Metallacarboranes in Catalysis. 2. Synthesis and Reactivity of Closo Icosahedral Bis(phosphine)hydridorhodacarboranes and the Crystal and Molecular Structures of Two Unusual *closo*-Phosphinerhodacarborane Complexes[1]

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Abstract: A series of closo icosahedral rhodacarboranes bearing substituents at carbon has been synthesized by the reaction of $[(PPh_3)_3RhCl]$ with the correspondingly C-substituted *nido*-carborane anions: [*closo*-1-R-2-R′-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_9$] from [*nido*-7-R-8-R′-7,8-$C_2B_9H_{10}$]$^-$ where R = R′ = H; R = R′ = D; R = H and R′ = Ph, Me, and *n*-Bu; [*closo*-1-R-2,2-$(PPh_3)_2$-2-H-2,1,7-$RhC_2B_9H_{10}$] from [*nido*-7-R-7,9-$C_2B_9H_{11}$]$^-$ where R = H, Ph, and Me; and [*closo*-2,2-$(PPh_3)_2$-2-H-2,1,12-$RhC_2B_9H_{11}$] from [*nido*-2,9-$C_2B_9H_{12}$]$^-$. These closo icosahedral rhodacarboranes are catalytically active in alkene isomerization and hydrogenation reactions, among others. The B–D–B bridge deuterated [*nido*-7,8-$C_2B_9H_{11}D$]$^-$ gave [*closo*-3,3-$(PPh_3)_2$-3-D-3,1,2-$RhC_2B_9H_{11}$] when reacted with $[(PPh_3)_3RhCl]$, establishing the regiospecific transfer of BHB hydrogen to Rh–H in the synthesis reaction. The complex [*closo*-1-*n*-Bu-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{10}$] is apparently transformed to [*closo*-8-*n*-Bu-2,2-$(PPh_3)_2$-2-H-2,1,8-$RhC_2B_9H_{10}$] by a polytopal rearrangement under mild conditions. The optically active catalyst [*d*-*closo*-1-Me-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{10}$] was employed to hydrogenate ethyl α-phenylacrylate to give ethyl α-phenylpropionate in 3% enantiomeric excess. In the absence of hydrogen this chiral catalyst reacted with certain esters of the acrylic type to yield alkyl chelates in which the alkene function of the ester had undergone migratory insertion into the Rh–H and the ester carbonyl oxygen became bound to Rh. One of these chelates, derived from the *d*-catalyst and *n*-butyl acrylate, was characterized crystallographically. The compound crystallizes in the space group $P2_12_12_1$ with unit cell parameters a = 24.578 (5) Å, b = 12.543 (2) Å, and c = 10.377 (2) Å, four molecules per unit cell. The structure was solved by conventional heavy-atom methods and refined to a final value of R = 0.069, R_w = 0.080 (3159 reflections). The absolute configuration of the *d*-catalyst and the [*l*-*nido*-7-Me-7,8-$B_9C_2H_{11}$]$^-$, from which it was derived, was thus established. Reaction of the unsubstituted compounds [*closo*-3,3-L_2-3-H-3,1,2-$RhC_2B_9H_{11}$] and [*closo*-2,2-L_2-2-H-2,1,7-$RhC_2B_9H_{11}$] (L = PPh_3) with more basic phosphines gave the corresponding L_2 compounds with L = PEt_3, PMe_2Ph, and for the 3,1,2-isomer, L_2 = $Ph_2PCH_2CH_2PPh_2$. Reaction of the unsubstituted 3,1,2-isomer (L = PPh_3) with HCl in $CHCl_3$ gave [*closo*-3,3-$(PPh_3)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$]. The analogous chloro compound in which L = PMe_2Ph was prepared by the reaction of the Rh–H species with CH_2Cl_2. Reaction of [*closo*-2,2-$(PPh_3)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$] with $HCl/CHCl_3$ produced the coordinatively unsaturated 16-electron species [*closo*-2-PPh_3-2-Cl-2,1,7-$RhC_2B_9H_{11}$]. This complex reacted with CO and other ligands to produce coordinatively saturated adducts. A crystallographic study of the 16-electron 2,1,7-chloride was carried out. This compound crystallizes in the monoclinic system $P2_1/n$, a = 13.840 (5) Å, b = 17.000 (7) Å, c = 13.771 (6) Å, and β = 118.98 (2)°, four molecules of complex and four molecules of benzene per unit cell. The structure was determined by conventional heavy-atom methods and refined to a final value of R = 0.039 (4173 reflections), R_w = 0.055. Although the electron deficiency seems to be metal centered, the molecule suffers little polyhedral distortion. The orientation of the Cl–Rh–PPh_3 plane is in strict agreement with the stereochemical predictions based upon the HOMO–LUMO treatment of Mingos. Reaction of [7-R-8-R′-7,8-$C_2B_9H_{10}$]$^-$ (R = R′ = Me; R = H, R′ = Ph; R = H, R′ = Me) with $(PPh_3)_3RhCl$, PPh_3, and aqueous HBF_4 produced the previously reported, but incorrectly formulated, species [*closo*-1-R-2-R′-3-PPh_3-8-PPh_3-3-Cl-3-H-3,1,2-$RhC_2B_9H_9$] in which one PPh_3 at Rh had formally interchanged with the terminal H at B(8) in a hypothetical [*closo*-1-R-2-R′-3,3-$(PPh_3)_2$-3-Cl-3,1,2-$RhC_2B_9H_9$] intermediate.

In 1974 we became intrigued by the possibility of discovering suitably constituted metallacarboranes that would activate small molecules and serve as homogeneous catalysts. The well-known structural diversity of metallacarboranes coupled with their normally high kinetic stabilities suggested that catalysts based upon this relatively new chemistry might find utility. Shortly after embarking upon this endeavor we developed a general synthesis route to metallacarboranes having dissociable phosphine ligands, namely the reaction of low-valent, coordinatively unsaturated transition-metal phosphine complexes with *nido*- or *arachno*-carboranes containing acidic hydrogen atoms.[3,4] We had previously reported[4] the synthesis of two catalytically active isomers of the complex [*closo*-$(PPh_3)_2Rh(H)C_2B_9H_{11}$] (Ia and IIa) by this means utilizing the reaction of $[(PPh_3)_3RhCl]$ with [*nido*-7,8-$C_2B_9H_{12}$]$^-$ or [*nido*-7,9-$C_2B_9H_{12}$]$^-$, respectively. These complexes may be formally considered to arise by oxidative addition of the B–H–B bridge system of the respective [*nido*-$C_2B_9H_{12}$]$^-$ anions to an unsaturated Rh(I) atom accompanied by η^5 bonding of the resulting Rh(III) moiety to the open carborane cage face. The structure of the 3,1,2-isomer, [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9B_{11}$] (Ia), is shown in Figure 1.[5] Complex Ia has been shown to be an active catalyst precursor for the homogeneous hydrogenation and isomerization of alkenes,[4,6a] the hydrosilylation

(1) For part 1, see: Jung, C. W.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1980**, *102*, 3024.

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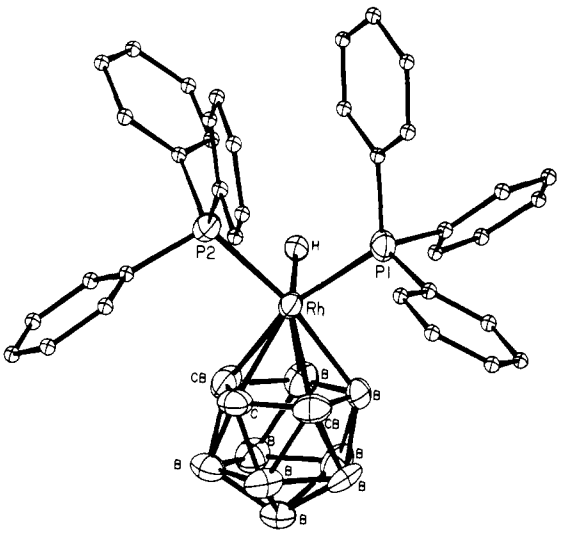
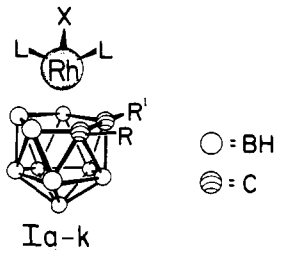


Figure 1. Molecular structure of [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$]. Thermal ellipsoids, except for phenyl carbon atoms, are shown at the 50% probability level. Hydrogen atoms, with the exception of the terminal hydride, have been omitted for clarity.

of ketones,[4] the hydrogenolysis of alkenyl acetates,[6b] and the exchange of terminal B–H bonds with deuterium gas.[6c,d] The ease of preparation, the versatility, and the stability of this formally 18-electron Rh(III) complex make it an extremely attractive homogeneous catalyst precursor and thus prompted us to explore the reactivity of the various isomers of Ia and their derivatives. An analogous complex, [*closo*-$(PPh_3)_2Rh(H)(SB_{10}H_{10})$], has also been described.[6e] We have reported[7a,b] the preparation and catalytic activity of a polymer-bound analogue of Ia, [*closo*-3,3-$(PPh_3)_2$-3-H-4-(polystyrylmethyl)-3,1,2-$RhC_2B_9H_{10}$], which can be recovered from catalytic hdyrogenation experiments by filtration. A similar polymer-bound catalyst was subsequently prepared by Rudolph et al.[8] In conjunction with our catalytic studies, we have examined the reactivity of the metal hydride present in Ia with strong acids. Reaction of Ia with H_2SO_4 or HNO_3 affords the versatile metallacarborane reagents [*closo*-$(PPh_3)_2(HSO_4)RhC_2B_9H_{11}$][9] and [*closo*-$(PPh_3)(NO_3)$-$RhC_2B_9H_{11}$],[10] respectively.

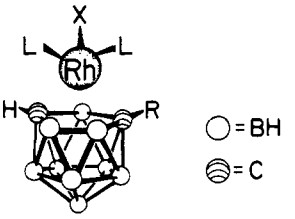
In order to further explore this unique chemistry, we have prepared a variety of complexes analogous to Ia using C-substituted carborane cages, various phosphine ligands, and the 2,9-isomer of [*nido*-$C_2B_9H_{12}$]$^-$ to generate the previously unreported 2,1,12-isomer of Ia, namely III. In the case of a mono-C-substituted or asymmetrically C,C′-disubstituted 1,2-$CRC'R'B_{10}H_{10}$ carborane, base degradation removes one of two chemically equivalent boron atoms[11] to generate a racemic mixture of chiral [*nido*-7,8-$CRC'R'B_9H_{10}$]$^-$ anions which can be resolved by the use of optically active cations.[12] It has thus proved possible to synthesize and study the optically active rhodacarborane catalyst precursor [*d-closo*-$(PPh_3)_2Rh(H)CMeC'HB_9H_9$] derived from optically pure (*l-nido*-7-Me-7,8-$C_2B_9H_{11}$]$^-$. Although preliminary results of the attempted asymmetry hydrogenation of prochiral



Ia-k

o) X=H, L=PPh_3, R=R'=H
b) X=H, L=PPh_3, R=R'=D
c) X=D, L=PPh_3, R=R'=H
d) X=H, L=PPh_3, R=H, R'=Ph
e) X=H, L=PPh_3, R=H, R'=Me
f) X=H, L=PPh_3, R=H, R'=Bu^n
g) X=H, L=PEt_3, R=R'=H
h) X=H, L=PMe_2Ph, R=R'=H
i) X=H, L_2=$(PPh_2CH_2)_2$, R=R'=H
j) X=Cl, L=PPh_3, R=R'=H
k) X=Cl, L=PMe_2Ph, R=R'=H

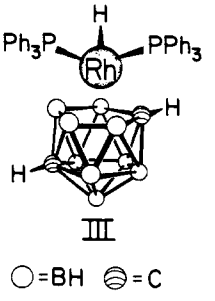
Figure 2. Schematic representation of closo complexes derived from *nido*-7,8-$C_2B_9H_{12}^-$.



IIa-e

a) X=H, L=PPh_3, R=R'=H
b) X=H, L=PPh_3, R=H, R'=Ph
c) X=H, L=PPh_3, R=H, R'=Me
d) X=H, L=PEt_3, R=R'=H
e) X=H, L=PMe_2Ph, R=R'=H

Figure 3. Schematic representation of closo complexes derived from *nido*-7,9-$C_2B_9H_{12}^-$.



III

○ = BH ⊛ = C

Figure 4. Schematic drawing of III derived from *nido*-2,9-$C_2B_9H_{12}^-$.

alkenes with this catalyst precursor gave alkane products in relatively low optical yields, these studies resulted in the isolation of several chelated alkyl rhodacarborane complexes, one of which has been characterized by an X-ray diffraction study described here.

We have recently reported[13] dynamic multinuclear FTNMR studies of hindered rotation of the metal vertex present in icosahedral metallacarboranes with respect to the pentagonal bonding face of the carborane ligand. In addition, we have discussed[14] the facile carborane cage exchange reaction which has provided a means of transferring the [$(PPh_3)_2Rh$] fragment from one carborane cage to another in a single, clean reaction. Both of these studies involved complexes described in this contribution. We have also shown that subtle modifications of these compounds can result in drastic changes in their gross structures and reactivities.[15,16]

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We now wish to report a detailed study of the synthesis of a series of icosahedral *closo*-bis(phosphine)hydridorhodacarboranes and to discuss their varied reactivity with esters of alkyl- and arylacrylic acids and chlorinating agents. The synthesis and reactivity of the iridium analogues of several of the complexes described will be reported in a subsequent paper.[17]

Results and Discussion

Synthesis of Icosahedral Hydridobis(phosphine)rhodacarboranes. Complexes Ia–f, IIa–c, and III [see Figures 2–4] were prepared by heating the corresponding [*nido*-$CRC'R'B_9H_{10}$]$^-$ anions with $[(PPh_3)_3RhCl]$ in absolute ethanol at the reflux temperature. The yellow to orange [*closo*-$(PPh_3)_2Rh(H)CRC'R'B_9H_9$] products precipitated from these reactions after several hours. These compounds were stable to air in the solid state but decomposed to a significant extent in solutions exposed to the atmosphere. Several of these compounds were prepared by stirring the two reactants in anhydrous methanol at room temperature for ca. 24 h. This procedure minimized the formation of undesired side products (e.g., $[(PPh_3)_2RhCl]_2$ and *trans*-$[(PPh_3)_2Rh(CO)Cl]$) which were obtained from prolonged heating of $[(PPh_3)_3RhCl]$ in ethanol. We have also prepared optically active Ie, henceforth referred to as Ie*, from the corresponding enantiomerically pure carborane anion [*l*-*nido*-7-CH_3-7,8-$C_2B_9H_{11}$]$^-$ (vide infra).[18]

The carbon-deuterated analogue of Ia, namely Ib, has proven useful as a means of monitoring cage exchange reactions.[14] The carbon-deuterated carborane anion was reacted with $[(PPh_3)_3RhCl]$ in ethanol at the reflux temperature to give Ib, which had no detectable carborane C–H resonance in the ^1H NMR spectrum. No loss of carborane C–D was observed after heating in ethanol for 1 week. We have also synthesized[19] the Rh–D analogue of Ia, namely Ic, by briefly heating the bridge-deuterated carborane anion[20] with $[(PPh_3)_3RhCl]$ in ethanol at the reflux temperature. Thus, the source of the rhodium hydride ligand of Ia and related species is indeed the bridging B–H–B of the incoming carborane monoanion.

