bond cleavage processes by metalloporphyrins.

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Supplementary Material Available: Tables of anisotropic temperature factors (Table SI), hydrogen coordinates and temperature factors (Table SII), bond lengths (Table SIII), bond angles (Table SIV), nonbonded distances (Table SV), and torsion angles (Table SVI) (9 pages); a table of observed and calculated structure factors (Table SVII) (10 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactions of Icosahedral Rhodacarboranes Bearing η^3-Allyl, Alkyl, and Acyl Moieties at the Metal Vertex[1]

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The rhodacarboranes [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (H(**1a**)) and [*closo*-2,2-$(PPh_3)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$] (H(**1b**)) are easily converted to the corresponding anionic **1a**$^-$ and **1b**$^-$ by abstraction of the hydrido ligand at Rh as a proton. The formal Rh(I) species **1a**$^-$ and **1b**$^-$ serve as apparent nucleophiles in reactions with allyl and methallyl chlorides or allyl acetate to afford the corresponding η^3-allyl derivatives. The crystal and molecular structure of [*closo*-3-PPh_3-3-(η^3-C_3H_5)-3,1,2-$RhC_2B_9H_{11}$] (**2a**) has been determined by X-ray diffraction techniques. The compound crystallizes in the monoclinic space group $P2_1/c$ with a = 12.678 (3) Å, b = 15.391 (4) Å, c = 15.454 (2) Å, β = 121.26 (1)°, and Z = 4. Diffraction data to 2θ(max) = 50° (Mo Kα radiation) were collected on a Syntex P$\bar{1}$ diffractometer, and the structure was solved by conventional Patterson, Fourier, and full-matrix least-squares techniques to a final discrepancy index of R = 0.041 for 3851 independent observed reflections. All atoms, including hydrogen atoms, were located. The molecule has the closo 12-vertex icosahedral geometry, and the rhodium atom exhibits pseudo-octahedral coordination with the dicarbollide ligand occupying three facial coordination sites, the triphenylphosphine occupying a fourth site, and the η^3-allyl ligand filling the remaining two sites. The molecule is monomeric, and there are no intermolecular distances shorter than van der Waals distances. Reactions of **1a**$^-$ and **1b**$^-$ with $(CH_3)_3OBF_4$ produced solvent-stabilized methyl derivatives **4a** and **4b**, [*closo*-3-PPh_3-3-CH_3-3-CH_3COCH_3-3,1,2-$RhC_2B_9H_{11}$] and [*closo*-2-PPh_3-2-CH_3-2-CH_3COCH_3-2,1,7-$RhC_2B_9H_{11}$], respectively. Both **4a** and **4b** were converted to $(PPh_3)_2$ derivatives by $(CH_3)_2CO$ displacement with PPh_3. Benzyl bromide and **1a**$^-$ produced [*closo*-3-PPh_3-3-$PhCH_2$-3-Br-3,1,2-$RhC_2B_9H_{11}$] (**6a**). The corresponding 2,1,7 derivative, **6b**, was similarly prepared. Dihydrogen reacts with complexes **2a**, **2b**, **4a**, and **4b** to produce unstable hydridic species **7a** and **7b** formulated as [*closo*-(PPh_3)(H)(solvent)$RhC_2B_9H_{11}$] isomers with solvent being $(CH_3)_2CO$ or CH_3CN. Complexes **4a** and **4b** react with CO (1 atm, 25 °C) to produce the corresponding isomers of [*closo*-(PPh_3)(CO)$(COCH_3)RhC_2B_9H_{11}$] (**8a** and **8b**, respectively). Similar benzoyl derivatives were obtained through alternative routes.

Introduction

In earlier publications[3,4] we have described the syntheses and structural characterization of the *closo*-rhodacarborane anions [*closo*-3-PPh_3-3-L-3,1,2-$RhC_2B_9H_{11}$]$^-$ (**1a**$^-$, L = PPh_3) and [*closo*-2-PPh_3-2-L-2,1,7-$RhC_2B_9H_{11}$]$^-$ (**1b**$^-$, L = PPh_3), which may be considered to contain formal d^8-$LRh(PPh_3)^+$ vertices combined with the corresponding [*nido*-$C_2B_9H_{11}$]$^{2-}$ ions. The ligand L may be comprised of any one of a number of uncharged electron-pair-donor species, such as η^2-C_2H_4 and CO. In this paper we describe reactions of **1a**$^-$ and **1b**$^-$ that produce novel icosahedral rhodacarborane derivatives bearing an η^3-allyl, alkyl, or acyl group attached to a formal d^6-Rh^{3+} vertex. The structure of [*closo*-3-PPh_3-3-(η^3-C_3H_5)-3,1,2-$RhC_2B_9H_{11}$] (**2a**) was elucidated by an X-ray diffraction study. Furthermore, the interconversions of certain of these conventional organometallic species are described along with the reactions of the η^3-allyl- and alkylrhodacarborane derivatives with H_2. The latter study proved the existence of H_2 activation pathways that appear to involve formal Rh^{5+} intermediates or cyclic concerted processes that require the simultaneous formation of C-H and Rh-H bonds in a cyclic transition state.

