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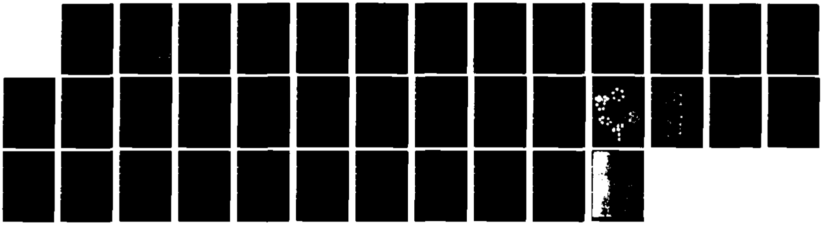

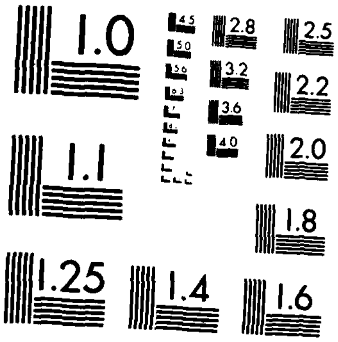

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Synthesis and Characterization of Anionic Halogen-Containing Rhodacarboranes. The Crystal and Molecular Structure of the Hydrogen Bonded Ion Pair, $[HPPh_3]$ $[\textit{closo}\text{-}3\text{-}(Ph_3P)\text{-}3,3\text{-}(Br)_2\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$.

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Synthesis and Characterization of Anionic Halogen-Containing Rhodacarboranes. The Crystal and Molecular Structure of the Hydrogen Bonded Ion Pair, $[HPPh_3]$ $[\underline{closo}\text{-}3\text{-}(Ph_3P)\text{-}3,3\text{-}(Br)_2\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$.

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Abstract

The title compound was obtained in low yield from the reaction of *closo*-3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$, **1**, and BBr_3 and was characterized by an x-ray diffraction study. Red crystals of $[HPPh_3]$ [*closo*-3-(Ph_3P)-3,3-$(Br)_2$-3,1,2-$RhC_2B_9H_{11}$]·1.5 C_6H_6, $[HPPH_3]$ **3** 1.5C_6H_6, were triclinic, space group $P\bar{1}$, with *a* = 12.591(5), *b* = 13.299(4), *c* = 17.568(5) Å, α = 111.77(2), β = 94.41(3), γ = 61.24(3)° and Z = 2. The structure was solved by conventional heavy atom techniques to a final discrepancy index of R = 0.046 for 6054 independent observed reflections. The rhodacarborane anion is pseudo-octahedral about the rhodium atom and the phosphonium cation is near the rhodium-bound bromine atoms with Br...H distances of 3.06(6) and 2.70(6) Å. It was suggested on the basis of nmr spectral data and solubility properties that ion pairing may also be significant for $[HPPh_3]$ **3** in solution. It was found that K[18-crown-6] **3** could be prepared in high yield from the anionic rhodacarborane K[18-crown-6] [*closo*-3,3-$(Ph_3P)_2$-3,1,2-$RhC_2B_9H_{11}$] and bromoform. The iodo analog of $\mathbf{3}^-$ could be isolated as the $(n\text{-}C_4H_9)_4N^+$ salt, in high yield, from the reaction of *closo*-3-(Ph_3P)-3,3-(NO_3)-3,1,2-$RhC_2B_9H_{11}$ and $(n\text{-}C_4H_9)_4NI$ and NaI in dichloromethane/water. The chloro analog of complex **3** could be prepared as the $[Et_4N]^+$ salt from the reaction of the 16-electron complex $[Et_4N]$ [*closo*-3-(Ph_3P)-3,1,2-$RhC_2B_9H_{11}$] (generated *in situ*) with CH_2Cl_2 in 60% yield.

Introduction

We recently reported the reaction of closo-3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$, 1, with benzoyl peroxide which afforded the asymmetric phosphinorhodacarborane dimer [closo-$(Ph_3P)RhC_2B_9H_{11}]_2$, 2, in modest yields (ca 40%).[2] In order to conduct a more thorough study of the chemical reactivity and catalytic properties of this dimeric complex we sought a more efficient conversion of 1 to 2 employing Lewis acids, (A), as shown in equation (1)

$$(Ph_3P)_2\text{-H-}RhC_2B_9H_{11} + A \text{ ----->} \ 1/2\ H_2 + A\ PPh_3 + [(Ph_3P)RhC_2B_9H_{11}]_2 \quad (1)$$

While the reactions of 1 with diborane and boron trifluoride did indeed proceed as per equation (1),[3] that with boron tribromide produced a bromine-containing phosphinorhodacarborane in low yield which was shown by X-ray crystallography to be the ionic complex $[HPPh_3]$[closo-3-(Ph_3P)-3,3-$(Br)_2$-3,1,2-$RhC_2B_9H_{11}$], $[HPPh_3]$ 3. Subsequent to the characterization of $[HPPh_3]$ 3 improved synthetic methods were developed which allowed the isolation of 3^- with a variety of supporting counterions in good yields. Moreover, it was found that the iodo and chloro analogs of 3^- could be easily prepared. Herein we report the details of these studies.

Results and Discussion

The reaction of complex 1 with a five-fold excess of BBr_3 in benzene at 25° C for 48 hours yielded a mixture of products. Column chromatography on Florisil with benzene elution yielded first a purple fraction and then a red fraction. The purple fraction was shown to consist of complex 2 and an unknown component. Red crystals could be isolated from the red fraction and were ultimately shown to be the ionic complex $[HPPh_3]$ $[$*closo*$\text{-}3\text{-}(Ph_3P)\text{-}3,3\text{-}(Br)_2\text{-}3,1,2\text{-}RhC_2B_9H_{11}]\cdot 1.5C_6H_6$, $[HPPh_3]$ 3•1.5 C_6H_6, by X-ray crystallography (*vide infra*). Although the elemental analyses correctly indicated the composition of $[HPPh_3]$ 3, the recognition of the ionic nature of this complex was clouded by its ready solubility in benzene and an osmometric molecular weight measurement in benzene which showed that this salt must exist as a tight ion pair in this solvent. As the mass, IR and nmr spectra did not fully elucidate the nature of this red complex an X-ray diffraction study was undertaken and showed the complex to be $[HPPh_3]$ 3•$1.5C_6H_6$.

The molecular structure of $[HPPh_3]$ 3 is shown in Figure 1 and some relevant bond distances and angles are presented in Tables I and II, respectively. The rhodium atom exhibits pseudo-octahedral coordination, with the dicarbollide ligand occupying three facial coordination sites and the two bromine atoms and a triphenylphosphine ligand occupying the remaining sites. The bonding of the rhodium atom to the five nearest carborane cage atoms is symmetrical and can be compared with 1 (2.22(1) to 2.28(1) Å)[4] or with $[$*closo*$\text{-}3\text{-}PPh_3\text{-}1,3\text{-}\mu\text{-}(\eta^2\text{-}3,4\text{-butenyl})\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{10}]$[5] (2.211(8) to 2.266(8) Å). In $[HPPh_3]$ 3 these distances range from Rh-C(1) = 2.152(6) to Rh-B(7) = 2.229(7)Å. Within the carborane polyhedron, bond distances reflect the positions of the heteroatoms. The C-C distance is 1.651(9) Å, the C-B distances in the five-membered face are 1.740(8) and 1.679(10) Å and B-B distances within the face are 1.819(10) and 1.819(10) Å. The average distances from C and B in the coordinated face to adjacent boron atoms in the lower pentagonal ring are 1.703(28) and 1.792(20)Å, respectively. The Rh-P(1) distance of 2.360(2) Å can be compared to the Rh-P distances of 2.301(1) and 2.357(3) Å in 1[4] and 2.338(2) and 2.360(2) Å in 2[2]. The two Rh-Br distances in $[HPPh_3]$ 3 are similar, 2.598(1) and 2.520(2) Å, with the shorter distance being between the rhodium and the hydrogen-bonded bromine atom. A comparable Rh-Br distance of 2.581 Å was found in tris-{tri(o-styryl)phosphine}rhodium bromide, $[\{P(C_8H_7)_3\}_3RhBr$.[6] The solvate molecules are not close to either ion, the closest approach of a benzene carbon atom to a nonsolvate atom being C71...H22 = 2.76 A. Distances within the cation are not unusual. The P-H distance of 1.36 Å can be compared with 1.42 in $(Bu^t{}_3PH)^+$,[7] 1.414 in PH_4I,[8] and 1.392 Å (neutron diffraction) in PH_4Br.[9] The P-C distance of 1.775 Å (av) is shorter than the comparable distance in the anion (1.843 Å (av)), as has also been found in $(Bu^t{}_3PH)[(Bu^t{}_3P)NiBr_3]$.[7] The C-P-C angles in the cation are also increased relative to those of the anion in both 3 and the nickel complex mentioned above. The bromine atoms of the anion in 3 are quite near the hydrogen atoms of the triphenylphosphonium cation (Br...H = 2.70(6) and 3.06(6) Å) and are indicative of an ion-pairing interaction in the solid state. The comparable Br...H distances for the ion-paired nickel complex referred to above are 3.06, 3.35 and 3.16 Å.[7] The sum of the van der Waals radii is Br...H = 3.0-3.45 Å.[10] This hydrogen-bonded ion pair interaction may also be important for 3 in solution, as the salt dissolves readily in benzene and the nmr resonances of the cation are broad at room temperature, possibly as a result of spin-coupling to the quadrupolar bromine nuclei of the anion (*vide infra*).

