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Metallacarboranes in Catalysis. 4. Structures of *closo*- and *exo*-*nido*-Phosphinerhodacarboranes and a $[(PPh_3)_3Rh]^+$[*nido*-7-R-7,8-$C_2B_9H_{11}$]$^-$ Salt[1]

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Abstract: In contrast to the observed equilibrium between the closo and exo-nido tautomers of the bis(triphenylphosphine)rhodacarborane formally derived from $(PPh_3)_2Rh^+$ and the [*nido*-7,8-μ-(1′,2′-$CH_2C_6H_4CH_2$-)-7,8-$C_2B_9H_{10}$]$^-$ ion, the crystalline solid obtained from this system has been determined to be pure [*closo*-1,2-μ-{1′,2′-$CH_2C_6H_4CH_2$-}-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_9$] (I). However, when one of these PPh_3 groups was replaced by $P(C_6H_{11})_3$ (PCy_3), [*exo-nido*-6,10-{$(PPh_3)(PCy_3)Rh$}-6,10-μ-$(H)_2$-7,8-μ-(1′,2′-$CH_2C_6H_4CH_2$-)-10,11-μ-(H)-7,8-$C_2B_9H_7$] (II) was the preferred isomer present in the solid. If the *o*-xylylene group bonded to the two carbon atoms of the C_2B_9 framework was replaced by a phenyl and a methyl group and the phosphine ligands were both PPh_3, [*exo-nido*-4,9-{$(PPh_3)_2Rh$}-4,9-μ-$(H)_2$-7-Me-8-Ph-7,8-$C_2B_9H_8$] (III), in which the BHB bridge was not located, was preferred in the solid. When this complex was heated in tetrahydrofuran solution in the presence of excess PEt_3 a polytopal rearrangement of the carborane icosahedron took place. The structure of the resulting complex, [*closo*-1-Me-2,2-$(PEt_3)_2$-2-H-8-Ph-2,1,8-$RhC_2B_9H_9$] (IV), is described. Reaction of the exo-nido complexes with certain two-electron donor ligands can result in displacement of the Rh from the carborane cage to generate an ion pair. The crystal structure of the salt $[(PPh_3)_3Rh]^+$[*nido*-7-R-7,8-$C_2B_9H_{11}$]$^-$ (R = (1′-*closo*-1′,2′-$C_2B_{10}H_{11}$)) (V) has been determined. Compound I crystallized in the monoclinic space group $P2_1/n$ with a = 17.803 (7) Å, b = 21.425 (6) Å, c = 13.010 (4) Å, β = 98.20 (2)°, and Z = 4. Observed and calculated densities were 1.36 and 1.44 g cm^{-3}, respectively. Diffraction data to 2θ = 45° (Mo Kα radiation) were collected on a Picker FACS-I diffractometer, and the structure was solved by conventional Patterson, Fourier, and full-matrix least-squares refinement techniques. The final discrepancy index was R = 0.0597, R_w = 0.0550, for 2864 independent reflections. The molecule possesses icosahedral geometry in which Rh occupies a vertex and is also bound to two triphenylphosphine ligands and to a terminal hydride ligand in a pseudooctahedral arrangement in which the carborane cage can be considered to occupy three coordination sites. Both carborane carbons, adjacent to each other in the closo-3,1,2 arrangement, are bridged by an *o*-xylylene group. Although this closo solid exhibited closo–exo-nido equilibrium in solution, the closo-3,1,2 geometry of the molecule in the crystal was normal in all respects. Compound II crystallized in the triclinic centrosymmetric space group $P\bar{1}$, with a = 11.565 (2) Å, b = 13.527 (5) Å, c = 18.313 (6) Å, α = 91.90 (4)°, β = 73.21 (4)°, γ = 102.10 (6)°, and Z = 2. Observed and calculated densities were 1.20 and 1.23 g cm^{-3}, respectively. Diffraction data to 2θ = 50° (Mo Kα radiation) were collected on a Picker FACS-I diffractometer, and the structure was solved by conventional Patterson, Fourier, and full-matrix least-squares refinement techniques. The final discrepancy index was R = 0.0561, R_w = 0.0529, for 5571 independent reflections. In II a $Rh(PPh_3)(PCy_3)$ moiety is attached to a *nido*-C_2B_9 icosahedral fragment through a pair of three-center, two-electron M–H–B bonds, and the conformation about Rh is distorted square planar. Another bridging hydrogen atom was found bound to two boron atoms of the open face of the carborane cage. Compound III crystallized in the monoclinic space group $C2/c$, a = 10.732 (3) Å, b = 23.610 (8) Å, c = 17.247 (6) Å, β = 91.32 (2)°, and Z = 4. Observed and calculated densities were 1.24 and 1.29 g cm^{-3}, respectively. Diffraction data to 2θ = 50° (Mo Kα) were collected on a Syntex $P2_1$ diffractometer, and the structure was solved by MULTAN, Fourier, and full-matrix least-squares techniques. The final discrepancy index was R = 0.0613, R_w = 0.0675, for 3104 independent reflections. In III the stereochemical configuration about Rh is the same as that seen in II; however, in the former species the attachment of $Rh(PPh_3)_2$ to the carborane fragment is through two B–H vertices which are adjacent to a single carbon atom. In III, as in II, this dual attachment is to a B–H vertex present in the open face and to a B–H vertex in the adjacent belt of five. In II neither of these boron atoms is adjacent to carbon. Compound IV crystallized in the monoclinic space group $P2_1/n$, a = 12.905 (3) Å, b = 13.855 (2) Å, c = 16.201 (3) Å, β = 91.46 (2)°, and Z = 4. Observed and calculated densities were 1.28 and 1.29 g cm^{-3}, respectively. Diffractometer data to 2θ = 50° were collected on a Syntex $P2_1$ diffractometer, and the structure was solved by Patterson, Fourier, and full-matrix least-squares techniques and refined to a discrepancy index R = 0.039, R_w = 0.049, for 3946 independent reflections. Although IV possesses icosahedral geometry resembling that of I, the bonding face in IV is CB_4 while that in I is C_2B_3. In IV, the carbon vertex bearing the phenyl substituent has migrated to a position in the lower belt of five atoms and is nonadjacent to the methyl-substituted carbon. Compound V crystallized in the monoclinic space group $P2_1/c$, a = 14.819 (4) Å, b = 25.429 (6) Å, c = 17.578 (4) Å, β = 98.65 (2)°, and Z = 4. Observed and calculated densities were 1.257 and 1.267 cm^{-3}, respectively. Rapid decomposition of the crystal forced discontinuation of data collection before a complete data set to 2θ = 45° had been collected. Data were collected on a Syntex $P\bar{1}$ diffractometer (Mo Kα radiation) and the structure was solved by heavy-atom techniques and refined to a discrepancy index of R = 0.0757, R_w = 0.0771, for 3319 independent reflections. The anion consists of a *closo*-$C_2B_{10}H_{11}$ icosahedron bonded to a *nido*-$C_2B_9H_{11}^-$ icosahedral fragment through carbon vertices. The $Rh(PPh_3)_3$ cation exhibits an unusual geometry: the ligand conformation about Rh is approximately planar with a T-shaped arrangement of the three PPh_3 ligands, and two of the carbon atoms of a phenyl ring occupy the remaining position of a very distorted square.

In the previous contribution of this series the syntheses and reactions of *exo-nido*-phosphinerhodacarboranes were presented[1] without a detailed description of the determination of the molecular structures of these new species and related compounds. The present contribution describes five X-ray diffraction studies which supply these details. The origin of each of the five species examined is briefly presented below.

A general synthesis of bis(phosphine)rhodacarborane complexes is simply the reaction of the Cs salt of the corresponding carborane nido monoanion $(RR'C_2B_9H_{10})^-$ with $[(PPh_3)_3RhCl]$ in benzene.[1]

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[1] For part 2 of this series see: Long, J. A.; Marder, T. B.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.*, second of five papers in this issue.

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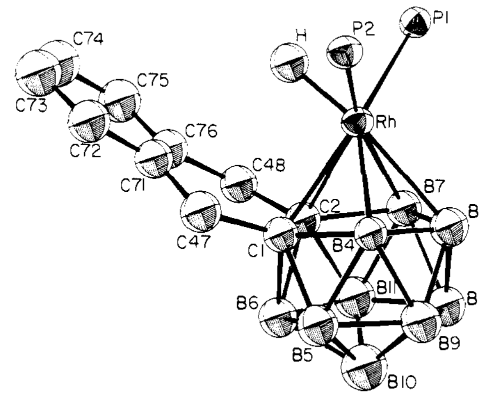

Figure 1. Molecular structure of [*closo*-1,2-μ-{1',2'-$CH_2C_6H_4CH_2$-}-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_9$] (I). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms, with the exception of the terminal hydride, and phenyl groups on phosphorus have been omitted for clarity.

The reaction of the *o*-xylylene-substituted carborane monoanion [*nido*-7,8-μ-(1',2'-$CH_2C_6H_4CH_2$-)-7,8-$C_2B_9H_{10}$]$^-$ with [$(PPh_3)_3RhCl$] in benzene produced a solution which contained species exhibiting closo-exo-nido tautomerism. However, crystals deposited from this solution were shown to be that of the closo tautomer (I). Factors affecting this equilibrium have been discussed in an accompanying paper.[1] When one of the PPh_3 groups in I was replaced by PCy_3 (Cy = cyclohexyl), the exo-nido isomer separated as the crystalline phase (II). When the *o*-xylylene group in the carborane anion was replaced with a methyl and a phenyl group and this anion was reacted with [$(PPh_3)_3RhCl$], the exo-nido form [*exo-nido*-4,9-{$(PPh_3)_2Rh$}-4,9-μ-$(H)_2$-7-Me-8-Ph-7,8-$C_2B_9H_8$] (III) was the crystalline product.

Ion-pair species such as [$(PEt_3)_4Rh$]$^+$[*nido*-7-R-8-R'-7,8-$C_2B_9H_{10}$]$^-$ react further to generate closo species[1] of the general formula [$(PEt_3)_2Rh(H)(C_2B_9H_9RR')$]. When R = Me and R' = Ph (but not when R, R' = μ-*o*-xylylene or μ-$CH_2CH_2CH_2$-) a polytopal rearrangement occurs, resulting in the formation of [*closo*-1-Me-2,2-$(PEt_3)_2$-2-H-8-Ph-2,1,8-$RhC_2B_9H_9$] (IV).

Reaction of the exo-nido complexes with two-electron donor ligands displaces the rhodium from the cage to give cationic species of the type [L_4Rh]$^+$, [L_3RhS]$^+$, and [$L_2Rh(CO)_3$]$^+$ (L = PPh_3) and [L_4Rh]$^+$ (L = PEt_3). When [$(PPh_3)_3RhCl$] reacted with Tl^+[*nido*-7-(1'-*closo*-1',2'-$C_2B_{10}H_{11}$)-7,8-$C_2B_9H_{11}$]$^-$ in benzene, instead of an exo-nido compound, the salt [$Rh(PPh_3)_3$]$^+$[*nido*-7-(1'-*closo*-1',2'-$C_2B_{10}H_{11}$)-7,8-$C_2B_9H_{11}$]$^-$ (V) was isolated as red crystals. The preparation and reactions of I-V are discussed in a companion paper[1] while the structures of species I-V are presented here.

Results and Discussion

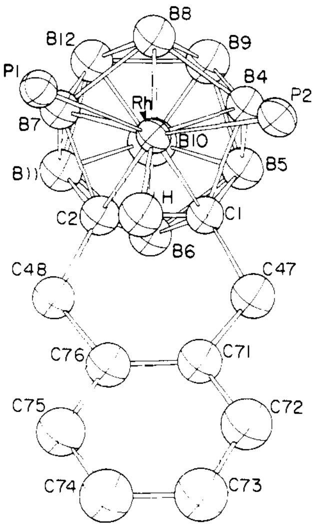

Figure 2. Another view of I. The disposition of the [RhP_2H] moiety with respect to the carborane fragment is depicted.

Molecular Structure of [*closo*-1,2-μ-(1',2'-$CH_2C_6H_4CH_2$-)-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_9$] (I). In solution, [*closo*-1,2-μ-(1',2'-$CH_2C_6H_4CH_2$-)-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_9$] (I) was found to be in equilibrium with its exo-nido tautomer, but the complex crystallized as the closo tautomer in which the hydride ligand is projected over, and bisects, the C-C bond of the carborane cage. In contrast, in the X-ray diffraction study of the unsubstituted isomer [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$][3] (Ia), only one of the atoms in the five-membered face coordinated to the Rh atom could be identified as a carbon atom, whereas the two adjacent atoms required assignment as statistically disordered carbon and boron atoms. Thus the conformational preference of the unsubstituted complex is low. The closo tautomer of I probably exists in solution in the symmetric conformation shown in Figures 1 and 2. The metal hydride H(3) is approximately trans to B(8), H(3)-Rh-B(8) = 168(3)°, and is nearly cis to the two carbon atoms on the C_2B_3 face. The two triphenylphosphine ligands are thus as far away from the bridging *o*-xylylene group as possible.

The overall geometry of the *closo*-RhC_2B_9 system is not unusual. Interatomic distances and angles are presented in Table I. The Rh atom exhibits pseudooctahedral coordination, with the carborane cage occupying three coordination sites and two phosphine ligands and the hydride ligand occupying the remaining sites. Bonding of the metal atom to the C_2B_3 face is highly symmetric, with distances in the range 2.23 (1)-2.33 (1) Å.

It is interesting to compare I to the unsubstituted isomer [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (Ia). In contrast to Ia, no asymmetry is found in the rhodium-phosphorus bonding, 2.335 (3) and 2.324 (3) Å. These distances are nearly the average of the distances found in Ia, 2.357 (3) and 2.301 (1) Å. As in Ia, there is no evidence of interaction of the hydride ligand with the carborane cage, and the Rh-H distance, 1.56 (9) Å, is the same as that found in Ia. The three angles around Rh involving the hydride ligand and the two phosphorus atoms are slightly smaller than in Ia, possible due to steric effects of the *o*-xylylene substituent. There is no crystallographic disorder in I because the *o*-xylylene substituent destroys the pseudosymmetry found in the C_2B_9 polyhedron in Ia. Indeed, the steric requirements of the *o*-xylylene substituent may also explain the apparent lack of rotation in solution of the [P_2RhH] vertex with respect to the C_2B_3 face of the carborane ligand.[4]

Molecular Structure of [*exo-nido*-6,10-{$(PPh_3)(PCy_3)Rh$}-6,10-μ-$(H)_2$-7,8-μ-(1',2'-$CH_2C_6H_4CH_2$-)-10,11-μ-(H)-7,8-$C_2B_9H_7$] (II). Three-center, two-electron M-H-B bonding (M = transition metal) is still a fairly uncommon phenomenon in exopolyhedral metallaborane and metallacarborane complexes.[5-10] The X-ray structure of the exopolyhedral Rh(I) carborane complex [$(PPh_3)_2Rh(C_2PhB_{10}H_{10})$] has previously been reported;[9] the Rh-cage interaction consists of a Rh-C σ bond and a Rh-H-B

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Table I. Interatomic Distances (Å) and Angles (deg) in [*closo*-1,2-μ-{1′,2′-$CH_2C_6H_4CH_2$-}-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_9$]·$2CH_2Cl_2$ (I)[a]

Interatomic Distances

Rh(3)–P(2)	2.335 (3)	C(1)–B(6)	1.757 (19)	B(7)–B(8)	1.821 (21)	C(47)–H(471)	0.826 (95)
Rh(3)–P(3)	2.324 (3)	C(1)–B(47)	1.518 (19)	B(7)–B(11)	1.768 (21)	C(47)–H(472)	0.789 (94)
Rh(3)–C(1)	2.292 (12)	C(2)–B(6)	1.730 (19)	B(7)–B(12)	1.798 (21)	C(47)–C(71)	1.484 (19)
Rh(3)–C(2)	2.310 (11)	C(2)–B(7)	1.740 (20)	B(7)–H(7)	1.022 (93)	C(48)–C(76)	1.482 (18)
Rh(3)–B(4)	2.229 (14)	C(2)–B(11)	1.691 (19)	B(8)–B(9)	1.726 (22)	C(48)–H(481)	1.017 (96)
Rh(3)–B(7)	2.238 (15)	C(2)–C(48)	1.518 (17)	B(8)–B(12)	1.798 (21)	C(48)–H(482)	0.877 (88)
Rh(3)–B(8)	2.331 (14)	B(4)–B(5)	1.823 (21)	B(8)–H(8)	1.063 (88)	C(12M)–Cl(1)	1.705 (19)
Rh(3)–H(3)	1.565 (88)	B(4)–B(8)	1.724 (23)	B(9)–B(10)	1.754 (24)	C(12M)–Cl(2)	1.802 (20)
P(2)–C(11)	1.831 (9)	B(4)–B(9)	1.795 (21)	B(9)–B(12)	1.781 (23)	C(34M)–Cl(3)	1.677 (43)
P(2)–C(21)	1.880 (8)	B(4)–H(4)	1.242 (87)	B(9)–H(9)	1.078 (87)	C(34M)–Cl(4)	1.629 (38)
P(2)–C(31)	1.861 (9)	B(5)–B(6)	1.744 (22)	B(10)–B(11)	1.754 (24)	C(71)–C(72)	1.390 (19)
P(3)–C(41)	1.853 (9)	B(5)–B(9)	1.746 (23)	B(10)–B(12)	1.792 (24)	C(71)–C(76)	1.372 (18)
P(3)–C(51)	1.846 (8)	B(5)–B(10)	1.716 (24)	B(10)–H(10)	1.142 (88)	C(72)–C(73)	1.418 (19)
P(3)–C(61)	1.846 (8)	B(5)–H(5)	1.134 (95)	B(11)–B(12)	1.759 (22)	C(73)–C(74)	1.409 (21)
C(1)–C(2)	1.593 (17)	B(6)–B(10)	1.687 (23)	B(11)–H(11)	1.016 (90)	C(74)–C(75)	1.356 (20)
C(1)–B(4)	1.802 (18)	B(6)–B(11)	1.717 (24)	B(12)–H(12B)	1.096 (91)	C(75)–C(76)	1.402 (17)
C(1)–B(5)	1.708 (19)	B(6)–H(6)	1.160 (86)				

