7440-16-6; B, 7440-42-8.

Supplementary Material Available: Listings of rigid-group parameters (Tables IVa and Va) and calculated and observed structure factors for **5** and **7**·5C$_6$H$_6$ (48 pages). Ordering information is given on any current masthead page.

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(28) Strouse, C. E. *Rev. Sci. Instrum.* **1976**, *47*, 871.

(29) Experimental and computational procedures used in this work have been previously described by: Callahan, K. P.; Strouse, C. E.; Sims, A. L.; Hawthorne, M. F. *Inorg. Chem.* **1974**, *13*, 1397. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma(F))^2$. $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$.