While the ν_{P-H} absorption was not detected in the 2450-2300 cm^{-1} region in the infrared,[11] the triphenylphosphonium cation proton was observed as a broad doublet ($W_{1/2} \gtrsim 220$ Hz) at ca 10.8δ in the ^1H nmr spectrum of 3 in $CDCl_3$. Cooling the sample to -33° C sharpened the resonance to a doublet at 10.73δ. The large value of J_{P-H} (557 Hz) is typical of phosphorus-hydrogen coupling constants in phosphonium salts.[12] In addition to the resonances at ca 7.6δ due to the phenyl protons of the coordinated triphenylphosphine ligand and the triphenylphosphonium cation, three carborane C-H resonances were observed and the intensities of these resonances were temperature-dependent, suggesting that more than one isomer of $\underline{3}^-$ was present in solution. The $^{31}P\{^1H\}$ nmr spectrum of $\underline{3}^-$ at 27° C was consistent with this notion and exhibited two doublets at 33.7 (P_1) and 27.5 ppm ($P_{1'}$) in a ratio ($P_1/P_{1'}$) of ca 10:1 due to the coordinated triphenylphosphine ligand and a broad singlet ($W_{1/2} \approx 75$ Hz) at -4.5 ppm (P_2) due to the triphenylphosphonium cation. At -33° C the doublet due to $P_{1'}$ became the major resonance ($P_1/P_{1'} \approx 1:1.8$) and the P_2 resonance sharpened considerably ($W_{1/2} \approx 35$ Hz).

Although the two isomers present in solutions of $\underline{3}^-$ could arise from ion-pairing interactions in solution, no evidence was obtained to support this possibility and only one resonance due to the phosphonium cation was observed in the ^1H and ^{31}P nmr spectra of $\underline{3}$. A more likely possibility is that two configurational isomers of the dibromophosphinorhodacarborane anion exist in solution, as depicted in Figure 2. The nmr data indicate that isomer A, for which only one carborane C-H proton resonance was observed, predominates at higher temperatures, while isomer B, for which two carborane C-H proton resonances were observed, is the major species at low temperature.[13] This assignment is consistent with the fact that only isomer B is observed in the solid state, although this may be a result of the intermolecular packing associated with the ion-pairing interactions. The broadness of the $^{31}P\{^1H\}$ and ^1H nmr resonances due to the triphenylphosphonium cation is unusual and may be the result of ion-pairing in solution, which would give rise to spin-coupling between the quadrupolar bromine nuclei of the anion and the phosphorus and hydrogen nuclei of the cation. Cooling the sample effects a degree of quadrupolar decoupling,[15] thus decreasing the line-widths of the observed resonances. Ten-fold dilution of the ^1H nmr sample of [$HPPh_3$] 3 had little effect on the line width of the P-H proton resonance.

The formation of [$HPPh_3$] 3 from complex 1 and BBr_3 was unexpected; however, monitoring this reaction by $^{31}P\{^1H\}$ nmr demonstrated that the formation of [$HPPh_3$] 3 was accompanied by the production of triphenylphosphine oxide. This observation suggests that adventitious moisture and oxygen may have disrupted the reaction sequence shown in equation (1) and caused the formation of [$HPPh_3$] 3. Although the exact mechanism for the formation of [$HPPh_3$] 3 was not determined it is conceivable that hydride-bromide exchange could first occur in complex 1 to produce closo-3,3-$(Ph_3P)_2$-3-Br-3,1,2-$RhC_2B_9H_{11}$, 4.[16] This exchange might be expected to be promoted by trace amounts of free radicals such as molecular oxygen. Although the direct conversion of 1 to 4 has never been observed it is noteworthy that complex 1 reacts in refluxing carbon tetrachloride and chloroform to produce closo-3,3-$(Ph_3)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$.[17] Complex 4 could then dissociate a triphenylphosphine ligand to produce the 16-electron complex "closo-3-(Ph_3P)-3-Br-3,1,2-$RhC_2B_9H_{11}$" and uncoordinated triphenylphosphine. Hydrogen bromide, produced from the hydrolysis of BBr_3, could then protonate the triphenylphosphine to produce [$HPPh_3$]Br. The 16-electron complex produced by the ligand dissociation from complex 4 could then react with the bromide ion to generate [$HPPh_3$] 3. In support of these final reaction steps, we have observed that dichloromethane solutions of complex 4 react immediately with concentrated HBr to quantitatively produce [$HPPh_3$] 3.

The initial characterization of [$HPPh_3$] 3 has since allowed its identification as a product in several other reactions. The known complex *closo*-3-(Ph_3P)-3,3-(NO_3)-3,1,2-$RhC_2B_9H_{11}$, 5,[16] reacts with a ten-fold excess of Et_4NBr in dichloromethane/water to produce [Et_4N] 3 in 65% yield. Inasmuch as complex 5 is derived from complex 1 in 60-70% yield the overall conversion of 1 to [Et_4N] 3 via complex 4 offers little preparative advantage over the original preparation. It has been found, however, that the anionic rhodacarborane K[18-crown-6] [*closo*-3,3-(Ph_3P)$_2$-3,1,2-$RhC_2B_9H_{11}$], K[18-crown-6] 6,[18] reacts smoothly with bromoform in dichloromethane to afford K[18-crown-6] 3 in 85% yield. The salt K[18-crown-6] 6 is easily produced from complex 1 in 90% yield which makes the overall conversion of 1 to K[18-crown-6] 3 via K[18-crown-6] 6 a quite serviceable reaction sequence.

The preparation of [Et_4N] 3 from complex 5 and Et_4NBr suggested to us that it might be possible to prepare chloro and iodo complexes analogous to [$HPPh_3$] 3 by the reaction of a suitable tetraalkylammonium halide with complex 5. Indeed, the reaction of one molar equivalent of (*n*-C_4H_9)$_4$NI and 6 molar equivalents of NaI in the two phase reaction medium CH_2Cl_2/H_2O generated [(*n*-C_4H_9)$_4$N][*closo*-3-(Ph_3P)-3,3-(I)$_2$-3,1,2-$RhC_2B_9H_{11}$], [*n*-C_4H_9)$_4$N] 7, in 90% yield.

An analogous reaction of complex 5 with Me_4NCl produced a red orange solid that appeared to be [Me_4N] [*closo*-3-(Ph_3P)-3,3-(Cl)$_2$-3,1,2-$RhC_2B_9H_{11}$]; however, this solid was not easily purified. It was later found that the reactive species generated from [Et_4N] [*closo*-3-(Ph_3P)-3-(CO)-3,1,2-$RhC_2B_9H_{11}$] by oxidative removal of the carbon monoxide ligand[19] readily reacted with dichloromethane to produce [Et_4N] [*closo*-3-(Ph_3P)-3,3-(Cl)$_2$-3,1,2-$RhC_2B_9H_{11}$], [Et_4N] 8, in 60% yield.