Results and Discussion

Syntheses and Characterization of η^3-Allylrhodacarboranes. The reaction of Li^+[*closo*-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{11}$]$^-$ (Li(**1a**)) or Li^+[*closo*-2,2-$(PPh_3)_2$-2,1,7-$RhC_2B_9H_{11}$]$^-$ (Li(**1b**)) with allyl chloride produced the respective yellow and pale yellow crystalline 18-electron η^3-allyl complexes [*closo*-3-PPh_3-3-(η^3-C_3H_5)-3,1,2-$RhC_2B_9H_{11}$] (**2a**) and [*closo*-2-PPh_3-2-(η^3-C_3H_5)-2,1,7-$RhC_2B_9H_{11}$] (**2b**). Similarly, Li(**1a**) and Li(**1b**) reacted with methallyl chloride to produce the corresponding η^3-methallyl complexes **3a** and **3b**, respectively; however, the latter reactions were complicated by the formation of additional chlororhodium complexes, and pure samples were difficult to obtain. However, a superior synthesis[5] of **2a** was developed by using the reaction of Li(**1a**) with allyl acetate in THF. Similar reactions of Li(**1b**) were more complex and offered no advantage in the preparation of **2b**. As seen in Figure 1, the 25 °C 200-MHz ^{1}H NMR spectrum of **2a** in CD_2Cl_2 displays the resonances expected to arise from the coordinated triphenylphosphine ligand and the two equivalent carboranyl C-H protons in addition to three resonances due to the η^3-allyl ligand. Following the assignments made in other (η^3-allyl)rhodium(III) complexes,[6] we assigned the complex multiplet of relative area equivalent to 1 H that appears at 4.97 ppm to the methine proton (H_1) of the allyl ligand. The two syn protons (H_2) appear as a doublet ($J_{H_1-H_2}$ = 8 Hz) at 4.10 ppm, while the triplet pattern at 2.53 ppm arises from the two anti protons (H_3). Decoupling experiments showed that the two H_3 protons were coupled to H_1 as well as to the phosphorus and rhodium nuclei. Inasmuch as the syn and anti protons have the same bond connectivity, this additional coupling is probably due to stronger "through-space" interactions of the anti protons with the phosphorus and rhodium nuclei compared to those of the syn protons. Indeed, X-ray structural analysis of **2a** (vide infra) supports this view. The ^{1}H NMR spectra of **2b**, **3a**, and **3b** exhibit comparable spectral features.

The formation of the η^3-allyl complex **2a** can be considered to arise from a nucleophilic displacement reaction of allyl chloride

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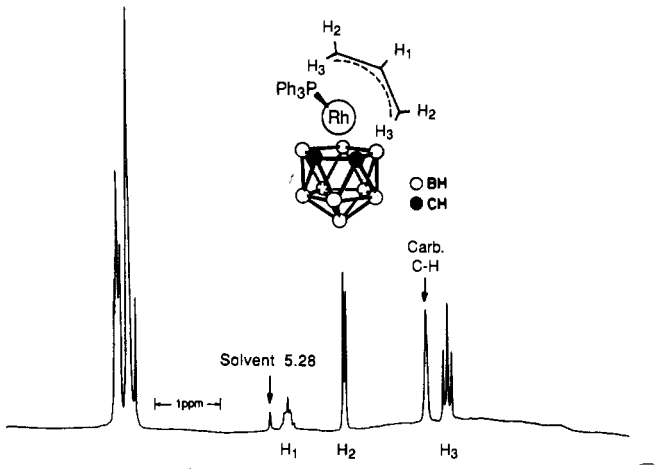

Figure 1. 200-MHz ^1H NMR spectrum of **2a** in CD_2Cl_2 at 25 °C. The peak labeled "Solvent" is due to undeuteriated CH_2Cl_2 present in the solvent.