Complexes Ig and Ih, [*closo*-3,3-(L_2)-3-H-3,1,2-$RhC_2B_9H_{11}$] (L = PEt_3 and PMe_2Ph, respectively), can be prepared by the reaction of the corresponding $\{L_3Rh^+BF_4^-\}$ salt[21] and [*nido*-7,8-$C_2B_9H_{12}$]$^-$ in methanol. A more convenient route, which has also been used to prepare the isomeric complexes [*closo*-2,2-(L_2)-2-H-2,1,7-$RhC_2B_9H_{11}$] (L = PEt_3, PMe_2Ph) (IId and IIe, respectively), as well as the chelated complex [*closo*-3,3-$(PPh_2CH_2CH_2PPh_2)$-3-H-3,1,2-$RhC_2B_9H_{11}$] (Ii), involved the reaction of the corresponding triphenylphosphine complexes with an excess of the appropriate phosphine in tetrahydrofuran (THF). The 3,1,2-complexes (Id, Ie, Ih, and Ii) were very sensitive to air in solution, darkening rapidly. NMR studies (^1H, $^{31}P\{^1H\}$, and ^{11}B)[22] suggest that complexes Id–h decompose to dimeric phosphinerhodacarboranes similar in nature to the purple complex prepared from Ia and characterized by NMR and X-ray crystallography.[23] Complex [*closo*-1-*n*-Bu-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (If), when heated to reflux in THF for 3 days in the presence of excess PPh_3, appeared to undergo a polytopal rearrangement. NMR spectroscopy (^1H, $^{31}P\{^1H\}$, and ^{11}B) suggested

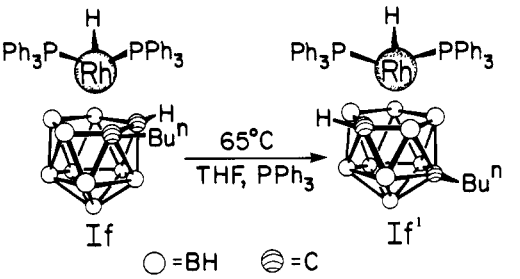

Figure 5. Polytopal rearrangement proposed for thermal conversion of If to If'.

the structure of the rearranged complex If' to be analogous to that of [*closo*-1-Me-2,2-$(PEt_3)_2$-2-H-8-Ph-2,1,8-$RhC_2B_9H_9$] whose structure has been determined by X-ray crystallography.[16] Complex If' would then be formulated as [*closo*-8-*n*-Bu-2,2-$(PPh_3)_2$-2-H-2,1,8-$RhC_2B_9H_{11}$] as shown in Figure 5.

Preparation of Optically Active [*d*-*closo*-1-Me-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{10}$] (Ie*) and Chelated Alkyl Complexes. Resolution of racemic [*nido*-7-Me-7,8-$C_2B_9H_{11}$]$^-$ was achieved by use of the *l*-*N*,*N*,*N*-trimethyl(α-phenylethyl)ammonium cation as the resolving agent in ethanol solvent. After 18 recrystallizations, optically pure [*l*-$Me_3NCH(Me)(Ph)$]$^+$(*l*-*nido*-7-Me-7,8-$C_2B_9H_{11}$]$^-$ was obtained ($[\alpha]^{25}_{579}$ −16.8°). The trimethylammonium salt was then prepared by ion exchange chromatography ($[\alpha]^{25}_{579}$ −5.9°). Reaction of this salt with $[(PPh_3)_3RhCl]$ in ethanol at room temperature produced optically active [*d*-*closo*-$(PPh_3)_2$Rh-$(H)(C_2B_9H_{10}Me)$] (Ie*) after recrystallization from THF/ethanol ($[\alpha]^{25}_{579}$ +5.3°).

In order to explore the potential of Ie* as a catalyst precursor for the asymmetric hydrogenation of prochiral alkenes, ethyl α-phenylacrylate was selected for study. Ethyl α-phenylacrylate appeared to be a favorable choice because (a) isomerization could not compete with hydrogenation and (b) Ia was an effective catalyst for the hydrogenation of acrylate esters.[6a] When a THF solution of Ie* containing ethyl α-phenylacrylate (6.45 mM in catalyst, 0.10 M in alkene) was stirred at 25 °C under 1 atm of H_2, no H_2 uptake was observed over 21 h. The experiment was repeated in an autoclave under 100 atm of H_2 at 25 °C. Although this resulted in complete reduction of the alkene to ethyl α-phenylpropionate, the measured optical rotation indicated an enantiomeric excess of only 3% ($[\alpha]^{25}_D$ +1.9° (lit.[24] 59.6 °)). It was not possible to recover the catalyst precursor since it had been converted to a blue rhodacarborane species (vide infra). Although Ie did not catalyze the reduction of ethyl α-phenylacrylate under ambient conditions, it was found to be an active catalyst for the hydrogenation of *n*-butyl acrylate (25 °C, 1 atm H_2) with an initial rate of ca. 5.8×10^{-2} mol H_2 mol^{-1} Rh s^{-1}. This result suggests that once the acrylate is coordinated to the rhodium, the sterically demanding α-phenyl group of the prochiral substrate, compared with the H atom of the unsubstituted acrylate, renders H_2 coordination unfavorable, and thus no hydrogenation is observed under mild conditions. However, it was noticed that upon injection of ethyl α-phenylacrylate into the orange solution of the catalyst precursor the color rapidly turned a deeper red-orange. The addition of ethanol formed red-orange crystals of IVa which were isolated. The same behavior was also observed in the absence of H_2. Complexes IVb and IVc were similarly prepared by reaction of Ie with *n*-butyl acrylate and methyl methacrylate, respectively. Furthermore, when [*exo*-*nido*-$(PPh_3)_2Rh(C_2B_9H_{10}Me_2)$][15] was reacted with methyl methacrylate in THF at room temperature, a red-orange product (IVd) was isolated which appeared to be analogous to IVa–c on the basis of analytical and spectroscopic data.

Elemental analyses of compounds IVa–c were consistent with products formed by the insertion of the acrylate or substituted acrylate ester C=C into the Rh–H bond of Ie accompanied by loss of a PPh_3 molecule. The product (IVd) derived from [*exo*-

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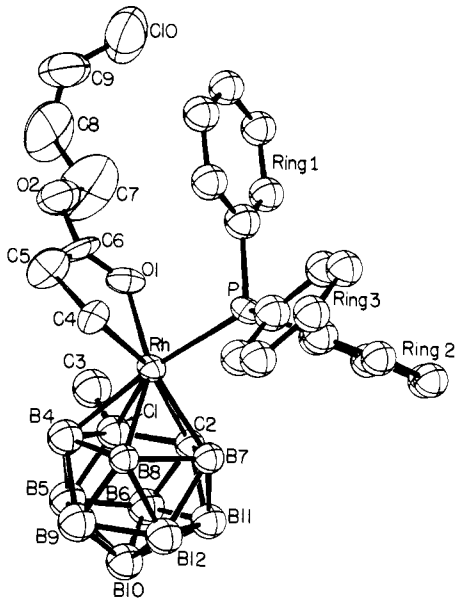

Figure 6. Molecular structure of [*closo*-1-Me-3,3-($CH_2CH_2C(O)OBu$-3-PPh_3-3,1,2-$RhC_2B_9H_{10}$] (IVb). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

nido-$(PPh_3)_2Rh(C_2B_9H_{10}Me_2)$][15] was formulated in an identical manner. Furthermore, IR spectra contained no evidence for the presence of Rh–H or B–H–B (bridge) bonds, but each compound exhibited an intense band in the region of 1615 cm^{-1}, attributed to $\nu_{C=O}$, fully 100 cm^{-1} lower in frequency than the carbonyl stretching frequency in the free acrylate ester. This result suggested that the ester carbonyl oxygen atom present in the substituted alkyl group attached to rhodium was chelated to rhodium, as well. This coordination of the ester carbonyl moiety to rhodium with weakening of the C=O bond should lower the stretching frequency of the ester carbonyl group with respect to free ester, as observed. A similar shift in $\nu_{C=O}$ has been reported[25] for a series of chelated alkenyl carboxylic esters derived from the reaction of $[H_2Ru(PPh_3)_4]$ with a variety of acrylate esters (RuCH=CHCOOR). The formation of a closo σ-bonded alkyl complex from [*exo-nido*-$(PPh_3)_2Rh(C_2B_9H_{10}Me_2)$] is explained[15] by a facile *exo–nido–closo* equilibrium that has been demonstrated to exist in solution.

In order to confirm the structural hypothesis presented above, an X-ray diffraction study of IVb was undertaken. The molecular structure is shown in Figure 6, and selected distances and angles are given in Table I. As predicted, the organic ligand is coordinated to the rhodium atom both through the oxygen atom of the ester carbonyl group and through an alkyl linkage. This results in distorted octahedral geometry about the 18-electron Rh(III) atom in which the cage is assumed to occupy three coordination sites. The C(4)–C(5) and C(5)–C(6) distances within the puckered 5-membered metallacycle are both 1.54 Å, typical of C–C single bonds. The Rh–C distance (2.10 (1) Å) is very similar to other Rh(III)–C bond lengths; for example, in $[Rh_2I_2(SMe_2)_3Me_4]$ and in $[RhCl_2(C_5H_5N)_2\{P(o\text{-}C_6H_4Me)_2(o\text{-}C_6H_4CH_2)\}]$ these distances are 2.08[26] and 2.083 (16) Å,[27] respectively. Rhodium–oxygen bond lengths vary widely, and the distance found here (2.185 (8) Å) is only slightly longer than Rh–O distances in various Rh(III) complexes, for example 2.098 (4) Å in $[RhCl(PhCONCS)_2(PPh_3)_2{\cdot}Et_2O]$[28] and in two recently characterized Rh(I) chelated cinnamate complexes (2.113 (5) and 2.185 (5) Å).[29,30] The C(6)–O(1) distance of 1.24 (2) Å is not significantly shorter than C–O distances (1.254 (12) and 1.248 (8) Å)[25,29] in analogous chelated complexes.

Table I. Selected Distances (Å) and Angles (deg) in [*closo*-1-CH_3-3,3-($CH_2CH_2C(O)OC_4H_9$)-3-PPh_3-3,1,2-$RhC_2B_9H_{10}$] (IVb)

A. Distances			
Rh–C(1)	2.24 (1)	Rh–O(1)	2.185 (8)
Rh–C(2)	2.27 (1)	Rh–C(4)	2.10 (1)
Rh–B(4)	2.25 (2)	Rh–P	2.323 (3)
Rh–B(7)	2.17 (2)	P-phenyl 1	1.81
Rh–B(8)	2.22 (2)	P-phenyl 2	1.80
		P-phenyl 3	1.82
C(4)–C(5)	1.53 (2)	O(2)–C(7)	1.54 (2)
C(5)–C(6)	1.51 (2)	C(7)–C(8)	1.50 (3)
C(6)–O(1)	1.24 (2)	C(8)–C(9)	1.32 (4)
C(6)–O(2)	1.32 (2)	C(9)–C(10)	1.57 (4)
C(1)–C(2)	1.63 (2)	B(5)–B(10)	1.80 (2)
C(1)–C(3)	1.57 (2)	B(6)–B(10)	1.78 (2)
C(1)–B(4)	1.69 (2)	B(6)–B(11)	1.81 (3)
C(1)–B(5)	1.70 (2)	B(7)–B(8)	1.89 (2)
C(1)–B(6)	1.79 (2)	B(7)–B(11)	1.81 (3)
C(2)–B(6)	1.71 (2)	B(7)–B(12)	1.85 (2)
C(2)–B(7)	1.76 (2)	B(8)–B(9)	1.74 (3)
C(2)–B(11)	1.69 (2)	B(8)–B(12)	1.83 (2)
B(4)–B(5)	1.76 (3)	B(9)–B(10)	1.75 (2)
B(4)–B(8)	1.79 (2)	B(9)–B(12)	1.75 (2)
B(4)–B(9)	1.81 (2)	B(10)–B(11)	1.90 (2)
B(5)–B(6)	1.85 (2)	B(10)–B(12)	1.79 (2)
		B(11)–B(12)	1.78 (2)
B. Angles			
Cn[a]–Rh–P	124	P–Rh–O(1)	85.4 (3)
Cn[a]–Rh–O(1)	124	P–Rh–C(4)	88.6 (4)
Cn[a]–Rh–C(4)	118	O(1)–Rh–C(4)	79.1 (4)
Rh–C(1)–C(3)	106.7 (7)	B(5)–C(1)–C(3)	117 (1)
C(2)–C(1)–C(3)	116 (1)	B(6)–C(1)–C(3)	112 (1)
B(4)–C(1)–C(3)	122 (1)		
Rh–C(4)–C(5)	109.5 (8)	C(6)–O(1)–Rh	113 (1)
C(4)–C(5)–C(6)	109 (1)	C(6)–O(2)–C(7)	116 (2)
C(5)–C(6)–O(1)	122 (1)	O(2)–C(7)–C(8)	105 (2)
O(2)–C(6)–O(1)	120 (2)	C(7)–C(8)–C(9)	119 (3)
C(5)–C(6)–O(2)	118 (2)	C(8)–C(9)–C(10)	123 (4)
Rh–P-phenyl 1	115	phenyl 1–P-phenyl 2	101
Rh–P-phenyl 2	118	phenyl 1–P-phenyl 3	105
Rh–P-phenyl 3	112	phenyl 2–P-phenyl 3	105

[a] Cn = centroid of the C_2B_3 face of the $C_2B_9H_{10}$ ligand. Estimated standard deviations in the least significant figure are given in parentheses. No estimated standard deviations are given for distances and angles involving members of rigid groups.