While the $^{31}P\{^1H\}$ nmr spectrum of [Et_4N] 8 in 20% CD_2Cl_2/CH_2Cl_2 did not change when the temperature was lowered to -73° C, the solution behavior of [*n*-C_4H_9)$_4$N] 7 was qualitatively similar to [$HPPh_3$] 3. In contrast to [$HPPh_3$] 3, solutions of [(*n*-C_4H_9)$_4$N] 7 contain only one isomer at 0° C. It thus appears that the metal vertex of [Et_4N] 8 freely rotates about the metal-carborane axis, while [$HPPh_3$] 3 and [($\underline{n}$-C_4H_9)$_4$N] 7 display restricted rotation about the metal carborane axis. Although this phenomenon has been observed before in many other rhodacarboranes with substituents on the carborane ligand this is apparently the first observation of hindered rotation about the metal-unsubstituted carborane ligand axis.[13]

These studies have shown that halogen-containing rhodacarboranes of the general formula $[(Ph_3P)-(X)_2-RhC_2B_9H_{11}]^-$ can be easily prepared and isolated. Although these complexes were inactive catalysts for the hydrogenation of vinyltrimethylsilane under mild conditions it is anticipated that complexes such as these might serve as useful intermediates in the synthesis of metallacarboranes containing metal-metal bonds.

Experimental Part

All operations were conducted under an inert atmosphere of dry nitrogen or argon unless otherwise indicated.

Physical Measurements

The ^1H (200.133 MHz) and $^{31}P\{^1H\}$ (81.02 MHz) nmr spectra 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 were recorded at 80.5 MHz on a Fourier transform instrument designed by Professor F.A.L. Anet and co-workers. The ^{31}P and ^{11}B nmr chemical shifts are reported in ppm downfield from D_3PO_4 and $BF_3.Et_2O$, respectively. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 137 Spectrophotometer. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, New York and melting points were determined on a Mel-Temp instrument in capillary tubes sealed in vacuo and are uncorrected. Glove box manipulations were performed in a Vacuum

Atmospheres HE-43 facility. The mass spectrum was recorded on an Associated Electrical Industries MS-9 instrument.

Materials

All solvents were reagent grade and when necessary were distilled from appropriate drying agents.[11] Boron tribromide (Alfa) was distilled *in vacuo* before use. The complexes *closo*-3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$,[17] K[18-cr -6] [*closo*-3,3-$(Ph_3P)_2$-3,1,2-$RhC_2B_9H_{11}$],[18] *closo*-3-(Ph_3P)-3,3-(NO_3)-3,1, ${}_2B_9H_{11}$,[16] *closo*-3,3-$(Ph_3P)_2$-3-Br-3,1,2-$RhC_2B_9H_{11}$[16] were prepared as previously described. Florisil (MCB) was heated to 120° C for 8 hours *in vacuo* prior to use.

→ Insert additional experimental material here.

Reaction of 1 with Boron Tribromide: Preparation of [HPPh$_3$] 3 Complex 1 (1.52g, 2.00 mmol) was slurried in 300 ml benzene and freeze-pump-thawed three times on the high vacuum line. Boron tribromide (0.8 ml, 8.44 mmol) was freeze-pump-thawed three times on the high vacuum line and distilled into the frozen reaction mixture. The reaction was thawed to ambient temperature and stirred for 48 h, affording a colorless solid and a deep red solution. The solution was concentrated by vacuum distillation to about 10 ml and the flask was transferred to the glove box. The solution was filtered to yield 150 mg $Ph_3P.BBr_3$ (identified by its IR spectrum[20]). The filtrate was mounted on a Florisil - benzene chromatographic column (2 x 20 cm) in the glove box and elution with benzene yielded a reddish purple band followed by a red band. Addition of heptane to both fractions and concentration *in vacuo* yielded 100 mg of a purple solid and 650 mg red crystals contaminated with $Ph_3P.BBr_3$. Recrystallization of the red product yielded 450 mg pure [$HPPh_3$] [*closo*-3-(Ph_3P)-3,3-$(Br)_2$-3,1,2-$RhC_2B_9H_{11}$]. (22%) m.p. 155-160 ° C. Anal. Calc'd for $C_{47}H_{51}B_9Br_2P_2Rh$: C, 54.39; H, 4.95; B, 9.38; Br, 15.40; P, 5.97; Rh, 9.91.

Insert

Reaction of 1 with BF_3: Preparation of 2

Complex 1 (810 mg, 1.07 mmol) was slurried in 300 mL benzene. BF_3 (purified by passage through a -91° C trap (heptane/nitrogen)) was bubbled through the solution for 5 min. The solution was stirred overnight, concentrated in vacuo to ca 10 mL and mounted on a silica gel/heptane chromatographic column (2 x 20 cm). Elution with benzene/heptane (1:1) yielded a dark purple band, which after concentration in vacuo, filtration and drying in vacuo afforded 320 mg 2 (60%). Elution of the chromatographic column with dichloromethane yielded a yellow band from which 30 mg unreacted 1 was isolated.

Reaction of 1 with B_2H_6: Preparation of 2

Complex 1 (620 mg, 0.82 mmol) was slurried in 300 mL benzene and diborane (generated from 6 mL 85% H_3PO_4 and 320 mg $NaBH_4$) was bubbled through the solution for 24 h. The solution was then purged with argon, evaporated in vacuo and treated as above to yield 300 mg 2 (74%), 10 mg $Ph_3P.BH_3$ (identified by IR) and 30 mg unreacted 1.

Found: C, 51.26; H, 4.88; B, 9.38; Br, 14.93; P, 6.04; Rh, 9.81. Osmometric molecular weight in benzene: 1144 (one determination) Calc'd for 3: 1037.93. The major ions observed in the mass spectrum of 3 are at m/e 384-397 and correspond to $[Br_2RhC_2B_9H_{11}]^+$. Infrared spectrum[21] (Nujol mull): 2525(vs), 1575(m), 1560(w), 1475(vs), 1430(vs), 1310(m), 1190(m), 1160(m), 1115(s), 1080(s), 1070(m), 1035(w), 1025(w), 1005(m), 985(m), 933(w), 908(w), 897(w), 862(w), 852(w), 823(w), 755(s,sh), 746(vs), 727(s), 692 cm^{-1} (vs). ^1H nmr spectra[21] ($CDCl_3$, 27° C):10.9 (d, br, $W_{1/2} \approx 220$ Hz, $J_{P-H} \approx 560$ Hz, P-H of $(HPPh_3)^+$), 7.58 (m, phenyl protons of $(HPPh_3)^+$ and coord. PPh_3), 4.30, 3.78 and 3.70 δ (br, s, carborane C-H). At -33° C: 10.73 (d, $J_{P-H}=552$ Hz), 7.58 (m), 4.32, 3.76 and 3.73 δ (br, s, carborane C-H). $^{31}P\{^1H\}$ nmr spectrum ($CDCl_3$): 33.7 (d, $J_{Rh-P}=151$ Hz), 27.5 (d, $J_{Rh-P}=134$ Hz) and -4.5 ppm (br, s, $J_{P-H}=550$ Hz in coupled spectrum). $^{11}B\{^1H\}$ nmr spectrum ($\{CD_3\}_2CO$): 16.3 (2), 3.8 (1), 1.4 (3), -3.8 (2) and -17.1 ppm (1).

Reaction of 1 with Boron Tribromide Monitored by $^{31}P\{^1H\}$ nmr Spectroscopy A 10 mm O.D. nmr tube was attached to a 14-20 joint and charged with 50 mg (66 mmol) of complex 1. Boron tribromide (50 ml, 527 mmol) was dissolved in 3 ml C_6D_6, freeze-pump-thawed three times, distilled into the nmr tube and the tube sealed off under vacuum. After six h the $^{31}P\{^1H\}$ nmr spectrum exhibited, in addition to a doublet at 41.2 ppm due to 1, two doublets at 35.6 andd 35.4 ppm ($J_{Rh-P}=131$ Hz for both doublets). After 3 days the doublets mentioned above were replaced by a broad resonance at -5.4 ppm due to $Ph_3.BBr_3$,[26] two doublets and a broad singlet due to $[HPPh_3]$ 3 and an intense resonance at 24.3 ppm due to triphenylphosphine oxide. Additionally, three resonances are observed at 50.8 ppm (dd, $J_{Rh-P}=137$ Hz, small splitting = 5 Hz), a doublet at 49.8 ppm ($J_{Rh-P}=139$ Hz) and a doublet at 38.0 ppm ($J_{Rh-P}=115$ Hz). Two of these resonances are assigned to complex 2 and the identity of the third component is unknown.

