Note Added in Proof.

The crystal structure of [Co(NH₃)₂(L-ala-gly-gly)] has been reported (Evans, E. J.; Hawkins, C. J.; Rodgers, J.; Snow, M. R. *Inorg. Chem.* **1983**, *22*, 34). The Co–N(amide) bond lengths average about 1.87 and 1.86 Å. A recent review on transition-metal complexes containing a metal–amide bond has appeared (Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 385).

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Synthesis and Characterization of Anionic Halogen-Containing Rhodacarboranes. Crystal and Molecular Structure of the Hydrogen-Bonded Ion Pair [HPPh₃][*closo*-3-Ph₃P-3,3-Br₂-3,1,2-RhC₂B₉H₁₁]
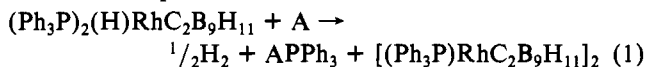
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The title compound was obtained in low yield from the reaction of *closo*-3,3-(Ph₃P)₂-3-H-3,1,2-RhC₂B₉H₁₁ (**1**) and BBr₃ and was characterized by an X-ray diffraction study. Red crystals of [HPPh₃][*closo*-3-Ph₃P-3,3-Br₂-3,1,2-RhC₂B₉H₁₁]·1.5C₆H₆, [HPPh₃][**3**]·1.5C₆H₆, were triclinic, space group P1̄, with *a* = 12.591 (5) Å, *b* = 13.299 (4) Å, *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 pseudooctahedral 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 [HPPh₃][**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-(Ph₃P)₂-3,1,2-RhC₂B₉H₁₁] and bromoform. The iodo analogue of **3**⁻ could be isolated as the (*n*-C₄H₉)₄N⁺ salt, in high yield, from the reaction of *closo*-3-Ph₃P-3,3-NO₃-3,1,2-RhC₂B₉H₁₁, (*n*-C₄H₉)₄NI, and NaI in dichloromethane/water. The chloro analogue of complex **3** could be prepared as the [Et₄N]⁺ salt from the reaction of the 16-electron complex [Et₄N][*closo*-3-Ph₃P-3,1,2-RhC₂B₉H₁₁] (generated in situ) with CH₂Cl₂ in 60% yield.

Introduction

We recently reported the reaction of *closo*-3,3-(Ph₃P)₂-3-H-3,1,2-RhC₂B₉H₁₁ (**1**) with benzoyl peroxide, which afforded the asymmetric (phosphine)rhodacarborane dimer [*closo*-(Ph₃P)RhC₂B₉H₁₁]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 eq 1.

$$(\text{Ph}_3\text{P})_2(\text{H})\text{RhC}_2\text{B}_9\text{H}_{11} + \text{A} \rightarrow$$
$$\tfrac{1}{2}\text{H}_2 + \text{APPh}_3 + [(\text{Ph}_3\text{P})\text{RhC}_2\text{B}_9\text{H}_{11}]_2 \quad (1)$$

While the reactions of **1** with diborane and boron trifluoride did indeed proceed as per eq 1,[3] that with boron tribromide produced in low yield a bromine-containing (phosphine)-rhodacarborane that was shown by X-ray crystallography to be the ionic complex [HPPh₃][*closo*-3-Ph₃P-3,3-Br₂-3,1,2-

RhC₂B₉H₁₁], [HPPh₃][**3**]. Subsequent to the characterization of [HPPh₃][**3**] improved synthetic methods were developed that allowed the isolation of **3**⁻ with a variety of supporting counterions in good yields. Moreover, it was found that the iodo and chloro analogues of **3**⁻ could be easily prepared. Herein we report the details of these studies.

Results and Discussion

The reaction of complex **1** with a 5-fold excess of BBr₃ in benzene at 25 °C for 48 h 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 [HPPh₃][*closo*-3-Ph₃P-3,3-Br₂-3,1,2-RhC₂B₉H₁₁]·1.5C₆H₆, [HPPh₃][**3**]·1.5C₆H₆, by X-ray crystallography (vide infra). Although the elemental analyses correctly indicated the composition of [HPPh₃][**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 that 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 [HPPh₃][**3**]·1.5C₆H₆.

The molecular structure of [HPPh₃][**3**] is shown in Figure 1, and some relevant bond distances and angles are presented