In addition to the mode of bonding seen in complex IVb the X-ray diffraction study of this complex establishes the absolute configuration of [*l-nido*-7-Me-7,8-$C_2B_9H_{11}$]$^-$ as well as the *d*-Ie* and IVb species derived from it. The fact that IVb contains a chiral carborane cage and a chiral rhodium center provides the possibility of obtaining IVb from *d*-Ie* in two diastereomerically related configurations. That IVb was apparently present as a pure diastereomer proves that the configuration of the rhodium center in crystalline IVb is rigorously controlled by the steric requirements of the carborane ligand. It is interesting to note that in none of the complexes IVa–d are diastereomers observed by variable-temperature ^1H or $^{31}P\{^1H\}$ NMR spectroscopy (vide infra). Thus, either the two sets of resonances are very close together in all cases or the barrier to interconversion of the diastereomers is quite low or both. It seems likely that interconversion might easily occur at the rhodium center by either dissociation of PPh_3 or cleavage of the rhodium–oxygen bond. However, the free energy difference between the two possible diastereomeric species may truly be large and subject to the stereochemical control fo the carborane ligand.

Although the complexes IVa–d are stable indefinitely in air in the solid state, they rapidly decompose under argon in solution at room temperature, presumably due to dissociation of the organic ligand via β-elimination to form Rh–H in the absence of PPh_3.

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(27) Mason, R.; Towl, D. C. *J. Chem. Soc. A* **1970**, 1601.
(28) Cowie, M.; Ibers, J. A. *Inorg. Chem.* **1973**, *15*, 552.
(29) Chan, A. S. C.; Pluth, J. J.; Halpern, J. *Inorg. Chim. Acta* **1979**, *37*, L477.
(30) Chan, A. S. C.; Pluth, J. J.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 5952.

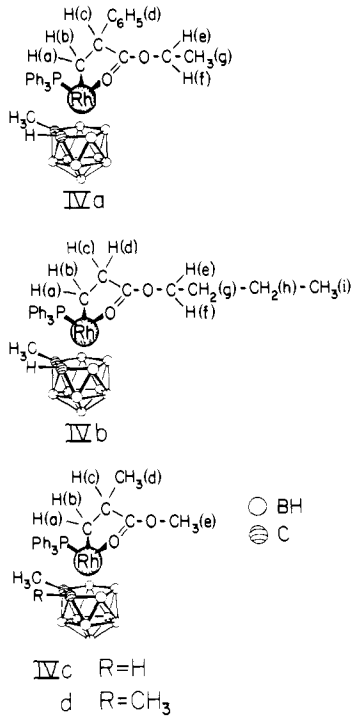

Figure 7. Schematic representation of chelate complexes IVa–d and labeling of protons for ^1H NMR assignment.

Recrystallization of the chelates could only be carried out in the presence of a large excess of acrylate ester in order to avoid total decomposition of these complexes.

The ^1H NMR spectra of the chelates (see Figure 7 and Experimental Section) were complex, but were assigned by means of a series of homonuclear and phosphorus decoupling experiments carried out at −33 °C to avoid decomposition. Spectra acquired rapidly at room temperature had shown there to be no observable dependence on temperature. In addition, the spectra indicated that the structure of the complexes in solution must be very similar to that found for IVb in the solid state.

In all four complexes the resonance due to H_a appears as a triplet ($^2J_{H_a\text{-}H_b} = {}^3J_{H_a\text{-}H_c}$) whereas H_b appears as a multiplet. The additional splitting is due to coupling to phosphorus, although the magnitude of the coupling could not be determined due to the complex nature of the resonances observed. H_b resonates ca. 2 ppm upfield from H_a, in keeping with observed chemical shift differences between methylenic protons in a variety of cyclic complexes.[31] Coupling of either H_a or H_b to Rh was not resolved and must presumably be less than 2 Hz. H_c also appears as a multiplet in complexes IVb–d, coupled to H_a, H_b, and H_d. In complex IVa the resonance is significantly shifted to low field due to the neighboring Ph group. The resonance of the Me protons of the ester group in IVc and IVd is a sharp singlet as expected, but in IVa and IVb the methylene protons are magnetically nonequivalent since no symmetry element exists between them. In IVa each proton gives rise to two overlapping quartets and in IVb two sets of overlapping triplets result ($^2J_{H_e\text{-}H_f} = 11$, $^3J_{H_e\text{-}H_g} = 6$ Hz in both cases).

An interesting feature of the spectra is the fact that in IVa–c the carborane C–Me protons appear as a doublet which collapses to a singlet upon phosphorus decoupling ($^4J_{P\text{-}H} = 2$ Hz). Examination of the structure of IVb indicates that C(1)–Me group to be approximately trans to the P atom bonded to Rh whereas the C(2) atom is cis to the P atom. In the case of IVd only one of the carborane C–Me groups shows coupling of its protons to phosphorus, which suggests that P–H coupling is only observed when the Me group is bonded to the trans C-atom, in agreement

(31) Booth, H. In "Progress in Nuclear Magnetic Resonance Spectroscopy"; Emsley, J. W., Feeney, J.; Sutcliffe, L. H., Eds., Pergamon Press: Oxford, 1969; Vol. 5, Chapter 3.

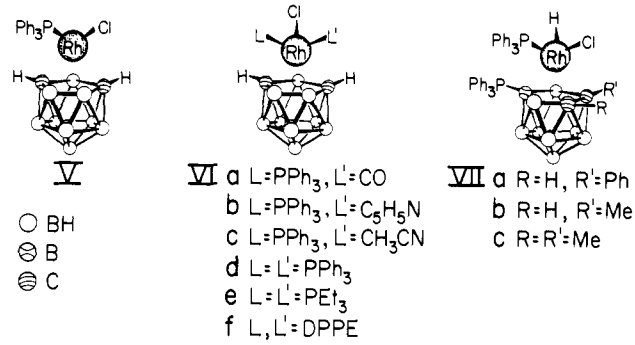

Figure 8. Schematic representation of structures of chloro complexes V, VIa–f, and VIIa–c.

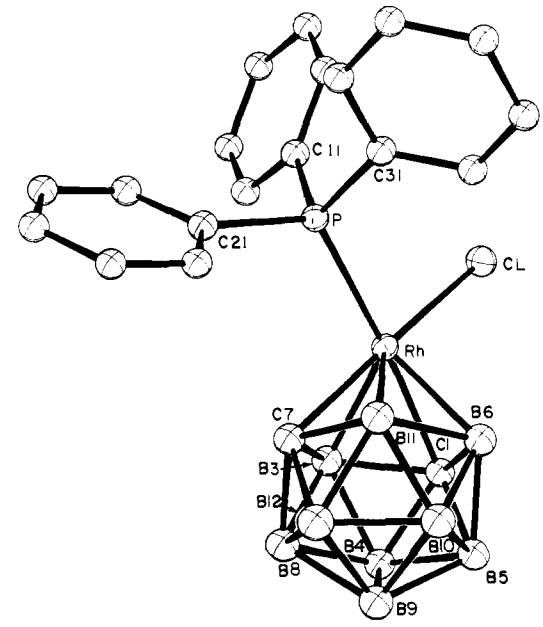

Figure 9. Molecular structure of [*closo*-2-Cl-2,1,7-$RhC_2B_9H_{11}$]·C_6H_6 (V). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

with the well-documented observation that trans coupling to phosphorus is significantly greater than cis coupling.[32] The $^{31}P\{^1H\}$ NMR spectra of the complexes exhibited one doublet ($J_{Rh\text{-}P}$ = 139 Hz) in all cases and were temperature independent. The ^{11}B NMR spectra were generally broad and uninformative.

Synthesis and Reactions of Rh–Cl Derivatives: Structure of [*closo*-2-PPh_3-2-Cl-2,1,7-$RhC_2B_9H_{11}$·C_6H_6] (V). Attempted recrystallization of the PMe_2Ph complex Ih from dichloromethane gave the chloro complex [*closo*-3,3-$(PMe_2Ph)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$] (Ik) in quantitative yield. We have been able to prepare the previously reported[33] PPh_3 analogue [*closo*-3,3-$(PPh_3)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$] (Ij) in 73% yield by heating Ia in $CHCl_3$/aqueous HCl. An attempt to prepare the isomeric [*closo*-2,2-$(PPh_3)_2$-2-Cl-2,1,7-$RhC_2B_9H_{11}$] complex by a similar procedure yielded instead the 16-electron *closo*-mono(triphenylphosphine) chloro complex (V) (see Figure 8). Skeletal electron counting formalisms[34] suggest that V contains 12 electron pairs for skeletal bonding and should exhibit a hyper-closo[35] geometry. Recent modifications of these rules by Nishimura[36] suggest that the effective atomic number of the metal center must

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(33) Siedle, A. R. *J. Organomet. Chem.* **1975**, *90*, 279.
(34) (a) Mingos, D. M. P. *Nature (London), Phys. Sci.* **1972**, *236*, 99. (b) Wade, K. *Prog. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (c) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446.
(35) Jung, C. W.; Baker, R. T.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1980**, *102*, 5782.
(36) Nishimura, E. K. *J. Chem. Soc., Chem. Commun.* **1978**, 858; private communication.

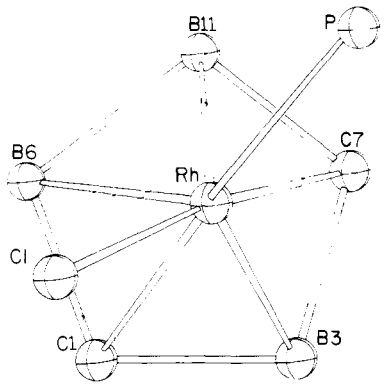


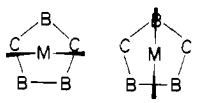
Figure 10. View of the RhPCl moiety and the C_2B_3 face coordinated to rhodium in V.

be considered in order to determine the geometry of the polyhedron. This approach suggested that V with formally 16-electron Rh(III) might possess 13 skeletal electron pairs available for cage bonding and thus exhibit closo geometry. In order to resolve the question of polyhedral geometry an X-ray diffraction study of V was undertaken.

Selected interatomic distances and angles in V are listed in Table II.

The structure of V, shown in Figure 9 together with the numbering system employed, unambiguously shows no distortion of the 12-vertex polyhedron. A different perspective illustrated in Figure 10 shows negligible movement of the metal center from the center of the bonding face of the cage.

The rotational conformation assumed by the P–Rh–Cl plane with respect to the bonding face of the carborane cage is the same as that predicted by Mingos[37] for an isoelectronic osmium complex (vide infra). For the hypothetical model compound [*closo*-2,2-$(PH_3)_2$-2,1,7-$PtC_2B_9H_{11}$], the HOMO–LUMO interaction between the hybrid (xz)–$5e_1(x)$ orbitals favors conformer B and



A B

the filled antibonding $5e_1(y)$–(yz)* orbital in B is lower in energy than the corresponding $5e_1(x)$–(yz)* orbital present in conformer A. It was also suggested that "compounds such as [*closo*-2,2-$(PR_3)_2$-2,1,7-$OsC_2B_9H_{11}$] may prove to be thermodynamically more stable than the corresponding platinum compounds"[37] because the loss of two electrons eliminates the antibonding interaction described above. It was inferred that the loss of two electrons should give rise to conformer A based on an examination of the HOMO–LUMO interaction diagram. Indeed, complex V, which is isoelectronic with [*closo*-$(PR_3)_2OsC_2B_9H_{11}$], exists as conformer A in the solid state. Consequently, it can be concluded that the electron deficiency of V is metal centered and that the molecule suffers little polyhedral distortion. This contrasts with the recently published X-ray crystallographic study of [*hypercloso*-2,3-$(CH_3)_2$-6-$(CH_2{=}CHCH_2C_6H_4PH_2P)$-6,2,3-$RuC_2B_7H_7$][35] in which the electronic unsaturation is delocalized over the polyhedral framework, resulting in a distorted triangulated closed polyhedral structure. At this point, the factors that determine whether electronic unsaturation will remain metal centered or be delocalized over the polyhedral framework are not clearly understood.

Compound V showed a wide range of reactivity with typical two-electron donors, demonstrating the unsaturation at the rhodium vertex (see Figure 8; $^{31}P\{^1H\}$ NMR data are presented in Table III). When a $CDCl_3$ solution of V was treated with CO, an immediate color change from dark red to light yellow occurred, giving the CO adduct VIa. The CO ligand could be easily removed by flushing the yellow solution with argon, thus regenerating V.

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Table II. Selected Distances (Å) and Angles (deg) in [*closo*-2-PPh_3-2-Cl-2,1,7-$RhC_2B_9H_{11}$] (V)

	1. Distances[a]		
Rh-P	2.329 (1)	Rh-C(1)	2.215 (4)
Rh-Cl	2.299 (1)	Rh-B(3)	2.106 (5)
P-C(11)	1.815[b]	Rh-B(6)	2.151 (5)
P-C(21)	1.844[b]	Rh-C(7)	2.165 (4)
P-C(31)	1.809[b]	B(4)-B(11)	2.139 (5)
C(1)-B(3)	1.731 (6)	B(4)-B(9)	1.778 (7)
C(1)-B(6)	1.675 (6)	B(4)-B(8)	1.765 (6)
C(1)-B(5)	1.679 (6)	C(7)-B(11)	1.686 (6)
C(1)-B(4)	1.692 (6)	C(7)-B(8)	1.708 (6)
B(3)-B(6)	1.785 (7)	C(7)-B(12)	1.699 (6)
B(3)-C(7)	1.740 (7)	B(11)-B(10)	1.785 (6)
B(3)-B(8)	1.789 (7)	B(11)-B(12)	1.795 (5)
B(6)-B(5)	1.803 (7)	B(10)-B(9)	1.798 (7)
B(6)-B(11)	1.887 (7)	B(10)-B(12)	1.784 (5)
B(6)-B(10)	1.777 (7)	B(9)-B(8)	1.774 (7)
B(5)-B(4)	1.759 (6)	B(9)-B(12)	1.758 (6)
B(5)-B(10)	1.776 (7)	B(8)-B(12)	1.759 (5)
B(5)-B(9)	1.749 (7)	C(7)-H(7)	0.92 (4)
C(1)-H(1)	0.98 (4)	B(11)-H(11)	1.17 (4)
B(3)-H(3)	1.13 (4)	B(10)-H(10)	1.10 (4)
B(6)-H(6)	1.14 (4)	B(9)-H(9)	1.09 (4)
B(5)-H(5)	1.07 (4)	B(8)-H(8)	1.13 (4)
B(4)-H(4)	1.13 (4)	B(12)-H(12)	1.10 (4)
	2. Angles[a]		
P-Rh-Cl	88.01 (3)	H(11)-B(11)-Rh	111 (2)
P-Rh-C(1)	175.2 (1)	H(11)-B(11)-C(7)	129 (2)
P-Rh-C(7)	96.7 (1)	H(11)-B(11)-B(4)	121 (2)
P-Rh-B(3)	128.5 (1)		
P-Rh-B(6)	136.1 (1)	H(6)-B(6)-Rh	122.2 (3)
P-Rh-B(11)	96.3 (1)	H(6)-B(6)-B(11)	125.1 (4)
		H(6)-B(6)-C(1)	127.9 (4)
Cl-Rh-C(1)	96.4 (1)		
Cl-Rh-C(7)	172.4 (1)	H(1)-C(1)-Rh	109 (3)
Cl-Rh-B(3)	124.4 (1)	H(1)-C(1)-B(6)	116 (3)
Cl-Rh-B(6)	98.6 (1)	H(1)-C(1)-B(3)	123 (3)
Cl-Rh-B(11)	139.5 (1)		
C(7)-B(11)-B(6)	104.9 (3)	H(3)-B(3)-Rh	108 (2)
B(11)-B(6)-B(1)	105.9 (3)	H(3)-B(3)-C(1)	127 (2)
B(6)-C(1)-B(3)	110.7 (3)	H(3)-B(3)-C(7)	122 (2)
C(1)-B(3)-C(7)	106.3 (3)		
B(3)-C(7)-B(11)	110.8 (3)	H(7)-C(7)-Rh	113 (3)
		H(7)-C(7)-B(3)	116 (2)
		H(7)-C(7)-B(11)	126 (2)

[a] Estimated standard deviations in the least significant figure are given in parentheses. [b] Estimated standard deviations are not given for member of rigid groups. The normal to the plane defined by P-Rh-Cl makes an angle of 79.32° with the normal to the least-squares plane through the C_2B_3 belt (i.e., the bonding face) of the carborane cage.