Preparation of K[18-crown-6] *3* To a solution of 3.30 g (3.10 mmol) of K[18-crown-6][*closo*-3,3-$(Ph_3P)_2$-3,1,2-$RhC_2B_9H_{11}$ in 200 ml CH_2Cl_2 was added 4.5 g (18 mmol) of bromoform and the reaction was stirred under N_2 for 24 h. The solution was then filtered and evaporated leaving a red residue which was washed three times with ether. The resultant residue was recrystallized from CH_2Cl_2/Et_2O several times producing a pure microcrystalline red solid. 2.5 g (83%). m.p. 175° (dec). Anal. Calcd for $C_{32}H_{50}B_9Br_2PRhKO_6$: C, 40.00; H, 5.25; B, 10.13; Br, 16.63; P, 3.22; Rh, 10.71; K, 4.07; O, 9.99. Found: C, 40.12; H, 5.30; B, 9.78; Br, 16.83; P, 3.25; Rh, 10.45; K, 4.02. IR (nujol) 2480(vs), 1575(w), 1560(w), 1300(m), 1250(w), 1215(m), 1165(w), 1070(vs,br), 970(w), 940(s), 880(w), 830(s), 745(s), 738(s), 695(s), 685(s). ^1H nmr (CD_2Cl_2, 25° C): 7.85(m), 7.28(m), (15H, phenyl protons), 4.56 (1H, s, carborane C-H), 3.47 (24H, s, CH_2 of 18-crown-6). $^{31}P\{^1H\}$ (CH_2Cl_2/d_6-benzene, 25° C): 33.7(d, J_{Rh-P} = -155 Hz); at -33° C: 34.5(d, J_{Rh-P} = 157 Hz); 34.1(d, J_{Rh-P} = 154 Hz). $^{11}B\{^1H\}$ (CH_2Cl_2, 25° C): 10.3(2), 7.42(3), -5.13 (2), -11.03 (1), -17.1 (1).

Preparation of [(*n*-Bu)$_4$N] [*closo*-3-(Ph_3P)-3,3-$(I)_2$-3,1,2-$RhC_2B_9H_{11}$], [(*n*-Bu)$_4$N] *7* To 200 ml CH_2Cl_2 was added 0.200 g (0.36 mmol) of *closo*-3-(Ph_3P)-3,3-(NO_3)-3,1,2-$RhC_2B_9H_{11}$, 0.15 g (0.14 mmol) of (*n*-Bu)$_4$NI and 0.35 g (2.3 mmol) of NaI producing a red solution. Approximately 80 ml distilled water was then added producing a very dark solution. The two phases were vigorously stirred for 2 h. After the organic phase was separated from the aqueous phase and dried over $MgSO_4$, the solvent was removed *in vacuo* producing a dark red oil. This oil was redissolved in CH_2Cl_2 and benzene producing a dark red solution which was evaporated *in vacuo*. This process was repeated until a solid residue was obtained. The solid so obtained was recrystallized from CH_2Cl_2/heptane producing pure elongated black-red needles. Yield 0.32 g, 90%, m.p. 180-185° C (dec). Anal. Calcd for $C_{36}H_{62}B_9RhPI_2$: C, 42.50; H, 6.28; B, 9.79; Rh, 10.36; P, 3.11; I, 25.53. Found: C, 43.69; H, 6.34; B, 9.70; Rh, 10.17, P, 3.11; I, 25.28. IR(nujol). 2500(s), 1575(w), 1560(w), 1375(s), 1310(w), 1210(w), 1190(m), 1155(m), 1085(s), 1170(w), 1025(ms), 1000(w), 985(s), 910(w), 895(w), 845(w), 755(vs), 690(vs), ^1H nmr (CD_2Cl_2, 25° C): 7.74 and 7.26(15H, m, phenyl protons), 4.96(2H, br, s, carborane C-H), 3.04 (8H, m, cation), 1.47(8H, m, cation); 1.29(8H, q, cation); .951(12H, t, cation). At -33° C: 7.8-7.16 (15H, broad envelope, phenyl protons); 5.18 (1H, br, s, carborane C-H); 4.70 (1H, br, s, carborane C-H); 2.96 (8H, m, cation); 1.26 (8H, q, cation); 0.917 (12H, t, cation). $^{31}P\{^1H\}$ (CH_2Cl_2/d_6-benzene, 25° C): 35.3(d, J_{Rh-P} = 154 Hz); 35.1(d, J_{Rh-P} = 154 Hz). At 0° C: 35.1(d, J_{Rh-P} = 154 Hz). $^{11}B\{^1H\}$ (CH_2Cl_2, 25° C): 8.16(1); 5.89(2); -4.86(2); -7.08(2); -13.83(1); -24.88(1).

Preparation of $[Et_4N][$*closo*$-3-(Ph_3P)-3,3-(Cl)_2-3,1,2-RhC_2B_9H_{11}]$ The cycloadduct formed between 0.500 g (0.76 mmol) $[Et_4N]$ $[$*closo*$-3-(Ph_3P)-3-(CO)-3,1,2-RhC_2B_9H_{11}]$ and 0.15 g benzhydroxamic acid chloride was isolated as previously described.[19] This solid was dissolved in 5 ml CH_2Cl_2 and 30 ml acetone and stirred for three hours at room temperature producing a cherry red solution. After the addition of 30 ml benzene the solution was concentrated *in vacuo* to 10 ml. The resultant orange microcrystalline product was then isolated by filtration and rinsed with pentane; yield 0.32 g, 60%. An analytical sample was obtained by recrystallization of the product from acetone/heptane. Anal. Calcd for $C_{28}H_{46}NRhPB_9Cl_2$: C, 48.13; H, 6.63; N, 2.00; Rh, 14.72; P, 4.43; B, 13.92; Cl, 10.14. Found: C, 48.34; H, 6.92; N, 3.92; Rh, 14.19; P, 4.44; B, 14.09; Cl, 10.06. IR(nujol): 2500(vs), 1575(w), 1560(w), 1185(m), 1170(s), 1150(m), 1090(s), 1060(w), 1040(w), 1025(w), 1020(m), 1005(m), 990(m), 930(w), 905(w), 888(w), 850(w), 785(m), 758(m), 751(m), 742(m), 695(s). ^{1}H nmr (CD_3COCD_3, 25° C): 8.07(m) and 7.35(15H, m, phenyl protons of PPh_3), 4.61 (1H, s, br, carborane C-H), 3.50 (8H, q, cation), 1.40 (12H, m, cation). $^{31}P\{^{1}H\}$ nmr (CD_3COCD_3, 25° C): 33.0 (d, J_{Rh-P} = 155 Hz). $^{11}B\{^{1}H\}$ (CD_3COCD_3, 25° C). 7.08(2), -4.18(1), -6.68(3), -12.75(2), -24.67(1).

X-ray Crystal and Molecular Structural Determination of [HPPh$_3$] [PPh$_3$Br$_2$RhC$_2$B$_9$H$_{11}$]•1.5 C$_6$H$_6$ A single crystal bounded by the (0 1 -1), (0 0 1), (1 1 0), (0 0 -1), (-1 -1 0) and (2 -1 0) faces with dimensions normal to these faces of 0.0, 0.0, 0.031, 0.0065, and 0.04 cm, respectively, was mounted on a glass fiber. From preliminary oscillation and Weissenberg photographs the space group was determined to be triclinic P1 or $P\bar{1}$. The automatic centering, autoindexing, and least-squares routines of a Syntex $P\bar{1}$ diffractometer were used to determine the unit cell parameters to be a = 12.591(5), b = 13.299(4), c = 17.568(5) Å, α= 111.77(2), β = 94.41(3), γ= 61.24(3)°, and V = 2376.1(1.3) Å^3, based on 15 high-angle reflections. A graphite crystal was used to provide monochromatic MoK$_\alpha$-radiation (0.7107 Å). The crystal density was found to be 1.37(2) by flotation in aqueous KI, while the calculated density was 1.450(1) g cm^{-3} based on Z = 2.