Table I. Selected Interatomic Distances (Å)

Rh–C(02)	2.130 (5)	B(6)–B(11)	1.756 (8)
Rh–C(03)	2.176 (5)	B(7)–C(2)	1.730 (7)
Rh–B(4)	2.180 (5)	B(7)–B(12)	1.780 (7)
Rh–C(1)	2.212 (4)	B(7)–B(8)	1.790 (7)
Rh–C(2)	2.227 (4)	B(7)–B(11)	1.790 (7)
Rh–B(7)	2.247 (5)	B(8)–B(12)	1.785 (7)
Rh–C(01)	2.250 (6)	B(8)–B(9)	1.786 (7)
Rh–B(8)	2.277 (5)	B(9)–B(10)	1.771 (8)
Rh–P	2.349 (1)	B(9)–B(12)	1.775 (8)
P–C(21)	1.827 (4)	B(10)–B(12)	1.773 (8)
P–C(11)	1.830 (4)	B(10)–B(11)	1.790 (8)
P–C(31)	1.838 (4)	B(11)–C(2)	1.690 (7)
B(4)–C(1)	1.738 (6)	B(11)–B(12)	1.781 (8)
B(4)–B(9)	1.796 (7)	C(1)–C(2)	1.601 (6)
B(4)–B(5)	1.800 (7)	C(01)–C(02)	1.382 (8)
B(4)–B(8)	1.807 (7)	C(02)–C(03)	1.392 (7)
B(5)–C(1)	1.703 (6)	Rh···H(01A)	2.90 (6)
B(5)–B(10)	1.766 (7)	Rh···H(01B)	2.59 (6)
B(5)–B(6)	1.766 (7)	Rh···H(02)	2.42 (6)
B(5)–B(9)	1.783 (7)	Rh···H(03A)	2.68 (6)
B(6)–C(2)	1.729 (7)	Rh···H(03B)	2.64 (6)
B(6)–C(1)	1.730 (7)	P···H(01B)	2.80 (7)
B(6)–B(10)	1.753 (8)	P···H(03B)	2.92 (7)

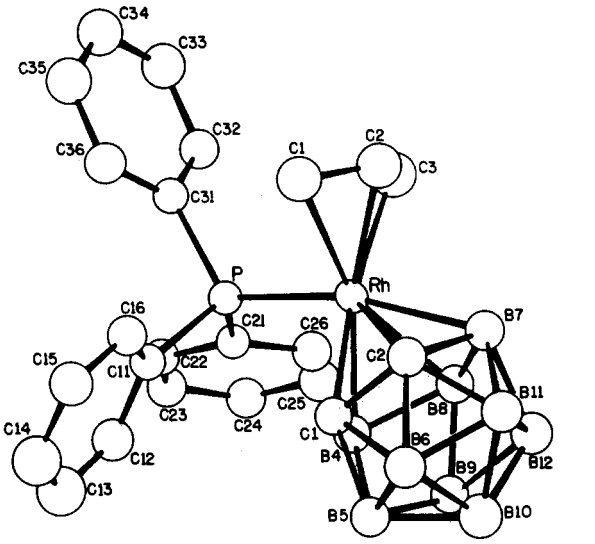

Figure 2. ORTEP projection of complex **2a** with hydrogen atoms omitted for clarity.

Table II. Selected Interatomic Angles (deg)

P–Rh–C(01)	87.4 (2)	B(4)–Rh–C(2)	76.8 (2)
P–Rh–C(02)	107.9 (1)	B(4)–Rh–B(7)	80.0 (2)
P–Rh–C(03)	92.6 (2)	B(4)–Rh–C(01)	153.2 (2)
P–Rh–B(4)	82.8 (1)	B(4)–Rh–B(8)	47.8 (2)
P–Rh–C(1)	99.8 (1)	C(1)–Rh–C(2)	42.3 (2)
P–Rh–C(2)	140.0 (1)	C(1)–Rh–B(7)	76.6 (2)
P–Rh–B(7)	159.2 (1)	C(1)–Rh–C(01)	111.7 (2)
P–Rh–B(8)	112.6 (1)	C(1)–Rh–B(8)	78.6 (2)
C(02)–Rh–B(4)	168.0 (2)	C(2)–Rh–B(7)	45.5 (2)
C(02)–Rh–C(1)	133.6 (2)	C(2)–Rh–C(01)	95.8 (2)
C(02)–Rh–C(2)	97.4 (2)	C(2)–Rh–B(8)	77.4 (2)
C(02)–Rh–B(7)	88.4 (2)	B(7)–Rh–C(01)	113.3 (2)
C(02)–Rh–B(8)	121.0 (2)	B(7)–Rh–B(8)	46.6 (2)
C(03)–Rh–B(4)	139.0 (2)	C(01)–Rh–B(8)	156.4 (2)
C(03)–Rh–C(1)	167.4 (2)	C(02)–C(01)–Rh	66.9 (3)
C(03)–Rh–C(2)	125.2 (2)	C(01)–C(02)–C(03)	120.9 (5)
C(03)–Rh–B(7)	92.8 (2)	C(01)–C(02)–Rh	76.4 (3)
C(03)–Rh–C(01)	66.0 (2)	C(03)–C(02)–Rh	73.0 (3)
C(03)–Rh–B(8)	99.2 (2)	C(02)–C(03)–Rh	69.3 (3)
B(4)–Rh–C(1)	46.6 (2)		