Addition of nitrogen donor solvents such as pyridine or acetonitrile to $CDCl_3$ solutions of V gave orange solutions of compounds VIb and VIc, respectively. Addition of PPh_3 (2.2 equiv) to $CDCl_3$ solutions of V showed only a slight color change and gave broad resonances in $^{31}P\{^1H\}$ NMR experiments at 27 °C, suggesting a rapid exchange process. Cooling the sample to −23 °C gave sharp resonances corresponding to the saturated bis(triphenylphosphine) complex (VId). Smaller and more basic phosphines such as PEt_3 or $Ph_2PCH_2CH_2PPh_2$ (DPPE) displaced the PPh_3 ligand of V, yielding the saturated bis(phosphine) complexes VIe and VIf, respectively. Compound V did not react with unsaturated organic ligands such as ethylene, cycloocta-1,5-diene, or ethynylbenzene under ambient conditions in $^{31}P\{^1H\}$ NMR experiments. A series of $^{31}P\{^1H\}$ NMR competition experiments demonstrated the order of coordination of the ligands to be DPPE, $PEt_3 \gg C_5H_5N > CO > CH_3CN > PPh_3 \gg$ unsaturated organic ligands.

Formation of Rhodium Hydrido Chlorides Accompanied by Migration of Triphenylphosphine from Rh to B. When the *C*-phenyl complex (Id) was recrystallized slowly by layering heptane over a dichloromethane solution of the complex, traces of bright orange crystalline material (VIIa) were found mixed with the Id which crystallized as large red-brown blocks. This orange material was mechanically separated from Id and a series of spectra ob-

Table III. 81.02-MHz $^{31}P\{^1H\}$ NMR Spectral Data for the 12-Vertex *closo*-Phosphinerhodacarborane Complexes[a]

complex	P_1 (J_{Rh-P_1})	P_2 (J_{Rh-P_2})	P_1' ($J_{Rh-P_1'}$)	P_2' ($J_{Rh-P_2'}$)	$^2J_{P_1-P_2}$, Hz	$^2J_{P_1-P_2'}$, Hz	T, °C
Ia[b]	39.5 (125)						−83
Id[b]	37.5 (134)	24.1 (110)	40.5 (127)	48.5 (158)	20	15	−88
Ie[c,f]	40.0 (131)	37.4 (131)			18		+100
Ie[b]	40.3 (134)	28.5 (108)	41.2 (122)	48.6 (153)	22	br	−88
If[b]	38.5 (134)	26.1 (110)	39.2 (122)	46.0 (159)	22	17	−88
Ig[d]	30.6 (120)						+27
Ih[e]	8.7 (118)						+27
Ii[e]	65.4 (120)						+27
Ij[e]	25.6 (129)						+27
Ik[d]	26.7 (129)						+27
IIa[b,f]	41.7 (125)						+27
IIa[b]	49.7 (139)	33.2 (112)			21		−83
IIb[b]	26.7 (112)	39.0 (147)	33.3 (127)	47.1 (157)	15	10	−88
IIc[e]	26.6 (116)	43.7 (143)	30.5 (122)	47.5 (145)	13	12	−83
IId[e,f]	30.5 (125)						+27
IId[e]	41.4 (129)	22.7 (115)			22		−103
IIe[e,f]	10.9 (127)						−23
IIe[e]	19.0 (134)	7.2 (110)			24		−103
III[b]	34.8 (112)						−83
IVa[b]	37.4 (139)						−33
IVb[b]	37.3 (139)						−33
IVc[b]	37.4 (139)						−33
IVd[e]	33.0 (139)						−33
V[d]	29.0 (142)						+27
VIa[d]	45.6 (103)						+27
VIb[d]	32.5 (125)						+27
VIc[d]	32.0 (120)						+27
VId[d]	26.5 (122)						+27
VIe[d]	26.7 (120)						+27
VIf[d]	70.6 (120)						+27
VIIa[b]	44.4 (134)	6.5 (br)			5[g]		+27
VIIb[d]	43.2 (130)	5.4 (br)			5[g]		+27
VIIc[d]	44.2 (131)	6.6 (br)			5[g]		+27

[a] P_1/P_1' is arbitrarily defined as the phosphine ligand pair with the smaller chemical shift difference. Coupling constants are in Hz. br = broad. [b] Spectra recorded in 20% CD_2Cl_2/CH_2Cl_2. [c] Spectrum recorded in 20% $C_6D_5CD_3/C_6H_5CH_3$. [d] Spectrum recorded in $CDCl_3$. [e] Spectrum recorded in 10% C_6D_6/tetrahydrofuran. [f] High-temperature limiting spectrum. [g] $^3J_{P_1-P_2}$.

tained which showed it to be a hydridophosphinerhodacarborane complex distinct from Id. This complex was also observed in sealed NMR samples of Id in CD_2Cl_2 after a period of several months. The spectra of the orange complex were identical with those of a complex described[38] as "3-PPh_3-3'-(Ph_2P-1-C_6H_4-)-3-H-3,1,2-$RhC_2B_9H_{10}$". It had been suggested[38] that one of the phosphine ligands was bound to the carborane cage through the carborane *C*-phenyl substituent. Complexes with similar modes of bonding had been proposed[38] for the *C*,*C*'-dimethyl and *C*-methyl, *C*'-ethyl derivatives that had been prepared[38] by heating a mixture of [$(PPh_3)_3RhCl$], PPh_3, aqueous HBF_4, and the appropriate carborane anion in ethanol. We have repeated this synthesis using the *nido*-7-phenyl-, -7-methyl-, and -7,8-dimethyl-7,8-carborane anions and have isolated the orange complexes VIIa–c. Complex VIIa isolated from this reaction proved to be identical with the orange complex observed when Id was allowed to stand in dichloromethane. Complexes VIIb and VIIc gave spectra similar to that of VIIa and also to those previously described.[38] The ^{11}B NMR spectra were broad with the exception of one doublet that remained unchanged upon broad-band proton decoupling. This suggested the possibility of a phosphine ligand attached to a cage boron atom with J_{B-P} of approximately 145 Hz. The $^{31}P\{^1H\}$ NMR spectra confirmed this hypothesis showing a sharp doublet of doublets at ca. 42–44 ppm [J_{Rh-P} = 136 Hz, J_{P-P} = 5 Hz] and a broad quartet at approximately 6 ppm that had been previously overlooked. The latter resonance is indicative of phosphorus coupling to ^{11}B. The fact that one phosphine is attached directly to a boron atom is in keeping with the very small phosphorus–phosphorus coupling constant observed (only resolved for the rhodium-bound phosphorus; see Figure 11 for the $^{31}P\{^1H\}$ NMR spectrum of VIIa). The ^1H NMR spectra all exhibited a doublet of doublets of doublets in the metal hydride region. Single-frequency ^{31}P decoupling of the metal hydride resonance in complex VIIa allowed the coupling constants to be determined as follows: J_{Rh-H} = 15 Hz; J_{P_1-H} = 42 Hz; J_{P_2-H} = 6 Hz (where P_1 is Rh bound and P_2 is bound to boron). The ^1H and $^1H\{^{31}P\}$ spectra of VIIb are similar and are shown in Figure 12. It seemed likely that a chlorine atom was albo bonded to the rhodium, and this was confirmed in all three cases by elemental analysis of samples (recrystallized from benzene–ethanol) that had not been exposed to chlorinated solvents. The proposed mechanism for the formation of complexes VIIa–c is shown in Figure 13. We believe that the first step of the reaction involves formation of the respective [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_9RR'$] complexes followed by exchange of the hydride ligand for a chloride through the agency of HCl formed in situ. It would appear that these carbon-substituted complexes then rapidly dissociate PPh_3, which subsequently attacks an activated boron atom and allows the terminal hydride attached to the boron atom to migrate to the

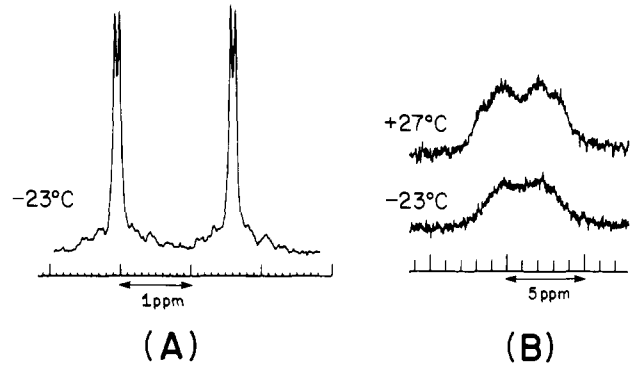

Figure 11. $^{31}P\{^1H\}$ NMR spectrum of [*closo*-1-Ph-3,8-$(PPh_3)_2$-3-Cl-3-H-3,1,2-$RhC_2B_9H_9$] VIIa showing (A) representative P_1 coupling to Rh and (B) representative P_2 coupling to boron.

(38) Brown, R. A. Ph.D. Dissertation, Cornell University, 1977.

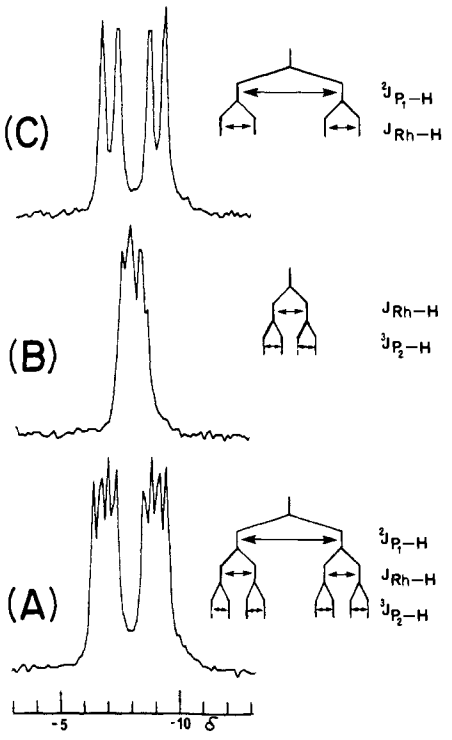

Figure 12. ^1H and $^1H\{^{31}P\}$ Spectra of [*closo*-1-Me-3,8-$(PPh_3)_2$-3-Cl-3-H-3,1,2-$RhC_2B_9H_9$] (VIIb): (A) no decoupling; (B) P_1 decoupled; (C) P_2 decoupled.

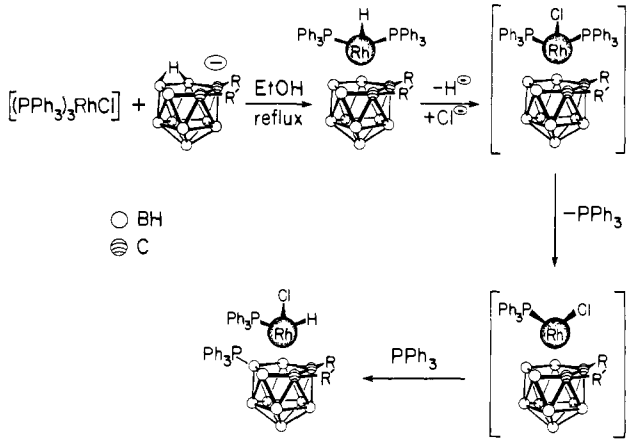

Figure 13. Proposed mechanism for the formation of complexes VIIa–c.

rhodium. This hypothesis is supported by the results of the reaction of complex Ie with aqueous HCl in ethanol at the reflux temperature which yields complex VIIb. It is also consistent with the instability of complexes Id and Ih in dichloromethane. Complex Id gave VIIa whereas complex Ih produced complex Ik. Therefore, 3,1,2-unsubstituted species do not rearrange readily, presumably due to the stability of the bis(phosphine) chlorides with respect to phosphine dissociation. Thus, complex Ia when reacted with PPh_3, HBF_4, and Me_4NCl in ethanol at the reflux temperature produced Ij.

It seemed likely that for complexes VIIa–c a boron atom on the pentagonal face of the carborane cage which bonds to metal also bonds to PPh_3 since coupling of both the metal-bound phosphorus and hydride to this phosphorus atom is observed (vide supra). This hypothesis has been confirmed by a recent X-ray diffraction study of complex VIIa[39] which shows the PPh_3 to be bonded to B(8), the unique boron atom on the C_2B_3 pentagonal face.

Similar metal-to-boron phosphine migrations have been reported for 10-[40] and 11-[1] vertex ruthena-, 11-[41] vertex platina- and 12-[42] vertex nickelacarboranes. Further studies are in progress to determine the nature of the unsaturated species formed by phosphine dissociation in nickel-triad, 12-vertex metallacarboranes.

(39) Day, V. W.; Thompson, M. R., private communication.