Intensity data were collected with a θ-2θ scan technique to limit of 2θ = 50°. Reflections were scanned at a constant rate of 2.0 deg/min from 1.15° below the K_{α_1} reflection to 1.15° above the K_{α_2} reflection. The total background counting time, measured at each end of the scan, was equal to the scan time for each reflection. The intensities of three standard reflections were measured after every 97 reflections. No significant deviations were observed. The data were corrected for Lorentz and polarization effects and for absorption[22] (mu=22.4 cm^{-1}, maximum, minimum, and average transmission factors of 0.9320, 0.7403, 0.8852). The intensity of a reflection, $\underline{I}(hkl)$, and its estimated standard deviation, sigma[$\underline{I}(hkl)$], were calculated as described previously.[22] Of the 8049 unique reflections, 1995 with intensities less than three times their standard deviations were considered to be unobserved and were omitted from subsequent calculations.

Solution and Refinement of the Structure The coordinates of the rhodium atom and two bromine atoms were determined by solution of a three-dimensional Patterson map, and a subsequent Fourier summation resulted in the location of all nonhydrogen atoms. The 6 phenyl groups and the benzene solvate were described as rigid C_6 hexagons with C-C = 1.39 Å and C-H = 1.0 Å. The 11 hydrogen atoms of the $C_2B_9H_{11}$ cage and the remaining hydrogen atom of the cation were located on difference maps. After several cycles of full-matrix least-squares refinement, with anisotropic thermal parameters for Rh, Br, P and the cage C_2B_9 atoms, and isotropic thermal parameters for the remaining atoms, convergence was reached with $R^{23} = 0.046$, $Rw = 0.054$. The refinement included positional and anisotropic thermal parameters for Rh, P, Br, and the C_2B_9 cage, positional and isotropic thermal parameters for the hydrogen atom of the cation, group and carbon isotropic thermal parameters for the phenyl groups and benzene molecules, and positional parameters for the remaining nongroup hydrogen atoms. For the latter hydrogen atoms, $\underline{B}$ was set at 1.0 plus $\underline{B}$ of the carbon atom to which the hydrogen atom is attached. The "goodness of fit" was 1.576, defined as $[\Sigma w(|Fo|-|Fc|)^2/(No - Nv)]^{1/2}$, with No (number of observations) = 6054 and Nv (number of variables) = 275. On a final difference map, the highest peak is 0.5 e/$Å^3$. There are 6 such peaks, all within 1 Å of PPh_3 or $HPPh_3^+$.

Scattering factors for Rh, Br, P, C, and B were taken from ref. 25 and for H from Stewart, Davidson and Simpson.[24] Real and imaginary terms for anomalous scattering were taken from ref. 25. The function $\sum w||Fo| - |Fc||^2$ was minimized in the refinement.

The final observed and calculated structure factors are available as supplementary material.

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Supplementary Material Available: A listing of structure factor amplitudes for $[HPPh_3][$*closo*$\text{-}3\text{-}(Ph_3P)\text{-}3,3\text{-}(Br)_2\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$ (21 pages). Ordering information is given on any current masthead page.

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21) Abbreviations for infrared spectra: vs-very strong, s-strong, m-medium, w-weak, br-broad, sh-shoulder. For nmr spectra: s-singlet, d-doublet, m-complex multiplet, br-broad, $W_{1/2}$-width of resonance at half-height.

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23) The function minimized during least-squares refinement was $w(|Fo| - |Fc|)^2$ where $w = [\sigma(|Fo|)]^{-2}$. The discrepancy indices are defined as:

$$R = [\Sigma||Fo| - |Fo||/\Sigma|Fo|]; \quad Rw = [\Sigma w||Fo| - |Fc||^2/\Sigma w|Fo|^2]^{1/2}$$

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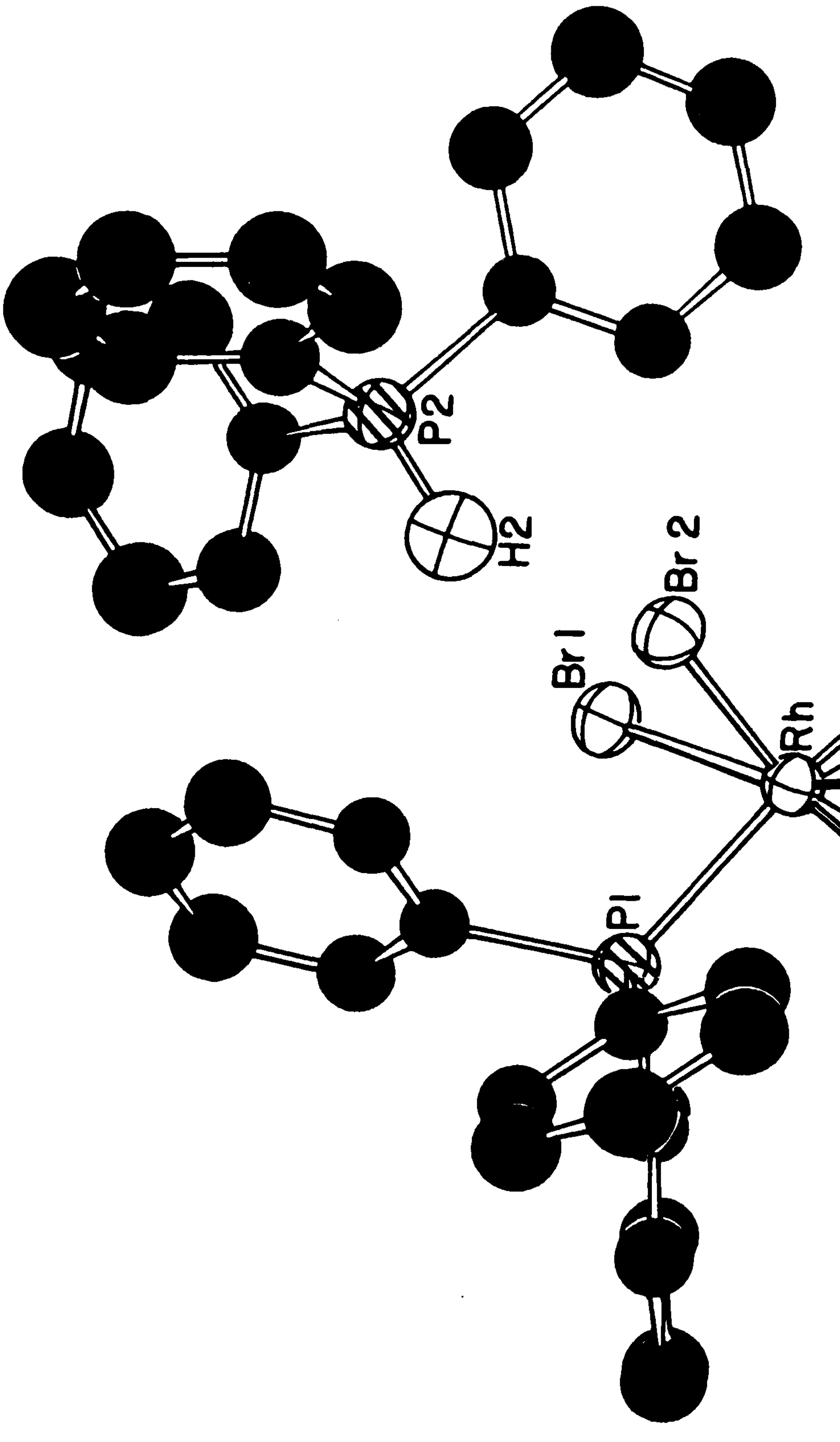
Figure Captions