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(3) The reaction of complex 1 with diborane and boron trifluoride produced 2 in yields of 74 and 60%, respectively. Baker, R. T. Ph.D. Thesis, University of California, Los Angeles. Numbering of compounds in this paper: **1**, *closo*-3,3-(Ph₃P)₂-3-H-3,1,2-RhC₂B₉H₁₁; **2**, [*closo*-(Ph₃P)-RhC₂B₉H₁₁]₂; **3**, [*closo*-3-Ph₃P-3,3-Br₂-3,1,2-RhC₂B₉H₁₁]⁻; **4**, *closo*-3,3-(Ph₃P)₂-3-Br-3,1,2-RhC₂B₉H₁₁; **5**, *closo*-3-Ph₃P-3,3-NO₃-3,1,2-RhC₂B₉H₁₁; **6**, [*closo*-3,3-(Ph₃P)₂-3,1,2-RhC₂B₉H₁₁]⁻; **7**, [*closo*-3-Ph₃P-3,3-I₂-3,1,2-RhC₂B₉H₁₁]⁻.
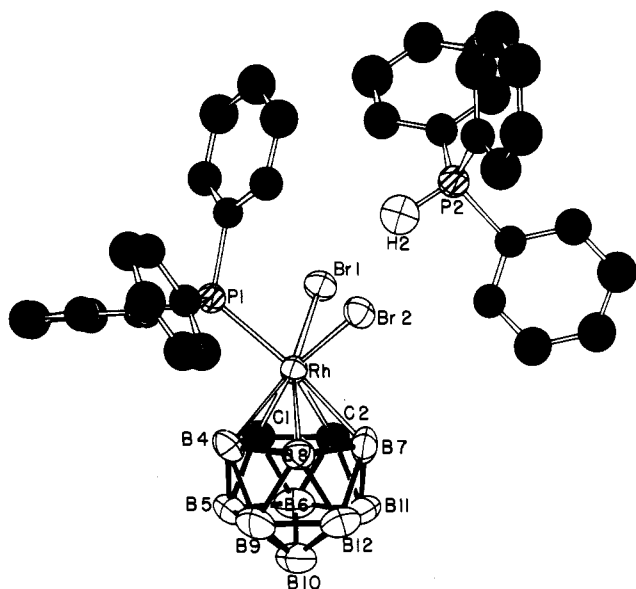
Figure 1. Structure of [HPPh$_3$][*closo*-3-Ph$_3$P-3,3-Br$_2$-3,1,2-RhC$_2$B$_9$H$_{11}$]. Hydrogen atoms of phenyl rings and carborane hydrogen atoms have been omitted for clarity. Thermal ellipsoids represent 50% probability.

Table I. Interatomic Distances (Å)

Rh–C(1)	2.152 (6)	B(8)–H(8)	1.25 (5)
Rh–B(4)	2.171 (6)	B(8)–B(12)	1.805 (10)
Rh–C(2)	2.183 (6)	B(8)–B(9)	1.806 (10)
Rh–B(8)	2.203 (6)	C(2)–H(2)	0.89 (6)
Rh–B(7)	2.229 (7)	C(2)–B(11)	1.678 (10)
Rh–P(1)	2.360 (2)	C(2)–B(7)	1.679 (10)
Rh–Br(2)	2.520 (2)	C(2)–B(6)	1.718 (10)
Rh–Br(1)	2.598 (1)	B(7)–H(7)	1.01 (6)
Rh···H(P2)	3.98	B(7)–B(12)	1.764 (10)
Br(1)···H(P2)	3.06 (6)	B(7)–B(11)	1.812 (11)
Br(2)···H(P2)	2.70 (6)	B(7)–B(8)	1.819 (10)
P(1)–C(11)	1.854^a	B(12)–H(12)	1.06 (6)
P(1)–C(21)	1.832	B(9)–H(9)	1.06 (6)
P(1)–C(31)	1.843	B(9)–B(10)	1.769 (11)
P(2)–H(P2)	1.36 (6)	B(9)–B(12)	1.798 (11)
P(2)–C(41)	1.780	B(5)–H(5)	1.03 (6)
P(2)–C(51)	1.764	B(5)–B(10)	1.752 (12)
P(2)–C(61)	1.782	B(5)–B(6)	1.753 (11)
C(1)–H(1)	0.90 (6)	B(5)–B(9)	1.762 (11)
C(1)–C(2)	1.651 (9)	B(6)–H(6)	1.06 (5)
C(1)–B(5)	1.681 (9)	B(6)–B(11)	1.735 (12)
C(1)–B(6)	1.735 (10)	B(6)–B(10)	1.758 (11)
C(1)–B(4)	1.740 (8)	B(10)–H(10)	1.05 (6)
B(4)–H(4)	1.06 (6)	B(10)–B(11)	1.760 (12)
B(4)–B(9)	1.771 (10)	B(10)–B(12)	1.775 (12)
B(4)–B(5)	1.795 (10)	B(11)–H(11)	1.03 (6)
B(4)–B(8)	1.819 (10)	B(11)–B(12)	1.748 (12)

^{a} Standard deviations are not given for distances involving atoms that are members of rigid groups.

in Tables I and II, respectively. The rhodium atom exhibits pseudooctahedral 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*-3-PPh$_3$-1,3-μ-(η^2-3,4-butenyl)-3-H-3,1,2-RhC$_2$B$_9$H$_{10}$][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 hetero atoms. 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*-styrylphosphine)rhodium bromide, [(P(C$_8$H$_7$)$_3$)$_3$]RhBr.[6] The solvate molecules are not close to either ion, the closest approach of a benzene carbon atom to a nonsolvate atom being C(71)···H(22) = 2.76 Å. Distances within the cation are not unusual. The P–H distance of 1.36 Å can be compared with 1.42 in (*t*-Bu$_3$PH)$^+$,[7] 1.414 in PH$_4$I,[8] and 1.392 Å (neutron diffraction) in PH$_4$Br.[9] The P–C distance of 1.775 Å (average) is shorter than the comparable distance in the anion (1.843 Å (average)), as has also been found in (*t*-Bu$_3$PH)[(*t*-Bu$_3$P)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 ($W_{1/2} \approx 220$ Hz) at ca. δ 10.8 in the ^{1}H NMR spectrum of 3 in CDCl$_3$. Cooling the sample to –33 °C sharpened the resonance to a doublet at δ 10.73. 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. δ 7.6 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 3$^-$ was present in solution. The ^{31}P{^{1}H} NMR spectrum of 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 3$^-$ could arise from ion-pairing interactions in solution, no evidence was