or acetate with $\mathbf{1a}^-$ to produce an intermediate species [*closo*-3,3-$(PPh_3)_2$-3-(η-C_3H_5)-3,1,2-$RhC_2B_9H_{11}$], which is unstable with respect to triphenylphosphine dissociation. Ligand dissociation is then followed by a η^1 to η^3 rearrangement of the allyl fragment to generate the observed product **2a**.

While many η^3-allyl complexes display fluxional solution behavior at room temperature,[6] the η^3-allyl complexes mentioned above were static at room temperature, and decreasing the temperature to −73 °C did not change the ^1H NMR spectrum of solutions of **2a**. The lack of fluxionality in these complexes indicates that the allyl ligand is tightly bound to the rhodium vertex. This strong interaction probably results from enhanced backbonding into the π^*-orbitals of the allyl ligand due to the electron-rich nature of the rhodium vertex. Although it is probable that fluxional solution behavior of these complexes may be observed at higher temperatures, experiments were not performed to verify this notion.

Crystal and Molecular Structure of 2a. In order to confirm the symmetrical nature of the bonding of the allyl ligand in one of these complexes, an X-ray crystal structure analysis was performed on **2a**. Single crystals of **2a** were grown by vapor diffusion of pentane into a 10% acetone–benzene solution of **2a**. An ORTEP plot of complex **2a** is shown in Figure 2, and Tables I and II list selected interatomic bond lengths and bond angles, respectively.

As can be seen from Figure 2, the rhodium atom exhibits pseudo-octahedral coordination with the dicarbollide ligand occupying three facial coordination sites and the triphenylphosphine ligand occupying a fourth site. The remaining two coordination sites are filled by the η^3-allyl ligand. The C(01)–C(02) bond length, 1.380 (8) Å, and the C(02)–C(03) bond length, 1.398 (7) Å, confirm the symmetrical nature of the allyl fragment. The structural analysis also verifies that the rhodium and phosphorus nuclei are substantially closer to the anti protons of the allyl ligand than to the syn protons (see Table I). Overall, the bond lengths and bond angles within the carborane ligand are not unusual.

Syntheses and Characterization of Methylrhodacarboranes. The reaction of K(**1a**) or K(**1b**) with 2.3 molar equiv of $(CH_3)_3OBF_4$ in acetonitrile at 0 °C produces in good yields, after chromatography on Florisil and recrystallization from acetone–heptane, the crystalline orange (**4a**) and the crystalline lemon yellow (**4b**) rhodacarboranes, respectively. The ^1H NMR spectrum of an acetone-d_6 solution of **4a** at −43 °C displays resonances assignable to one triphenylphosphine ligand and two equivalent carboranyl C–H protons. Additionally, the observation of a doublet-of-doublets resonances at 1.70 ppm of relative area equivalent to 3 H indicates the presence of a Rh–CH_3 linkage (J_{P-H} = 8, J_{Rh-H} = 2 Hz), and a resonance of relative area equivalent to 6 H at 1.95 ppm is assigned to a coordinated acetone molecule. Taken together, these spectral observations indicate the formulation of **4a** in acetone at −43 °C to be the chiral, 18-electron solvated alkylrhodacarborane [*closo*-3-PPh_3-3-CH_3-3-CH_3COCH_3-3,1,2-$RhC_2B_9H_{11}$]. The IR spectrum of **4a** (Nujol) displays absorptions expected to arise from the dicarbollide and triphenylphosphine ligands; however, only weak absorptions or no absorptions are observed for the acetone ligand in **4a**, suggesting that in the solid state **4a** might exist as a 16-electron unsolvated species or as a