Angles

P(2)–Rh(3)–P(3)	98.7 (1)	C(1)–C(2)–B(7)	110.0 (9)	Rh(3)–B(7)–B(11)	123.4 (9)	B(6)–B(11)–B(7)	111.0 (11)
C(1)–Rh(3)–P(2)	106.2 (3)	B(6)–C(2)–B(7)	111.7 (9)	C(2)–B(7)–B(11)	57.6 (8)	C(2)–B(11)–B(10)	105.6 (11)
C(1)–Rh(3)–P(3)	151.9 (3)	Rh(3)–C(2)–B(11)	123.3 (8)	B(8)–B(7)–B(11)	106.7 (10)	B(6)–B(11)–B(10)	58.1 (9)
C(2)–Rh(3)–P(2)	144.3 (3)	C(1)–C(2)–B(11)	111.1 (10)	Rh(3)–B(7)–B(12)	124.2 (9)	B(7)–B(11)–B(10)	108.9 (11)
C(2)–Rh(3)–P(3)	111.9 (3)	B(6)–C(2)–B(11)	60.2 (8)	C(2)–B(7)–B(12)	105.1 (10)	C(2)–B(11)–B(12)	109.0 (11)
C(2)–Rh(3)–C(1)	40.5 (4)	B(7)–C(2)–B(11)	62.0 (8)	B(8)–B(7)–B(12)	59.6 (8)	B(6)–B(11)–B(12)	110.2 (11)
B(4)–Rh(3)–P(2)	87.8 (4)	Rh(3)–C(2)–C(48)	109.6 (8)	B(11)–B(7)–B(12)	59.1 (9)	B(7)–B(11)–B(12)	61.3 (9)
B(4)–Rh(3)–P(3)	148.9 (4)	C(1)–C(2)–C(48)	117.2 (10)	Rh(3)–B(7)–H(7)	108.0 (50)	B(10)–B(11)–B(12)	61.3 (9)
B(4)–Rh(3)–C(1)	47.0 (5)	B(6)–C(2)–C(48)	110.6 (10)	C(2)–B(7)–H(7)	119.8 (50)	C(2)–B(11)–H(11)	117.8 (50)
B(4)–Rh(3)–C(2)	75.6 (5)	B(7)–C(2)–C(48)	126.6 (10)	B(8)–B(7)–H(7)	128.6 (50)	B(6)–B(11)–H(11)	117.1 (50)
B(7)–Rh(3)–P(2)	159.8 (4)	B(11)–C(2)–C(48)	117.6 (10)	B(11)–B(7)–H(7)	114.8 (50)	B(7)–B(11)–H(11)	120.3 (50)
B(7)–Rh(3)–P(3)	87.0 (4)	Rh(3)–B(4)–C(1)	68.4 (6)	B(12)–B(7)–H(7)	120.2 (50)	B(10)–B(11)–H(11)	125.5 (50)
B(7)–Rh(3)–C(1)	74.1 (5)	Rh(3)–B(4)–B(5)	120.8 (9)	Rh(3)–B(8)–B(4)	64.7 (7)	B(12)–B(11)–H(11)	124.7 (50)
B(7)–Rh(3)–C(2)	45.0 (5)	C(1)–B(4)–B(5)	56.2 (8)	Rh(3)–B(8)–B(7)	63.9 (7)	B(7)–B(12)–B(8)	60.9 (8)
B(7)–Rh(3)–B(4)	77.8 (5)	Rh(3)–B(4)–B(8)	71.0 (7)	B(4)–B(8)–B(7)	104.5 (10)	B(7)–B(12)–B(9)	105.2 (11)
B(8)–Rh(3)–P(2)	113.1 (4)	C(1)–B(4)–B(8)	107.5 (10)	Rh(3)–B(8)–B(9)	121.1 (9)	B(8)–B(12)–B(9)	57.7 (8)
B(8)–Rh(3)–P(3)	106.3 (3)	B(5)–B(4)–B(8)	105.8 (10)	B(4)–B(8)–B(9)	62.7 (9)	B(7)–B(12)–B(10)	106.0 (11)
B(8)–Rh(3)–C(1)	75.9 (5)	Rh(3)–B(4)–B(9)	123.2 (9)	B(7)–B(8)–B(9)	106.4 (11)	B(8)–B(12)–B(10)	105.8 (11)
B(8)–Rh(3)–C(2)	76.4 (5)	C(1)–B(4)–B(9)	102.0 (9)	Rh(3)–B(8)–B(12)	119.3 (9)	B(9)–B(12)–B(10)	58.8 (9)
B(8)–Rh(3)–B(4)	44.4 (5)	B(5)–B(4)–B(9)	57.7 (8)	B(4)–B(8)–B(12)	110.3 (11)	B(7)–B(12)–B(11)	59.6 (9)
B(8)–Rh(3)–B(7)	46.9 (5)	B(8)–B(4)–B(9)	58.7 (8)	B(7)–B(8)–B(12)	59.6 (8)	B(8)–B(12)–B(11)	108.2 (11)
P(2)–Rh(3)–H(3)	78.1 (32)	Rh(3)–B(4)–H(4)	111.9 (39)	B(9)–B(8)–B(12)	60.7 (9)	B(9)–B(12)–B(11)	105.7 (11)
P(3)–Rh(3)–H(3)	75.1 (32)	C(1)–B(4)–H(4)	107.4 (40)	Rh(3)–B(8)–H(8)	109.5 (47)	B(10)–B(12)–B(11)	59.2 (9)
C(1)–Rh(3)–H(3)	97.1 (32)	B(5)–B(4)–H(4)	103.3 (40)	B(4)–B(8)–H(8)	125.2 (47)	B(7)–B(12)–H(12B)	125.0 (47)
C(2)–Rh(3)–H(3)	91.9 (32)	B(8)–B(4)–H(4)	143.1 (40)	B(7)–B(8)–H(8)	121.9 (47)	B(8)–B(12)–H(12B)	119.0 (47)
B(4)–Rh(3)–H(3)	135.8 (32)	B(9)–B(4)–H(4)	123.9 (40)	B(9)–B(8)–H(8)	121.4 (47)	B(9)–B(12)–H(12B)	119.8 (47)
B(7)–Rh(3)–H(3)	122.1 (32)	C(1)–B(5)–B(4)	61.3 (8)	B(12)–B(8)–H(8)	117.5 (47)	B(10)–B(12)–H(12B)	123.3 (47)
B(8)–Rh(3)–H(3)	168.0 (32)	C(1)–B(5)–B(6)	61.2 (8)	B(4)–B(9)–B(5)	61.9 (9)	B(11)–B(12)–H(12B)	126.5 (47)
Rh(3)–P(2)–C(11)	114.5 (3)	B(4)–B(5)–B(6)	111.7 (11)	B(4)–B(9)–B(8)	58.6 (8)	Rh(3)–C(47)–C(1)	43.5 (6)
Rh(3)–P(2)–C(21)	118.1 (3)	C(1)–B(5)–B(9)	108.1 (11)	B(5)–B(9)–B(8)	109.1 (11)	Rh(3)–C(47)–H(471)	95.1 (65)
C(11)–P(2)–C(21)	99.5 (3)	B(4)–B(5)–B(9)	60.3 (9)	B(4)–B(9)–B(10)	109.0 (11)	C(1)–C(47)–H(471)	115.3 (66)
Rh(3)–P(2)–C(31)	115.9 (3)	B(6)–B(5)–B(9)	108.8 (11)	B(5)–B(9)–B(10)	58.7 (9)	Rh(3)–C(47)–H(472)	139.7 (68)
C(11)–P(2)–C(31)	106.7 (4)	C(1)–B(5)–B(10)	106.6 (11)	B(8)–B(9)–B(10)	110.8 (11)	C(1)–C(47)–H(472)	96.3 (68)
C(21)–P(2)–C(31)	100.0 (3)	B(4)–B(5)–B(10)	109.5 (11)	B(4)–B(9)–B(12)	107.9 (11)	H(471)–C(47)–H(472)	109.5 (94)
Rh(3)–P(3)–C(41)	122.3 (3)	B(6)–B(5)–B(10)	58.4 (9)	B(5)–B(9)–B(12)	107.6 (11)	Rh(3)–C(47)–C(71)	91.6 (8)
Rh(3)–P(3)–C(51)	109.7 (3)	B(9)–B(5)–B(10)	60.9 (10)	B(8)–B(9)–B(12)	61.7 (9)	C(1)–C(47)–C(71)	116.0 (12)
C(41)–P(3)–C(51)	101.1 (3)	C(1)–B(5)–H(5)	102.6 (45)	B(10)–B(9)–B(12)	60.9 (9)	H(471)–C(47)–C(71)	110.3 (66)
Rh(3)–P(3)–C(61)	119.0 (3)	B(4)–B(5)–H(5)	119.3 (45)	B(4)–B(9)–H(9)	118.5 (47)	H(472)–C(47)–C(71)	108.2 (68)
C(41)–P(3)–C(61)	96.4 (3)	B(6)–B(5)–H(5)	106.3 (45)	B(5)–B(9)–H(9)	121.3 (47)	Rh(3)–C(48)–C(2)	43.5 (6)
C(51)–P(3)–C(61)	105.8 (3)	B(9)–B(5)–H(5)	141.4 (46)	B(8)–B(9)–H(9)	118.9 (47)	Rh(3)–C(48)–C(76)	93.7 (7)
Rh(3)–C(1)–C(2)	70.4 (6)	B(10)–B(5)–H(5)	130.7 (46)	B(10)–B(9)–H(9)	123.6 (47)	C(2)–C(48)–C(76)	118.0 (11)
Rh(3)–C(1)–B(4)	64.7 (6)	C(1)–B(6)–C(2)	54.4 (7)	B(12)–B(9)–H(9)	123.6 (47)	Rh(3)–C(48)–H(481)	80.6 (50)
C(2)–C(1)–B(4)	110.0 (9)	C(1)–B(6)–B(5)	58.4 (8)	B(5)–B(10)–B(6)	61.6 (10)	C(2)–C(48)–H(481)	102.3 (50)
Rh(3)–C(1)–B(5)	123.1 (8)	C(2)–B(6)–B(5)	102.2 (10)	B(5)–B(10)–B(9)	60.4 (9)	C(76)–C(48)–H(481)	113.0 (50)
C(2)–C(1)–B(5)	109.9 (9)	C(1)–B(6)–B(10)	105.7 (11)	B(6)–B(10)–B(9)	111.1 (12)	Rh(3)–C(48)–H(482)	144.8 (59)
B(4)–C(1)–B(5)	62.5 (8)	C(2)–B(6)–B(10)	106.9 (11)	B(5)–B(10)–B(11)	106.7 (12)	C(2)–C(48)–H(482)	104.3 (59)
Rh(3)–C(1)–B(6)	127.5 (8)	B(5)–B(6)–B(10)	60.0 (9)	B(6)–B(10)–B(11)	59.8 (9)	C(76)–C(48)–H(482)	118.6 (60)
C(2)–C(1)–B(6)	62.0 (8)	C(1)–B(6)–B(11)	102.5 (10)	B(9)–B(10)–B(11)	107.0 (12)	H(481)–C(48)–H(482)	97.6 (77)
B(4)–C(1)–B(6)	112.0 (9)	C(2)–B(6)–B(11)	58.8 (8)	B(5)–B(10)–B(12)	108.5 (12)	Cl(1)–C(12M)–Cl(2)	108.0 (10)
B(5)–C(1)–B(6)	60.4 (8)	B(5)–B(6)–B(11)	107.2 (11)	B(6)–B(10)–B(12)	110.0 (12)	Cl(3)–C(34M)–Cl(4)	109.3 (21)
Rh(3)–C(1)–C(47)	109.4 (8)	B(10)–B(6)–B(11)	62.0 (10)	B(9)–B(10)–B(12)	60.3 (9)	C(72)–C(71)–C(47)	116.4 (12)
C(2)–C(1)–C(47)	118.4 (10)	C(1)–B(6)–H(6)	104.8 (43)	B(11)–B(10)–B(12)	59.4 (9)	C(76)–C(71)–C(47)	124.1 (12)
B(4)–C(1)–C(47)	125.6 (10)	C(2)–B(6)–H(6)	109.4 (43)	B(5)–B(10)–H(10)	120.1 (44)	C(76)–C(71)–C(72)	119.4 (12)
B(5)–C(1)–C(47)	117.4 (10)	B(5)–B(6)–H(6)	121.6 (43)	B(6)–B(10)–H(10)	111.5 (44)	C(71)–C(72)–H(72)	119.7 (12)
B(6)–C(1)–C(47)	111.7 (10)	B(10)–B(6)–H(6)	141.8 (43)	B(9)–B(10)–H(10)	128.0 (44)	C(71)–C(72)–C(73)	120.7 (12)
Rh(3)–C(2)–C(1)	69.1 (6)	B(11)–B(6)–H(6)	131.2 (43)	B(11)–B(10)–H(10)	119.5 (44)	H(72)–C(72)–C(73)	119.6 (12)
Rh(3)–C(2)–B(6)	127.9 (8)	Rh(3)–B(7)–C(2)	69.7 (6)	B(12)–B(10)–H(10)	126.6 (44)	H(73)–C(73)–C(72)	120.9 (13)
C(1)–C(2)–B(6)	63.7 (8)	Rh(3)–B(7)–B(8)	69.2 (7)	C(2)–B(11)–B(6)	61.0 (8)	C(74)–C(73)–C(72)	118.1 (13)
Rh(3)–C(2)–B(7)	65.3 (6)	C(2)–B(7)–B(8)	107.4 (10)	C(2)–B(11)–B(7)	60.4 (8)	C(74)–C(73)–H(73)	121.0 (13)

Table I (*Continued*)

Angles							
H(74)-C(74)-C(73)	119.7 (14)	C(76)-C(75)-H(75)	119.6 (12)	P(2)-C(11)-C(16)	118.0 (6)	P(3)-C(41)-C(42)	115.2 (5)
C(73)-C(74)-C(75)	120.5 (13)	C(71)-C(76)-C(48)	122.7 (11)	P(2)-C(21)-C(22)	120.3 (5)	P(3)-C(41)-C(46)	124.8 (6)
H(74)-C(74)-C(75)	119.8 (14)	C(75)-C(76)-C(48)	116.8 (11)	P(2)-C(21)-C(26)	119.7 (5)	P(3)-C(51)-C(52)	119.4 (5)
H(75)-C(75)-C(74)	119.6 (12)	C(75)-C(76)-C(71)	120.4 (11)	P(2)-C(31)-C(32)	122.3 (6)	P(3)-C(51)-C(56)	120.5 (5)
C(76)-C(75)-C(74)	120.8 (12)	P(2)-C(11)-C(12)	122.0 (6)	P(2)-C(31)-C(36)	117.3 (6)		

[a] Esd in parentheses in units of least significant digit of the corresponding value in this and in following tables.

bridge bond. Prior to the discovery of the Ir exo-nido complexes[11] and the Rh species reported here, M–H–B bonding of exopolyhedral B–H units of *nido*-carborane fragments was only known with main group elements, the fluxional [*exo-nido*-9,10-(R_2M)-9,10-μ-$(H)_2$-10,11-μ-(H)-7,8-$C_2B_9H_9$] (M = Al, Ga, R_2 = Me and Et).[12] The structure of another exopolyhedral *nido*-metallacarborane, [*nido*-4,8-μ-$\{(Me_3P)_2Pt\}$-8,8-$(Me_3P)_2$-7,8,10-$CPtCB_8H_{10}$], has been reported[13] in which one of the two Pt atoms is attached to a C_2PtB_8 icosahedral fragment through one boron atom adjacent to the apical boron and through Pt in the open face of the cage.