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Table II. Interatomic Angles (deg)[a]

Angle	deg	Angle	deg	Angle	deg	Angle	deg
C(1)-Rh(3)-B(4)	47.5 (2)	B(5)-C(1)-Rh(3)	125.1 (4)	H(6)-B(6)-B(10)	132 (3)	B(10)-B(9)-B(8)	109.6 (5)
C(1)-Rh(3)-C(2)	44.8 (2)	B(6)-C(1)-B(4)	114.6 (5)	C(2)-B(6)-C(1)	57.1 (4)	B(4)-B(9)-B(12)	108.4 (5)
C(1)-Rh(3)-B(8)	80.6 (2)	B(6)-C(1)-Rh(3)	126.4 (4)	C(2)-B(6)-B(11)	58.1 (4)	B(4)-B(9)-B(8)	61.1 (4)
C(1)-Rh(3)-B(7)	79.0 (3)	B(4)-C(1)-Rh(3)	66.8 (3)	C(2)-B(6)-B(5)	102.9 (5)	B(12)-B(9)-B(8)	60.1 (4)
C(1)-Rh(3)-P(1)	108.5 (2)	H(2)-C(2)-C(1)	113 (4)	C(2)-B(6)-B(10)	103.6 (6)	H(10)-B(10)-B(5)	127 (3)
C(1)-Rh(3)-Br(2)	164.3 (2)	H(2)-C(2)-B(11)	121 (4)	C(1)-B(6)-B(11)	105.1 (5)	H(10)-B(10)-B(6)	117 (3)
C(1)-Rh(3)-Br(1)	94.6 (2)	H(2)-C(2)-B(7)	124 (4)	C(1)-B(6)-B(5)	57.6 (4)	H(10)-B(10)-B(11)	114 (3)
B(4)-Rh(3)-C(2)	79.4 (3)	H(2)-C(2)-B(6)	111 (4)	C(1)-B(6)-B(10)	104.3 (5)	H(10)-B(10)-B(9)	129 (3)
B(4)-Rh(3)-B(8)	49.1 (3)	H(2)-C(2)-Rh(3)	104 (4)	B(11)-B(6)-B(5)	108.0 (6)	H(10)-B(10)-B(12)	121 (3)
B(4)-Rh(3)-B(7)	83.2 (3)	C(1)-C(2)-B(11)	111.7 (5)	B(11)-B(6)-B(10)	60.5 (5)	B(5)-B(10)-B(6)	59.9 (5)
B(4)-Rh(3)-P(1)	88.1 (2)	C(1)-C(2)-B(7)	113.6 (5)	B(5)-B(6)-B(10)	59.9 (5)	B(5)-B(10)-B(11)	106.9 (5)
B(4)-Rh(3)-Br(2)	129.7 (2)	C(1)-C(2)-B(6)	62.0 (4)	H(7)-B(7)-C(2)	116 (3)	B(5)-B(10)-B(9)	60.1 (4)
B(4)-Rh(3)-Br(1)	137.0 (2)	C(1)-C(2)-Rh(3)	66.6 (3)	H(7)-B(7)-B(12)	119 (3)	B(5)-B(10)-B(12)	107.8 (5)
C(2)-Rh(3)-B(8)	78.4 (3)	B(11)-C(2)-B(7)	85.4 (5)	H(7)-B(7)-B(11)	105 (3)	B(6)-B(10)-B(11)	59.1 (5)
C(2)-Rh(3)-B(7)	44.7 (3)	B(11)-C(2)-B(6)	61.4 (5)	H(7)-B(7)-B(8)	138 (3)	B(6)-B(10)-B(9)	108.4 (5)
C(2)-Rh(3)-P(1)	150.8 (2)	B(11)-C(2)-Rh(3)	128.4 (5)	H(7)-B(7)-Rh(3)	120 (3)	B(6)-B(10)-B(12)	106.9 (5)
C(2)-Rh(3)-Br(2)	122.2 (2)	B(7)-C(2)-B(6)	116.8 (5)	C(2)-B(7)-B(12)	102.3 (5)	B(11)-B(10)-B(9)	108.4 (5)
C(2)-Rh(3)-Br(1)	85.0 (2)	B(7)-C(2)-Rh(3)	69.1 (3)	C(2)-B(7)-B(11)	57.3 (4)	B(11)-B(10)-B(12)	59.3 (5)
B(8)-Rh(3)-B(7)	48.5 (3)	B(6)-C(2)-Rh(3)	125.5 (4)	C(2)-B(7)-B(8)	104.8 (5)	B(9)-B(10)-B(12)	61.0 (5)
B(8)-Rh(3)-P(1)	112.7 (2)	H(4)-B(4)-C(1)	125 (3)	C(2)-B(7)-Rh(3)	66.2 (3)	H(11)-B(11)-C(2)	121 (3)
B(8)-Rh(3)-Br(2)	88.2 (2)	H(4)-B(4)-B(9)	118 (3)	B(12)-B(7)-B(11)	58.5 (5)	H(11)-B(11)-B(6)	120 (3)
B(8)-Rh(3)-Br(1)	160.7 (2)	H(4)-B(4)-B(5)	115 (3)	B(12)-B(7)-B(8)	60.5 (4)	H(11)-B(11)-B(12)	125 (3)
B(7)-Rh(3)-P(1)	159.5 (2)	H(4)-B(4)-B(8)	127 (3)	B(12)-B(7)-Rh(3)	118.5 (5)	H(11)-B(11)-B(10)	126 (3)
B(7)-Rh(3)-Br(2)	85.4 (2)	H(4)-B(4)-Rh(3)	115 (3)	B(11)-B(7)-B(8)	107.5 (5)	H(11)-B(11)-B(7)	119 (3)
B(7)-Rh(3)-Br(1)	112.3 (2)	C(1)-B(4)-B(9)	102.9 (5)	B(11)-B(7)-Rh(3)	118.7 (5)	C(2)-B(11)-B(6)	60.4 (4)