mixture of solvated and unsolvated species. The analytical data obtained for **4a** support the 18-electron formulation for this species, but the difference in the compositions of the 16-electron structure and the 18-electron structure of complex **4a** may not be large enough to conclusively differentiate between these two species by elemental analyses. Regardless of the precise solid-state composition of **4a**, the ^{1}H NMR data presented above unequivocally establish the solution structure of this species, and inasmuch as stable solutions of **4a** only exist at reduced temperatures in polar coordinating solvents such as acetone or acetonitrile, the solvated formulation of **4a** is the best operational structure for this species. Complex **4b** appears to be analogous to **4a**.

The initial alkylation of K(**1a**) or K(**1b**) by $(CH_3)_3OBF_4$ would be expected to produce the respective isomers of the general formula $[(PPh_3)_2CH_3RhC_2B_9H_{11}]$. These complexes apparently are unstable with respect to triphenylphosphine dissociation to produce the solvent-stabilized species **4a** or **4b**. Furthermore, the subsequent alkylation of the free dissociated triphenylphosphine ligands with $(CH_3)_3OBF_4$ would drive this reaction to completion. The stabilities of **4a** and **4b** are quite surprising and apparently result from the stabilizing effect of the donor solvents that are used in conjunction with these complexes. Solutions of **4a** or **4b** were unstable in the absence of acetone or acetonitrile. For example, it was noted that complex **4b** was cleanly converted to the known complex [*closo*-2-PPh_3-2-Cl-2,1,7-$RhC_2B_9H_{11}$][7] in CH_2Cl_2. Finally, it was observed that air oxidation of acetone-d_6 solutions of **4a** gave rise to the known dimeric species [3-PPh_3-3,1,2-$RhC_2B_9H_{11}]_2$,[8,9] as evidenced by its characteristic purple color and ^{31}P NMR spectrum.

Acetone solutions of **4a** and **4b** were observed to react with triphenylphosphine to respectively produce in high yields the insoluble species formulated on the basis of elemental analyses as [*closo*-3,3-$(PPh_3)_2$-3-CH_3-3,1,2-$RhC_2B_9H_{11}$] (**5a**) and [*closo*-2,2-$(PPh_3)_2$-2-CH_3-2,1,7-$RhC_2B_9H_{11}$]·CH_3COCH_3 (**5b**). The very low solubility of these complexes precluded the acquisition of NMR spectra, but the chemical reactivity (vide infra) of **5a** and **5b** provides further support for their suggested formulations. The presence of acetone in the crystal lattice of **5b** was verified by the observation of a strong carbonyl band at 1700 cm^{-1} in the IR spectrum of **5b** and by elemental analyses. Heating complex **5b** in vacuo to 50 °C for 3 h did not remove the acetone solvate.

Syntheses and Characterization of Benzylrhodacarboranes. The reaction of K[18-crown-6](**1a**) with benzyl bromide in benzene produced a red ionic precipitate that has been formulated as K[18-crown-6][*closo*-3-PPh_3-3-$PhCH_2$-3-Br-3,1,2-$RhC_2B_9H_{11}$] (**6a**) on the basis of analytical and spectroscopic data. The room-temperature 200-MHz ^{1}H NMR spectrum of **6a** in CD_2Cl_2 displays the usual resonances due to the triphenylphosphine ligand, the cation, and the two inequivalent carboranyl C–H protons. Additionally, the inequivalent benzylic protons appear as six-line multiplets at 3.61 and 1.74 ppm. The inequivalence of the carboranyl C–H protons and the benzylic protons is consistent with the chiral nature of the rhodium vertex of **6a**. Further support for the existence of a chiral rhodium vertex in this complex is provided by the 127-MHz ^{11}B{^{1}H} NMR spectrum of **6a** in CD_2Cl_2, which displays seven separate resonances indicating the lack of mirror symmetry in this complex.

The formation of **6a** could result from initial alkylation of K[18-crown-6](**1a**) to form an intermediate neutral species [*closo*-3,3-$(PPh_3)_2$-3-$PhCH_2$-3,1,2-$RhC_2B_9H_{11}$], which then dissociates a triphenylphosphine ligand. The 16-electron complex so formed is attacked by the bromide ion to generate **6a**.