Although a variety of structural types have been established for 12-vertex *nido*-metallacarboranes[14] the spectroscopic and analytical data available for the *nido*-rhodacarboranes described here did not allow unambiguous conclusions to be drawn concerning their structure and bonding. For example, cleavage of a C–B bond in the pentagonal bonding face would result in the Rh vertex interactin, with a "carbadiborallyl" fragment analogous to the structure of the tetracarbon metallacarborane [$(\eta^5$-$C_5H_5)FeMe_4C_4B_7H_8$][15] or the Rh atom could occupy a position bridging a B–B edge above the open face, as found for main group complexes [*exo-nido*-9,10-(R_2M)-9,10-μ-$(H)_2$-10,11-μ-(H)-7,8-$C_2B_9H_9$] (M = Al, Ga, R = Me, Et), referred to above,[12] in which the metal is bonded to the cage via a pair of three-center, two-electron M–H–B bonds.[16] Consequently, in order to characterize these *nido*-rhodacarboranes, an X-ray structural analysis of II was undertaken.

The empirical formula of II is identical with that of I except for replacement of one triphenylphosphine ligand by tricyclohexylphosphine. However, in II a $(PPh_3)(PCy_3)Rh$ moiety is attached to a *nido*-C_2B_9 icosahedral fragment through two exopolyhedral three-center, two-electron M–H–B bonds. Neither of the two boron atoms involved in bridge bonding, B(10) on the open C_2B_3 face and B(6) on the lower B_5 belt parallel to that face, is bonded to carbon. The stereochemical configuration about rhodium is distorted square planar, as shown in Figure 3.

The greatest deviation of an atom from the least-squares plane through RhP_2B_2 is 0.262 (8) Å (for B(10)), but the greatest deviation of an atom from the plane through RhP_2H_2 is 0.08 (5) Å (for H(10)). A bridging hydride is found bound to two boron atoms of the open face. One of these boron atoms (B(10)) is also bonded to an M–H–B bridging hydride. Interatomic distances and angles are listed in Table II.

The most striking difference in the nature of the *o*-xylylene substituents in I and II is at the points of attachment to the carborane cage. The angle between the normals to the least-squares planes defined by the two methylene carbon atoms and the two carborane carbon atoms and by the C_2B_3 face is 23.8° (I) and 34.7° (II) while the angle between the normals to the least-squares planes through the eight *o*-xylylene carbon atoms and through the C_2B_3 face is 38.7° (I) and 81.0° (II), as shown in Figures 1 and 3.

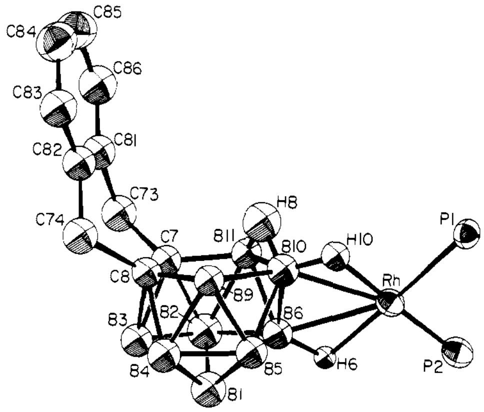

Figure 3. Molecular structure of [*exo-nido*-6,10-$\{(PPh_3)(PCy_3)Rh\}$-6,10-μ-$(H)_2$-7,8-μ-$(1',2'$-$CH_2C_6H_4CH_2-)$-7,8-$C_2B_9H_8$] (II). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms, with the exception of bridging hydrides, and phenyl and cyclohexyl groups on phosphorus have been omitted for clarity.

Molecular Structure of [*exo-nido*-4,9-$\{(PPh_3)_2Rh\}$-4,9-μ-$(H)_2$-7-Me-8-Ph-7,8-$C_2B_9H_8$] (III). Some features of III can be inferred from $^{11}B\{^1H\}$ NMR spectroscopy; e.g., the two upfield resonances, one of which is very broad in the decoupled spectrum, are reminiscent of upfield resonances in spectra of the parent *nido*-7,8-$C_2B_9H_{12}^-$ ion, where one resonance is assigned to apical atom B(1) and the other to the central boron atom in the open face B(10).[17] Atom B(10) is bonded to the bridging proton which tautomerizes between two positions, bridging either B(9) and B(10) or B(10) and B(11). The resonance usually appears to be broadened due to poorly resolved coupling to the fluxional bridging proton. In the ^1H NMR spectrum of III, a broad resonance at -2.15 ppm can be assigned to a bridging B–H–B. When the sample solution is cooled to -88 °C, a broad singlet appears at -5.39 ppm, which can be attributed to Rh–H–B bridging protons. The sharp doublet in the $^{31}P\{^1H\}$ NMR spectrum indicates the apparent equivalence of the two phosphine ligands. The Rh is bonded to an asymmetric cage; therefore, a process must occur which makes the two phosphines equivalent on the NMR time scale, such as rotation of the $\{RhL_2\}$ moiety perhaps coupled with a migration of the $\{RhL_2\}$ fragment about the polytopal surface of the carborane ligand. Similar processes obviously occur in II, III and the various exo-nido species which we have previously discussed[1] as determined by variable-temperature ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The lack of an apparent terminal Rh–H stretch in the IR spectrum suggests that III exists purely in the exo-nido form in the solid state.

The molecular structure of III is shown in Figure 4 and distances and angles are presented in Table III. The structure formally consists of a discrete $[(PPh_3)_2Rh]^+$ fragment bonded to two terminal B–H bonds of a [*nido*-7-Me-8-Ph-7,8-$C_2B_9H_{10}$]$^-$ ion. The Rh atom interacts with B(4)–H(4) and B(9)–H(9) through two three-center, two-electron Rh–H–B bonds, each of which may be formally considered as a two-electron donor to the metal, thus completing the 16-e$^-$ configuration at the Rh(I) center.

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Table II. Interatomic Distances (Å) and Angles (deg) in [*exo-nido*-6,10-{$(PPh_3)(PCy_3)Rh$}-6,10-μ-$(H)_2$-7,8-μ-(1′,2′-$CH_2C_6H_4CH_2$)-10,11-μ-(H)-7,8-$C_2B_9H_7$] (II)[a]

Interatomic Distances

Rh-P(1)	2.247 (2)	B(2)-H(2)	1.077 (51)	B(9)-H(9)	1.125 (56)	C(61)-C(66)	1.512 (11)
Rh-P(2)	2.256 (2)	B(3)-B(4)	1.749 (11)	B(10)-B(11)	1.851 (11)	C(62)-C(63)	1.535 (11)
Rh-B(6)	2.338 (8)	B(3)-C(7)	1.712 (11)	B(10)-H(10)	1.129 (55)	C(63)-C(64)	1.500 (13)
Rh-B(10)	2.398 (8)	B(3)-C(8)	1.742 (10)	B(10)-HB	1.056 (63)	C(64)-C(65)	1.505 (12)
Rh-H(6)	1.842 (47)	B(3)-H(3)	1.120 (55)	B(11)-H(11)	1.073 (51)	C(65)-C(66)	1.558 (11)
Rh-H(10)	1.832 (50)	B(4)-B(5)	1.732 (12)	B(11)-HB	1.526 (60)	C(73)-H(73A)	0.975 (74)
P(1)-C(11)	1.840 (4)	B(4)-C(8)	1.725 (10)	C(41)-H(41)	0.986 (64)	C(73)-H(73B)	1.028 (70)
P(1)-C(21)	1.843 (5)	B(4)-B(9)	1.780 (12)	C(41)-C(42)	1.542 (10)	C(73)-C(81)	1.511 (10)
P(1)-C(31)	1.828 (4)	B(4)-H(4)	1.141 (67)	C(41)-C(46)	1.503 (10)	C(8)-C(74)	1.539 (9)
P(2)-C(41)	1.861 (7)	B(5)-B(6)	1.818 (11)	C(42)-C(43)	1.533 (12)	C(74)-H(74A)	1.038 (61)
P(2)-C(51)	1.864 (8)	B(5)-B(9)	1.736 (11)	C(43)-C(44)	1.482 (13)	C(74)-H(74B)	1.002 (71)
P(2)-C(61)	1.861 (7)	B(5)-B(10)	1.789 (12)	C(44)-C(45)	1.493 (12)	C(74)-C(82)	1.500 (10)
B(1)-B(2)	1.730 (12)	B(5)-H(5)	1.076 (42)	C(45)-C(46)	1.532 (11)	C(83)-H(83)	0.892 (55)
B(1)-B(3)	1.747 (11)	B(6)-B(10)	1.712 (11)	C(51)-H(51)	1.060 (73)	C(83)-C(84)	1.377 (13)
B(1)-B(4)	1.775 (12)	B(6)-B(11)	1.754 (10)	C(51)-C(52)	1.507 (9)	C(83)-C(82)	1.381 (10)
B(1)-B(5)	1.778 (11)	B(6)-H(6)	1.167 (47)	C(51)-C(56)	1.520 (10)	C(84)-H(84)	0.849 (84)
B(1)-B(6)	1.770 (12)	C(7)-C(8)	1.558 (9)	C(52)-C(53)	1.500 (11)	C(84)-C(85)	1.370 (14)
B(1)-H(1)	1.017 (57)	C(7)-B(11)	1.602 (10)	C(53)-C(54)	1.503 (11)	C(85)-C(86)	1.389 (12)
B(2)-B(3)	1.719 (12)	C(7)-C(73)	1.527 (9)	C(54)-C(55)	1.449 (12)	C(85)-H(85)	1.013 (85)
B(2)-B(6)	1.760 (11)	C(8)-B(9)	1.626 (10)	C(55)-C(56)	1.552 (13)	C(86)-H(86)	0.986 (61)
B(2)-C(7)	1.725 (10)	C(8)-C(74)	1.539 (9)	C(61)-H(61)	0.958 (74)	C(81)-C(82)	1.381 (10)
B(2)-B(11)	1.811 (12)	B(9)-B(10)	1.811 (12)	C(61)-C(62)	1.528 (10)	C(81)-C(86)	1.396 (11)

Angles

P(1)-Rh-P(2)	99.3 (1)		
P(1)-Rh-B(6)	149.0 (2)	Rh-B(10)-H(10)	47.3 (26)
P(2)-Rh-B(6)	111.3 (2)	B(5)-B(10)-H(10)	117.4 (27)
P(1)-Rh-B(10)	106.7 (2)	B(6)-B(10)-H(10)	113.8 (27)
P(2)-Rh-B(10)	153.0 (2)	B(9)-B(10)-H(10)	129.6 (27)
B(6)-Rh-B(10)	42.4 (3)	B(11)-B(10)-H(10)	123.4 (27)
P(1)-Rh-H(6)	177.4 (14)	Rh-B(10)-HB	116.2 (34)
P(2)-Rh-H(6)	82.6 (14)	B(5)-B(10)-HB	138.5 (35)
B(6)-Rh-H(6)	29.5 (14)	B(6)-B(10)-HB	114.4 (35)
B(10)-Rh-H(6)	71.7 (14)	B(9)-B(10)-HB	87.7 (34)
P(1)-Rh-H(10)	80.2 (16)	B(11)-B(10)-HB	55.5 (34)
P(2)-Rh-H(10)	177.3 (16)	H(10)-B(10)-HB	101.8 (43)
B(6)-Rh-H(10)	69.1 (16)	Rh-B(11)-B(2)	103.6 (4)
B(10)-Rh-H(10)	27.0 (16)	Rh-B(11)-B(6)	48.2 (3)
H(6)-Rh-H(10)	98.1 (22)	B(2)-B(11)-B(6)	59.1 (4)
Rh-P(1)-C(11)	112.6 (1)	Rh-B(11)-C(7)	149.1 (5)
Rh-P(1)-C(21)	110.0 (2)	B(2)-B(11)-C(7)	60.4 (4)
C(11)-P(1)-C(21)	103.9 (2)	B(6)-B(11)-C(7)	104.2 (5)
Rh-P(1)-C(31)	125.7 (1)	Rh-B(11)-B(10)	50.5 (3)
C(11)-P(1)-C(31)	100.4 (2)	B(2)-B(11)-B(10)	106.1 (5)
C(21)-P(1)-C(31)	101.6 (2)	B(6)-B(11)-B(10)	56.6 (4)
Rh-P(2)-C(41)	114.5 (2)	C(7)-B(11)-B(10)	105.7 (5)
Rh-P(2)-C(51)	112.9 (2)	Rh-B(11)-H(11)	87.2 (26)
C(41)-P(2)-C(51)	104.7 (3)	B(2)-B(11)-H(11)	118.7 (26)
Rh-P(2)-C(61)	115.0 (2)	C(7)-B(11)-H(11)	123.4 (26)
C(41)-P(2)-C(61)	105.0 (3)	B(10)-B(11)-H(11)	124.8 (26)
C(51)-P(2)-C(61)	103.7 (3)	Rh-B(11)-HB	72.4 (24)
B(2)-B(1)-B(3)	59.3 (5)	B(2)-B(11)-HB	132.8 (24)
B(2)-B(1)-B(4)	108.3 (6)	B(6)-B(11)-HB	91.4 (24)
B(3)-B(1)-B(4)	59.5 (5)	C(7)-B(11)-HB	98.6 (24)
B(2)-B(1)-B(5)	110.7 (6)	B(10)-B(11)-HB	34.8 (24)
B(3)-B(1)-B(5)	106.5 (6)	H(11)-B(11)-HB	108.2 (35)
B(4)-B(1)-B(5)	58.4 (5)	P(1)-C(11)-C(12)	121.4 (3)
B(2)-B(1)-B(6)	60.4 (5)	P(1)-C(11)-C(16)	118.6 (3)
B(3)-B(1)-B(6)	105.7 (6)	P(1)-C(21)-C(22)	120.8 (3)
B(4)-B(1)-B(6)	106.8 (6)	P(1)-C(21)-C(26)	119.1 (3)
B(5)-B(1)-B(6)	61.7 (5)	P(1)-C(31)-C(32)	119.6 (3)
B(2)-B(1)-H(1)	117.6 (33)	P(1)-C(31)-C(36)	120.3 (3)
B(3)-B(1)-H(1)	124.0 (33)	P(2)-C(41)-H(41)	106.5 (34)
B(4)-B(1)-H(1)	125.8 (33)	P(2)-C(41)-C(42)	117.6 (5)
B(5)-B(1)-H(1)	122.4 (33)	H(41)-C(41)-C(42)	93.0 (34)
B(6)-B(1)-H(1)	119.9 (33)	P(2)-C(41)-C(46)	113.2 (5)
B(1)-B(2)-B(3)	60.9 (5)	H(41)-C(41)-C(46)	114.7 (34)
B(1)-B(2)-B(6)	60.9 (5)	C(42)-C(41)-C(46)	110.4 (6)
B(3)-B(2)-B(6)	107.4 (6)	C(41)-C(42)-H(42A)	109.1 (7)
B(1)-B(2)-C(7)	104.5 (6)	C(41)-C(42)-H(42B)	109.1 (7)
B(3)-B(2)-C(7)	59.6 (4)	C(41)-C(42)-C(43)	110.9 (7)
B(6)-B(2)-C(7)	99.0 (5)	H(42A)-C(42)-C(43)	109.2 (7)
B(1)-B(2)-B(11)	108.3 (6)	H(42B)-C(42)-C(43)	109.1 (7)
B(3)-B(2)-B(11)	105.7 (6)	C(42)-C(43)-H(43A)	109.0 (7)
B(6)-B(2)-B(11)	58.8 (4)	C(42)-C(43)-H(43B)	109.1 (7)
C(7)-B(2)-B(11)	53.8 (4)	C(42)-C(43)-C(44)	111.3 (7)
B(1)-B(2)-H(2)	130.4 (28)	C(44)-C(43)-H(43A)	109.0 (8)

Table II (*Continued*)