P(1)-Rh(3)-Br(2)	85.93 (5)	C(1)-B(4)-B(5)	56.8 (4)	B(8)-B(7)-Rh(3)	65.0 (3)	C(2)-B(11)-B(12)	103.0 (5)
P(1)-Rh(3)-Br(1)	86.54 (4)	C(1)-B(4)-B(8)	104.5 (5)	H(8)-B(8)-B(12)	110 (3)	C(2)-B(11)-B(10)	105.2 (6)
Br(2)-Rh(3)-Br(1)	92.47 (4)	C(1)-B(4)-Rh(3)	65.7 (3)	H(8)-B(8)-B(9)	117 (3)	C(2)-B(11)-B(7)	57.3 (4)
Rh(3)-Br(1)-H(P2)	89 (1)	B(9)-B(4)-B(5)	59.2 (4)	H(8)-B(8)-B(4)	133 (3)	B(6)-B(11)-B(12)	109.1 (6)
Rh(3)-Br(2)-H(P2)	99 (1)	B(9)-B(4)-B(8)	60.4 (4)	H(8)-B(8)-B(7)	118 (3)	B(6)-B(11)-B(10)	60.4 (5)
Rh(3)-P(1)-C(1-1)	115.5	B(9)-B(4)-Rh(3)	120.1 (4)	H(8)-B(8)-Rh(3)	120 (3)	B(6)-B(11)-B(7)	109.2 (5)
Rh(3)-P(1)-C(2-1)	118.1	B(5)-B(4)-B(8)	107.3 (5)	B(12)-B(8)-B(9)	59.7 (4)	B(12)-B(11)-B(10)	60.8 (5)
Rh(3)-P(1)-C(3-1)	113.0	B(5)-B(4)-Rh(3)	118.2 (4)	B(12)-B(8)-B(4)	106.0 (5)	B(12)-B(11)-B(7)	59.4 (4)
C(1-1)-P(1)-C(2-1)	100.5	B(8)-B(4)-Rh(3)	66.3 (3)	B(12)-B(8)-B(7)	58.2 (4)	B(10)-B(11)-B(7)	108.6 (6)
C(1-1)-P(1)-C(3-1)	103.8	H(5)-B(5)-C(1)	118 (3)	B(12)-B(8)-Rh(3)	117.8 (4)	H(12)-B(12)-B(11)	117 (3)
C(2-1)-P(1)-C(3-1)	104.1	H(5)-B(5)-B(10)	127 (3)	B(9)-B(8)-B(4)	58.5 (4)	H(12)-B(12)-B(7)	117 (3)
H(P2)-P(2)-C(4-1)	104	H(5)-B(5)-B(6)	120 (3)	B(9)-B(8)-B(7)	106.0 (5)	H(12)-B(12)-B(10)	122 (3)
H(P2)-P(2)-C(5-1)	109	H(5)-B(5)-B(9)	125 (3)	B(9)-B(8)-Rh(3)	116.8 (4)	H(12)-B(12)-B(9)	127 (3)
H(P2)-P(2)-C(6-1)	113	H(5)-B(5)-B(4)	116 (3)	B(4)-B(8)-B(7)	106.9 (5)	H(12)-B(12)-B(8)	122 (3)
C(4-1)-P(2)-C(5-1)	111.7	C(1)-B(5)-B(10)	106.9 (5)	B(4)-B(8)-Rh(3)	64.5 (3)	B(11)-B(12)-B(7)	62.1 (5)
C(4-1)-P(2)-C(6-1)	109.8	C(1)-B(5)-B(6)	60.7 (4)	B(7)-B(8)-Rh(3)	66.5 (3)	B(11)-B(12)-B(10)	59.9 (5)
C(5-1)-P(2)-C(6-1)	109.2	C(1)-B(5)-B(9)	105.7 (5)	H(9)-B(9)-B(5)	122 (3)	B(11)-B(12)-B(9)	107.6 (6)
H(1)-C(1)-C(2)	116 (4)	C(1)-B(5)-B(4)	60.0 (4)	H(9)-B(9)-B(10)	122 (3)	B(11)-B(12)-B(8)	111.0 (5)
H(1)-C(1)-B(5)	119 (4)	B(10)-B(5)-B(6)	60.2 (5)	H(9)-B(9)-B(4)	120 (3)	B(7)-B(12)-B(10)	110.1 (6)
H(1)-C(1)-B(6)	110 (4)	B(10)-B(5)-B(9)	60.5 (5)	H(9)-B(9)-B(12)	123 (3)	B(7)-B(12)-B(9)	108.7 (5)
H(1)-C(1)-B(4)	127 (4)	B(10)-B(5)-B(4)	109.5 (6)	H(9)-B(9)-B(8)	120 (3)	B(7)-B(12)-B(8)	61.3 (4)
H(1)-C(1)-Rh(3)	108 (4)	B(6)-B(5)-B(9)	109.0 (6)	B(5)-B(9)-B(10)	59.5 (5)	B(10)-B(12)-B(9)	59.4 (5)
C(2)-C(1)-B(5)	109.1 (5)	B(6)-B(5)-B(4)	111.0 (5)	B(5)-B(9)-B(4)	61.0 (4)	B(10)-B(12)-B(8)	109.3 (6)
C(2)-C(1)-B(6)	60.9 (4)	B(9)-B(5)-B(4)	59.7 (4)	B(5)-B(9)-B(12)	106.3 (5)	B(9)-B(12)-B(8)	60.1 (4)
C(2)-C(1)-B(4)	110.1 (5)	H(6)-B(6)-C(2)	121 (3)	B(5)-B(9)-B(8)	109.3 (5)	P(2)-H(P2)-Br(2)	141 (3)
C(2)-C(1)-Rh(3)	68.6 (3)	H(6)-B(6)-C(1)	115 (3)	B(10)-B(9)-B(4)	109.8 (5)	P(2)-H(P2)-Br(1)	127 (3)
B(5)-C(1)-B(6)	61.7 (4)	H(6)-B(6)-B(11)	128 (3)	B(10)-B(9)-B(12)	59.7 (5)	Br(2)-H(P2)-Br(1)	80 (2)
B(5)-C(1)-B(4)	63.2 (4)	H(6)-B(6)-B(5)	121 (3)				