On the basis of preliminary observations, a similar reaction of K[18-crown-6](**1b**) with benzyl bromide in acetonitrile produced a neutral rhodacarborane formulated as [*closo*-2-PPh_3-2-$PhCH_2$-2,1,7-$RhC_2B_9H_{11}$] (**6b**). Complex **6b** was found to be stable in CH_3CN but rapidly decomposed in acetone or THF. That a species similar to **6a** is not produced in this reaction apparently is a consequence of the carborane ligand. The preference for an icosahedral 2,1,7-rhodacarborane to adopt a five-coordinate geometry has been previously observed in the complex [*closo*-2-PPh_3-2-Cl-2,1,7-$RhC_2B_9H_{11}$],[7] and the formation of these five-coordinate complexes may indicate that the $[7,9\text{-}C_2B_9H_{11}]^{2-}$ is a stronger trans-labilizing ligand than its 7,8-isomer.

Reactions of η^3-Allyl- and Alkylrhodacarboranes with Hydrogen. The hydridorhodacarborane[7] that serves as the precursor[3,4] of **1a**$^-$, [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (H(**1a**)), has been shown to be an effective homogeneous catalyst for the hydrogenation of rearrangement inert, blocked terminal olefins such as 3-methyl-3-phenylbutene-1. As a result of a lengthy and detailed kinetic and mechanistic study[7,10-14] of the behavior of this catalyst system, it is currently believed that a spectroscopically undetectable, catalytically active exo–nido Rh(I) tautomer of H(**1a**) exists in solution in which the Rh–H proton is transferred to the carborane ligand to produce a B–H–B moiety while the metal simultaneously migrates to a B–H–Rh position of lower hapticity on the carborane ligand, i.e., η^5 to η^x (x = 1, 2).[10-14] Thus, this Rh(I) species is capable of binding alkenes and activating hydrogen to produce alkylrhodacarboranes of a totally different structural class than the simple *closo*-alkylrhodacarboranes whose syntheses and characterization were described above. While the mechanism that involves the reactive exo-nido Rh(I) tautomer of H(**1a**) appears to be corroborated by many independent observations, it was nevertheless of interest to determine whether a simple closo Rh(III) species such as complex **4a** could activate molecular hydrogen. We have therefore examined the reactivity of the previously described η^3-allyl- and alkylrhodacarboranes with molecular hydrogen.

Complex **2a** reacts with hydrogen (1 atm, 25 °C) in THF to quantitatively produce the known dimeric complex [3-PPh_3-3,1,2-$RhC_2B_9H_{11}]_2$[8,9] and a mixture of propene and propane. A similar reaction in the presence of 1 molar equiv of triphenylphosphine produces the known hydrido complex H(**1a**). Complex **2b** also reacts with hydrogen in benzene to produce a mixture of four different hydridorhodacarborane species, as judged by the high-field NMR spectrum of the reaction mixture. The exact identity of the components of this mixture remains unknown, but these products appear to be similar to the products formed upon treatment of [*closo*-2-PPh_3-2,2-CH_3CO_2-2,1,7-$RhC_2B_9H_{11}$] with hydrogen.[5]

The mode of hydrogen activation by these Rh(III) complexes is unclear, but hydrogen activation by other Rh(III) rhodacarboranes has been previously observed.[5,15] A η^3 to η^1 rearrangement of the η^3-allyl ligand of **2a** or **2b** would produce a 16-electron Rh(III) species. The hydrogen reaction might then occur by oxidative addition of H_2 to produce an unstable Rh(V) alkyl dihydride species that could rapidly eliminate propene to produce the unstable 16-electron rhodium hydride species [*closo*-3-PPh_3-3-H-3,1,2-$RhC_2B_9H_{11}$] (**7a**). An equivalent mechanism would consist of a four-center transition state involving the Rh η^1-allyl ligand and H_2 that would produce propene and the unstable species **7a** in concert. Regardless of the detailed mechanism of this process, the facility of this transformation clearly highlights

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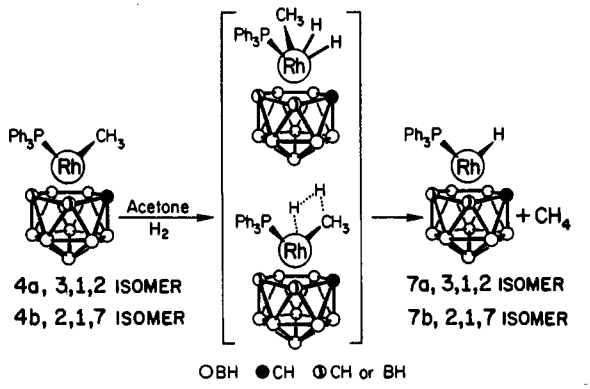

Figure 3. Two possible intermediates in the hydrogenolysis of Rh–CH_3 rhodacarboranes.

the ability of certain Rh(III) rhodacarboranes to activate hydrogen without prior tautomerization to Rh(I) intermediates.