B(3)-B(2)-H(2)	123.9 (28)	C(44)-C(43)-H(43B)	109.0 (8)
B(6)-B(2)-H(2)	126.0 (28)	C(43)-C(44)-H(44A)	108.9 (8)
C(7)-B(2)-H(2)	119.8 (27)	C(43)-C(44)-H(44B)	109.0 (8)
B(11)-B(2)-H(2)	115.2 (27)	C(43)-C(44)-C(45)	111.6 (8)
B(1)-B(3)-B(2)	59.9 (5)	C(45)-C(44)-H(44A)	108.9 (8)
B(1)-B(3)-B(4)	61.0 (5)	C(45)-C(44)-H(44B)	109.0 (8)
B(2)-B(3)-B(4)	110.0 (6)	C(44)-C(45)-H(45A)	109.0 (7)
B(1)-B(3)-C(7)	104.3 (5)	C(44)-C(45)-H(45B)	108.9 (7)
B(2)-B(3)-C(7)	60.4 (4)	C(44)-C(45)-C(46)	111.4 (7)
B(4)-B(3)-C(7)	103.9 (5)	C(46)-C(45)-H(45A)	109.0 (7)
B(1)-B(3)-C(8)	103.4 (5)	C(46)-C(45)-H(45B)	109.0 (7)
B(2)-B(3)-C(8)	103.3 (5)	C(41)-C(46)-C(45)	112.1 (6)
B(4)-B(3)-C(8)	59.2 (4)	C(41)-C(46)-H(46A)	108.8 (6)
C(7)-B(3)-C(8)	53.6 (4)	C(41)-C(46)-H(46B)	108.8 (6)
B(1)-B(3)-H(3)	133.1 (28)	C(45)-C(46)-H(46A)	108.8 (6)
B(2)-B(3)-H(3)	120.0 (28)	C(45)-C(46)-H(46B)	108.8 (6)
B(4)-B(3)-H(3)	126.9 (28)	P(2)-C(51)-H(51)	103.4 (38)
C(7)-B(3)-H(3)	115.0 (28)	P(2)-C(51)-C(52)	111.8 (5)
C(8)-B(3)-H(3)	119.9 (28)	H(51)-C(51)-C(52)	110.5 (39)
B(1)-B(4)-B(3)	59.5 (5)	P(2)-C(51)-C(56)	118.4 (5)
B(1)-B(4)-B(5)	60.9 (5)	C(56)-C(51)-H(51)	100.3 (39)
B(3)-B(4)-B(5)	108.5 (6)	C(56)-C(51)-C(52)	111.4 (6)
B(1)-B(4)-C(8)	102.9 (6)	C(51)-C(52)-H(52A)	108.7 (6)
B(3)-B(4)-C(8)	60.2 (4)	C(51)-C(52)-H(52B)	108.6 (6)
B(5)-B(4)-C(8)	100.7 (5)	C(51)-C(52)-C(53)	112.8 (6)
B(1)-B(4)-B(9)	107.4 (6)	H(52A)-C(52)-C(53)	108.6 (6)
B(3)-B(4)-B(9)	107.7 (6)	H(52B)-C(52)-C(53)	108.6 (6)
B(5)-B(4)-B(9)	59.2 (5)	C(52)-C(53)-H(53A)	108.8 (6)
C(8)-B(4)-B(9)	55.2 (4)	C(52)-C(53)-H(53B)	108.9 (6)
B(1)-B(4)-H(4)	128.5 (31)	C(52)-C(53)-C(54)	111.9 (7)
B(3)-B(4)-H(4)	118.0 (31)	C(54)-C(53)-H(53A)	108.9 (7)
B(5)-B(4)-H(4)	128.9 (31)	C(54)-C(53)-H(53B)	108.9 (7)
C(8)-B(4)-H(4)	119.8 (31)	C(53)-C(54)-H(54A)	108.5 (7)
B(9)-B(4)-H(4)	119.9 (31)	C(53)-C(54)-H(54B)	108.7 (7)
B(1)-B(5)-B(4)	60.7 (5)	C(53)-C(54)-C(55)	112.7 (7)
B(1)-B(5)-B(6)	58.9 (4)	C(55)-C(54)-H(54A)	108.6 (8)
B(4)-B(5)-B(6)	106.5 (6)	C(55)-C(54)-H(54B)	108.7 (8)
B(1)-B(5)-B(9)	109.2 (6)	C(54)-C(55)-H(55A)	108.5 (8)
B(4)-B(5)-B(9)	61.8 (5)	C(54)-C(55)-H(55B)	108.6 (8)
B(6)-B(5)-B(9)	104.9 (5)	C(54)-C(55)-C(56)	113.1 (8)
B(1)-B(5)-B(10)	107.3 (6)	C(56)-C(55)-H(55A)	108.6 (8)
B(4)-B(5)-B(10)	111.2 (6)	C(56)-C(55)-H(55B)	108.5 (8)
B(6)-B(5)-B(10)	56.7 (4)	C(51)-C(56)-C(55)	109.9 (7)
B(9)-B(5)-B(10)	61.8 (5)	C(51)-C(56)-H(56A)	109.4 (7)
B(1)-B(5)-H(5)	122.0 (24)	C(55)-C(56)-H(56A)	109.4 (7)
B(4)-B(5)-H(5)	129.0 (24)	C(51)-C(56)-H(56B)	109.3 (7)
B(6)-B(5)-H(5)	116.8 (24)	C(55)-C(56)-H(56B)	109.3 (7)
B(9)-B(5)-H(5)	125.2 (24)	P(2)-C(61)-H(61)	106.6 (44)
B(10)-B(5)-H(5)	114.4 (24)	P(2)-C(61)-C(62)	112.8 (5)
Rh-B(6)-B(1)	151.3 (5)	C(62)-C(61)-H(61)	107.1 (44)
Rh-B(6)-B(2)	148.4 (5)	P(2)-C(61)-C(66)	113.6 (5)
B(1)-B(6)-B(2)	58.7 (5)	C(66)-C(61)-H(61)	105.1 (45)
Rh-B(6)-B(5)	102.2 (4)	C(62)-C(61)-C(66)	111.1 (6)
B(1)-B(6)-B(5)	59.4 (4)	C(61)-C(62)-H(62A)	109.0 (6)
B(2)-B(6)-B(5)	107.5 (5)	C(61)-C(62)-H(62B)	109.1 (6)
Rh-B(6)-B(10)	70.7 (4)	C(61)-C(62)-C(63)	111.1 (6)
B(1)-B(6)-B(10)	111.2 (6)	H(62A)-C(62)-C(63)	109.0 (6)
B(2)-B(6)-B(10)	114.9 (6)	H(62B)-C(62)-C(63)	109.2 (6)
B(5)-B(6)-B(10)	60.8 (4)	C(62)-C(63)-H(63A)	108.8 (7)
Rh-B(6)-B(11)	97.7 (4)	C(62)-C(63)-H(63B)	108.9 (7)
B(1)-B(6)-B(11)	109.0 (5)	C(62)-C(63)-C(64)	111.8 (7)
B(2)-B(6)-B(11)	62.0 (5)	C(64)-C(63)-H(63A)	108.9 (7)
B(5)-B(6)-B(11)	109.9 (5)	C(64)-C(63)-H(63B)	108.9 (7)
B(10)-B(6)-B(11)	64.5 (5)	C(63)-C(64)-H(64A)	108.9 (7)
Rh-B(6)-H(6)	51.0 (23)	C(63)-C(64)-H(64B)	108.9 (7)
B(1)-B(6)-H(6)	116.5 (23)	C(63)-C(64)-C(65)	111.7 (7)
B(2(-B(6)-H(6)	118.1 (23)	H(64A)-C(64)-C(65)	108.8 (7)
B(5)-B(6)-H(6)	120.7 (23)	H(64B)-C(64)-C(65)	109.0 (7)
B(10)-B(6)-H(6)	121.3 (23)	C(64)-C(65)-H(65A)	109.3 (7)
B(11)-B(6)-H(6)	123.8 (23)	C(64)-C(65)-H(65B)	109.3 (7)
B(2)-C(7)-B(3)	60.0 (4)	C(64)-C(65)-C(66)	110.1 (7)
B(2)-C(7)-C(8)	111.4 (5)	C(66)-C(65)-H(65A)	109.3 (7)
B(3)-C(7)-C(8)	64.2 (4)	C(66)-C(65)-H(65B)	109.3 (7)
B(2)-C(7)-B(11)	65.8 (5)	C(61)-C(66)-C(65)	111.2 (6)
B(3)-C(7)-B(11)	116.2 (5)	C(61)-C(66)-H(66A)	109.1 (6)
C(8)-C(7)-B(11)	111.7 (5)	C(65)-C(66)-H(66A)	109.1 (6)
B(2)-C(7)-C(73)	123.0 (6)	C(61)-C(66)-H(66B)	109.0 (6)
B(3)-C(7)-C(73)	115.9 (5)	C(65)-C(66)-H(66B)	109.0 (6)
C(8)-C(7)-C(73)	115.1 (5)	C(7)-C(73)-H(73A)	104.2 (40)

Table II (*Continued*)

B(11)-C(7)-C(73)	120.6 (6)	C(7)-C(73)-H(73B)	103.9 (37)
B(3)-C(8)-B(4)	60.6 (4)	H(73A)-C(73)-H(73B)	118.4 (54)
B(3)-C(8)-C(7)	62.2 (4)	C(7)-C(73)-C(81)	109.7 (6)
B(4)-C(8)-C(7)	112.2 (5)	C(81)-C(73)-H(73A)	108.2 (40)
B(3)-C(8)-B(9)	115.4 (5)	C(81)-C(73)-H(73B)	112.0 (37)
B(4)-C(8)-B(9)	64.1 (5)	C(8)-C(74)-H(74A)	107.5 (33)
C(7)-C(8)-B(9)	116.0 (5)	C(8)-C(74)-H(74B)	103.9 (39)
B(3)-C(8)-C(74)	115.5 (5)	H(74A)-C(74)-H(74B)	110.9 (51)
B(4)-C(8)-C(74)	121.6 (6)	C(8)-C(74)-C(82)	110.6 (6)
C(7)-C(8)-C(74)	113.7 (5)	C(82)-C(74)-H(74A)	110.9 (33)
B(9)-C(8)-C(74)	120.4 (6)	C(82)-C(74)-H(74B)	112.7 (39)
B(4)-B(9)-B(5)	59.0 (5)	C(84)-C(83)-H(83)	122.0 (35)
B(4)-B(9)-C(8)	60.7 (4)	C(82)-C(83)-H(83)	117.6 (35)
B(5)-B(9)-C(8)	104.7 (5)	C(82)-C(83)-C(84)	120.0 (8)
B(4)-B(9)-B(10)	108.0 (5)	C(83)-C(84)-H(84)	115.2 (60)
B(5)-B(9)-B(10)	60.5 (4)	C(83)-C(84)-C(85)	120.8 (9)
C(8)-B(9)-B(10)	103.5 (5)	H(84)-C(84)-C(85)	123.9 (60)
B(4)-B(9)-H(9)	119.3 (29)	C(84)-C(85)-C(86)	119.6 (9)
B(5)-B(9)-H(9)	125.2 (29)	C(84)-C(85)-H(85)	128.1 (48)
C(8)-B(9)-H(9)	121.4 (29)	C(86)-C(85)-H(85)	112.3 (48)
B(10)-B(9)-H(9)	125.8 (29)	C(81)-C(86)-C(85)	120.0 (8)
Rh-B(10)-B(5)	100.8 (4)	C(85)-C(86)-H(86)	121.5 (35)
Rh-B(10)-B(6)	66.9 (4)	C(81)-C(86)-H(86)	118.5 (35)
B(5)-B(10)-B(6)	62.5 (5)	C(73)-C(81)-C(86)	121.2 (7)
Rh-B(10)-B(9)	156.1 (5)	C(73)-C(81)-C(82)	119.3 (6)
B(5)-B(10)-B(9)	57.7 (4)	C(82)-C(81)-C(86)	119.5 (7)
B(6)-B(10)-B(9)	106.2 (5)	C(74)-C(82)-C(83)	121.9 (6)
Rh-B(10)-B(11)	93.0 (4)	C(74)-C(82)-C(81)	118.0 (6)
B(5)-B(10)-B(11)	106.9 (5)	C(81)-C(82)-C(83)	120.1 (6)
B(6)-B(10)-B(11)	58.8 (4)	Rh-H(6)-B(6)	99.5 (29)
B(9)-B(10)-B(11)	102.9 (5)	Rh-H(10)-B(10)	105.7 (35)
		B(10)-HB-B(11)	89.7 (42)

[a] Esd in parentheses in units of least significant digit of the corresponding value.

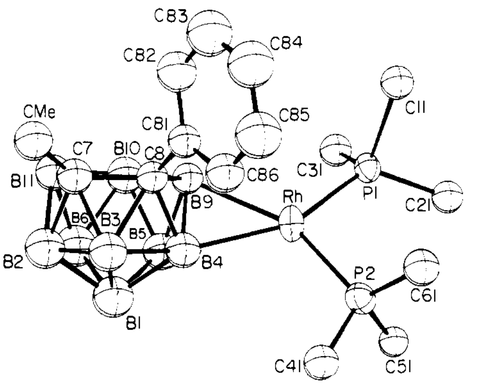

Figure 4. Molecular structure of [*exo-nido*-4,9-{$(PPh_3)_2Rh$}-4,9-μ-$(H)_2$-7-Me-8-Ph-7,8-$C_2B_9H_8$] (III). Thermal ellipsoids are depicted at the 50% probability level. All hydrogen atoms and the phenyl groups of the triphenylphosphine ligands have been omitted for clarity.

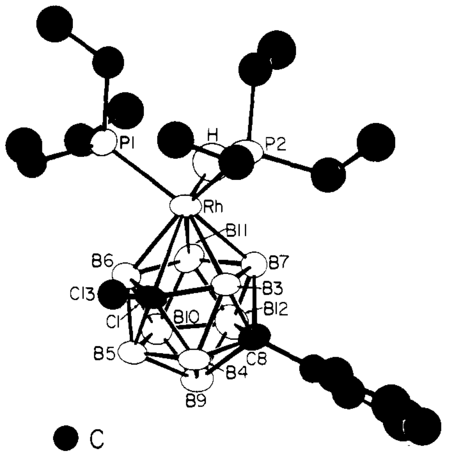

Figure 5. Molecular structure of [*closo*-1-Me-2,2-$(PEt_3)_2$-2-H-8-Ph-2,1,8-$RhC_2B_9H_9$] (IV). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms, with the exception of the terminal hydride, have been omitted for clarity.

In III, Rh is joined to the cage through two boron atoms which are adjacent to the phenyl-bonded carbon atom: B(9) on the open C_2B_3 face and B(4) on the lower B_5 belt, parallel to that face, at distances of 2.40 (1) and 2.36 (1) Å, respectively. These distances are somewhat longer than Rh(III)-B distances found in the closo compound (I) of 2.24 (1), 2.23 (1), and 2.33 (1) Å, but are very similar to those found in the exo-nido compound (II) where Rh-B is 2.338 (8) and 2.398 (8) Å. Rh-P distances in III are 2.231 (4) and 2.232 (5) Å while in II they are 2.247 (2) and 2.256 (2) Å and in the closo compound (I) they are 2.335 (3) and 2.324 (3) Å. In each compound, P-Rh-P is nearly orthogonal, 95.6 (1)° (III), 99.3 (1)° (II), and 98.7 (1)° (I), respectively. In III B(4) is approximately trans to P(1), B(4)-Rh-P(1) 151.6 (4)°, and cis to P(2), B(4)-Rh-P(2) 111.9 (3)°, and B(9) is approximately trans to P(2), B(9)-Rh-P(2) 154.9 (3)° and cis to P(1), B(9)-Rh-P(1) 109.3 (3)°. The hydrogen atoms bridging B(10) and either B(9) or B(11) and Rh and B(4) were not located although the hydrogen bridging the Rh and B(9) was evident. The B(10)-B(11) distance, 1.84 (2) Å, is not significantly different from B(9)-B(10), 1.81 (2) Å, but is not normally found to be appreciably affected by the presence of B-H-B bridges.

Although the bridging B-H-B proton on the open pentagonal face of the carborane cage was not located, spectroscopic data clearly indicated its presence.[1] The carborane cage retains the expected geometry of an 11-vertex icosahedral fragment, with no significant distortions induced by the exopolyhedral metal moiety; i.e., the geometry of this fragment is not unlike that found in *closo*-3,1,2-RhC_2B_9 icosahedra. Furthermore, a recent crystallographic study[11] of [*exo-nido*-4,9-{$(H)_2(P(p\text{-tolyl})_3)_2Ir$}-4,9-$\mu$-$(H)_2$-7,8-$C_2B_9H_{10}$] (IIa) showed it to possess entirely analogous metal-cage bonding interactions, and in this case both M-H-B hydrogen atoms were located.