[a] Units of each esd, in parentheses, are those of the least-significant digit of the corresponding parameter. Standard deviations are not given for angles involving atoms that are members of rigid groups.

obtained to support this possibility, and only one resonance due to the phosphonium cation was observed in the ^{1}H and ^{31}P NMR spectra of **3**. A more likely possibility is that two configurational isomers of the dibromo(phosphine)-rhodacarborane 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.[13,14] 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
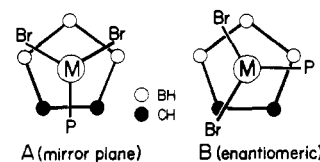

A (mirror plane)   B (enantiomeric)

Figure 2. Configurational isomers of the dibromo(phosphine)-rhodacarborane anion which exist in solution.

associated with the ion-pairing interactions. The broadness of the ^{31}P{^{1}H} and ^{1}H 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

(13) The configurations depicted in Figure 2 are consistent with a previously reported correlation between J_{Rh-P} and the portion of the carborane bonding face trans to the Rh–P bond in pseudooctahedral Rh^{III} rhodacarborane complexes. See ref 14.

(14) Marder, T. B.; Baker, R. T.; Long, J. A.; Doi, J. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1981**, *103*, 2988.

(15) Beall, H.; Bushweller, C. H. *Chem. Rev.* **1973**, *73*, 467 and references cited therein.

decreasing the line widths of the observed resonances. A 10-fold dilution of the ^{1}H 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{^{1}H} 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 eq 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$_3$P)$_2$-3-Br-3,1,2-RhC$_2$B$_9$H$_{11}$ (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$_3$P)$_2$-3-Cl-3,1,2-RhC$_2$B$_9$H$_{11}$.[17] Complex 4 could then dissociate a triphenylphosphine ligand to produce the 16-electron complex "*closo*-3-Ph$_3$P-3-Br-3,1,2-RhC$_2$B$_9$H$_{11}$" 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$_3$P-3,3-NO$_3$-3,1,2-RhC$_2$B$_9$H$_{11}$ (5)[16] reacts with a 10-fold excess of Et$_4$NBr in dichloromethane/water to produce [Et$_4$N][3] in 65% yield. Inasmuch as complex 5 is derived from complex 1 in 60–70% yield, the overall conversion of 1 to [Et$_4$N][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$_3$P)$_2$-3,1,2-RhC$_2$B$_9$H$_{11}$], 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$_4$N][3] from complex 5 and Et$_4$NBr 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 1 mol equiv of (*n*-C$_4$H$_9$)$_4$NI and 6 mol equiv of NaI in the two-phase reaction medium CH$_2$Cl$_2$/H$_2$O generated [(*n*-C$_4$H$_9$)$_4$N][*closo*-3-Ph$_3$P-3,3-I$_2$-3,1,2-RhC$_2$B$_9$H$_{11}$], [*n*-C$_4$H$_9$)$_4$N][7], in 90% yield.