Complexes **4a** and **4b** when dissolved in acetone each react with hydrogen (1 atm, 0 °C) to produce unstable hydridorhodacarboranes **7a** and **7b**, respectively, and presumably methane gas. The ^1H NMR spectrum of **7a** in acetone-d_6 at −73 °C shows a four-line rhodium hydride resonance at −6.84 ppm, and warming this sample to −23 °C produces two equal-intensity four-line rhodium hydride signals at −6.84 and −7.61 ppm. At room temperature the NMR sample is slightly discolored, but the ^1H NMR spectrum only shows the two hydride signals; the lower field signal predominates (ca. 85%). This behavior is consistent with the formation of the solvated species [*closo*-3-PPh_3-3-H-3-CH_3COCH_3-3,1,2-$RhC_2B_9H_{11}$] at low temperatures, which then dissociates the solvent at room temperature to produce the thermally unstable 16-electron species, **7a**, which in turn slowly produces the dimeric species [3-PPh_3-3,1,2-$RhC_2B_9H_{11}$]$_2$. It is noteworthy that complex **7a** was not observed in the reaction of **2a** with H_2 in THF or in the similar reaction of [*closo*-3-PPh_3-3,3-CH_3CO_2-3,1,2-$RhC_2B_9H_{11}$] with H_2[5] in THF. This is undoubtedly due to the stabilization of **7a** by the more coordinating solvents used in the study of **4a** and **4b**.

Complex **7b** appears to be similar to **7a** but is slightly more stable than **7a**. A white microcrystalline solid sample of **7b** can be obtained by the slow addition of heptane to a homogeneous acetone solution of **7b** at 0 °C. This solid exhibits a Rh–H absorption at 2005 cm^{-1} in the IR spectrum. As this complex possesses only modest thermal stability, an elemental analysis was not obtained. The observation and isolation of **7b** is in contrast to the earlier results obtained for the reaction of **2b** with hydrogen and again demonstrates the stabilizing effects of donor solvents on 16-electron hydridorhodacarboranes.

Figure 3 depicts two plausible intermediates in the reactions of complexes **4a** and **4b** with H_2. The concerted addition of molecular hydrogen to the Rh–CH_3 linkage to produce methane and a rhodium hydride is attractive because this step does not require a change in the formal oxidation state of the rhodium atom; however, hydrogenolysis of metal alkyl complexes is generally thought to proceed by initial oxidative addition of molecular hydrogen followed by reductive elimination of alkane.[16] Oxidative addition of molecular hydrogen by **4a** and **4b** would produce a transitory Rh(V) alkylrhodacarborane dihydrido intermediate. Although organometallic Rh(V) species are generally thought to be unstable, the isolation[17] of the Rh(V) species such as [(η^5-$C_5(CH_3)_5$)Rh($SiEt_3$)$_2H_2$] adds credence to the existence of the Rh(V) intermediate mentioned above.

Previously, it has been observed[18] that the rhodium(III) complexes [*closo*-3-PPh_3-3,3-(X)-3,1,2-$RhC_2B_9H_{11}$] (X = NO_3^-,[15] $CH_3CO_2^-$[5]) were also capable of activating molecular hydrogen, and these precursor complexes were found to provide extremely active, but short-lived, homogeneous catalysts for the hydrogenation of blocked terminal olefins. It is likely that treatment of the acetate or nitrate complexes mentioned above initially gives rise to complex **7a** and HX (X = $CH_3CO_2^-$, NO_3^-) and that complex **7a** is the functional hydrogenation catalyst or, more likely, a precursor. In view of the extreme ease of the hydrogenolysis of the *closo*-alkylrhodacarboranes (**4a**, **4b**), it appears very likely that catalyst systems based upon complex **7a** operate between Rh(III) and Rh(V) oxidation states. It is hoped that further studies will provide more data to support this hypothesis.