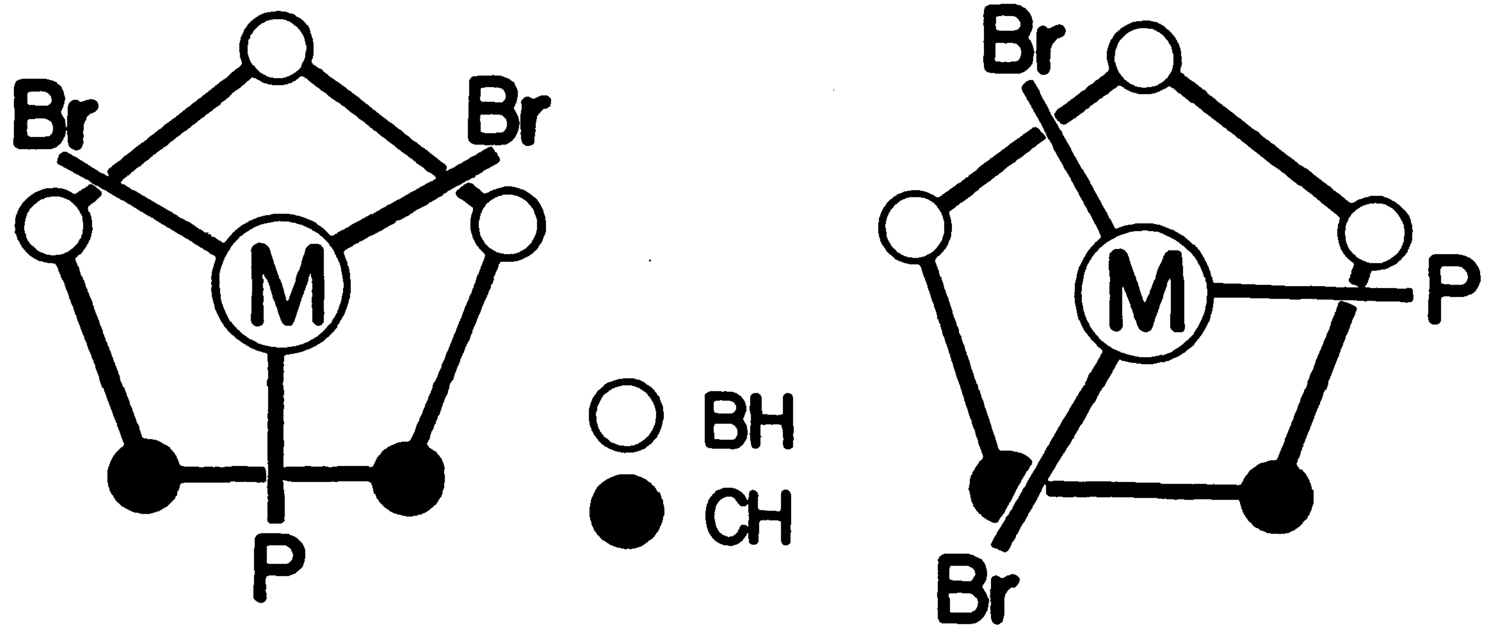
Figure 1. Structure of $[HPPh_3]$ [*closo*-3-(Ph_3P)-3,3-$(Br)_2$-3,1,2-$RhC_2B_9H_{11}$] 3. Hydrogen atoms of phenyl rings and carborane hydrogen atoms have been omitted for clarity. Thermal ellipsoids represent 50% probability.

Figure 2. Configurational isomers of the dibromophosphinorhodacarborane anion which exist in solution.

Numbering of compounds in this paper:

1. *closo*-3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$
2. [*closo*-$(Ph_3P)RhC_2B_9H_{11}]_2$
3. [*closo*-3-(Ph_3P)-3,3-$(Br)_2$-3,1,2-$RhC_2B_9H_{11}]^-$
4. *closo*-3,3-$(Ph_3P)_2$-3-Br-3,1,2-$RhC_2B_9H_{11}$
5. *closo*-3-(Ph_3P)-3,3-(NO_3)-3,1,2-$RhC_2B_9H_{11}$
6. [*closo*-3,3-$(Ph_3P)_2$-3,1,2-$RhC_2B_9H_{11}]^-$
7. [*closo*-3-(Ph_3P)-3,3-$(I)_2$-3,1,2-$RhC_2B_9H_{11}]^-$


H2
P2
Br 2
Br 1
Rh
P1
C2
C1
B7
B11
B12
B8
B6
B10
B9
B4
B5



A (mirror plane)

B (enantiomeric)

Table I. Interatomic Distances, A

Rh-C(1)	2.152(6)
Rh-B(4)	2.171(6)
Rh-C(2)	2.183(6)
Rh-B(8)	2.203(6)
Rh-B(7)	2.229(7)
Rh-P(1)	2.360(2)
Rh-Br(2)	2.520(2)
Rh-Br(1)	2.598(1)
Rh...H(P2)	3.98
Br(1)..H(P2)	3.06(6)
Br(2)..H(P2)	2.70(6)
P(1)-C(11)	1.854 *
P(1)-C(21)	1.832
P(1)-C(31)	1.843
P(2)-H(P2)	1.36(6)
P(2)-C(41)	1.780
P(2)-C(51)	1.764
P(2)-C(61)	1.782
C(1)-H(1)	0.90(6)
C(1)-C(2)	1.651(9)
C(1)-B(5)	1.681(9)
C(1)-B(6)	1.735(10)
C(1)-B(4)	1.740(8)
B(4)-H(4)	1.06(6)
B(4)-B(9)	1.771(10)
B(4)-B(5)	1.795(10)
B(4)-B(8)	1.819(10)
B(8)-H(8)	1.25(5)
B(8)-B(12)	1.805(10)
B(8)-B(9)	1.806(10)
C(2)-H(2)	0.89(6)
C(2)-B(11)	1.678(10)
C(2)-B(7)	1.679(10)
C(2)-B(6)	1.718(10)
B(7)-H(7)	1.01(6)
B(7)-B(12)	1.764(10)
B(7)-B(11)	1.812(11)
B(7)-B(8)	1.819(10)
B(12)-H(12)	1.06(6)
B(9)-H(9)	1.06(6)
B(9)-B(10)	1.769(11)
B(9)-B(12)	1.798(11)
B(5)-H(5)	1.03(6)
B(5)-B(10)	1.752(12)
B(5)-B(6)	1.753(11)
B(5)-B(9)	1.762(11)
B(6)-H(6)	1.06(5)
B(6)-B(11)	1.735(12)
B(6)-B(10)	1.758(11)
B(10)-H(10)	1.05(6)
B(10)-B(11)	1.760(12)
B(10)-B(12)	1.775(12)

B(11)-H(11)	1.03(6)
B(11)-B(12)	1.748(12)

(*) Standard deviations are not given for distances involving atoms which are members of rigid groups.

Table II Interatomic Angles (deg)