An analogous reaction of complex 5 with Me$_4$NCl produced a red-orange solid that appeared to be [Me$_4$N][*closo*-3-Ph$_3$P-3,3-Cl$_2$-3,1,2-RhC$_2$B$_9$H$_{11}$]; however, this solid was not easily purified. It was later found that the reactive species generated from [Et$_4$N][*closo*-3-Ph$_3$P-3-CO-3,1,2-RhC$_2$B$_9$H$_{11}$] by oxidative removal of the carbon monoxide ligand[19] readily reacted with dichloromethane to produce [Et$_4$N][*closo*-3-

Ph$_3$P-3,3-Cl$_2$-3,1,2-RhC$_2$B$_9$H$_{11}$], [Et$_4$N][8], in 60% yield.

While the ^{31}P{^{1}H} NMR spectrum of [Et$_4$N][8] in 20% CD$_2$Cl$_2$/CH$_2$Cl$_2$ did not change when the temperature was lowered to –73 °C, the solution behavior of [(*n*-C$_4$H$_9$)$_4$N][7] was qualitatively similar to that of [HPPh$_3$][3]. In contrast to [HPPh$_3$][3], solutions of [(*n*-C$_4$H$_9$)$_4$N][7] contain only one isomer at 0 °C. It thus appears that the metal vertex of [Et$_4$N][8] freely rotates about the metal–carborane axis, while [HPPh$_3$][3] and [(*n*-C$_4$H$_9$)$_4$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$_3$P-(X)$_2$-RhC$_2$B$_9$H$_{11}$]$^-$ 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 Section

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

Physical Measurements. The ^{1}H (200.133 MHz) and ^{31}P{^{1}H} (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$_3$PO$_4$ and BF$_3$·Et$_2$O, respectively. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 137 spectrophotometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY, and melting points were determined on a Mel-Temp instrument in capillary tubes sealed in vacuo and are uncorrected. Glovebox 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$_3$P)$_2$-3-H-3,1,2-RhC$_2$B$_9$H$_{11}$,[17] K[18-crown-6][*closo*-3,3-(Ph$_3$P)$_2$-3,1,2-RhC$_2$B$_9$H$_{11}$],[18] *closo*-3-Ph$_3$P-3,3-NO$_3$-3,1,2-RhC$_2$B$_9$H$_{11}$,[16] and *closo*-3,3-(Ph$_3$P)$_2$-3-Br-3,1,2-RhC$_2$B$_9$H$_{11}$[16] were prepared as previously described. Florisil (MCB) was heated to 120 °C for 8 h in vacuo prior to use.

Reaction of 1 with BF$_3$: Preparation of 2. Complex 1 (810 mg, 1.07 mmol) was slurried in 300 mL of 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 × 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 of 2 (60%). Elution of the chromatographic column with dichloromethane yielded a yellow band from which 30 mg of unreacted 1 was isolated.

Reaction of 1 with B$_2$H$_6$: Preparation of 2. Complex 1 (620 mg, 0.82 mmol) was slurried in 300 mL of benzene, and diborane (generated from 6 mL of 85% H$_3$PO$_4$ and 320 mg of 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 of 2 (74%), 10 mg of Ph$_3$P·BH$_3$ (identified by IR), and 30 mg of unreacted 1.

Reaction of 1 with Boron Tribromide: Preparation of [HPPh$_3$][3]. Complex 1 (1.52 g, 2.00 mmol) was slurried in 300 mL of benzene and freeze-pump-thawed 3 times on the high-vacuum line. Boron tribromide (0.8 mL, 8.44 mmol) was freeze-pump-thawed 3 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

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was concentrated by vacuum distillation to about 10 mL and the flask was transferred to the glovebox. The solution was filtered to yield 150 mg of $Ph_3P \cdot BBr_3$ (identified by its IR spectrum[20]). The filtrate was mounted on a Florisil–benzene chromatographic column (2 × 20 cm) in the glovebox, 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 of red crystals contaminated with $Ph_3P \cdot BBr_3$. Recrystallization of the red product yielded 450 mg of pure $[HPPh_3][closo$-3-Ph_3P-$3,3$-Br_2-$3,1,2$-$RhC_2B_9H_{11}]$ (22%), mp 155–160 °C. Anal. Calcd 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. 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); calcd for 3 1037.93. The major ions observed in the mass spectrum of **3** are at m/e 384–397 and correspond to $[Br_2RhC_2B_9H_{11}]^+$: IR[21] (Nujol) 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); ^{1}H NMR[21] (CDCl$_3$, 27 °C) δ 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 coordinated PPh$_3$), 4.30, 3.78, and 3.70 (br, s, carborane C–H); at -33 °C δ 10.73 (d, J_{P-H} = 552 Hz), 7.58 (m), 4.32, 3.76, and 3.73 (br, s, carborane C–H); ^{31}P{^{1}H} NMR (CDCl$_3$) 33.7 (d, J_{Rh-P} = 151 Hz), 27.5 (d, J_{Rh-P} = 134 Hz), and -4.5 (br, s, J_{P-H} = 550 Hz in coupled spectrum); ^{11}B{^{1}H} NMR ((CD$_3$)$_2$CO) 16.3 (2), 3.8 (1), 1.4 (3), -3.8 (2), and -17.1 (1).