Unlike the *exo-nido*-Rh (1+) structures, the formal iridium (3+) complex (IIa) has two mutually cis terminal hydride ligands (not located crystallographically) bonded to Ir; thus the configuration around Ir would be expected to differ from that around Rh. However, there are many similarities, including the near

Table III. Interatomic Distances (A) and Angles (deg) in [*exo-nido*-4,9-{$(PPh_3)_2Rh$}-4,9-μ-$(H)_2$-7-Me-8-Ph-7,8-$C_2B_9H_8$] (III)

Interatomic Distances

Rh-P(1)	2.231 (4)	B(1)-B(3)	1.76 (2)	B(5)-B(6)	1.82 (2)	C(7)-C(8)	1.60 (1)
Rh-P(2)	2.232 (5)	B(1)-B(4)	1.74 (2)	B(5)-B(9)	1.77 (2)	C(7)-B(11)	1.63 (2)
Rh-B(4)	2.36 (1)	B(1)-B(5)	1.77 (2)	B(5)-B(10)	1.81 (2)	C(7)-CMe	1.47 (2)
Rh-B(9)	2.40 (1)	B(1)-B(6)	1.85 (2)	B(5)-H(5)	1.02 (9)	C(8)-B(9)	1.62 (1)
Rh-H(9)	1.92 (8)	B(1)-H(1)	1.25 (9)	B(6)-B(10)	1.83 (2)	C(8)-C(71)	1.49 (1)
P(1)-C(11)	1.835 (5)	B(3)-B(4)	1.79 (2)	B(6)-B(11)	1.79 (2)	B(9)-B(10)	1.81 (2)
P(1)-C(21)	1.845 (5)	B(3)-C(7)	1.76 (1)	B(2)-B(3)	1.70 (2)	B(9)-H(9)	1.00 (8)
P(1)-C(31)	1.828 (6)	B(3)-C(8)	1.82 (2)	B(2)-B(6)	1.78 (2)	B(10)-B(11)	1.84 (2)
P(2)-C(41)	1.837 (6)	B(4)-B(5)	1.76 (2)	B(2)-C(7)	1.70 (2)	B(10)-H(10)	0.99 (8)
P(2)-C(51)	1.817 (5)	B(4)-C(8)	1.74 (1)	B(2)-B(11)	1.79 (2)	B(11)-H(11)	1.19 (8)
B(1)-B(2)	1.78 (2)	B(4)-B(9)	1.74 (1)	B(2)-H(2)	1.12 (9)		

Angles

P(1)-Rh-P(2)	95.6 (1)	B(5)-B(6)-B(10)	59.6 (7)
P(1)-Rh-B(4)	151.6 (4)	B(2)-B(6)-B(10)	109.9 (10)
P(2)-Rh-B(4)	111.9 (3)	B(1)-B(6)-B(11)	105.6 (10)
P(1)-Rh-B(9)	109.3 (3)	B(5)-B(6)-B(11)	104.7 (9)
P(2)-Rh-B(9)	154.9 (3)	B(2)-B(6)-B(11)	60.1 (7)
B(4)-Rh-B(9)	43.0 (3)	B(10)-B(6)-B(11)	61.1 (7)
P(1)-Rh-H(9)	90 (4)	B(1)-B(2)-B(3)	60.8 (8)
P(2)-Rh-H(9)	169 (4)	B(1)-B(2)-B(6)	62.6 (8)
B(4)-Rh-H(9)	64 (6)	B(3)-B(2)-B(6)	112.3 (11)
B(9)-Rh-H(9)	24 (5)	B(1)-B(2)-C(7)	107.7 (10)
Rh-P(1)-C(11)	114.2 (2)	B(3)-B(2)-C(7)	62.3 (7)
Rh-P(1)-C(21)	124.2 (2)	B(6)-B(2)-C(7)	105.5 (9)
C(11)-P(1)-C(21)	101.8 (3)	B(1)-B(2)-B(11)	108.7 (10)
Rh-P(1)-C(31)	108.7 (3)	B(3)-B(2)-B(11)	108.8 (10)
C(11)-P(1)-C(31)	103.4 (3)	B(6)-B(2)-B(11)	60.0 (8)
C(21)-P(1)-C(31)	102.1 (3)	C(7)-B(2)-B(11)	55.8 (7)
Rh-P(2)-C(41)	113.6 (3)	H(2)-B(2)-B(1)	129 (4)
Rh-P(2)-C(51)	112.3 (3)	H(2)-B(2)-B(3)	121 (5)
C(41)-P(2)-C(51)	103.5 (3)	H(2)-B(2)-B(6)	123 (4)
Rh-P(2)-C(61)	115.1 (2)	H(2)-B(2)-C(7)	116 (4)
C(41)-P(2)-C(61)	100.1 (3)	H(2)-B(2)-B(11)	116 (5)
C(51)-P(2)-C(61)	111.1 (3)	B(2)-C(7)-B(3)	58.9 (8)
B(3)-B(1)-B(4)	61.4 (8)	B(3)-C(7)-C(8)	65.1 (6)
B(3)-B(1)-B(5)	109.4 (10)	B(2)-C(7)-C(8)	109.4 (8)
B(4)-B(1)-B(5)	60.1 (7)	B(3)-C(7)-B(11)	113.3 (9)
B(3)-B(1)-B(6)	106.5 (10)	B(2)-C(7)-B(11)	64.7 (7)
B(4)-B(1)-B(6)	107.4 (10)	C(8)-C(7)-B(11)	106.8 (8)
B(5)-B(1)-B(6)	60.3 (8)	B(3)-C(7)-CMe	116.9 (8)
B(2)-B(1)-B(3)	57.5 (8)	B(2)-C(7)-CMe	121.6 (9)
B(2)-B(1)-B(4)	105.5 (10)	C(8)-C(7)-CMe	120.1 (9)
B(2)-B(1)-B(5)	106.6 (10)	B(11)-C(7)-CMe	121.6 (9)
B(2)-B(1)-B(6)	58.9 (8)	B(3)-C(8)-B(4)	60.3 (7)
B(1)-B(3)-B(4)	58.7 (7)	B(3)-C(8)-C(7)	61.7 (6)
B(1)-B(3)-B(2)	61.8 (8)	B(4)-C(8)-C(7)	111.2 (7)
B(2)-B(3)-B(4)	106.7 (10)	B(3)-C(8)-B(9)	113.6 (8)
B(1)-B(3)-C(7)	105.8 (10)	B(4)-C(*)-B(9)	62.4 (5)
B(4)-B(3)-C(7)	102.2 (8)	C(7)-C(8)-B(9)	115.7 (8)
B(2)-B(3)-C(7)	58.8 (7)	B(3)-C(8)-C(71)	116.5 (7)
B(1)-B(3)-C(8)	102.0 (9)	B(4)-C(8)-C(71)	119.0 (6)
B(4)-B(3)-C(8)	57.9 (7)	C(7)-C(8)-C(71)	117.7 (8)
B(2)-B(3)-C(8)	100.0 (9)	B(9)-C(8)-C(71)	118.8 (8)
C(7)-C(3)-C(8)	53.2 (6)	Rh-B(9)-B(4)	67.1 (5)
Rh-B(4)-B(1)	145.4 (8)	Rh-B(9)-B(5)	91.1 (6)
Rh-B(4)-B(3)	154.6 (8)	Rh-B(9)-C(8)	103.6 (6)
B(1)-B(4)-B(3)	59.9 (8)	B(4)-B(9)-B(5)	60.0 (6)
Rh-B(4)-B(5)	93.0 (7)	B(4)-B(9)-C(8)	62.3 (6)
B(1)-B(4)-B(5)	60.7 (7)	B(5)-B(9)-C(8)	107.3 (8)
B(3)-B(4)-B(5)	108.8 (9)	Rh-B(9)-B(10)	143.2 (7)
Rh-B(4)-C(8)	101.4 (5)	B(4)-B(9)-B(10)	110.8 (8)
B(1)-B(4)-C(8)	105.9 (8)	B(5)-B(9)-B(10)	60.8 (7)
B(3)-B(4)-C(8)	61.8 (7)	C(8)-B(9)-B(10)	107.2 (8)
B(5)-B(4)-C(8)	102.5 (7)	H(9)-B(9)-Rh	50 (5)
Rh-B(4)-B(9)	69.9 (6)	H(9)-B(9)-B(4)	112 (5)
B(1)-B(4)-B(9)	109.5 (9)	H(9)-B(9)-B(5)	134 (5)
B(3)-B(4)-B(9)	109.0 (8)	H(9)-B(9)-C(8)	106 (5)
B(5)-B(4)-B(9)	60.7 (6)	H(9)-B(9)-B(10)	134 (5)
C(8)-B(4)-B(9)	55.3 (5)	B(6)-B(10)-B(5)	59.8 (7)
B(1)-B(5)-B(4)	59.1 (7)	B(5)-B(10)-B(9)	58.4 (6)
B(1)-B(5)-B(6)	62.1 (8)	B(6)-B(10)-B(9)	104.3 (9)
B(4)-B(5)-B(6)	108.0 (9)	B(5)-B(10)-B(11)	102.8 (8)
B(1)-B(5)-B(9)	107.1 (9)	B(6)-B(10)-B(11)	58.2 (7)
B(4)-B(5)-B(9)	59.3 (6)	B(9)-B(10)-B(11)	99.1 (8)
B(6)-B(5)-B(9)	106.6 (9)	B(5)-B(10)-H(10)	111 (5)
B(1)-B(5)-B(10)	112.2 (9)	B(6)-B(10)-H(10)	116 (5)
B(4)-B(5)-B(10)	110.2 (9)	B(9)-B(10)-H(10)	124 (5)

Table III (*Continued*)

B(6)-B(5)-B(10)	60.6 (7)	B(11)-B(10)-H(10)	135 (5)
B(9)-B(5)-B(10)	60.7 (7)	B(6)-B(11)-B(2)	59.9 (8)
H(5)-B(5)-B(1)	98 (5)	B(6)-B(11)-C(7)	108.4 (9)
H(5)-B(5)-B(4)	115 (5)	B(2)-B(11)-C(7)	59.5 (7)
H(5)-B(5)-B(6)	111 (5)	B(6)-B(11)-B(10)	60.7 (7)
H(5)-B(5)-B(9)	142 (6)	B(2)-B(11)-B(10)	109.5 (9)
H(5)-B(5)-B(10)	134 (5)	C(7)-B(11)-B(10)	111.0 (9)
B(1)-B(6)-B(5)	57.6 (7)	B(6)-B(11)-H(11)	119 (4)
B(1)-B(6)-B(2)	58.6 (8)	B(2)-B(11)-H(11)	119 (4)
B(2)-B(6)-B(5)	104.2 (10)	C(7)-B(11)-H(11)	122 (4)
B(1)-B(6)-B(10)	107.6 (10)	B(1)-B(11)-H(11)	121 (4)
		Rh-H(9)-B(9)	106 (6)

orthogonality of H-M-P, 94 (2) and 95 (3)° in IIa, 90 (4)° in III, and 83 (1) and 80 (2)° in II. In the latter two, H is also trans to the other phosphorus atom, H-Rh-P is 169 (4)° in III and 177 (1) and 177 (2)° in II. Angles around the bridging M-H-B hydride are also similar: 98 (4) and 94 (6)° in IIa, 106 (6)° in III, and 100 (3)° and 105 (3)° in II. The B-M-B angles in the three compounds are also notably similar: 40.8 (4)° in IIa, 43.0 (3)° in III, and 42.4 (3)° in II. The M-H distances are nearly the same, 1.92 (8) Å in III and 1.84 (5) and 1.83 (5) Å in II.

Molecular Structure of [*closo*-1-Me-2,2-$(PEt_3)_2$-2-H-8-Ph-2,1,8-$RhC_2B_9H_9$] (IV). Polytopal rearrangement is a common reaction in both carborane and metallacarborane chemistry.[18] The carbon atoms are generally found to migrate apart, and the driving force for the rearrangements is partially due to the electrostatic repulsion between the formally electropositive carbon atoms.[19] For example, the predicted[20,21] and the observed[22,23] ordering of stability for the *closo*-$C_2B_{10}H_{12}$ isomers is 1,2- < 1,7- < 1,12-$C_2B_{10}H_{12}$. Although Coulombic considerations are undoubtedly important, steric repulsions of the substituents on adjacent polyhedral carbon atoms are often found to play a crucial role. For example, the cisoid isomer of [3-$(1,2\text{-}Me_2C_2B_9H_9)_2Ni^{IV}$], in which the cage carbon atoms are almost eclipsed, undergoes a remarkably facile carbon atom migration at 0 °C to produce the isomer in which one of the C-Me vertices has moved away from the C-Me groups on the adjacent polyhedron.[24] In contrast to this, the unsubstituted complex [3-$(1,2\text{-}C_2B_9H_{11})_2Ni^{IV}$] is found to rearrange only when heated to 300 °C in vacuo. Consequently, the formation[1] of IV from $[(PEt_3)_4Rh]^+$[*nido*-7-Me-8-Ph-7,8-$C_2B_9H_{10}]^-$ may involve the initial production of [*closo*-1-Me-2-Ph-3,3-$(PEt_3)_2$-3-H-3,1,2-$RhC_2B_9H_9$] which then undergoes rapid polytopal rearrangement. In order to obtain proof of this rearrangement, regardless of its mechanism, an X-ray diffraction study of IV was undertaken.

The molecular structure of IV is shown in Figure 5 and interatomic distances and angles are listed in Table IV. The most striking feature of the structure is the position of the two carbon atoms, which define the complex as a member of the closo 2,1,8-isomer series. The carbon vertex bearing the phenyl substituent has migrated to a position on the lower pentagonal belt of the cage, nonadjacent to the methyl-substituted carbon or the rhodium. This results in a decrease in both electrostatic repulsions and steric interactions between the two substituted carbon atoms and the sterically encumbered $(PEt_3)_2RhH$ vertex. An X-ray diffraction study[25] of the complex obtained upon rearrangement of the 3,1,2-isomer of [*closo*-$(PPh_3)_2Ir(H)(C_2B_9H_{10}Ph)$] (IVa) proved it to be the 2,1,8-isomer (IVa) which results from migration of the phenyl-substituted carbon vertex to the lower belt.

Table IV. Selected Distances (Å) and Angles (deg) in [*closo*-1-Me-2,2-$(PEt_3)_2$-2-H-8-Ph-2,1,8-$RhC_2B_9H_9$] (IV)

A. Distances

Rh-P(1)	2.357 (1)	Rh-P(2)	2.346 (1)
Rh-H	1.530 (51)	Rh-C(1)'	2.332 (4)
Rh-B(3)	2.159 (5)	Rh-B(6)	2.207 (5)
Rh-B(7)	2.189 (5)	Rh-B(11)	2.221 (5)
P(1)-C(1)	1.847 (6)	P(1)-C(3)	1.840 (6)
P(1)-C(5)	1.846 (5)	P(2)-C(7)	1.827 (6)
P(2)-C(9)	1.843 (6)	P(2)-C(11)	1.847 (6)
C(1)-C(2)	1.519 (8)	C(3)-C(4)	1.507 (10)
C(5)-C(6)	1.501 (8)	C(7)-C(8)	1.454 (8)
C(9)-C(10)	1.518 (9)	C(11)-C(12)	1.478 (9)
C(1)'-C(13)	1.517 (6)	C(1)'-B(3)	1.681 (6)
C(1)'-B(4)	1.684 (6)	C(1)'-B(5)	1.699 (6)
C(1)'-B(6)	1.745 (7)	C(8)'-C(14)	1.509 (6)
C(8)'-B(3)	1.739 (6)	C(8)'-B(4)	1.696 (7)
C(8)'-B(7)	1.742 (6)	C(8)'-B(9)	1.739 (7)
C(8)'-B(12)	1.735 (7)	B(3)-B(4)	1.804 (6)
B(3)-B(7)	1.839 (7)	B(4)-B(5)	1.736 (8)
B(4)-B(9)	1.744 (8)	B(5)-B(6)	1.800 (7)
B(5)-B(9)	1.753 (8)	B(5)-B(10)	1.765 (8)
B(6)-B(10)	1.795 (7)	B(6)-B(11)	1.814 (7)
B(7)-B(11)	1.801 (7)	B(7)-B(12)	1.768 (7)
B(9)-B(10)	1.766 (8)	B(9)-B(12)	1.764 (8)
B(10)-B(11)	1.788 (8)	B(10)-B(12)	1.758 (9)
B(11)-B(12)	1.766 (8)	C(14)-C(15)	1.379 (7)
C(15)-C(16)	1.405 (8)	C(16)-C(17)	1.321 (8)
C(17)-C(18)	1.339 (9)	C(18)-C(19)	1.408 (9)

B. Angles

P(1)-Rh-P(2)	102.47 (4)	B(6)-Rh-B(11)	48.4 (2)
P(1)-Rh-H	79.5 (19)	B(7)-Rh-B(11)	48.2 (2)
P(2)-Rh-H	78.7 (18)	C(13)-C(1)'-Rh	114.7 (3)
C(1)'-Rh-B(3)	43.8 (2)	C(13)-C(1)'B(3)	122.1 (4)
C(1)'-Rh-B(6)	45.1 (2)	C(13)-C(1)'-B(4)	114.2 (4)
C(1)'-Rh-B(7)	79.6 (2)	C(13)-C(1)'-B(5)	113.7 (4)
C(1)'-Rh-B(11)	79.5 (2)	C(13)-C(1)'-B(6)	122.1 (4)
B(3)-Rh-B(6)	78.8 (2)	C(14)-C(8)'-B(3)	119.4 (3)
B(3)-Rh-B(7)	50.0 (2)	C(14)-C(8)'-B(4)	116.3 (4)
B(3)-Rh-B(11)	82.7 (2)	C(14)-C(8)'-B(7)	119.0 (4)
B(6)-Rh-B(7)	81.8 (2)	C(14)-C(8)'-B(9)	118.0 (4)
		C(14)-C(8)'-B(12)	121.0 (4)