Conclusion

While we have not specifically discussed the catalytic properties of the set of three isomeric [*closo*-$(PPh_3)_2(H)RhC_2B_9H_{11}$] rhodacarborantes and their derivatives, this subject will be treated along with mechanistic details in a later paper in this series.[6a] However, at this point we have shown that these closo 18-electron, formal Rh(III) species are readily available and that they undergo characteristic reactions at the Rh vertex of the icosahedral cluster. The possible intervention of novel *nido*-Rh(I) tautomers as intermediates in some of these reactions is quite likely, and this subject will be addressed in the following contributions to this series.[15]

Experimental Section

Physical Measurements. The ^1H (200.133 MHz) and $^{31}P\{^1H\}$ (81.02 MHz) NMR spectra[43] were recorded on a Bruker WP-200 Fourier transform instrument utilizing a deuterium lock and a B-VT-1000 temperature controller for variable-temperature measurements. The ^{11}B NMR spectra[44] were recorded at 80.5, 118.0, or 127.0 MHz on a Fourier transform instrument designed by Professor F. A. L. Anet of this department. IR spectra were recorded as Nujol mulls on a Perkin-Elmer 137 spectrophotometer. Optical rotations were measured with a Perkin-Elmer 241MC polarimeter. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY. Glovebox manipulations were performed in a Vacuum Atmosphere HE-43 facility.

Materials. All solvents were reagent grade (Mallinckrodt) and were distilled from an appropriate drying agent under argon as follows: methanol (magnesium methoxide), diethyl ether (sodium–potassium alloy), benzene and tetrahydrofuran (potassium metal), toluene and heptane (sodium metal). Tetrahydrofuran and diethyl ether were also pretreated with activity 1 alumina (Merck) to remove peroxides. NMR solvents were obtained from commercial sources and dried and degassed prior to use. Triethylphosphine, dimethylphenylphosphine, 1,2-bis(diphenylphosphine)ethane (Strem), fluoboric acid (MCB), tetramethylammonium chloride, triphenylphosphine (Aldrich), hydrogen chloride, carbon monoxide (Liquid Carbonic), and rhodium trichloride trihydrate (Matthey Bishop) were purchased from commercial sources and used as received. Sodium borohydride (Alfa) was dried in vacuo prior to use. Inhibited *n*-butyl acrylate (Eastman) and methyl methacrylate (Aldrich) were passed down a column of alumina and then vacuum distilled from calcium hydride immediately before use. Precursor α-phenylacrylic acid was prepared from phenylmalonic acid (Aldrich) according to literature procedures[45,46] and converted to its ethyl ester by the method of Raber and Gariano.[47] The product was purified by fractional distillation (0.2 mmHg, 56 °C) and then vacuum distilled from calcium hydride prior to use. Salts of the [*nido*-$C_2B_9H_{10}RR'$] anions,[12,48] $[Rh_2(OAc)_4 \cdot 2MeOH]$[21] and $[(PPh_3)_3RhCl]$,[49] were prepared by literature procedures. The resolving agent *l*-*N*,*N*,*N*-trimethyl(α-phenylethyl)ammonium iodide was prepared from *l*-α-phenylethylamine (Aldrich) as previously described.[12,50] Thin-layer chromatography was performed on Kodak 13181 silica gel with fluorescent indicator. Baker silica gel (60–200 mesh) was employed for column chromatography.

Preparation of [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (Ia). General Procedure for Preparation of *closo*-Bis(phosphine)hydrido-

(40) Jung, C. W.; Baker, R. T.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1981**, *103*, 810.
(41) Barker, G. K.; Green, M.; Stone, F. G. A.; Welch, A. J.; Wolsey, W. C. *J. Chem. Soc., Chem. Commun.* **1980**, 627.
(42) Miller, S. B.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1976**, 786.
(43) $^{31}P\{^1H\}$ NMR spectra are referenced to external 85% H_3PO_4 as described in ref 13.
(44) ^{11}B NMR spectra are referenced to external BF_3OEt_2 with downfield shifts taken as positive. The ^{11}B NMR spectrum of complex (Ig) has been completely assigned: Kalb, W. C.; Kreimendahl, C. W.; Busby, D. C.; Hawthorne, M. F. *Inorg. Chem.* **1980**, *19*, 1590.
(45) Mannich, C.; Gang, E. *Chem. Ber.* **1922**, *55*, 3486.
(46) Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, *82*, 1886.
(47) Raber, D. J.; Gariano, P. *Tetrahedron Lett.* **1971**, *49*, 4741. Raber, D. J.; Gariano, P.; Brod, A. O.; Gariano, A. L.; Guida, W. C. *Org. Synth.* **1977**, *56*, 59.
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(49) Osborn, J.; Wilkinson, G. *Inorg. Synth.* **1967**, *10*, 67.
(50) Icke, R. N.; Wisengarver, B. B.; Alles, G. A. *Org. Synth.* **1945**, *25*, 89.

Table IV. Yields and Rh-H Stretching Frequencies (Nujol Mull) of $[closo\text{-}(PPh_3)_2(H)Rh(C_2B_9H_{10}R)]$ Species Obtained from $(PPh_3)_3RhCl$ and $[nido\text{-}C_2B_9H_{11}R^-]$ Ions

complex	% yield	$\bar{\nu}_{Rh-H}$, cm^{-1}
Ia	95	2120, 2080
Id	76	2170
Ie	88	2110, 2030
If	74	2080
If'[a]	15	2030
IIa	97	2110, 2070
IIb	81	2125
IIc	67	2070
III	89	2070

[a] From polytopal rearrangement of If.

rhodacarboranes. To a solution of $[Me_3NH][nido\text{-}7,8\text{-}C_2B_9H_{12}]$ (0.46 g, 2.38 mmol) in ethanol (100 mL) was added $[(PPh_3)_3RhCl]$ (2.0 g, 2.16 mmol) and the mixture heated at the reflux temperature for ca. 2 h. The reaction mixture was cooled to 40 °C, and the resulting yellow precipitate was separated by filtration and washed with ethanol, yielding Ia (1.49 g, 91%). In order to remove traces of Rh metal initially present in $[(PPh_3)_3RhCl]$, the crude product was chromatographed on silica gel, eluting with CH_2Cl_2. The recovered product was recrystallized from CH_2Cl_2/ethanol or CH_2Cl_2/heptane. This preparation has been scaled up to produce as much as 19 g of Ia in yields of 97%. Complexes Ib–e, IIa–c, and III were all prepared by analogous routes from the respective carborane anions. Only complexes Ia, IIa, and III were chromatographed as above. An alternative preparation involved reaction of $[(PPh_3)_3RhCl]$ with the carborane anion in methanol at room temperature overnight, followed by heating to the reflux temperature for ca. 1 h. This method was used for the preparation of complexes Id-f. Yields and ν_{Rh-H} are shown in Table IV.

The carbon-deuterated *closo*-carborane 1,2-D_2-1,2-$C_2B_{10}H_{10}$ was prepared by hyrolysis of 1,2-Li_2-1,2-$C_2B_{10}H_{10}$[51] using D_2O and degraded to the $[nido\text{-}7,8\text{-}D_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ using excess $NaOC_2H_5$ in C_2H_5OD at the reflux temperature. Prior to removal of excess base, C_2H_5OH followed by H_2O was added to back-exchange the B–D–B bridge deuteron by a proton. The carbon-deuterated anion was reacted with $[(PPh_3)_3RhCl]$ in C_2H_5OH at the reflux temperature to give Ib, which had no detectable carborane C–H resonance in the ^1H NMR spectrum. No attempt was made to optimize yields of reactions leading to the carbon-deuterated complex. As the precursor *closo*-1-Me-1,7-$C_2B_{10}H_{11}$ could not be prepared completely free from traces of *closo*-1,7-$C_2B_{10}H_{12}$, complex IIc was always contaminated with IIa and hence no elemental analysis was obtained for IIc. Analytical data for the remaining compounds are shown in Table V, while $^{31}P\{^1H\}$ and ^1H NMR spectra are summarized in Tables III and VI, respectively.[52] ^{11}B NMR spectra were often broad and uninformative;[53] however, those spectra that were relatively well resolved are tabulated (Table VII).

Resolution of $[dl\text{-}nido\text{-}7\text{-}Me\text{-}7,8\text{-}C_2B_9H_{11}]^-$ and the Preparation of $[d\text{-}closo\text{-}1\text{-}Me\text{-}3,3\text{-}(PPh_3)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{10}]$ (Ie*). Racemic $[nido\text{-}7,8\text{-}C_2B_9H_{11}]^-$ was resolved by slight modification of the procedure used[12] to resolve $[nido\text{-}7\text{-}Ph\text{-}7,8\text{-}C_2B_9H_{11}]^-$. Aqueous solutions of *l*-*N*,*N*,*N*-trimethyl(α-phenylethyl)ammonium iodide (81.0 g, 0.278 mol in 350 mL of H_2O) and crude $K[nido\text{-}7\text{-}Me\text{-}7,8\text{-}C_2B_9H_{11}]$ (50.0 g, 0.268 mol dissolved in 400 mL of H_2O) were mixed. The resulting white precipitate of $[l\text{-}Me_3NCH(Me)(Ph)][dl\text{-}nido\text{-}7\text{-}Me\text{-}7,8\text{-}C_2B_9H_{11}]$ was separated by filtration, washed with H_2O, and dried in vacuo: yield 76.7 g, 92%, $[\alpha]^{25}_{579}$ −9.0°. All rotations were measured in acetonitrile solvent. The product was recrystallized 18 times from ethanol, after which the total amount recovered was 13.0 g (16%) of $[l\text{-}Me_3NCH(Me)(Ph)][l\text{-}nido\text{-}7\text{-}Me\text{-}7,8\text{-}C_2B_9H_{11}]$: mp 138.5–140 °C, $[\alpha]^{25}_{579}$ −16.8°. The NMe_3H salt was obtained by cation exchange chromatography as previously described.[12] The crude yield of $[NMe_3H][l\text{-}nido\text{-}7\text{-}Me\text{-}7,8\text{-}C_2B_9H_{11}]$ was 7.64 g (86%). After recrystallization from hot H_2O, 6.68 g were obtained: mp 243–245 °C; $[\alpha]^{25}_{579}$ −5.9°. Complex Ie* was prepared from $[NMe_3H][l\text{-}nido\text{-}7\text{-}Me\text{-}7,8\text{-}C_2B_9H_{11}]$ as described above, giving $[\alpha]^{25}_{579}$ +5.3°.

Hydrogenation Studies of Ethyl α-Phenylacrylate Employing Chiral Ie* as the Catalyst Precursor. (a) At 25 °C under 1 atm of H_2. The apparatus employed has been previously described.[54] A 100-mL flask with side arm, containing a solution of Ie* (150 mg, 0.19 mmol) in THF (30 mL), was attached to the apparatus and three freeze–pump–thaw cycles were carried out. Hydrogen was then admitted to attain a total pressure of 1 atm and the system allowed to equilibrate at room temperature with vigorous stirring. The alkene (0.5 mL, 2.98 mmol) was injected through a septum on the side arm of the flask. The solution at once turned a deeper orange. After 21 h no H_2 uptake had been observed. Ethanol was then added to the solution, and when the volume was reduced in vacuo, orange crystals appeared which were identified as complex Ie* by ^1H NMR and IR spectroscopy. When a larger volume of alkene was used (1 mL) orange-red crystals of IVa were isolated from the solution (vide infra).

(b) At 25 °C and 100 atm of H_2. The glass liner of a 100-mL autoclave was charged with a solution of Ie* (120 mg, 0.155 mmol) and ethyl α-phenylacrylate (1 mL, 5.96 mmol) in THF (30 mL) in an argon-filled glove bag. The autoclave was assembled and tightened by hand. After removal from the glove bag, the autoclave was fastened securely and H_2 was admitted to a pressure of 1400 psi. After 48 h the autoclave was almost completely vented and then was dismantled in the glove bag. The volatile components were distilled from the green-brown solution on a high-vacuum line and the THF then distilled away from the higher boiling residue to yield 0.5 mL of a viscous, colorless liquid identified as ethyl α-phenylpropionate by ^1H NMR spectroscopy; $[\alpha]^{25}_D$ 1.9°. Preparative thick-layer chromatography of the solid, metal-containing residue, eluting with 1:1 CH_2Cl_2/heptane, afforded ca. 20 mg of a blue rhodacarborane complex which was not further examined.

Preparation of $[closo\text{-}1\text{-}Me\text{-}3,3\text{-}(CH_2C(H)PhC(O)OEt)\text{-}3\text{-}PPh_3\text{-}3,1,2\text{-}RhC_2B_9H_{10}]$ (IVa). Ethyl α-phenylacrylate (1 mL, 5.96 mmol) was added to a solution of Ie (144 mg, 0.186 mmol) in THF (2 mL), causing an immediate deepening of the color to red-orange. The solution was stirred at room temperature for 12 h and then concentrated in vacuo to 10 mL. On addition of ethanol (10 mL) red-orange crystals of IVa formed. These were recrystallized from CH_2Cl_2/ethanol containing ethyl α-phenylacrylate (0.5 mL) to prevent decomposition of the product to give IVa (45 mg, 35%). ^1H NMR 7.48 (m, 15 H, phenyl protons of coordinated PPh_3), 7.13, 6.46 (m, 5 H, Hd), 4.44 (t, 1 H, Hc, $^3J_{Ha-Hc}$ = 9, $^3J_{Hb-Hc}$ = 9 Hz), 4.25 (t, 1 H, Ha, $^2J_{Ha-Hb}$ = 9, $^3J_{Ha-Hc}$ = 9 Hz), 4.09 (overlapping quartet, 1 H, He, $^2J_{He-Hf}$ = 11, $^3J_{He-Hg}$ = 6 Hz), 3.8m (overlapping quartet, 1 H, Hf, $^2J_{He-Hf}$ = 11, $^3J_{Hf-Hg}$ = 6 Hz), 2.43 (s, br, 1 H, carborane C–H), 2.24 (m, 1 H, Hb, $^2J_{Ha-Hb}$ = 9, $^3J_{Hb-Hc}$ = 9 Hz), 1.59 (d, 3 H, carborane C–Me, $^4J_{P-H}$ = 2 Hz), 1.00 ppm (t, 3 H, Hg, $^3J_{He-Hg}$ = 6, $^3J_{Hf-Hg}$ = 6 Hz).