Reaction of 1 with Boron Tribromide Monitored by ^{31}P{^{1}H} 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 of C$_6$D$_6$, freeze–pump–thawed 3 times, and distilled into the NMR tube, and the tube was sealed off under vacuum. After 6 h the ^{31}P{^{1}H} spectrum exhibited, in addition to a doublet at 41.2 ppm due to **1**, two doublets at 35.6 and 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 PPh$_3 \cdot$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 of CH$_2$Cl$_2$ 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 that was washed 3 times with ether. The resultant residue was recrystallized from CH$_2$Cl$_2$/Et$_2$O several times, producing a pure microcrystalline red solid: yield 2.5 g (83%); mp 175 °C dec; 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); ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ 7.85, 7.28 (15 H, m, phenyl protons), 4.56 (1 H, s, carborane C–H), 3.47 (24 H, s, CH$_2$ of 18-crown-6); ^{31}P{^{1}H} (CH$_2$Cl$_2$/benzene-d_6, 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{^{1}H} (CH$_2$Cl$_2$, 25 °C) 10.3 (2), 7.42 (3), -5.13 (2), -11.03 (1), -17.1 (1). Anal. Calcd for C$_{32}$H$_{50}$B$_9$Br$_2$PRhKO$_6$: 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.

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 of CH$_2$Cl$_2$ were 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 of 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$_2$Cl$_2$ 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$_2$Cl$_2$/heptane, producing pure elongated black-red needles: yield 0.32 g (90%); mp 180–185 °C dec; 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); ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ 7.74 and 7.26 (15 H, m, phenyl protons), 4.96 (2 H, br, s, carborane C–H), 3.04 (8 H, m, cation), 1.47 (8 H, m, cation), 1.29 (8 H, q, cation), 0.951 (12 H, t, cation); at -33 °C δ 7.8–7.16 (15 H, br envelope, phenyl protons), 5.18 (1 H, br, s, carborane C–H), 4.70 (1 H, br, s, carborane C–H), 2.96 (8 H, m, cation), 1.26 (8 H, q, cation), 0.917 (12 H, t, cation); ^{31}P{^{1}H} (CH$_2$Cl$_2$/benzene-d_6, 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{^{1}H} (CH$_2$Cl$_2$, 25 °C) 8.16 (1), 5.89 (2), -4.86 (2), -7.08 (2), -13.83 (1), -24.88 (1). Anal. Calcd for C$_{36}$H$_{62}$B$_9$RhPI$_2$: 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.

Preparation of [Et$_4$N][$closo$-3-Ph_3P-$3,3$-Cl_2-$3,1,2$-$RhC_2B_9H_{11}$]. The cycloadduct formed between 0.500 g (0.76 mmol) of [Et$_4$N][$closo$-3-Ph_3P-3-CO-$3,1,2$-$RhC_2B_9H_{11}$] and 0.15 g of benzhydroxamic acid chloride was isolated as previously described.[19] This solid was dissolved in 5 mL of CH$_2$Cl$_2$ and 30 mL of acetone and stirred for 3 h at room temperature, producing a cherry red solution. After the addition of 30 mL of 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: 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 (w), 695 (s); ^{1}H NMR (CD$_3$COCD$_3$, 25 °C) δ 8.07, 7.35 (15 H, m, phenyl protons of PPh$_3$), 4.61 (1 H, s, br, carborane C–H), 3.50 (8 H, q, cation), 1.40 (12 H, m, cation); ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$, 25 °C) 33.0 (d, J_{Rh-P} = 155 Hz); ^{11}B{^{1}H} NMR (CD$_3$COCD$_3$, 25 °C) 7.08 (2), -4.18 (1), -6.68 (3), -12.75 (2), -24.67 (1). Anal. Calcd for C$_{28}$H$_{46}$NRhPB$_9$Cl$_2$: 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.

X-ray Crystal and Molecular Structural Determination of [HPPh$_3$][PPh$_3$Br$_2$RhC$_2$B$_9$H$_{11}$]·1.5C$_6$H$_6$. A single crystal bounded by the $(01\bar{1})$, (001), (110), $(00\bar{1})$, $(\overline{1}10)$, and $(2\overline{1}0)$ 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) Å, b = 13.299 (4) Å, 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 Mo Kα radiation (0.7107 Å). The crystal density was found to be 1.37 (2) g cm^{-3} 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 a limit of 2θ = 50°. Reflections were scanned at a constant rate of 2.0°/min from 1.15° below the Kα_1 reflection to 1.15° above the Kα_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 3 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] (μ = 22.4 cm^{-1}; maximum, minimum, and average transmission factors of 0.9320, 0.7403, and 0.8852). The intensity of a reflection, $I(hkl)$, and its estimated standard deviation, $\sigma[I(hkl)]$, were calculated as described previously.[22] Of the 8049 unique reflections, 1995 with intensities

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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 $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma(|F_o|)]^{-2}$. The discrepancy indices are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum_w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$.