As expected, the Rh atom in IV exhibits pseudooctahedral coordination; the carborane cage occupies three coordination sites and the two PEt_3 ligands and the hydride occupy the remaining sites. The Rh-H distance (1.53 (5) Å) is very similar to that found for [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (Ia) (1.54 (9) Å).[3] The structure also indicates that there is no fundamental distortion from the usual 12-vertex closo icosahedral geometry. Variable-temperature solution $^{31}P\{^1H\}$ NMR spectra of IV indicate the presence of hindered rotation of the $[P_2RhH)$ vertex with respect to the CB_4 face of the carborane ligand.[1]

Molecular Structure of $[Rh(PPh_3)_3]^+$[*nido*-7-(1'-*closo*-1',2'-$C_2B_{10}H_{11}$)-7,8-$C_2B_9H_{11}]^-$ (V). The $[Rh(PPh_3)_3]^+$ cation in V has the geometry previously described in the structural study of tris(triphenylphosphine)rhodium(I) perchlorate (Va).[26] The

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Table V. Comparison of Tris(triphenylphosphine)rhodium(I) Cation in the Perchlorate and [*nido*-7-(1′-*closo*-1′,2′-$C_2B_{10}H_{11}$)-7,8-$C_2B_9H_{11}$]$^-$ (V) Salts[a]

	ClO_4	V
Rh-P(1)[b]	2.21	2.212 (4)
Rh-P(3)[b]	2.24	2.236 (4)
Rh···C(91)[b]	2.48 (2)	2.502 (8)
Rh···C(92)[b]	2.62 (2)	2.611 (9)
Rh···H(92)[b]	2.56	2.57
P(3)-C(91)[b]	1.78	1.810 (9)
P(1)-Rh-P(2)[c]	97.7 (2)	99.5 (1)
P(1)-Rh-P(3)[c]	102.4 (2)	101.4 (1)
P(2)-Rh-P(3)[c]	159.3 (2)	158.2 (1)
Rh-P(3)-C(91)[c]	75.6 (5)	75.6 (3)
Rh-P(3)-C(71)[c]	124.3 (6)	123.3 (4)
Rh-P(3)-C(81)[c]	126.7 (5)	126.2 (3)
torsion angle Rh-P3-C91-C92[c]	57	60

[a] Numbering for the perchlorate salt has been changed to correspond to the numbering in V. [b] Distances in Å. [c] Angles in deg.

coordination about Rh is planar and approximately T-shaped, with a close approach of one phenyl ring to the metal atom, R···C(92) 2.611 (9) Å, Rh···C(91) 2.502 (8) Å, Rh···H(92) 2.57 Å (H in calculated position), and P(1)-Rh-P(2) 99.5 (1)°, P(1)-Rh-P(3) 101.4 (1)° and P(2)-Rh-P(3) 158.2 (1)°. The Rh-P(3)-C(91) angle is only 75.6 (3)°, while Rh-P(3)-C(71) and Rh-P(3)-C(81) are 126.2 (3) and 123.3 (4)°, respectively. Although the P-C bond is shortened in the ClO_4^- salt, the P(3)-C(91) bond in V is not unusual, 1.810 (9) Å. There are no close nonbonding contacts (<3.0 Å) between the cations, anions, or solvate. Features of the cation geometry of V and Va are summarized in Tables V and VI. The molecular structure is shown in Figure 6 and the detailed conformation about Rh is depicted in Figure 7.

Displacement of Substituents from Their Idealized Positions in Icosahedral Geometry. In the exo-nido structures we present here, substituents placed on the carbon atoms of the C_2B_3 face tend to be located farther from the C_2B_3 plane than are the corresponding substituents in closo complexes. For example, in III, the phenyl carbon and the methyl carbon which are bonded to the carborane cage are 0.770 and 0.668 Å, respectively, from the C_2B_3 plane. In II, the two methylene C atoms are 0.743 and 0.809 Å from the C_2B_3 plane. However, in I, the two methylene C atoms are only 0.522 and 0.517 Å from the C_2B_3 plane. Furthermore, the *o*-xylylene group extends to 4.452 and 4.478 Å from this plane for the exo-nido complex (II) and to 2.762 and 2.828 Å for the closo complex (I). In the closo compound (IV), the methyl carbon is only 0.420 Å from the C_2B_3 plane. The latter compound does not have the bulky PPh_3 and *o*-xylylene groups which are expected to affect the geometry of I. It thus appears as though substituents on the open nido face are preferentially directed toward the empty vertex.

Perhaps a better way to compare the positions of carbon substituents on an icosahedral carborane or an icosahedral fragment is to compare the angle between (1) the vector described by a vertex atom and its exopolyhedral substituent and (2) the normal to the C_2B_3 plane which passes through the vertex. For a regular icosahedral structure, such as that of $B_{12}H_{12}^{2-}$, this angle is 63.4°. A substituent on the open face of a nido icosahedral fragment generates angles of 59.3 and 58.4° (II), 60.2 and 61.8° (III), and 60.1° (IV). In the case of a substituent on the closo metal-bonded face the angles are 68.9 and 69.2° (I) and 71.0° (IV). In the closo system, for a face not bonded to metal, the angle is 57.6° (IV). Thus the greatest deviation from the regular icosahedral geometry is found for substituents on the pentagonal face which is bonded to metal in closo complexes, and the effect is a compression toward the plane.

Conclusions

In each of the structures reported here, the basic geometry of the icosahedron is preserved and the C_2B_9 fragment has essentially the same form. Substituents on carbon atoms of the 3,1,2-closo system seem to be closer to the C_2B_3 plane than are substituents in the exo-nido system, and the orientation of the *o*-xylylene group with respect to the carborane fragment in the two systems is very different.

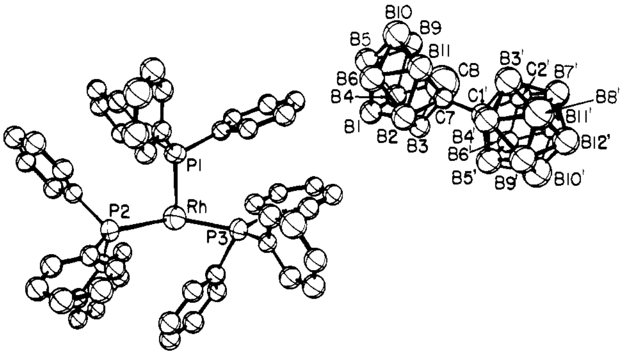

Figure 6. Crystal structure of the salt $[(PPh_3)_3Rh]^+$ [*nido*-7-(1′-*closo*-1′,2′-$C_2B_{10}H_{11}$)-7,8-$C_2B_9H_{11}$]$^-$ (V). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

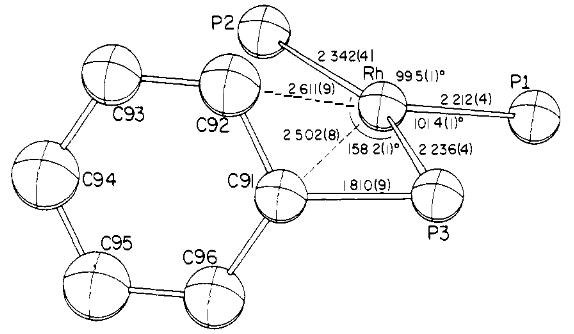

Figure 7. Details of the conformation about rhodium in V.

The points of attachment of rhodium through B-H-Rh bonds to the carborane fragment in the exo-nido compounds varies. In II, the B-H-B hydrogen and an M-H-B hydride are bonded to the same boron atom and the *o*-xylylene group is across the C_2B_3 face, and thus far removed from this point of attachment. In III the point of attachment of the Rh is to a pair of BH groups both of which are adjacent to the phenyl-bonded carbon atom, and in IIa, Ir is also bonded to two BH groups adjacent to a single cage carbon atom.

The charge distribution on the polyhedral surface of the carborane anions and the associated electron density in the B-H bonds undoubtedly influence the preferred site of attachment of the cationic metal fragment to the carborane cage in the exo-nido complexes. In solution, the exo-nido Rh complexes exhibit dynamic behavior[1] consistent with a migration of the $[L_2Rh]^+$ moiety about the polyhedral surface of the carborane anion. Therefore, it is impossible, at this time, to rationalize the site of attachment of the metal to the carborane cage. It is interesting to note that in complexes IIa and III, the $[(PPh_3)_2Rh(H)_2]^+$ and $[(PPh_3)_2Rh]^+$ fragments, respectively, are bound to identical positions on the carborane anion (adjacent to cage-carbon atoms). However, in II, the $[(PCy_3)(PPh_3)Rh]^+$ fragment is bound to a different set of two B-H groups (neither adjacent to cage-carbon atoms). Although this distinction may be largely influenced by steric considerations (i.e., the bulk of the PCy_3 and *o*-xylylene moieties), the increased basicity of the PCy_3 ligand over the PPh_3 ligand may favor the different mode of attachment found in II. Indeed, the basic PCy_3 ligand is trans to the central boron atom on the open face of the carborane anion which is involved in the B-H-B interaction.

Stereochemical Configuration about Rhodium. In the closo compounds, I and IV, the conformation about Rh is very similar; the expected pseudooctahedral coordination is exhibited and P-Rh-P is 98.7 (1) and 102.47 (4)°, respectively, while P-Rh-H is 78 (3) and 75 (3)° for I and 80 (2) and 79 (2)° for IV. In I the terminal hydride is cis to the two cage-carbon atoms, H-Rh-C

Table VI. Interatomic Distances (Å) and Angles (deg) in $[(PPh_3)_3Rh]^+[$*nido*-7-(1'-*closo*-1',2'-$C_2B_{10}H_{11}$)-7,8-$C_2B_9H_{11}]^-$ (V)

Interatomic Distances

Rh-P(1)	2.212 (4)	B(2)-B(6)	1.74 (3)	B(9)-B(10)	1.76 (3)	B(5)'-B(9)'	1.70 (3)
Rh-P(2)	2.342 (4)	B(2)-C(7)	1.71 (2)	B(10)-B(11)	1.72 (3)	B(5)'-B(10)'	1.83 (3)
Rh-P(3)	2.236 (4)	B(2)-B(11)	1.82 (3)	C(1)'-C(2)'	1.67 (2)	B(6)'-B(10)'	1.81 (3)
P(1)-C(11)	1.838 (9)	B(3)-B(4)	1.76 (3)	C(1)'-B(3)'	1.77 (2)	B(6)'-B(11)'	1.87 (3)
P(1)-C(21)	1.826 (10)	B(3)-C(7)	1.70 (2)	C(1)'-B(4)'	1.74 (3)	B(7)'-B(8)'	1.79 (3)
P(1)-C(31)	1.840 (12)	B(3)-C(8)	1.76 (2)	C(1)'-B(5)'	1.68 (2)	B(7)'-B(11)'	1.77 (3)
P(2)-C(41)	1.811 (10)	B(4)-B(5)	1.79 (3)	C(1)'-B(6)'	1.72 (3)	B(7)'-B(12)'	1.75 (3)
P(2)-C(51)	1.840 (10)	B(4)-C(8)	1.79 (2)	C(2)'-B(3)'	1.72 (3)	B(8)'-B(9)'	1.73 (3)
P(2)-C(61)	1.834 (10)	B(4)-B(9)	1.86 (3)	C(2)'-B(6)'	1.81 (3)	B(8)'-B(12)'	1.74 (3)
P(3)-C(71)	1.792 (11)	B(5)-B(6)	1.85 (3)	C(2)'-B(7)'	1.68 (2)	B(9)'-B(10)'	1.77 (4)
P(3)-C(81)	1.804 (10)	B(5)-B(9)	1.73 (3)	C(2)'-B(11)'	1.78 (3)	B(9)'-B(12)'	1.77 (3)
P(3)-C(91)	1.810 (9)	B(5)-B(10)	1.80 (3)	B(3)'-B(4)'	1.69 (3)	B(10)'-B(11)'	1.82 (3)
B(1)-B(2)	1.77 (3)	B(6)-B(10)	1.82 (3)	B(3)'-B(7)'	1.85 (3)	B(10)'-B(12)'	1.77 (3)
B(1)-B(3)	1.78 (3)	B(6)-B(11)	1.77 (3)	B(3)'-B(8)'	1.82 (3)	B(11)'-B(12)'	1.84 (3)
B(1)-B(4)	1.84 (3)	C(7)-C(8)	1.63 (2)	B(4)'-B(5)'	1.87 (3)	C-Cl(1)	1.91 (3)
B(1)-B(5)	1.78 (3)	C(7)-B(11)	1.63 (2)	B(4)'-B(8)'	1.85 (3)	C-Cl(2)	1.71 (3)
B(1)-B(6)	1.73 (3)	C(7)-C(1)'	1.53 (2)	B(4)'-B(9)'	1.86 (3)		
B(2)-B(3)	1.81 (3)	C(8)-B(9)	1.74 (2)	B(5)'-B(6)'	1.82 (3)		

Angles

B(2)-C(7)-B(3)	64 (1)	Rh-P(3)-C(91)	75.6 (3)
B(2)-C(7)-C(8)	116 (1)	C(71)-P(3)-C(81)	107.1 (4)
B(3)-C(7)-C(8)	64 (1)	C(71)-P(3)-C(91)	110.1 (5)
B(2)-C(7)-B(11)	66 (1)	C(81)-P(3)-C(91)	105.5 (4)
B(3)-C(7)-B(11)	116 (1)	P(1)-C(11)-C(12)	122.0 (3)
C(8)-C(7)-B(11)	109 (1)	P(1)-C(11)-C(16)	117.7 (3)
B(2)-C(7)-C(1)'	121 (1)	P(1)-C(21)-C(22)	116.8 (3)
B(3)-C(7)-C(1)'	116 (2)	P(1)-C(21)-C(26)	123.1 (3)
C(8)-C(7)-C(1)'	114 (2)	P(1)-C(31)-C(32)	120.6 (3)
B(11)-C(7)-C(1)'	123 (2)	P(1)-C(31)-C(36)	119.4 (3)
B(3)-C(8)-B(4)	60 (1)	P(2)-C(41)-C(42)	121.6 (3)
B(3)-C(8)-C(7)	60 (1)	P(2)-C(41)-C(46)	118.4 (3)
B(4)-C(8)-C(7)	109 (1)	P(2)-C(51)-C(52)	120.5 (2)
B(3)-C(8)-B(9)	112 (1)	P(2)-C(51)-C(56)	119.4 (3)
B(4)-C(8)-B(9)	64 (1)	P(2)-C(61)-C(62)	116.0 (3)
C(7)-C(8)-B(9)	111 (2)	P(2)-C(61)-C(66)	124.0 (3)
B(4)-B(9)-B(5)	60 (1)	P(3)-C(71)-C(72)	119.4 (3)
B(4)-B(9)-C(8)	59 (1)	P(3)-C(71)-C(76)	120.6 (3)
B(5)-B(9)-C(8)	104 (1)	P(3)-C(81)-C(82)	121.3 (3)
B(4)-B(9)-B(10)	109 (2)	P(3)-C(81)-C(86)	118.7 (3)
B(5)-B(9)-B(10)	62 (1)	P(3)-C(91)-C(92)	113.3 (3)
C(8)-B(9)-B(10)	103 (2)	P(3)-C(91)-C(96)	126.0 (3)
B(5)-B(10)-B(6)	61 (1)	B(2)-B(1)-B(3)	61 (1)
B(5)-B(10)-B(9)	58 (1)	B(2)-B(1)-B(4)	109 (1)
B(6)-B(10)-B(9)	108 (2)	B(3)-B(1)-B(4)	58 (1)
B(5)-B(10)-B(11)	107 (2)	B(2)-B(1)-B(5)	110 (1)
B(6)-B(10)-B(11)	60 (1)	B(3)-B(1)-B(5)	106 (1)
B(9)-B(10)-B(11)	107 (2)	B(4)-B(1)-B(5)	59 (1)
B(2)-B(11)-B(6)	58 (1)	B(2)-B(1)-B(6)	59 (1)
B(2)-B(11)-C(7)	59 (1)	B(3)-B(1)-B(6)	108 (2)
B(6)-B(11)-C(7)	105 (2)	B(4)-B(1)-B(6)	111 (2)
B(2)-B(11)-B(10)	111 (2)	B(5)-B(1)-B(6)	64 (1)
B(6)-B(11)-B(10)	63 (1)	B(1)-B(2)-B(3)	60 (1)
C(7)-B(11)-B(10)	110 (2)	B(1)-B(2)-B(6)	59 (1)
C(7)-C(1)'-C(2)'	119 (1)	B(3)-B(2)-B(6)	106 (2)
C(7)-C(1)'-B(3)'	112 (2)	B(1)-B(2)-C(7)	103 (1)
C(2)'-C(1)'-B(3)'	60 (1)	B(3)-B(2)-C(7)	58 (1)
C(7)-C(1)'-B(4)'	114 (2)	B(6)-B(2)-C(7)	103 (1)
C(2)'-C(1)'-B(4)'	108 (1)	B(1)-B(2)-B(11)	104 (1)
B(3)'-C(1)'-B(4)'	57 (1)	B(3)-B(2)-B(11)	102 (2)
C(7)-C(1)'-B(5)'	124 (1)	B(6)-B(2)-B(11)	60 (1)
C(2)'-C(1)'-B(5)'	112 (1)	C(7)-B(2)-B(11)	55 (1)
B(3)'-C(1)'-B(5)'	112 (1)	B(1)-B(3)-B(2)	59 (1)
B(4)'-C(1)'-B(5)'	66 (1)	B(1)-B(3)-B(4)	62 (1)
C(7)-C(1)'-B(6)'	120 (2)	B(2)-B(3)-B(4)	111 (2)
C(2)'-C(1)'-B(6)'	65 (1)	B(1)-B(3)-C(7)	103 (2)
B(3)'-C(1)'-B(6)'	116 (2)	B(2)-B(3)-C(7)	58 (1)
B(4)'-C(1)'-B(6)'	120 (2)	B(4)-B(3)-C(7)	107 (1)
B(5)'-C(1)'-B(6)'	65 (1)	B(1)-B(3)-C(8)	106 (1)
C(1)'-C(2)'-B(3)'	63 (1)	B(2)-B(3)-C(8)	105 (1)
C(1)'-C(2)'-B(6)'	59 (1)	B(4)-B(3)-C(8)	61 (1)
B(3)'-C(2)'-B(6)'	114 (2)	C(7)-B(3)-C(8)	56 (1)
C(1)'-C(2)'-B(7)'	114 (2)	B(1)-B(4)-B(3)	59 (1)
B(3)'-C(2)'-B(7)'	66 (1)	B(1)-B(4)-B(5)	59 (1)
B(6)'-C(2)'-B(7)'	113 (1)	B(3)-B(4)-B(5)	106 (2)
C(1)'-C(2)'-B(11)'	111 (1)	B(1)-B(4)-C(8)	103 (1)
B(3)'-C(2)'-B(11)'	117 (2)	B(3)-B(4)-C(8)	60 (1)
B(6)'-C(2)'-B(11)'	63 (1)	B(5)-B(4)-C(8)	100 (1)