The other alkyl complexes were similarly prepared as follows:

$[closo\text{-}1\text{-}Me\text{-}3,3\text{-}(CH_2CH_2C(O)OBu)\text{-}3\text{-}PPh_3\text{-}3,1,2\text{-}RhC_2B_9H_{10}]$ (IVb). By use of Ie (250 mg, 0.32 mmol) and *n*-butyl acrylate (5.0 mL, 34.80 mmol) in THF (20 mL), 70 mg (34%) of IVb was obtained after recrystallization from CH_2Cl_2/ethanol. The crystal for the X-ray study was also grown from this solvent combination. ^1H NMR 7.44 (m, 15 H, phenyl protons of coordinated PPh_3), 4.07 (t, 1 H, Ha, $^2J_{Ha-Hb}$ = 10, $^3J_{Ha-Hc}$ = 10 Hz), 3.68 (overlapping triplet, 1 H, He, $^2J_{He-Hf}$ = 11, $^3J_{He-Hg}$ = 6 Hz), 3.25 (overlapping triplet, 1 H, Hf, $^2J_{He-Hf}$ = 11, $^3J_{Hf-Hg}$ = 6 Hz), 3.01 (m, 1 H, Hc, $^3J_{Ha-Hc}$ = 10, $^2J_{Hc-Hd}$ = 6 Hz), 2.42 (d, 1 H, Hd, $^2J_{Hc-Hd}$ = 6 Hz), 2.31 (m, 1 H, Hb, $^2J_{Ha-Hb}$ = 10 Hz), 2.23 (s, br, 1 H, carborane C–H), 1.49 (d, 3 H, carborane C–Me, $^4J_{P-H}$ = 2 Hz), 1.25,

(51) Grimes, R. N. "Carboranes"; Academic Press: New York, 1970; and references contained therein.

(52) Proton chemical shifts were referenced to residual protons in the solvent (dichloromethane, δ 5.32, toluene methyl, δ 2.09, tetrahydrofuran δ 3.58, with respect to tetramethylsilane). Phosphorus chemical shifts were determined as follows: because the spectrometer was locked on different solvent deuterium resonances (i.e., CD_2Cl_2, C_6D_6, or $C_6D_5CD_3$), it was necessary to calibrate spectra obtained with the use of each of these lock signals. This was achieved by determining the chemical shift of PPh_3 in all the solvent systems used under spectrometer conditions identical with those employed in this study. The ^{31}P chemical shifts are reported with respect to 85% H_3PO_4 by taking the chemical shift of PPh_3 with respect to 85% H_3PO_4 as −6 ppm as described in: Mann, B. E. *J. Chem. Soc., Perkin Trans.* **1972**, *2*, 30.

(53) Very broad ^{11}B NMR resonances are typical of metallacarboranes containing bulky ligands (e.g., PPh_3, $AsPh_3$, $P(p\text{-tolyl})_3$).[a-f] The analogous complexes with smaller ligands exhibit ^{11}B NMR spectra with normal line widths. This effect may be due to the size or molecular volume of the metallacarborane molecule.[d] Metallacarboranes with large ligands tumble more slowly and lower rates of molecular reorientation result in more efficient quadrupolar relaxation of the boron nuclei and therefore larger line widths in the ^{11}B NMR spectrum. This effect can be duplicated by lowering the temperature or by increasing the viscosity of the solution. (a) Paxson, T. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1974**, *96*, 4674. (b) Hoel, E. L.; Hawthorne, M. F. *Ibid.* **1973**, *95*, 2712; **1975**, *97*, 6388. (c) Klanberg, F.; Wegner, P. A.; Parshall, G. W.; Muetterties, E. L. *Inorg. Chem.* **1968**, *1*, 2072. (d) Beall, H.; Bushweller, C. H. *Chem. Rev.* **1973**, *73*, 465 and references cited therein. (e) Baker, R. T.; King, R. E., III; Knobler, C. B.; O'Con, C. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1978**, *100*, 8266. (f) Kalb, W. C.; Kreimendahl, C. W.; Busby, D. C.; Hawthorne, M. F. *Inorg. Chem.* **1980**, *19*, 1590 (ref 46).

(54) Potential catalysts are screened utilizing a previously reported procedure and apparatus described: Baker, R. T.; King, R. E., III; Knobler, C. B.; O'Con, C. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1978**, *100*, 8266.

Table V. Analytical Data for 12-Vertex *closo*-Phosphinerhodacarborane Complexes[a]

complex	C	H	B	P	Rh	Cl	N
Ia	60.25	6.29	12.57	8.24	12.77		
	(59.98)	(5.57)	(12.78)	(8.14)	(13.52)		
Id	62.76	5.75	10.82	7.27	11.78		
	(63.14)	(5.54)	(11.62)	(7.40)	(12.29)		
Ie	60.67	5.99	13.23	7.99	12.67		
	(60.44)	(5.73)	(12.55)	(7.99)	(13.28)		
If	61.80	6.48	11.60	7.55	12.06		
	(61.74)	(6.17)	(11.92)	(7.58)	(12.60)		
If[b]	58.19	5.81	10.27	7.21	11.31	7.35	
	(57.26)	(5.81)	(10.79)	(6.83)	(11.41)	(7.86)	
Ig	35.58	8.90	20.68	13.03	21.77		
	(35.58)	(8.96)	(20.59)	(13.11)	(21.77)		
Ih	42.44	6.79	18.63	12.00	19.64		
	(42.18)	(6.69)	(18.98)	(12.09)	(20.07)		
Ii	53.17	5.97	14.91	9.39	15.80		
	(52.98)	(5.72)	(15.33)	(9.76)	(16.21)		
Ij	57.34	5.42	11.88	7.86	12.73	4.38	
	(57.38)	(5.20)	(12.24)	(7.29)	(12.94)	(4.46)	
Ik	39.20	6.30	16.69	10.58	18.60	6.46	
	(39.52)	(6.08)	(17.79)	(11.32)	(18.81)	(6.48)	
IIa[c]	52.83	5.27	11.17	6.88	11.65	11.78	
	(53.21)	(4.93)	(11.05)	(7.04)	(11.69)	(12.08)	
IIb	62.90	5.64	11.45	7.53	12.18		
	(63.14)	(5.54)	(11.62)	(7.40)	(12.29)		
IId[d]	34.69	8.87	18.51	12.74	20.85	3.62	
	(34.65)	(8.67)	(19.71)	(12.54)	(20.83)	(3.59)	
IIe	42.16	6.73	18.69	11.57	19.70		
	(42.17)	(6.68)	(18.99)	(12.08)	(20.07)		
III	61.37	5.36	12.65	8.15	12.99		
	(59.98)	(5.57)	(12.78)	(8.14)	(13.52)		
IVa	55.66	5.90	14.12	4.13	15.04		
	(55.80)	(6.00)	(14.12)	(4.50)	(15.04)		
IVb	52.18	6.55	14.71	4.90	15.24		
	(52.48)	(6.45)	(15.18)	(4.83)	(16.06)		
IVc	51.02	6.23	16.16	5.20	17.15		
	(50.96)	(6.09)	(15.88)	(5.05)	(16.79)		
IVd	51.95	6.46	15.60	5.16	16.18		
	(51.74)	(6.27)	(15.52)	(4.94)	(16.42)		
V	50.16	5.32	15.11	4.91	16.00	7.01	
	(51.09)	(5.28)	(15.93)	(5.07)	(16.84)	(5.80)	
VIa	44.69	4.66	17.23	5.68	18.34	6.43	
	(44.96)	(4.67)	(17.34)	(5.52)	(18.34)	(6.32)	
VIb	48.32	5.02	15.79	4.90	16.05	7.21	2.41
	(49.04)	(5.10)	(15.91)	(5.06)	(16.81)	(5.79)	(2.29)
VIIa[e]	61.88	5.59	10.81	6.89	11.31	3.23	
	(62.00)	(5.31)	(10.69)	(6.80)	(11.30)	(3.89)	
VIIb	58.09	5.31	12.07	7.33	12.48	4.17	
	(57.88)	(5.35)	(12.02)	(7.65)	(12.71)	(4.38)	
VIIc	58.29	5.80	11.70	7.32	12.42	4.52	
	(58.35)	(5.51)	(11.82)	(7.52)	(12.50)	(4.31)	

[a] Found values are given first; calculated values are given in parentheses. [b] Calcd for CH_2Cl_2. [c] Calcd for $CHCl_3$. [d] Calcd for CH_2Cl_2. [e] Calcd for C_6H_6.

1.12 (m, 4 H, Hg, Hh), 0.77 ppm (t, 3 H, Hi, $^2J_{Hh-Hi}$ = 7 Hz).

[*closo*-1-Me-3,3-($CH_2C(H)MeC(O)OMe$)-3-PPh_3-3,1,2-$RhC_2B_9H_{10}$] (IVc). By use of Ie (300 mg, 0.387 mmol) and methyl methacrylate (3.0 mL, 32.10 mmol) in THF (20 mL), 65 mg (27%) of IVc was isolated after recrystallization from CH_2Cl_2/ethanol. ^1H NMR 7.43 (m, 15 H, phenyl protons of coordinated PPh_3), 4.21 (t, 1 H, Ha, $^2J_{Ha-Hb}$ = 9, $^3J_{Ha-Hc}$ = 9 Hz), 3.27 (s, 3 H, He), 3.17 (m, 1 H, Hc, $^3J_{Ha-Hc}$ = 9, $^3J_{Hc-Hd}$ = 7 Hz), 2.28 (s, br, carborane C–He, 2.05 (m, 1 H, Hb, $^2J_{Ha-Hb}$ = 9 Hz), 1.50 (d, 3 H, carborane C–Me, $^4J_{P-H}$ = 2 Hz), 0.91 ppm (d, 3 H, Hd, $^3J_{Hc-Hd}$ = 7 Hz).

[*closo*-1,2-$(Me)_2$-3,3-($CH_2C(H)MeC(O)OMe$-3-PPh_3-3,1,2-$RhC_2B_9H_9$] (IVd). By use of [*exo-nido*-$(PPh_3)_2Rh(C_2B_9H_{10}Me_2)$][15] (200 mg, 0.254 mmol) and methyl methacrylate (1.5 mL, 16.10 mmol in THF (20 mL), 28 mg (18%) of IVd was isolated after recrystallization from CH_2Cl_2/ethanol. ^1H NMR 7.50, 7.35 (m, 15 H, phenyl protons of coordinated PPh_3), 3.87 (t, 1 H, Ha, $^2J_{Ha-Hb}$ = 10, $^3J_{Ha-Hc}$ = 10 Hz), 3.75 (s, 3 H, He), 3.00 (m, 1 H, Hc, $^3J_{Hc-Hd}$ = 7, $^3J_{Ha-Hc}$ = 10 Hz), 1.60 (m, 1 H, Hb, $^2J_{Ha-Hb}$ = 10 Hz), 1.42 (d, 3 H, carborane C–Me, $^4J_{P-H}$ = 3 Hz), 1.36 (s, 3 H, carborane C–Me), 0.51 ppm (d, 3 H, Hd, $^3J_{Hc-Hd}$ = 7 Hz).

Thermal Rearrangement of [*closo*-1-*n*-Bu-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{10}$] (If to If'). A solution containing If (0.50 g, 0.61 mmol) and PPh_3 (0.81 g, 3.09 mmol) in THF (50 mL) was heated at the reflux temperature for 72 h. The solvent was then removed in vacuo and the resulting solid was recrystallized from CH_2Cl_2/heptane, affording off-white crystals of If' (75 mg, 15%).[55] The $^{31}P\{^1H\}$ NMR spectra of If' in 20% CD_2Cl_2/CH_2Cl_2 displayed the second-order ABM portion of an ABMX spin system centered at 31.6 ppm (A = B = ^{31}P, $I = {}^1/_2$; M = ^{103}Rh, $I = {}^1/_2$; X = ^1H, $I = {}^1/_2$).

Preparation of [*closo*-3,3-$(PEt_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (Ig). Method A. To a solution of [$Rh_2(OAc)_4$·2MeOH] (275 mg, 0.54 mmol) in methanol (30 mL) was added 48% aqueous HBF_4 (1 mL), and the blue solution was held at 60 °C for 16 h, yielding a green solution of $[Rh_2][BF_4]_4$. The solution was transferred to the glovebox, PEt_3 (400 mg, 3.40 mmol) added, and the resulting bright yellow solution stirred for 2 h. The solvent was removed and the residue dried on a high-vacuum line to remove water and acetic acid. The residue was then dissolved in methanol (50 mL) and [Me_3NH][*nido*-7,8-$C_2B_9H_{12}$] (215 mg, 1.10 mmol) added. The solution turned orange; yellow crystals of Ig precipitated which were separated by filtration, washed with methanol (2 × 20 mL), and dried in vacuo, yielding 420 mg (82%) of Ig (ν_{Rh-H} 2040 cm^{-1}).

Method B. Complex Ia (761 mg, 1.00 mmol) was dissolved in THF (200 mL) and PEt_3 (265 mg, 3.08 mmol) added in the glovebox. The reaction was stirred for 10 h and then heated to reflux for 1 h. Addition

(55) Delaney, M. S.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1981**, *20*, 1341.

Table VI. 200.133-MHz ^1H NMR Spectral Data for the 12-Vertex *closo*-Phosphinerhodacarborane Complexes

complex	M-H	M-H′	J_{Rh-H}	$J_{Rh-H'}$	$^2J_{P-H}$	$^2J_{P-H'}$	T, °C
Ia[a]	−8.40		17		29		−83
Id[a]	−10.19	−8.47	20	4	20/37	32[e]	−88
Ie[a,g]	−9.25		14		28/33		+42
Ie[a]	−9.73 (br)[h]	−8.36 (br)[h]					−88
If	−10.10	−8.05	22	<4	22/30	31[e]	−83
If′[a]	−8.69		15		27		+27
Ig[a]	−10.27		20		32		+27
Ih[b]	−9.57		20		32		+27
Ii[c]	−8.95		23		29		+27
IIa[a]	−10.74		15		24[e]		−83
IIb[a]	−13.79	−12.37	13	4	30[e]		−88
IIc[b]	−12.14	−12.57	16	10	27[e]		−88
IId[a,g]	−14.16		16		29		+27
IIe[a,g]	−12.22		17		31		+27
III[a,g]	−8.74		15		27		−83
VIIa[a]	−8.39		15		42/6[f]		+27
VIIb[d]	−8.05		13		43/6[f]		+27
VIIc[d]	−8.30		15		42/7[f]		+27

[a] Spectrum recorded in CD_2Cl_2. [b] Spectrum recorded in THF-d_8. [c] Spectrum recorded in C_6D_6. [d] Spectrum recorded in $CDCl_3$. [e] $^2J_{P_1-H} = {}^2J_{P_2-H}$. [f] $^3J_{P-H}$. [g] High-temperature limiting spectrum. [h] br = broad.