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Table IIIA. Atomic Positional Parameters for 3^a

atom	x	y	z
Rh(3)	0.10808 (4)	0.44528 (4)	0.29666 (2)
Br(1)	0.15686 (5)	0.32874 (5)	0.39598 (3)
Br(2)	0.28032 (5)	0.26288 (6)	0.18850 (4)
P(1)	−0.00997 (13)	0.34912 (13)	0.23514 (8)
P(2)	0.47492 (14)	0.01962 (14)	0.28169 (9)
C(1)	−0.0097 (6)	0.6248 (5)	0.3893 (3)
C(2)	0.1356 (6)	0.5829 (6)	0.3986 (4)
B(4)	−0.0380 (6)	0.6157 (6)	0.2891 (4)
B(5)	−0.0772 (8)	0.7591 (7)	0.3747 (5)
B(6)	0.0300 (8)	0.7374 (7)	0.4451 (5)
B(7)	0.2183 (7)	0.5399 (7)	0.3107 (5)
B(8)	0.1088 (6)	0.5638 (6)	0.2365 (4)
B(9)	−0.0047 (7)	0.7261 (7)	0.2799 (5)
B(10)	0.0353 (8)	0.8006 (7)	0.3745 (5)
B(11)	0.1699 (9)	0.6886 (8)	0.3951 (6)
B(12)	0.1530 (8)	0.6791 (8)	0.2934 (5)
H(P2)	0.3672 (54)	0.1037 (53)	0.2673 (33)
H(1)	−0.0486 (55)	0.6139 (55)	0.4237 (35)
H(2)	0.1633 (55)	0.5478 (55)	0.4354 (35)
H(4)	−0.1129 (54)	0.6084 (52)	0.2616 (33)
H(5)	−0.1691 (54)	0.8178 (54)	0.3955 (33)
H(6)	0.0014 (51)	0.7787 (52)	0.5098 (34)
H(7)	0.3099 (56)	0.4926 (52)	0.3094 (33)
H(8)	0.1490 (49)	0.5185 (50)	0.1621 (33)
H(9)	−0.0510 (52)	0.7733 (52)	0.2406 (33)
H(10)	0.0244 (51)	0.8903 (55)	0.3994 (33)
H(11)	0.2346 (53)	0.7046 (52)	0.4290 (34)
H(12)	0.2122 (53)	0.6942 (52)	0.2653 (33)

^{a} Units of each esd, in parentheses, are those of the least-significant digit of the corresponding parameter.

less than 3 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 non-hydrogen atoms. The six phenyl groups and the benzene solvate were described as rigid C_6

hexagons with C–C = 1.39 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 $R^{23} = 0.046$ and $R_w = 0.054$. 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 (Table IIIA). For the latter hydrogen atoms, B was set at 1.0 + B of the carbon atom to which the hydrogen atom is attached. The "goodness of fit" was 1.576, defined as $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, with N_o (number of observations) = 6054 and N_v (number of variables) = 275. On a final difference map, the highest peak is 0.5 e/Å^3. There are six 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 $\sum w||F_o| - |F_c||^2$ was minimized in the refinement.

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

Notes

Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514, and the U.S. Army Research Office, Research Triangle Park, North Carolina 27709

Crystal and Molecular Structure of (η^5-Pentamethylcyclopentadienyl)(trifluoromethanesulfonato)iron(II) Dicarbonyl: A Strong Electrostatic Iron–Triflate Interaction

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We wish to report here the X-ray crystallographic study of (η^5-pentamethylcyclopentadienyl)(trifluoromethanesulfonato)iron(II) dicarbonyl (**1**), the first transition-metal triflate to be so characterized.

Although a wide range of organometallic complexes containing sulfur–oxygen ligands has been reported in recent years,[1] a relatively small number of sulfonato complexes of

1
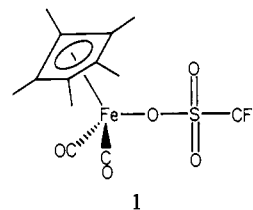
transition metals has been described.[2–6] Much of the interest in these complexes stems from the behavior of the sulfonate group, which has the capacity to function as a mono-, di-, or tridentate ligand and to vary its mode of bonding. Thus, in (CO)$_5$Re(OSO$_2$R) (R = CH$_3$, C$_6$H$_5$, p-CH$_3$C$_6$H$_4$),[4] normal monodentate coordination appears to be observed. Multidentate behavior is observed with titanium in (TiCl$_2$(OSO$_2$-CF$_3$)$_2$)$_2$[2] and (TiCl$_3$(OSO$_2$CF$_3$))$_x$.[2]

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