Table VI (*Continued*)

B(7)'-C(2)'-B(11)'	61 (1)	B(1)-B(4)-B(9)	104 (2)
C(1)'-B(3)'-C(2)'	57 (1)	B(3)-B(4)-B(9)	106 (1)
C(1)'-B(3)'-B(4)'	60 (1)	B(5)-B(4)-B(9)	57 (1)
C(2)'-B(3)'-B(4)'	109 (2)	C(8)-B(4)-B(9)	57 (1)
C(1)'-B(3)'-B(7)'	102 (2)	B(1)-B(5)-B(4)	62 (1)
C(2)'-B(3)'-B(7)'	56 (1)	B(1)-B(5)-B(6)	57 (1)
B(4)'-B(3)'-B(7)'	111 (2)	B(4)-B(5)-B(6)	108 (2)
C(1)'-B(3)'-B(8)'	104 (2)	B(1)-B(5)-B(9)	112 (2)
C(2)'-B(3)'-B(8)'	103 (2)	B(4)-B(5)-B(9)	64 (1)
B(4)'-B(3)'-B(8)'	64 (1)	B(6)-B(5)-B(9)	108 (2)
B(7)'-B(3)'-B(8)'	58 (1)	B(1)-B(5)-B(10)	107 (2)
C(1)'-B(4)'-B(3)'	62 (1)	B(4)-B(5)-B(10)	110 (2)
C(1)'-B(4)'-B(5)'	56 (1)	B(6)-B(5)-B(10)	60 (1)
B(3)'-B(4)'-B(5)'	107 (2)	B(9)-B(5)-B(10)	60 (1)
C(1)'-B(4)'-B(8)'	104 (2)	B(1)-B(6)-B(2)	61 (1)
B(3)'-B(4)'-B(8)'	62 (1)	B(1)-B(6)-B(5)	59 (1)
B(5)'-B(4)'-B(8)'	101 (2)	B(2)-B(6)-B(5)	108 (2)
C(1)'-B(4)'-B(9)'	97 (2)	B(1)-B(6)-B(10)	108 (2)
B(3)'-B(4)'-B(9)'	104 (2)	B(2)-B(6)-B(10)	110 (2)
B(5)'-B(4)'-B(9)'	54 (1)	B(5)-B(6)-B(10)	59 (1)
B(8)'-B(4)'-B(9)'	56 (1)	B(1)-B(6)-B(11)	108 (2)
C(1)'-B(5)'-B(4)'	58 (1)	B(2)-B(6)-B(11)	62 (1)
C(1)'-B(5)'-B(6)'	59 (1)	B(5)-B(6)-B(11)	103 (2)
B(4)'-B(5)'-B(6)'	109 (2)	B(10)-B(6)-B(11)	57 (1)
C(1)'-B(5)'-B(9)'	106 (2)	B(11)'-B(7)'-B(12)'	63 (1)
B(4)'-B(5)'-B(9)'	63 (1)	B(3)'-B(8)'-B(4)'	55 (1)
B(6)'-B(5)'-B(9)'	108 (2)	B(3)'-B(8)'-B(7)'	62 (1)
C(1)'-B(5)'-B(10)'	105 (2)	B(4)'-B(8)'-B(7)'	107 (2)
B(4)'-B(5)'-B(10)'	111 (2)	B(3)'-B(8)'-B(9)'	105 (2)
B(6)'-B(5)'-B(10)'	60 (1)	B(4)'-B(8)'-B(9)'	63 (1)
B(9)'-B(5)'-B(10)'	60 (1)	B(7)'-B(8)'-B(9)'	106 (2)
C(1)'-B(6)'-C(2)'	57 (1)	B(3)'-B(8)'-B(12)'	110 (2)
C(1)'-B(6)'-B(5)'	57 (1)	B(4)'-B(8)'-B(12)'	113 (2)
C(2)'-B(6)'-B(5)'	101 (2)	B(7)'-B(8)'-B(12)'	59 (1)
C(1)'-B(6)'-B(10)'	104 (2)	B(9)'-B(8)'-B(12)'	61 (2)
C(2)'-B(6)'-B(10)'	101 (2)	B(4)'-B(9)'-B(5)'	63 (1)
B(5)'-B(6)'-B(10)'	60 (1)	B(4)'-B(9)'-B(8)'	62 (1)
C(1)'-B(6)'-B(11)'	105 (2)	B(5)'-B(9)'-B(8)'	113 (2)
C(2)'-B(6)'-B(11)'	58 (1)	B(4)'-B(9)'-B(10)'	114 (2)
B(5)'-B(6)'-B(11)'	107 (2)	B(5)'-B(9)'-B(10)'	64 (2)
B(10)'-B(6)'-B(11)'	59 (1)	B(8)'-B(9)'-B(10)'	110 (2)
C(2)'-B(7)'-B(3)'	58 (1)	B(4)'-B(9)'-B(12)'	111 (2)
C(2)'-B(7)'-B(8)'	105 (2)	B(5)'-B(9)'-B(12)'	112 (2)
B(3)'-B(7)'-B(8)'	60 (1)	B(8)'-B(9)'-B(12)'	60 (1)
C(2)'-B(7)'-B(11)'	62 (1)	B(10)'-B(9)'-B(12)'	60 (2)
B(3)'-B(7)'-B(11)'	111 (2)	B(5)'-B(10)'-B(6)'	60 (1)
B(8)'-B(7)'-B(11)'	111 (2)	B(5)'-B(10)'-B(9)'	56 (1)
C(2)'-B(7)'-B(12)'	108 (2)	B(6)'-B(10)'-B(9)'	105 (2)
B(3)'-B(7)'-B(12)'	108 (2)	B(5)'-B(10)'-B(11)'	109 (2)
B(8)'-B(7)'-B(12)'	59 (1)	B(6)'-B(10)'-B(11)'	62 (1)
P(1)-Rh-P(3)	101.4 (1)	B(9)'-B(10)'-B(11)'	108 (2)
P(1)-Rh-P(2)	99.5 (1)	B(5)'-B(10)'-B(12)'	106 (2)
P(2)-Rh-P(3)	158.2 (1)	B(6)'-B(10)'-B(12)'	110 (2)
P(1)-Rh···C(91)	142.4 (3)	B(9)'-B(10)'-B(12)'	60 (2)
P(2)-Rh···C(91)	113.7 (2)	B(11)'-B(10)'-B(12)'	62 (1)
P(3)-Rh···C(91)	44.5 (2)	C(2)'-B(11)'-B(6)'	59 (1)
P(9)-Rh···C(92)	165.4 (2)	C(2)'-B(11)'-B(7)'	57 (1)
P(2)-Rh···C(92)	93.3 (2)	B(6)'-B(11)'-B(7)'	106 (2)
P(3)-Rh···C(92)	66.8 (2)	C(2)'-B(11)'-B(10)'	102 (2)
P(1)-Rh···H(92)	145.5[a]	B(6)'-B(11)'-B(10)'	59 (1)
P(2)-Rh···H(92)	96.2[a]	B(7)'-B(11)'-B(10)'	104 (2)
P(3)-Rh···H(92)	69.6[a]	C(2)'-B(11)'-B(12)'	100 (2)
Rh-P(1)-C(11)	115.5 (3)	B(6)'-B(11)'-B(12)'	105 (2)
Rh-P(1)-C(21)	113.9 (3)	B(7)'-B(11)'-B(12)'	58 (1)
Rh-P(1)-C(31)	115.2 (3)	B(10)'-B(11)'-B(12)'	58 (1)
C(11)-P(1)-C(21)	103.7 (4)	B(7)'-B(12)'-B(8)'	62 (1)
C(11)-P(1)-C(31)	100.5 (4)	B(7)'-B(12)'-B(9)'	106 (2)
C(21)-P(1)-C(31)	106.5 (4)	B(8)'-B(12)'-B(9)'	59 (2)
Rh-P(2)-C(41)	125.3 (3)	B(7)'-B(12)'-B(10)'	107 (2)
Rh-P(2)-C(51)	113.6 (3)	B(8)'-B(12)'-B(10)'	109 (2)
Rh-P(2)-C(61)	105.9 (3)	B(9)'-B(12)'-B(10)'	60 (1)
C(41)-P(2)-C(51)	99.8 (4)	B(7)'-B(12)'-B(11)'	59 (1)
C(41)-P(2)-C(61)	104.1 (4)	B(8)'-B(12)'-B(11)'	110 (2)
C(51)-P(2)-C(61)	106.5 (4)	B(9)'-B(12)'-B(11)'	107 (2)
Rh-P(3)-C(71)	126.2 (3)	B(10)'-B(12)'-B(11)'	60 (1)
Rh-P(3)-C(81)	123.3 (4)	Cl(1)-C-Cl(2)	92 (1)

[a] Parameters for H(92) were not refined.

Table VII. Some Important Parameters for the Crystal Structures Described in this Paper

compd	I	II	III	IV	V
crystal system	$P2_1/n$	$P\bar{1}$	$C2/c$	$P2_1/n$	$P2_1/c$
cell a, Å	17.803 (7)	11.565 (2)	10.732 (3)	12.905 (3)	14.819 (4)
b, Å	21.425 (6)	13.527 (5)	23.610 (8)	13.855 (2)	25.429 (6)
c, Å	13.010 (4)	18.313 (6)	17.247 (6)	16.201 (3)	17.578 (4)
α, deg		91.90 (4)			
β, deg	98.20 (2)	73.21 (4)	91.32 (2)	91.46 (2)	98.65 (2)
γ, deg		102.10 (6)			
V, Å^3	4912 (3)	2680	4370 (3)	2896 (1)	6549 (3)
Z	4	2	4	4	4
density (calcd), g cm^{-3}	1.44	1.23	1.29	1.29	1.267
density (obsd), g cm^{-3}	1.36	1.20	1.24	1.28	1.257
2θ maximum	45	50	50	50	45 (incomplete)
scan rate, deg min^{-1}	2.0	2.0	2.55	2.5–29.3	2.0
scan range	$2.2(1 + 0.692 \tan\theta)$	$2.2(1 + 0.692 \tan\theta)$	1.0 below Kα1 1.0 above Kα2	1.5 below Kα1 1.5 above Kα2	1.0 below Kα1 1.0 above Kα2
background	20 s total	20 s total	= scan time	= 0.5 scan time	= scan time
scan mode	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
obsd reflections, $I > 3\sigma(I)$	2864	5571	3104	3946	3319
absorption coeff	5.55	3.57	4.19	6.95	3.96
agreement factors, R	0.0597	0.0561	0.0613	0.039	0.0757
R_w	0.0550	0.0529	0.0675	0.049	0.0771
goodness of fit	2.11	1.48	1.68	1.71	2.30
data/parameters	10.2	14.8	16.7	11.1	12.6

97 (3) and 92 (3)°, and it is nearly trans to B(8), H–Rh–B 168 (3)°. Distances around Rh are Rh–H 1.56 (9) Å, Rh–P 2.335 (3) and 2.324 (3) Å, and Rh to C_2B_3 atoms 2.23 to 2.33 (1) Å. In IV, the terminal hydride is nearly trans to C(1′) and cis to B(7) and B(11), with angles of 160 (2), 86 (2), and 82 (2)°, respectively, and distances around Rh are Rh–H 1.53 (5) Å, Rh–P 2.357 (1) and 2.346 (1) Å, and Rh to CB_4 atoms range from 2.16 to 2.33 (5) Å. Although the terminal hydride ligand in the corresponding Ir compound IVa has not been located, it also must be trans to the carbon atom of the bonding face.

The conformation about Rh in the two exo-nido compounds is approximately square-planar RhP_2H_2, with the maximum distance from the least-squares plane through these five atoms of only 0.08 Å (II). Again, P–Rh–P is nearly orthogonal, 95.6° in III and 99.3° in II. The RhP_2B_2 is also nearly planar, with maximum distances from the least-squares plane through these five atoms 0.18 (1) Å in III and 0.262 (8) Å in II. Distances from Rh to P are somewhat shorter than for the closo compounds and distances from Rh to B are slightly longer than for the closo compounds. Rh to bridging hydride distances are considerably longer than those of terminal Rh hydrides.

In the cation V only two of the P–Rh–P angles retain near orthogonality, while the third opens to 158.2°. Also involved in the conformation about Rh are two carbon atoms of a phenyl group, at distances of 2.502 (8) and 2.611 (9) Å and one phenyl hydrogen, H(92), at a distance of 2.57 Å (all phenyl hydrogen atoms are in calculated positions as described in the Experimental Section).

Experimental Section

Some of the more important parameters for the crystal structures described below, including unit cell parameters and conditions of data collection, are summarized in Table VII.

Collection and Reduction of X-ray Data for I·2CH_2Cl_2. An air-stable single crystal, obtained from CH_2Cl_2/heptane solution, with faces (–3,0,5), (3,0,–5), (0,1,1), (0,–1,–1), (4,0,2), and (–4,0,–2) and approximately 0.25 mm on an edge, was mounted in an arbitrary orientation and transferred to a Picker FACS-I diffractometer. Orientation of the crystal and space group determination followed autoindexing of 11 accurately centered reflections found photographically. Preliminary data were collected to identify the intense high-angle data. Accurate cell constants were obtained by a least-squares fit of 14 of these reflections ($24° < 2\theta < 34°$) and the 11 low-angle reflections. Data were collected in the θ–2θ scan mode to a $(\sin\theta)/\lambda$ limit of 0.54 Å with Zr-filtered Mo Kα radiation. Three intense reflections (2,3,10), (4,14,3), and (4,4,–7) were monitored every 100 reflections to check the stability of the experiment. Intensities of these reflections fluctuated only slightly during the course of the experiment. A constant scan rate of 2° min^{-1} and scan range of $2.2(1 + 0.692 \tan\theta)$ were employed. A 10-s background count was taken at each end of the scan. A total of 6943 reflections were collected; of these, 2594 were considered observed ($I \geq 3(\sigma I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz, polarization, and absorption effects. The observed systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, indicate the space group to be $P2_1/n$.