Table VII. $^{11}B\{^1H\}$ NMR Spectral Data for the 12-Vertex *closo*-Phosphinerhodacarborane Complexes[a]

complex	shift (integral)
Ig[b]	−2.8 (1), −3.9 (1), −9.0 (2), −10.9 (2), −21.1 (3)
Ih[b]	−1.8 (1), −4.4 (1), −8.5 (2), −10.0 (2), −21.3 (3)
Ii[b]	−1.1 (2), −8.1 (3), −10.1 (2), −19.4 (2)
Ik[b]	+6.9 (1), −2.6 (1), −3.7 (2), −6.0 (2), −18.1 (3)
IId[c]	−0.1 (2), −8.6 (1), −12.5 (1), −14.6 (2), −18.0 (2), −21.2 (1)
IIe[c]	−4.1 (2), −9.3 (1), −12.5 (1), −15.6 (2), −18.8 (2), −21.6 (1)
V[d]	+11.86 (1), +7.99 (2), +4.6 (1), −7.8 (1), −9.1 (1), −13.6 (2), −17.2 (1)
VI[d]	+16.0 (3), +5.6 (2), +0.6 (1), −2.6 (2), −8.7 (1)

[a] The number of boron atoms represented by each resonance is given in parentheses; chemical shifts are in ppm with respect to external BF_3:OEt_2. [b] Spectrum recorded at 127.1 MHz in tetrahydrofuran. [c] Spectrum recorded at 111.7 MHz in CH_2Cl_2. [d] Spectrum recorded at 111.7 MHz in $CDCl_3$.

Table VIII. Some Important Parameters for the Crystal Structures of Compounds V and IVb

Crystal Data for [*closo*-2-Cl-2-PPh_3-2,1,7-$RhC_2B_9H_{11}$·C_6H_6] (V)	
crystal system	monoclinic, $P2_1/n$, $Z = 4$
cell system	$a = 13.840$ (5) Å
	$b = 17.000$ (7) Å
	$c = 13.771$ (6) Å
	$\beta = 118.98$ (2)°
volume	2834 Å^3
calcd density (119 K)	1.43 g/cm^3
obsd density (298 K)	1.33 g/cm^3
2θ collection limit	50 (Mo Kα)
agreement factors	$R = 0.039$ (4173 reflections)
	$R_w = 0.055$
goodness of fit	1.94
Crystal Data for [*closo*-3-PPh_3-3,3-$(CH_3CH_2C(O)OC_4H_9)$-1-CH_3-3,1,2-$RhC_2B_9H_{10}$] (IVb)	
crystal system	orthorhombic, $P2_12_12_1$, $Z = 4$
	$a = 24.578$ (5) Å
	$b = 12.543$ (2) Å
	$c = 10.377$ (2) Å
	$V = 3202$ Å^3
calcd density	1.33 g/cm^3
obsd density	1.31 g/cm^3
2θ data collection limit	50°
absorption coefficient	5.964 cm^{-1}
variation in transmission coefficient	0.9410–0.9455
agreement factor	$R = 0.69$ (3159 reflections)
	$R_w = 0.80$
goodness of fit	2.38

of absolute ethanol (100 mL) followed by concentration of the solution to 70 mL in vacuo afforded a light yellow powder which on recrystallization from CH_2Cl_2/heptane yielded 430 mg (91%) of Ig.

Preparation of [*closo*-3,3-(PMe_2Ph)-3-H-3,1,2-$RhC_2B_9H_{11}$] (Ih). Complex Ih could be prepared by method A or B above.

Method A. By use of $[Rh_2(OAc)_4·2MeOH]$ (275 mg, 0.54 mmol), HBF_4 (1 mL), PMe_2Ph (470 mg, 3.40 mmol), and $[Me_3NH][nido$-7,8-$C_2B_9H_{12}]$ (215 mg, 1.10 mmol), 440 mg (79%) of Ih was obtained after recrystallization from THF/heptane (ν_{Rh-H} 2040, 2060 cm^{-1}).

Method B. A yield of 470 mg (92%) of complex Ih was obtained from Ia (761 mg, 1.00 mmol) and PMe_2Ph (425 mg, 3.08 mmol) after recrystallization from THF/heptane.

Preparation of [*closo*-3,3-$(Ph_2PCH_2CH_2PPh_2)$-3-H-3,1,2-$RhC_2B_9H_{11}$] (Ii). Complex Ii was prepared according to method B from Ia (761 mg, 1.00 mmol) and $Ph_2PCH_2CH_2PPh_2$ (410 mg, 1.03 mmol). Recrystallization of the resulting yellow powder from THF/heptane, yielded 580 mg (91%) of Ii (ν_{Rh-H} 2050 cm^{-1}).

Preparation of [*closo*-3,3-$(PPh_3)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$] (Ij). Complex Ia (102 mg, 0.134 mmol) was heated to the reflux temperature for 2 h in $CHCl_3$ solution (40 mL) in the presence of concentrated aqueous HCl (10 mL), yielding an orange-red solution. The organic layer was separated, washed with H_2O (5 × 20 mL), and dried over anhydrous $MgSO_4$. Concentration of the filtered $CHCl_3$ solution, followed by addition of ethanol gave 78 mg (73%) of crystalline Ij.

Preparation of [*closo*-3,3-$(PMe_2Ph)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$] (Ik). Complex Ih (256 mg, 0.50 mmol) was dissolved in CH_2Cl_2 (10 mL). The resulting solution was stirred for 12 h and layered with heptane to yield large red-orange blocks of Ik (260 mg, 95%).

Preparation of [*closo*-2,2-$(PEt_3)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$] (IId). To a stirred solution of IIa (1.52 g, 2.00 mmol) in benzene (200 mL) was added PEt_3 (0.94 g, 4.00 mmol). The solution was stirred for 8 h and the solvent then extracted in vacuo. The resulting yellow oil was extracted with CH_2Cl_2, filtered, and layered with heptane, affording light yellow crystals of IId (709 mg, 75%) (ν_{Rh-H} 2040, 2080 cm^{-1}).

Preparation of [*closo*-2,2-$(PMe_2Ph)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$] (IIe). To a benzene (200 mL) solution of IIa (1.52 g, 2.00 mmol) PMe_2Ph (1.10 g, 4.00 mmol) was added and the solution stirred for 8 h. Addition of ethanol (100 mL) followed by slow evaporation to 100 mL yielded a light yellow microcrystalline solid, which on recrystallization from CH_2Cl_2/heptane afforded light yellow crystals of IIe (0.820 g, 80%) (ν_{Rh-H} 2033 cm^{-1}).

Preparation of [*closo*-2-PPh_3-2-Cl-2,1,7-$RhC_2B_9H_{11}$] (V). A solution of IIa (2.28 g, 3.00 mmol) in benzene (200 mL) containing CCl_4 (10 mL) was heated to the reflux temperature for 12 h, during which time the initial yellow solution became dark red. The solution was reduced to dryness on silica gel, applied to a silica gel column, and eluted with 5:1 heptane/benzene to collect the red band (elution with CH_2Cl_2 gives IIa). On evaporation of the solvent, followed by extraction with benzene, filtration, and addition of heptane, traces of IIa were obtained after 24 h. Filtration, further addition of heptane, and concentration in vacuo yielded V (565 mg, 35%).

Preparation of [*closo*-2-PPh_3-2-CO-2-Cl-2,1,7-$RhC_2B_9H_{11}$] (VIa). When CO was passed through a red solution of V (500 mg, 0.938 mmol) in benzene (25 mL) the color gradually became light yellow. Addition of heptane precipitated a yellow powder that was recrystallized from

Table IX. Positional[a] (in fractional coordinates) and Thermal Parameters for [1-CH_3-3,3-($CH_2CH_2C(O)OC_4H_9$)-3-PPh_3-3,1,2-$RhC_2B_9H_{10}$] (IVb)

non-group atoms	x	y	z	B, Å²
Rh	0.42071 (3)	0.13583 (7)	−0.01029 (9)	b
P	0.3474 (1)	0.1485 (3)	−0.1499 (3)	b
O(1)	0.4116 (4)	−0.0360 (7)	−0.0328 (10)	b
O(2)	0.3852 (5)	−0.1835 (9)	0.0663 (12)	b
C(4)	0.3661 (5)	0.1019 (10)	0.1391 (11)	b
C(5)	0.3712 (7)	−0.0155 (12)	0.1772 (16)	b
C(6)	0.3908 (7)	−0.0789 (13)	0.0629 (18)	b
C(7)	0.4101 (11)	−0.2460 (14)	−0.0471 (24)	b
C(8)	0.4011 (14)	−0.3609 (17)	−0.0152 (31)	b
C(9)	0.3533 (13)	−0.4061 (21)	−0.0331 (37)	b
C(10)	0.3298 (12)	−0.4329 (18)	−0.1693 (19)	b
C(1)	0.5112 (4)	0.1272 (9)	0.0021 (13)	3.5 (2)
C(2)	0.4932 (6)	0.1989 (11)	−1210 (13)	3.4 (3)
C(3)	0.5274 (6)	0.0086 (10)	−0.0270 (14)	4.7 (3)
B(4)	0.4834 (6)	0.1639 (12)	0.1440 (14)	3.0 (3)
B(5)	0.5511 (9)	0.1965 (15)	0.1064 (18)	4.8 (4)
B(6)	0.5582 (8)	0.2189 (14)	−0.0684 (16)	4.2 (4)
B(7)	0.4446 (8)	0.2935 (14)	−0.0738 (16)	3.5 (4)
B(8)	0.4426 (8)	0.2775 (14)	0.1070 (16)	3.6 (4)
B(9)	0.5083 (8)	0.2985 (14)	0.1622 (17)	4.2 (4)
B(10)	0.5550 (7)	0.3284 (12)	0.0403 (16)	4.4 (4)
B(11)	0.5140 (8)	0.3268 (15)	−0.1143 (18)	5.0 (4)
B(12)	0.4867 (7)	0.3771 (13)	0.0328 (15)	4.8 (4)

Anisotropic Temperature Factors[c]

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	7.2 (1)	50.1 (6)	56.4 (9)	−0.6 (3)	−2.3 (5)	−0.3 (9)
P	5.1 (1)	56 (3)	69 (3)	0 (1)	−6 (1)	0 (3)
O(1)	14 (2)	45 (6)	123 (12)	0 (3)	−19 (5)	−23 (7)
O(2)	23 (3)	55 (9)	264 (22)	−12 (4)	−18 (6)	58 (11)
C(4)	2 (2)	64 (12)	71 (13)	5 (4)	27 (5)	−2 (9)
C(5)	23 (4)	60 (13)	128 (20)	6 (5)	10 (8)	−4 (13)
C(6)	14 (4)	67 (16)	177 (25)	−7 (5)	−9 (8)	72 (15)
C(7)	68 (9)	69 (15)	325 (47)	39 (10)	38 (17)	−76 (20)
C(8)	98 (12)	67 (15)	349 (48)	41 (13)	6 (29)	104 (31)
C(9)	59 (9)	182 (29)	460 (63)	−73 (13)	−55 (22)	179 (37)
C(10)	67 (10)	150 (23)	142 (26)	−2 (11)	−46 (14)	42 (20)

Rigid Group Parameters[d]

name	10^4x	10^4y	10^4z	ϕ	θ	ρ	B, Å²
Phenyl 1	3096 (4)	258 (6)	−1719 (9)	−1.988 (9)	2.179 (5)	−0.120 (9)	4.6 (1)
Phenyl 2	2934 (4)	2395 (6)	−1102 (10)	−0.961 (7)	−2.304 (5)	2.777 (8)	4.9 (1)
Phenyl 3	3690 (4)	1867 (7)	−3113 (6)	−2.442 (5)	3.155 (5)	−2.030 (5)	4.3 (1)

[a] Estimated standard deviations are given in parentheses. [b] Anisotropic thermal parameters. [c] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ all parameters have been multiplied by 10^4. [d] x, y, and z are the fractional coordinates of the group origin and ϕ, θ, and ρ, the rotation angles, in radians, as defined by: Scheringer, C. *Acta Crystallogr.* **1963**, *16*, 546.

CO-saturated benzene/heptane at ca. 5 °C, affording 244 mg (46%) of VIa. Attempted recrystallization from argon-saturated solvents regenerated the red color of the starting material (ν_{CO} 2060 cm^{-1}).

Preparation of [*closo*-2-PPh_3-2-C_5H_5N-2-Cl-2,1,7-$RhC_2B_9H_{11}$] (VIb). The pyridine adduct of V, namely VIb, could be precipitated as orange plates from benzene/pyridine solution by addition of heptane. A sample thus isolated was recrystallized from CH_2Cl_2/heptane/pyridine and an elemental analysis confirmed the proposed stoichiometry. Attempted recrystallizations from solution not containing pyridine resulted in a darkening of the solution from orange to red ($\nu_{C_5H_5N}$ 1610 cm^{-1}).

Preparation of [*closo*-1-Ph-3,8-(PPh_3)$_2$-3-Cl-3-H-3,1,2-$RhC_2B_9H_9$] (VIIa). A 250-mL Schlenk flask was charged with [$(PPh_3)_3RhCl$] (2.00 g, 2.16 mmol), PPh_3 (0.566 g, 2.16 mmol), and [Me_4N][*nido*-7-Ph-7,8-$C_2B_9H_{11}$] (0.625 g, 2.18 mmol). Ethanol (150 mL) was added, followed by 48% aqueous HBF_4 (1.75 mL, 8.75 mmol). The reaction mixture was heated to the reflux temperature for 7 h and allowed to cool to ca. 40 °C. The light orange precipitate was isolated by filtration and washed with ethanol and diethyl ether to give VIIa (1.56 g, 83%). The complex was recrystallized from benzene/ethanol to give bright orange fluffy crystals (ν_{Rh-H} 2100 cm^{-1}).

Preparation of [*closo*-1-Me-3,8-(PPh_3)$_2$-3-Cl-3-H-3,1,2-$RhC_2B_9H_9$] (VIIb). Method A. To a solution containing PPh_3 (87 mg, 0.33 mmol) and concentrated hydrochloric acid (0.14 mL, 1.65 mmol) in ethanol (40 mL) was added complex Ie (256 mg, 0.33 mmol). After the mixture was heated to the reflux temperature for 1 h a deep red solution had formed from which an orange solid rapidly precipitated. The mixture was then stirred at room temperature overnight. The precipitate was isolated by filtration and recrystallized from benzene/ethanol, affording 125 mg (47%) of VIIb (ν_{Rh-H} 2100 cm^{-1}). A higher yield of VIIb was obtained (185 mg, 69%) employing 48% aqueous HBF_4 (0.7 mL, 3.3 mmol) and NMe_4Cl (72 mg, 0.67 mmol) in place of the HCl.

Method B. To a solution of [NMe_3H][*nido*-7-Me-7,8-$C_2B_9H_{11}$] (624 mg, 3.00 mmol) in ethanol (100 mL) was added [$(PPh_3)_3RhCl$] (2.778 g, 3.00 mmol), PPh_3 (786 mg, 3.00 mmol), and 48% HBF_4 (2.4 mL, 12.00 mmol). The mixture was heated to the reflux temperature. After 15 min an orange precipitate began to replace the red suspension of [$(PPh_3)_3RhCl$] and after 2 h the precipitate was completely orange. Heating was continued for 10 h. The precipitate was then isolated by filtration, washed with ethanol, and recrystallized from benzene/ethanol to yield bright orange crystals of VIIb (1.65 g, 68%).