C(1)-Rh(3)-B(4)	47.5(2)	H(P2)-P(2)-C(4 1)	104.
C(1)-Rh(3)-C(2)	44.8(2)	H(P2)-P(2)-C(5 1)	109.
C(1)-Rh(3)-B(8)	80.6(2)	H(P2)-P(2)-C(6 1)	113.
C(1)-Rh(3)-B(7)	79.0(3)	C(4 1)-P(2)-C(5 1)	111.7
C(1)-Rh(3)-P(1)	108.5(2)	C(4 1)-P(2)-C(6 1)	109.8
C(1)-Rh(3)-Br(2)	164.3(2)	C(5 1)-P(2)-C(6 1)	109.2
C(1)-Rh(3)-Br(1)	94.6(2)	H(1)-C(1)-C(2)	116.(4)
B(4)-Rh(3)-C(2)	79.4(3)	H(1)-C(1)-B(5)	119.(4)
B(4)-Rh(3)-B(8)	49.1(3)	H(1)-C(1)-B(6)	110.(4)
B(4)-Rh(3)-B(7)	83.2(3)	H(1)-C(1)-B(4)	127.(4)
B(4)-Rh(3)-P(1)	88.1(2)	H(1)-C(1)-Rh(3)	108.(4)
B(4)-Rh(3)-Br(2)	129.7(2)	C(2)-C(1)-B(5)	109.1(5)
B(4)-Rh(3)-Br(1)	137.0(2)	C(2)-C(1)-B(6)	60.9(4)
C(2)-Rh(3)-B(8)	78.4(3)	C(2)-C(1)-B(4)	110.1(5)
C(2)-Rh(3)-B(7)	44.7(3)	C(2)-C(1)-Rh(3)	68.6(3)
C(2)-Rh(3)-P(1)	150.8(2)	B(5)-C(1)-B(6)	61.7(4)
C(2)-Rh(3)-Br(2)	122.2(2)	B(5)-C(1)-B(4)	63.2(4)
C(2)-Rh(3)-Br(1)	85.0(2)	B(5)-C(1)-Rh(3)	125.1(4)
B(8)-Rh(3)-B(7)	48.5(3)	B(6)-C(1)-B(4)	114.6(5)
B(8)-Rh(3)-P(1)	112.7(2)	B(6)-C(1)-Rh(3)	126.4(4)
B(8)-Rh(3)-Br(2)	88.2(2)	B(4)-C(1)-Rh(3)	66.8(3)
B(8)-Rh(3)-Br(1)	160.7(2)	H(2)-C(2)-C(1)	113.(4)
B(7)-Rh(3)-P(1)	159.5(2)	H(2)-C(2)-B(11)	121.(4)
B(7)-Rh(3)-Br(2)	85.4(2)	H(2)-C(2)-B(7)	124.(4)
B(7)-Rh(3)-Br(1)	112.3(2)	H(2)-C(2)-B(6)	111.(4)
P(1)-Rh(3)-Br(2)	85.93(5)	H(2)-C(2)-Rh(3)	104.(4)
P(1)-Rh(3)-Br(1)	86.54(4)	C(1)-C(2)-B(11)	111.7(5)
Br(2)-Rh(3)-Br(1)	92.47(4)	C(1)-C(2)-B(7)	113.6(5)
Rh(3)-Br(1)-H(P2)	89.(1)	C(1)-C(2)-B(6)	62.0(4)
Rh(3)-Br(2)-H(P2)	99.(1)	C(1)-C(2)-Rh(3)	66.6(3)
Rh(3)-P(1)-C(1 1)	115.5	B(11)-C(2)-B(7)	85.4(5)
Rh(3)-P(1)-C(2 1)	118.1	B(11)-C(2)-B(6)	61.4(5)
Rh(3)-P(1)-C(3 1)	113.0	B(11)-C(2)-Rh(3)	128.4(5)
C(1 1)-P(1)-C(2 1)	100.5	B(7)-C(2)-B(6)	116.8(5)
C(1 1)-P(1)-C(3 1)	103.8	B(7)-C(2)-Rh(3)	69.1(3)
C(2 1)-P(1)-C(3 1)	104.1	B(6)-C(2)-Rh(3)	125.5(4)

H(4)-B(4)-C(1)	125.(3)	C(2)-B(6)-B(5)	102.9(5)
H(4)-B(4)-B(9)	118.(3)	C(2)-B(6)-B(10)	103.6(6)
H(4)-B(4)-B(5)	115.(3)	C(1)-B(6)-B(11)	105.1(5)
H(4)-B(4)-B(8)	127.(3)	C(1)-B(6)-B(5)	57.6(4)
H(4)-B(4)-Rh(3)	115.(3)	C(1)-B(6)-B(10)	104.3(5)
C(1)-B(4)-B(9)	102.9(5)	B(11)-B(6)-B(5)	108.0(6)
C(1)-B(4)-B(5)	56.8(4)	B(11)-B(6)-B(10)	60.5(5)
C(1)-B(4)-B(8)	104.5(5)	B(5)-B(6)-B(10)	59.9(5)
C(1)-B(4)-Rh(3)	65.7(3)	H(7)-B(7)-C(2)	116.(3)
B(9)-B(4)-B(5)	59.2(4)	H(7)-B(7)-B(12)	119.(3)
B(9)-B(4)-B(8)	60.4(4)	H(7)-B(7)-B(11)	105.(3)
B(9)-B(4)-Rh(3)	120.1(4)	H(7)-B(7)-B(8)	138.(3)
B(5)-B(4)-B(8)	107.3(5)	H(7)-B(7)-Rh(3)	120.(3)
B(5)-B(4)-Rh(3)	118.2(4)	C(2)-B(7)-B(12)	102.3(5)
B(8)-B(4)-Rh(3)	66.3(3)	C(2)-B(7)-B(11)	57.3(4)
H(5)-B(5)-C(1)	118.(3)	C(2)-B(7)-B(8)	104.8(5)
H(5)-B(5)-B(10)	127.(3)	C(2)-B(7)-Rh(3)	66.2(3)
H(5)-B(5)-B(6)	120.(3)	B(12)-B(7)-B(11)	58.5(5)
H(5)-B(5)-B(9)	125.(3)	B(12)-B(7)-B(8)	60.5(4)
H(5)-B(5)-B(4)	116.(3)	B(12)-B(7)-Rh(3)	118.5(5)
C(1)-B(5)-B(10)	106.9(5)	B(11)-B(7)-B(8)	107.5(5)
C(1)-B(5)-B(6)	60.7(4)	B(11)-B(7)-Rh(3)	118.7(5)
C(1)-B(5)-B(9)	105.7(5)	B(8)-B(7)-Rh(3)	65.0(3)
C(1)-B(5)-B(4)	60.0(4)	H(8)-B(8)-B(12)	110.(3)
B(10)-B(5)-B(6)	60.2(5)	H(8)-B(8)-B(9)	117.(3)
B(10)-B(5)-B(9)	60.5(5)	H(8)-B(8)-B(4)	133.(3)
B(10)-B(5)-B(4)	109.5(6)	H(8)-B(8)-B(7)	118.(3)
B(6)-B(5)-B(9)	109.0(6)	H(8)-B(8)-Rh(3)	120.(3)
B(6)-B(5)-B(4)	111.0(5)	B(12)-B(8)-B(9)	59.7(4)
B(9)-B(5)-B(4)	59.7(4)	B(12)-B(8)-B(4)	106.0(5)
H(6)-B(6)-C(2)	121.(3)	B(12)-B(8)-B(7)	58.2(4)
H(6)-B(6)-C(1)	115.(3)	B(12)-B(8)-Rh(3)	117.8(4)
H(6)-B(6)-B(11)	128.(3)	B(9)-B(8)-B(4)	58.5(4)
H(6)-B(6)-B(5)	121.(3)	B(9)-B(8)-B(7)	106.0(5)
H(6)-B(6)-B(10)	132.(3)	B(9)-B(8)-Rh(3)	116.8(4)
C(2)-B(6)-C(1)	57.1(4)	B(4)-B(8)-B(7)	106.9(5)
C(2)-B(6)-B(11)	58.1(4)	B(4)-B(8)-Rh(3)	64.5(3)

(CONTINUED)