Solution and Refinement of the Structure of I. The rhodium and phosphorus atoms were located from a Patterson map.^{27} All non-hydrogen atoms, including two methylene chloride molecules, were located by difference electron density maps. Full-matrix least-squares refinement converged to an agreement factor of 0.065. During this refinement, the six phenyl rings of the two triphenylphosphine ligands were treated as rigid groups with C–C and C–H set at 1.39 and 1.08 Å, respectively, and all C–C–C and C–C–H angles set at 120°. The positional, rotational, and individual isotropic thermal (carbon) parameters were allowed to vary. The Rh, P, and solvent atoms were allowed to vibrate anisotropically; all other nongroup atoms were allowed to vibrate isotropically. Scattering factors for H were obtained from Stewart et al.^{28} and for other atoms were taken from "International Tables for X-ray Crystallography", Vol. IV.^{29} Anomalous dispersion terms^{30} were applied to scattering of Rh, Cl, and P. The hydride ligand and all hydrogen atoms on the carborane cage were located on a difference electron density map. Least-squares refinement converged to the final agreement factor^{31} $R = 0.0597$, $R_w = 0.0550$. The standard deviation of an observation of unit weight was 2.11, based on refinement of 282 parameters.^{32} Final positional and thermal parameters are given in Table VIII, and a table of structure factors is available.^{33}

Collection and Reduction of X-ray Data for II·1.5(C_6H_6). Preliminary photographs of air-stable red prismatic crystals of II, obtained from benzene/ethanol solution (liquid diffusion), indicated triclinic symmetry. The density, measured by flotation in aqueous KI, was 1.20 g cm^{-3}, in reasonable agreement with the calculated density of 1.23 g cm^{-3} based on $Z = 2$.

The crystal used for data collection was bounded by faces (3,–2,2), (0,0,1), (0,1,0), (0,–1,1), (0,–1,0), (0,0,–1), and (–2,1,–1). Crystal dimensions normal to these faces were 0, 0, 0, 0.0038, 0.015, 0.025, and

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(27) Programs used in this work include locally written data reduction and absorption programs and locally revised versions of ORFLS, ORFFE, ORTEP, MULTAN, and SHELX-76.

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(29) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(30) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.

(31) The function $\sum w||F_o| - |F_c||^2$ was minimized in the least-squares refinements and the discrepancy indices were defined as $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = [1/\sigma(F_o)]^2$

(32) The final "goodness of fit" is defined as $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o is the number of observed reflections and N_v is the number of variable parameters.

(33) Supplementary materials.

0.043 cm. Intensity data were collected on a Picker FACS-I diffractometer. Lattice parameters, determined by a least-squares fit of 15 accurately centered reflections, were a = 11.565 (2) Å, b = 13.527 (5) Å, c = 18.313 (6) Å, α = 91.90 (4)°, β = 73.21 (4)°, and γ = 102.10 (6)°.

Data were collected in the θ-2θ scan mode, with a scan range of 2.2(1 + 0.692 tan θ), at 2° min^{-1}, to a 2θ limit of 50° with Zr-filtered Mo Kα radiation. A 10-s background count was taken at each end of the scan. Three intense reflections, monitored every 100 reflections, fluctuated in intensity only slightly during the measured period.

Of 10 292 reflections measured, including standards and duplicates, 5571 unique reflections were considered to be observed ($I \geq 3(\sigma I)$) and were used in the structure analysis. Data were corrected for Lorentz, polarization, and absorption effects. The absorption coefficient is 3.57 cm^{-1} and the maximum and minimum transmission factors are 0.9749 for (0,-1,-3) and 0.9570 for (3,1,0).

Solution and Refinement of the Structure of II. Rhodium and phosphorus atoms were located by conventional Patterson methods and the remaining atoms (including H with the exception of those on the benzene of solvation) were located on electron density or difference electron density maps. In order to reduce the number of parameters refined, the three phenyl groups on phosphorus and the solvate benzene molecules were described as rigid C_6H_5 and C_6H_6 regular hexagons, respectively, with C–C constrained to be 1.395 and C–H constrained to be 1.08 Å, and the CH_2 fragments of the cyclohexyl groups were constrained to have C–H distances of 1.08 Å and H–C–H angles of 109.5°. In addition, three isotropic thermal parameters for H on phenyl rings were refined: one each for H bonded to C ortho, meta, or para to C bonded to P. The thermal parameters for hydrogen atoms of the benzene solvate were arbitrarily set at u = 0.2. Least-squares refinement for positional parameters for all remaining atoms, anisotropic thermal parameters of Rh, P, and C of the benzene solvate and the two outermost C atoms of the xylylene substituent, isotropic thermal parameters for other nongroup atoms, and the constrained parameters described above resulted in convergence at R = 0.0561 and R_w = 0.0529. The standard deviation of an observation of unit weight is 1.48. Anomalous dispersion terms[30] were applied to scattering of Rh and P. Scattering factors for H were obtained from Stewart, Davidson, and Simpson[28] and for other atoms were taken from "International Tables", Vol. IV.[29] Positional and thermal parameters are given in Table IX, and a table of structure factors is available.[33]

Collection and Reduction of X-ray Data for III. A prismatic-shaped crystal of III measuring 0.30 × 0.22 × 0.20 mm was obtained from the slow evaporation of a benzene/heptane solution of III. Crystallographic data were collected at room temperature with a Syntex P2$_1$ diffractometer. Experimental and data handling techniques were analogous to those described in the following section for IV. Experimental parameters are summarized in Table VII. Systematic absences were found in hkl with $h + k = 2n + 1$ and in $h0l$ with $l = 2n + 1$, indicating the space group to be Cc or $C2/c$. A statistical analysis of the intensity distribution indicated the space group to be $C2/c$, which was confirmed by the successful structure determination.

Solution and Refinement of the Structure of III. Direct methods (MULTAN), Fourier, difference Fourier, and least-squares refinement techniques were used in the solution of the structure. In the final refinement, positional and anisotropic thermal parameters of Rh and P, positional and isotropic thermal parameters of carborane atoms, and positional parameters for H atoms were refined. The methyl group was treated as a rigid tetrahedron with C–H distances of 1.08 Å; an isotropic thermal parameter for C and a single isotropic thermal parameter for the three H atoms were refined. Phenyl groups were treated as rigid hexagons with C–C distances of 1.395 and C–H distances of 1.08 Å. Individual isotropic thermal parameters for carbon and isotropic thermal parameters for ortho, meta, and para H were refined. Only six hydrogen atoms on the carborane cage were located. Positions for each of these and a single overall thermal parameter were refined. Although the space group is $C2/c$, there are only four molecules in the unit cell. The molecule is asymmetric and the structure is disordered, with eight molecules, each at half occupancy. Positional and thermal parameters are listed in Table X.[33]

In all, 186 parameters were varied and 3104 reflections were included. Anomalous dispersion terms were applied to Rh and P.[30] Scattering factors for H are from Stewart[28] and for the other atoms are from "International Tables", Vol. IV.[29] Refinement converged at R = 0.0613, R_w = 0.0675. The standard deviation of an observation of unit weight is 1.68. Structure factor tables are available.[33]

Collection and Reduction of X-ray Data for IV. A well-formed transparent crystal, obtained from THF/ethanol solution, was mounted on the end of a thin glass fiber and coated with epoxy cement, placed on an xyz goniometer, and optically centered on a Syntex P2$_1$ diffractometer equipped with a molybdenum tube ($\lambda_{MoK\alpha}$ = 0.71069 Å) and a graphite monochromator. Preliminary cell parameters were obtained from 15 centered reflections. Reflections of relatively strong intensity at higher values of θ were chosen after a rapid-scan abbreviated data set was collected, and 15 of these reflections were centered in order to obtain improved cell parameters. Systematic absences were found for $h0l$ with $h + l = 2n + 1$ and $0k0$ with $k = 2n + 1$, indicating the space group $P2_1/n$. Unit cell parameters are given in Table VII.

The 6126 reflections, including standards, were measured with a Syntex P2$_1$ diffractometer at 21 °C over a 2θ range of 0–50°. Of the reflections measured, 3946 unique reflections were considered observed with $I \geq 3\sigma(I)$. Three standard reflections were measured after every 50 reflections; there was no observable decay. No absorption correction was applied. The crystal measured 0.48 × 0.16 × 0.20 mm and the absorption coefficient is 6.25 cm^{-1} for Mo Kα radiation.

Solution and Refinement of the Structure of IV. The position of the rhodium atom was determined from three high peaks on a three-dimensional Patterson map. All 32 non-hydrogen atoms were located by Fourier and least-squares methods. The location of methyl and phenyl groups bonding to the carborane icosahedron allowed early discrimination between carbon and boron atoms. Rh, P, and icosahedron atoms were allowed to vibrate anisotropically, and the remaining carbon atoms were allowed to vibrate isotropically. Hydrogen atoms were located from a difference electron density map. Hydrogen atoms on methyl and phenyl groups were assigned an isotropic B value of 6; all positional parameters, anisotropic thermal parameters of Rh, P, and icosahedral atoms, and isotropic thermal parameters of all other atoms were allowed to vary. The final unweighted value of R was 0.039 and R_w was 0.049;[31] the standard deviation of an observation of unit weight is 1.71.

Scattering factors and anomalous dispersion terms for Rh and P were taken from "International Tables for X-ray Crystallography".[29] Final positional and thermal parameters are listed in Table XI. Structure factor tables are available.[33]

Collection and Refinement of X-ray Data for V·CH_2Cl_2. A nearly cube-shaped crystal of V·CH_2Cl_2, which measured approximately 0.25 mm on an edge, was obtained from CH_2Cl_2/ethanol solution (liquid diffusion), placed on the end of a thin glass fiber, and coated with a layer of glue. Preliminary room-temperature photographs indicated that this compound crystallizes in the monoclinic system with space group $P2_1/c$. Lattice parameters, determined by a least-squares fit of 15 accurately centered reflections, are a = 14.819 (4) Å, b = 25.429 (6) Å, c = 17.578 (4) Å, and β = 98.65 (2)°. The room temperature density, measured by flotation in aqueous KI, was 1.257 g cm^{-3}, in reasonable agreement with the calculated density of 1.267 g cm^{-3} based on Z = 4. X-ray diffraction data were collected on a Syntex P$\bar{1}$ diffractometer with Mo Kα radiation (graphite crystal monochromator) up to a 2θ maximum of 45° using the θ–2θ scan technique. Data collection was discontinued when the intensity of the three standard reflections dropped approximately 40%; 5808 reflections including standards and $0,k,-l$ duplicates had been measured. Freshly prepared clear red crystals of this compound become opaque dark red with time, and the onset of opacity seems to be hastened with X-rays. An empirical correction, linear in time, was applied after reflections were corrected for Lorentz and polarization effects. No absorption correction was applied. Reflections having intensities less than three times their standard deviations were defined as unobserved and were not included in subsequent calculations.

Solution and Refinement of the Structure of V. Least-squares refinement of the positional parameters for non-hydrogen non-phenyl atoms, group positional parameters for C_6H_5 groups, anisotropic thermal parameters for Rh, P, and Cl, isotropic thermal parameters for the remaining nonhydrogen atoms, and overall isotropic thermal parameters for hydrogen on phenyl groups (depending on whether H bonds to C ortho, meta, or para to C bonded to P), with anomalous dispersion terms applied to scattering of Rh, P, and Cl, resulted in convergence at R = 0.076, R_w = 0.077. In all, 263 parameters were varied and 3319 reflections were included. The standard deviation of an observation of unit weight is 2.3. Scattering factors for H are from Stewart et al.[28] and for the other atoms are from "International Tables", Vol. IV[29] and real and imaginary terms for anomalous scattering were taken from Cromer.[30] The structure was solved by heavy-atom methods. All non-hydrogen atoms were located. All phenyl rings were included as rigid C_6H_5 hexagons with C–C = 1.395 Å and C–H = 1.08 Å. Although peaks corresponding to some cage hydrogen atoms appeared on the final difference map, hydrogen atoms on the cage were not included in the structure factor calculation. There is evidence of disorder in the anion; a peak appears in the "unoccupied" twelfth-vertex position of the second cage. No attempt to describe this disorder was attempted. In the 12-vertex cage, isotropic u values are rather large; with the exception of u = 0.06 at the carbon atom bonding to the other cage, u ranges from 0.09 to 0.14. Positional and thermal parameters are listed in Table XII. Structure factor tables are available.[33]

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Registry No. I, 76287-19-9; I·$2CH_2Cl_2$, 89437-70-7; II, 89414-09-5; II·$1.5(C_6H_6)$, 89414-10-8; III, 89397-42-2; IV, 89302-17-0; V, 89397-43-3; V·CH_2Cl_2, 89397-44-4.

Supplementary Material Available: Tables of observed and calculated structure factors and tables (Tables VIII-XII) of final positional and thermal parameters for I-V (115 pages). Ordering information is given on any current masthead page.

Metallacarboranes in Catalysis. 5. Interconversion of *closo*-Bis(phosphine)hydridorhodacarboranes by Rhodium Transfer between η^5-*nido*-Carborane Anions[1]

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Abstract: Both the hydride and dicarbollide ligands of a series of closo, formally six-coordinate Rh(III), bis(triphenylphosphine)hydrido η^5-(*nido*-$C_2B_9H_9RR'$) complexes were easily replaced by a series of [*nido*-$C_2B_9H_{12}$]$^-$ ligands using thermal reactions. The following trend for ease of displacement of the *nido*-carborane anion in cage-carbon-substituted [*closo*-$(PPh_3)_2Rh(H)(C_2RR'B_9H_9)$] complexes has been found: 7,8-disubstituted > 7,8-monosubstituted > 7,8-unsubstituted > 7,9-unsubstituted ~ 2,9-unsubstituted. Kinetic studies of the reaction of [*closo*-3,3-$(PPh_3)_2$-3-H-1-R-2-R′-3,1,2-$RhC_2B_9H_9$] (R = Me, R′ = H) (IVd) with [*nido*-7,8-$C_2B_9H_{12}$]$^-$ (Ia) and [*nido*-2,9-$C_2B_9H_{12}$]$^-$ (III) in THF at 29 °C showed no anion concentration dependence and a common first-order rate constant for the two reactions although in the case of [*nido*-7,9-$C_2B_9H_{12}$]$^-$ (II), anion dependence was observed. Similar kinetic studies of the reaction of [*exo-nido*-$(PPh_3)_2$Rh-7-Me-8-Ph-7,8-$C_2B_9H_{10}$] (IVf) with anions Ia, II, and III in THF at -63 °C proved these exchanges with exo-nido substrates to be much faster than the reactions involving closo substrates. In the cases of Ia and II, the less stable kinetic product of the reaction, the exo-nido tautomer, was initially observed along with its conversion to the more stable closo tautomer. Analysis of the anion concentration dependence of the rates of these reactions suggested the existence of a spectroscopically invisible intermediate, presumably an isomer of the exo-nido starting complex. Formation of an analogous intermediate appears to be the rate-determining step in reactions of *closo*-IVd with anions Ia and III. In addition, the dissociation of either PPh_3 or *nido*-carborane anion does not appear to be involved in any of these cage exchange reactions. Anion III was found to be a more effective nucleophile than Ia which, in turn, was more nucleophilic than II.

One of the more fascinating mechanistic problems associated with organometallic chemistry is that of the occasionally observed displacement of η^6 or η^5 ligands by other ligands of high hapticity or by electron-pair donors. Such processes have an important bearing upon the mechanisms of reactions which employ η^6 or η^5 organometallics as homogeneous catalysts or catalyst precursors.

There have been a number of reports concerning thermal ligand exchange reactions of ferrocene and related complexes.[3] The conditions required were vigorous, and Lewis acid catalysis was necessary. Khan and Dormond have reported[4] facile thermal exchange of cyclopentadienyl rings in certain titanium complexes, and Brubaker has studied[5] photolytic exchanges using $[(\eta^5\text{-}C_5H_5)_2MCl_n]$ (M = V, Ti, Zr, Hf; $n = 0, 1, 2$). A recent study[6] of the complex $\{Ru(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5(CO_2Me)_5]\}$ showed that the bonding between the $C_5(CO_2Me)_5$ group and the ruthenium is relatively weak and thus the $C_5(CO_2Me)_5$ ligand can be displaced by 2-e$^-$ donor ligands under mild conditions.

An interest in arene exchange reactions[7] has also developed, particularly in view of the discovery of homogeneous catalysts for the hydrogenation of aromatic hydrocarbons.[8] The experimental conditions required for the arene exchange reactions varied widely. For example, it was found[9] that reasonable rates for arene exchanges in $[(arene)Cr(CO)_3]$ complexes could be obtained at temperatures of ca. 140 °C when promoted by electron donor solvents. In contrast to these rather vigorous conditions, the toluene ligand in $[(\eta^6\text{-}C_6H_5CH_3)Ni(C_6F_5)_2]$ is so labile that it can be rapidly exchanged with other arene ligands at room temperature.[10]

The exact means by which the cyclopentadienyl or arene ligand is removed from the metal center is thus far unanswered. The assumption that dissociation is a stepwise process, perhaps of the type η^5-η^3-η^1-η^0 for cyclopentadienyl ligands and η^6-η^4-η^2-η^0 for arene ligands, is not at all unreasonable.

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