Preparation of [*closo*-1,2-$(Me)_2$-3,8-(PPh_3)$_2$-3-Cl-3-H-3,1,2-$RhC_2B_9H_8$] (VIIc). Method B, above, was employed with [NMe_3H]-[*nido*-7,8-Me_2-7,8-$C_2B_9H_{10}$] (442 mg, 2.00 mmol), [$(PPh_3)_3RhCl$] (1.852 g, 2.00 mmol), PPh_3 (524 mg, 2.00 mmol), and 48% aqueous HBF_4 (1.6 mL, 8.00 mmol) in ethanol (45 mL). After the mixture was heated to the reflux temperature for 2 h the resulting orange precipitate was recrystallized from benzene/ethanol to yield 1.06 g (64%) of VIIc (ν_{Rh-H} 2050 cm^{-1}).

Reaction of Ia with HBF_4, PPh_3, and NMe_4Cl. A mixture of Ia (380 mg, 0.50 mmol), NMe_4Cl (60 mg, 0.525 mmol), PPh_3 (131 mg, 0.50 mmol), and 48% aqueous HBF_4 (1.0 mL, 5.0 mmol) in ethanol (40 mL) was heated at the reflux temperature for 16 h, forming an orange precipitate. This was extracted into benzene (100 mL) and heptane (25 mL) added. On concentration of the solution in vacuo, a mixture of orange

Table X. Positional (in Fractional Coordinates) and Thermal Parameters[a] for the Non-Group Atoms of [*closo*-2-Cl-2-PPh_3-2,1,7-$RhC_2B_9H_{11}$·C_6H_6] (V)

atom	*x*	*y*	*z*	*B*, Å^2
Rh	0.42814 (2)	0.30898 (2)	0.63474 (2)	*b*
Cl	0.25520 (8)	0.29392 (6)	0.61700 (2)	*b*
P	0.46963 (8)	0.39393 (6)	0.78249 (8)	*b*
C(1)	0.4036 (3)	0.2266 (2)	0.5001 (3)	1.58 (6)
B(3)	0.5240 (4)	0.2162 (3)	0.6252 (4)	1.75 (7)
B(4)	0.5120 (4)	0.1834 (3)	0.4966 (4)	1.75 (7)
B(5)	0.4255 (4)	0.2507 (3)	0.3941 (4)	1.94 (8)
B(6)	0.3809 (4)	0.3213 (3)	0.4619 (4)	1.96 (8)
C(7)	0.5920 (3)	0.3062 (2)	0.6517 (3)	1.78 (7)
B(8)	0.6320 (4)	0.2344 (3)	0.5919 (4)	2.11 (8)
B(9)	0.5686 (4)	0.2582 (3)	0.4487 (4)	2.14 (8)
B(10)	0.4876 (4)	0.3452 (3)	0.4304 (4)	2.23 (2)
B(11)	0.5091 (4)	0.3758 (3)	0.5634 (4)	1.98 (8)
B(12)	0.6203 (4)	0.3330 (3)	0.5494 (4)	2.37 (8)
H(1)	0.3375 (38)	0.1944 (25)	0.4799 (36)	2.62 (95)
H(3)	0.5399 (32)	0.1734 (23)	0.6940 (31)	1.54 (80)
H(4)	0.5069 (31)	0.1183 (23)	0.4795 (31)	1.63 (80)
H(5)	0.3671 (39)	0.2306 (30)	0.3124 (41)	3.89 (96)
H(6)	0.3014 (39)	0.3501 (27)	0.3996 (40)	1.04 (72)
H(7)	0.6468 (34)	0.3141 (22)	0.7237 (35)	1.75 (86)
H(8)	0.7147 (38)	0.2046 (25)	0.6430 (37)	2.90 (99)
H(9)	0.6073 (33)	0.2434 (25)	0.3983 (33)	2.22 (89)
H(10)	0.4672 (37)	0.3889 (27)	0.3638 (37)	3.35 (96)
H(11)	0.5064 (35)	0.4432 (25)	0.5790 (35)	2.64 (93)
H(12)	0.6937 (36)	0.3703 (27)	0.5759 (37)	3.20 (98)

Anisotropic Thermal Parameters[c]

atom	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Rh	221 (3)	107 (1)	255 (2)	−9 (1)	100 (2)	−31 (1)
Cl	251 (7)	183 (4)	403 (7)	−56 (4)	155 (6)	86 (4)
P	238 (7)	104 (3)	236 (6)	1 (4)	94 (5)	−12 (4)

Rigid-Group Parameters[d]

group	*x*	*y*	*z*	ϕ	θ	ρ	*B*, Å^2
Phenyl 1	0.4321 (2)	0.3450 (1)	0.8766 (2)	0.734 (1)	3.080 (1)	2.445 (1)	1.79 (2)
Phenyl 2	0.6143 (2)	0.4247 (2)	0.8699 (2)	2.482 (2)	−2.237 (1)	1.938 (3)	1.93 (3)
Phenyl 3	0.3977 (2)	0.4871 (1)	0.7414 (2)	2.677 (4)	1.964 (1)	−0.717 (3)	1.72 (3)
Phenyl 4	0.4222 (2)	−0.0558 (1)	0.1311 (2)	1.443 (1)	−2.906 (2)	0.437 (2)	2.80 (3)

[a] Estimated standard deviations in the least significant figures are given in parentheses. [b] Anisotropic thermal parameters. [c] The expression for the anisotropic temperature is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [d] *x*, *y*, and *z* are the fractional coordinates of the origin of the rigid group and ϕ, θ, and ρ, the rotation angles, in radians, described by: Scheringer, C. *Acta Crystallogr.* 1963, *16*, 546.

and yellow crystals formed. When a second recrystallization was attempted, only the orange product redissolved. Addition of heptane afforded 150 mg (38%) of **1j** identified by comparison of its IR spectrum and a thin-layer chromatogram with those of an authentic sample of **1j**. The yellow crystals were identified as starting complex **1a** by IR and ^{1}H NMR spectroscopy.

Molecular Structure Determination for Complex IVb. The crystal chosen for data collection was in the shape of an elongated octahedron (0.30 mm × 0.40 mm) and was bounded by faces of the forms {3,0,2}, {−3,0,2}, [1,1,0], and {−1,1,0}. The crystal was mounted in a arbitrary direction and transferred to a Picker FACS-1 automated diffractometer. Orientation of the crystal and crystal system followed autoindexing eight accurately centered reflections found photographically. The orthorhombic nature of the unit cell was confirmed by the observation of mirror planes perpendicular to each reciprocal axis. Preliminary data were then collected to identify the intense high-angle data. Accurate cell constants (Table VIII) were obtained by a least-squares fit of 19 reflections in the range $5° \leq 2\theta \leq 34°$.

Data were collected in the θ–2θ scan mode to a $(\sin\theta)/\lambda$ limit of 0.595 Å^{-1} with Zr-filtered Mo Kα radiation. Three intense reflections, 290, 526, and 13, 2, −6 were monitored every 101 reflections as a check on the stability of the experiment. Intensities of these standards fluctuated only slightly during the course of data collection. A constant scan rate of 2°/min was used with a scan range of $(2.0 + 0.692 \tan\theta)°$. A 10-s background count was taken at each end of the scan. One quadrant of data ($+h,+k,+/-l$, 5897 reflections) were collected. Of this total, 3159 reflections were considered observed (i.e., $I > 3\sigma(I)$) and were corrected for Lorentz, polarization, and absorption effects. One octant of data (3196 reflections) was extracted and of this total, 2161 were considered observed (i.e., $I > 3\sigma(I)$) and were corrected for Lorentz, polarization, and absorption effects. The observed systematic absences $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, and $00l$, $l = 2n + 1$ indicated the space group to be $P2_12_12_1$. The structure was solved by using one octant ($+h$, $+k$, $+l$) of observed data by standard Patterson-Fourier techniques[56] and refined in several cycles of full-matrix least-squares. In these and subsequent refinements, the Rh and P atoms were treated as anomalous scatterers,[57] the positional and isotropic thermal parameters of the cage atoms, the positional and anisotropic thermal parameters of the remaining non-hydrogen non-phenyl carbon atoms, and the scale factor were allowed to vary. The phenyl rings on the phosphorus atoms were treated as rigid groups with C–C and C–H set as 1.39 and 1.00 Å, respectively. The positional, rotational, and overall thermal parameters of these groups were allowed to vary.

At this point, refinement was continued on the originally chosen isomer with the full data set ($+h,+k,\pm l$) and also on its enantiomer. Refinement converged to an agreement factor of 0.069 for the former and 0.070 for the latter (the corresponding weighted agreement factors are 0.080 and 0.081, respectively). This represents a certainty at the 99% confidence level that the originally chosen molecule is the correct stereoisomer.[58] Final positional and thermal parameters are given in Table IX.

Molecular Structure Determination of Complex V. A representative crystal (0.35 mm × 0.22 mm × 0.27 mm) was chosen for data collection and was mounted in an arbitrary orientation and transferred to a Syntex $P\bar{1}$ automated diffractometer. The crystal was maintained at 119 K during the preliminary experiments and data collection. Orientation of

(56) Programs used in this work include locally written data reduction and absorption programs and locally revised versions of ORFLS, ORFFE, ORTEP, and MULTAN.

(57) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(58) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

the crystal and crystal system determination followed the autoindexing of seven accurately centered reflections found photographically. An axial photograph of the b axis revealed a mirror plane. The orientation matrix obtained from these data was used to index 15 accurately centered high-angle reflections ($18° < 2\theta < 27°$). A least-squares fit of these reflections yielded the cell constants found in Table VIII.

Data were collected in the θ–2θ scan mode to a $(\sin\theta)/\lambda$ limit of 0.60 $Å^{-1}$ with graphite-monochromatized Mo Kα radiation. Three intense reflections, 2,–2,6, 1,6,–5, and –5,5,–3, were monitored every 100 reflections as a check on the stability of the experiment. Intensities of these standards fluctuated only slightly during the course of the experiment. A constant scan rate of 3°/min was used with a scan range of 1.1° on either side of Mo $K\alpha_1$ and Mo$K\alpha_2$. The background time to scan ratio was 1. One quadrant of data (5298 reflections) were collected and of this total 4389 were considered observed (i.e., $I > 3\sigma(I)$) and were corrected for Lorentz and polarization effects. The raw data were also corrected for absorption by an empirical method based on the variation in intensity of three reflections about $\chi = 270°$. The reflections used and their 2θ values are 5,–1,1, 18.89°; 7,–1,3, 30.19°; and 10,–2,3, 40.61°. The systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, indicated the space group to be $P2_1/n$. The Rh, P, and Cl atoms were located from a Patterson map and Fourier syntheses phased by these and successively added atoms allowed the location of all non-hydrogen atoms, including the benzene of crystallization. At this point the phenyl groups were treated as rigid groups with C–C and C–H set at 1.39 and 1.00 Å, respectively. In subsequent refinement, the positional parameters and overall temperature factor of each group were allowed to vary. Full-matrix least-squares varying all positional and isotropic thermal parameters and the scale factor resulted in an agreement factor of 0.066. The carbon atom positions of the carborane fragment were clearly distinguishable at this point, corresponding to their larger scattering ability. Difference maps at this point revealed the locations of all the carborane hydrogens. Two more cycles of full-matrix least-squares converged to an agreement factor of 0.039. In these final cycles of refinement all atomic positions and thermal parameters (anisotropic for the Rh, P, and Cl atoms, isotropic for all other atoms), and the scale factor were allowed to vary. In the final cycle of least-squares the largest shift to standard deviation ratio was 0.13 and most were less than 0.05. A final difference Fourier synthesis revealed no significant peaks. Final positional and thermal parameters are given in Table X.

Scattering factors were taken from the "International Tables for X-ray Crystallography", and anomalous dispersion terms were included for the Rh, P, and Cl atoms.[57]

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Registry No. Ia, 53687-46-0; Ib, 76270-74-1; Ic, 82808-04-6; Id, 65337-89-5; Ie, 76287-17-7; Ie*, 89363-52-0; If, 76146-56-0; If', 89363-60-0; Ig, 73246-82-9; Ih, 89363-53-1; Ii, 89363-54-2; Ij, 56465-07-7; Ik, 89363-55-3; IIa, 53754-45-3; IIb, 77330-46-2; IIc, 77319-39-2; IId, 77319-38-1; IIe, 77319-37-0; IIl, 76287-18-8; IVa, 89363-56-4; IVb, 89363-57-5; IVc, 89363-58-6; IVd, 89363-59-7; V, 89437-63-8; VIa, 89437-64-9; VIb, 89437-65-0; VIc, 89437-66-1; VId, 89437-67-2; VIe, 89437-68-3; VIf, 89437-69-4; VIIa, 89462-05-5; VIIb, 89509-59-1; VIIc, 89486-19-1; *exo-nido*-$(PPh_3)_2Rh(C_2B_9H_{10}Me_2)$, 89345-76-6; $[Me_3NH][nido\text{-}7,8\text{-}C_2B_9H_{12}]$, 89321-03-9; $1,2\text{-}D_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, 57584-38-0; $1,2\text{-}Li_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, 22220-85-5; $[nido\text{-}7,8\text{-}D_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$, 76448-54-9; *closo*-1-Me-1,7-$C_2B_{10}H_{11}$, 17378-55-1; K[*nido*-7-Me-7,8-$C_2B_9H_{11}$], 39333-04-5; [*l*-$Me_3NCH(Me)(Ph)$][*dl-nido*-7-Me-7,8-$C_2B_9H_{11}$], 89321-05-1; [*l*-$Me_3NCH(Me)(Ph)$][*l-nido*-7-Me-7,8-$C_2B_9H_{11}$), 89321-07-3; $[Me_4N][nido\text{-}7\text{-}Ph\text{-}7,8\text{-}C_2B_9H_{11}]$, 39336-45-3; $[NMe_3H][l\text{-}nido\text{-}7\text{-}Me\text{-}7,8\text{-}C_2B_9H_{11}]$, 89414-08-4; $(PPh_3)_3RhCl$, 14694-95-2; $[Rh_2(OAc)_4{\cdot}2MeOH]$, 41772-64-9; $[Rh_2][BF_4]_4$, 30935-54-7; ethyl α-phenylacrylate, 22286-82-4; α-phenylpropionate, 39192-74-0; *n*-butyl acrylate, 141-32-2; methyl methacrylate, 80-62-6; $[NMe_3H][nido\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_{10}]$, 89321-09-5.

Supplementary Material Available: Tables of observed and calculated structure factors for IVb and V (25 pages). Ordering information is given on any current masthead page.