B(7)-B(8)-Rh(3)	66.5(3)	H(11)-B(11)-B(6)	120.(3)
H(9)-B(9)-B(5)	122.(3)	H(11)-B(11)-B(12)	125.(3)
H(9)-B(9)-B(10)	122.(3)	H(11)-B(11)-B(10)	126.(3)
H(9)-B(9)-B(4)	120.(3)	H(11)-B(11)-B(7)	119.(3)
H(9)-B(9)-B(12)	123.(3)	C(2)-B(11)-B(6)	60.4(4)
H(9)-B(9)-B(8)	120.(3)	C(2)-B(11)-B(12)	103.0(5)
B(5)-B(9)-B(10)	59.5(5)	C(2)-B(11)-B(10)	105.2(6)
B(5)-B(9)-B(4)	61.0(4)	C(2)-B(11)-B(7)	57.3(4)
B(5)-B(9)-B(12)	106.3(5)	B(6)-B(11)-B(12)	109.1(6)
B(5)-B(9)-B(8)	109.3(5)	B(6)-B(11)-B(10)	60.4(5)
B(10)-B(9)-B(4)	109.8(5)	B(6)-B(11)-B(7)	109.2(5)
B(10)-B(9)-B(12)	59.7(5)	B(12)-B(11)-B(10)	60.8(5)
B(10)-B(9)-B(8)	109.6(5)	B(12)-B(11)-B(7)	59.4(4)
B(4)-B(9)-B(12)	108.4(5)	B(10)-B(11)-B(7)	108.6(6)
B(4)-B(9)-B(8)	61.1(4)	H(12)-B(12)-B(11)	117.(3)
B(12)-B(9)-B(8)	60.1(4)	H(12)-B(12)-B(7)	117.(3)
H(10)-B(10)-B(5)	127.(3)	H(12)-B(12)-B(10)	122.(3)
H(10)-B(10)-B(6)	117.(3)	H(12)-B(12)-B(9)	127.(3)
H(10)-B(10)-B(11)	114.(3)	H(12)-B(12)-B(8)	122.(3)
H(10)-B(10)-B(9)	129.(3)	B(11)-B(12)-B(7)	62.1(5)
H(10)-B(10)-B(12)	121.(3)	B(11)-B(12)-B(10)	59.9(5)
B(5)-B(10)-B(6)	59.9(5)	B(11)-B(12)-B(9)	107.6(6)
B(5)-B(10)-B(11)	106.9(5)	B(11)-B(12)-B(8)	111.0(5)
B(5)-B(10)-B(9)	60.1(4)	B(7)-B(12)-B(10)	110.1(6)
B(5)-B(10)-B(12)	107.8(5)	B(7)-B(12)-B(9)	108.7(5)
B(6)-B(10)-B(11)	59.1(5)	B(7)-B(12)-B(8)	61.3(4)
B(6)-B(10)-B(9)	108.4(5)	B(10)-B(12)-B(9)	59.4(5)
B(6)-B(10)-B(12)	106.9(5)	B(10)-B(12)-B(8)	109.3(6)
B(11)-B(10)-B(9)	108.4(6)	B(9)-B(12)-B(8)	60.1(4)
B(11)-B(10)-B(12)	59.3(5)	P(2)-H(P2)-Br(2)	141.(3)
B(9)-B(10)-B(12)	61.0(5)	P(2)-H(P2)-Br(1)	127.(3)
H(11)-B(11)-C(2)	121.(3)	Br(2)-H(P2)-Br(1)	80.(2)

NOTE: Units of each e.s.d., in parentheses, are those of the least significant digit of the corresponding parameter. Standard deviations are not given for angles involving atoms which are members of rigid groups.

TABLE III POSITION AND VIBRATION PARAMETERS FOR **3**

ATOM	X	Y	Z	U11 OR B	U22	U33	U12	U13	U23	EQUIV B
Rh(3)	0.10808(4)	0.44528(4)	0.29666(2)	350(2)	369(2)	385(3)	-174(2)	-70(2)	192(2)	2.8
Br(1)	0.15686(5)	0.32874(5)	0.39598(3)	488(4)	468(4)	463(3)	-227(3)	-101(3)	258(3)	3.6
Br(2)	0.28032(5)	0.26288(6)	0.10850(4)	450(4)	488(4)	508(4)	-166(3)	26(3)	186(3)	4.0
P(1)	-0.00997(13)	0.34912(13)	0.23514(8)	386(8)	413(8)	389(8)	-201(7)	-59(6)	172(6)	3.1
P(2)	0.47492(14)	0.01962(14)	0.28169(9)	476(9)	472(9)	507(9)	-247(8)	-109(7)	248(7)	3.6
C(1)	-0.0097 (6)	0.6248 (5)	0.3893 (3)	518(38)	462(35)	422(33)	-226(30)	-8(27)	167(27)	3.7
C(2)	0.1356 (6)	0.5829 (6)	0.3986 (4)	703(45)	542(39)	596(38)	-411(36)	-315(33)	315(32)	4.3
B(4)	-0.0380 (6)	0.6157 (6)	0.2891 (4)	436(39)	433(39)	474(37)	-160(32)	-94(31)	240(32)	3.6
B(5)	-0.0772 (8)	0.7591 (7)	0.3747 (5)	552(47)	405(41)	672(49)	-121(36)	-84(39)	237(36)	4.6
B(6)	0.0300 (8)	0.7374 (7)	0.4451 (5)	930(64)	466(44)	528(44)	-386(45)	-101(42)	148(36)	5.0
B(7)	0.2183 (7)	0.5399 (7)	0.3107 (5)	398(40)	640(49)	705(49)	-277(38)	-125(36)	359(41)	4.3
B(8)	0.1088 (6)	0.5638 (6)	0.2365 (4)	546(44)	475(41)	539(41)	-243(35)	-32(34)	259(34)	3.9
B(9)	-0.0047 (7)	0.7261 (7)	0.2799 (5)	672(51)	510(45)	603(45)	-259(39)	-153(39)	335(38)	4.5
B(10)	0.0353 (8)	0.8006 (7)	0.3745 (5)	854(61)	403(43)	746(53)	-325(43)	-175(45)	248(39)	5.2
B(11)	0.1699 (9)	0.6886 (8)	0.3951 (6)	821(61)	622(52)	879(60)	-522(49)	-308(48)	332(46)	5.5
B(12)	0.1530 (8)	0.6791 (8)	0.2934 (5)	707(55)	618(51)	867(58)	-421(45)	-114(45)	414(45)	5.1
H(P(2))	0.3672(54)	0.1037(53)	0.2673(33)	5.5(14)						
H(1)	-0.0486(55)	0.6139(55)	0.4237(35)	5.0						
H(2)	0.1633(55)	0.5478(55)	0.4354(35)	5.0						
H(4)	-0.1129(54)	0.6084(52)	0.2616(33)	5.0						
H(5)	-0.1691(54)	0.8178(54)	0.3955(33)	5.0						
H(6)	0.0014(51)	0.7787(52)	0.5098(34)	5.0						
H(7)	0.3099(56)	0.4926(52)	0.3094(33)	5.0						
H(8)	0.1490(49)	0.5185(50)	0.1621(33)	5.0						
H(9)	-0.0510(52)	0.7733(52)	0.2406(33)	5.0						
H(10)	0.0244(51)	0.8903(55)	0.3994(33)	5.0						
H(11)	0.2346(53)	0.7046(52)	0.4290(34)	5.0						
H(12)	0.2122(53)	0.6942(52)	0.2653(33)	5.0						

NOTE: U-Values have been multiplied by 10000.0.
Units of u and isotropic B are Angstroms squared.
Units of each e.s.d., in parentheses, are those of the least significant digit of the corresponding parameter.
Thermal parameters of hydrogen atoms 1-12 were assigned to be 5.

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Abstract

The title compound was obtained in low yield from the reaction of *closo*-3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$, **1**, and BBr_3 and was characterized by an x-ray diffraction study. Red crystals of $[HPPh_3]$ [*closo*-3-(Ph_3P)-3,3-$(Br)_2$-3,1,2-$RhC_2B_9H_{11}$]·1.5 C_6H_6, $[HPPH_3]$ **3** 1.5C_6H_6, were triclinic, space group $P\bar{1}$, with *a* = 12.591(5), *b* = 13.299(4), *c* = 17.568(5) Å, α = 111.77(2), β = 94.41(3), γ = 61.24(3)° and Z = 2. The structure was solved by conventional heavy atom techniques to a final discrepancy index of R = 0.046 for 6054 independent observed reflections. The rhodacarborane anion is pseudo-octahedral about the rhodium atom and the phosphonium cation is near the rhodium-bound bromine atoms with Br...H distances of 3.06(6) and 2.70(6) Å. It was suggested on the basis of nmr spectral data and solubility properties that ion pairing may also be significant for $[HPPh_3]$ **3** in solution. It was found that K[18-crown-6] **3** could be prepared in high yield from the anionic rhodacarborane K[18-crown-6] [*closo*-3,3-$(Ph_3P)_2$-3,1,2-$RhC_2B_9H_{11}$] and bromoform. The iodo analog of **3**$^-$ could be isolated as the $(n\text{-}C_4H_9)_4N^+$ salt, in high yield, from the reaction of *closo*-3-(Ph_3P)-3,3-(NO_3)-3,1,2-$RhC_2B_9H_{11}$ and $(n\text{-}C_4H_9)_4NI$ and NaI in dichloromethane/water. The chloro analog of complex **3** could be prepared as the $[Et_4N]^+$ salt from the reaction of the 16-electron complex $[Et_4N]$ [*closo*-3-(Ph_3P)-3,1,2-$RhC_2B_9H_{11}$] (generated *in situ*) with CH_2Cl_2 in 60% yield.

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