An alternative mode of hydrogen activation by Rh(III) rhodacarboranes involves the heterolysis of molecular hydrogen into H^- and H^+. This type of hydrogen activation is exemplified by the formation of [$(PPh_3)_3RuHCl$] from [$(PPh_3)_4RuCl_2$] and molecular hydrogen in the presence of triethylamine.[19] If the hydrogenolysis of complexes **4a** and **4b** proceeds by heterolysis of molecular hydrogen, either the solvent or the carborane ligand must trap the released proton prior to methane elimination. At this point there is insufficient experimental evidence to indicate exactly how some Rh(III) rhodacarboranes activate hydrogen, but the facility with which this process occurs demonstrates the electronic flexibility of rhodacarboranes.

Syntheses and Characterization of Acylrhodacarboranes. The interaction of carbon monoxide with alkylmetal complexes has been a widely studied reaction because of its importance in the synthesis of valuable industrial commodities such as acetic acid, ethylene glycol, and butyraldehyde, among others.[20,21] The insertion of carbon monoxide into metal–carbon bonds (or more correctly characterized as alkyl migration to coordinated carbon monoxide) provides a necessary pathway for the homologation of metal-bound organic moieties. A current goal in metallacarborane chemistry is the development of homogeneous metallacarborane catalysts capable of activating carbon monoxide, and it is through the study of the interaction of carbon monoxide with metallacarboranes that such catalysts might be discovered. Thus, we have examined the reactivity of the alkyl- and η^3-allylrhodacarboranes described above with carbon monoxide.

Acetone solutions of complex **4a** rapidly react with CO (1 atm, 25 °C) to produce in high yields the orange crystalline acyl complex [*closo*-3-PPh_3-3-CO-3-$COCH_3$-3,1,2-$RhC_2B_9H_{11}$] (**8a**). Similarly, complex **4b** reacts with CO to produce the crystalline, lemon yellow complex [*closo*-2-PPh_3-2-CO-2-$COCH_3$-2,1,7-$RhC_2B_9H_{11}$] (**8b**). Complexes **8a** and **8b** could also be prepared either by treatment of acetone suspensions of **5a** and **5b**, respectively, with carbon monoxide or by the reaction of methyl iodide with the 3,1,2- and 2,1,7-isomers of K[18-crown-6][*closo*-(PPh_3)(CO)$RhC_2B_9H_{11}$] (**9a** and **9b**, respectively)[4] in methanol under an atmosphere of CO. The latter route was the most synthetically useful method of preparing **8a** or **8b**. The IR spectrum of **8a** displays absorptions expected to arise from the coordinated dicarbollide ligand and the triphenylphosphine ligand. Strong absorptions at 2050 and 1700 cm^{-1} are assigned to the terminal carbonyl stretch and the acyl carbonyl stretch, respectively. The ^1H NMR spectrum of CD_2Cl_2 solutions of **8a** displays resonances assignable to the triphenylphosphine ligand and the two inequivalent carboranyl C–H protons. The methyl substituent gives rise to a singlet at 2.06 ppm. Complex **8b** displays comparable spectral features.

Complex **9b** reacts with benzyl bromide in methanol under an atmosphere of CO to produce in good yield the crystalline, lemon yellow complex [*closo*-2-PPh_3-2-CO-2-$COCH_2C_6H_5$-2,1,7-$RhC_2B_9H_{11}$] (**10b**). A similar reaction of **9a** with benzyl bromide apparently produces the 3,1,2 complex, **10a**, analogous to **10b**, but because **10a** was easily decarbonylated during attempted isolation, this complex was not obtained in an analytically pure state. The IR spectra of **10a** and **10b** are consistent with their

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formulations, as are their corresponding ^1H NMR spectra.

The facile formation of acylrhodacarboranes from alkylrhodacarboranes represents an example of alkyl migration to coordinated carbon monoxide. This general reaction has substantial precedent in the chemical literature;[22] however, the isolation of the acylrhodacarboranes described above represents the first example in metallacarborane chemistry of alkyl migration to coordinated carbon monoxide. The reverse of this reaction, the deinsertion of carbon monoxide, also seems to be quite facile in some instances, notably for complex **10a**. The deinsertion of carbon monoxide requires a vacant coordination site on the metal, which is probably formed via dissociation of a terminal carbonyl ligand from the Rh(III) species, **10a**. The available evidence for such a dissociation is provided by the observation that complex **8a** was found to react with K[18-crown-6]I in the absence of CO to produce an orange crystalline species formulated as K[18-crown-6][*closo*-3-PPh_3-3-$COCH_3$-3-I-3,1,2-$RhC_2B_9H_{11}$] (**11a**). This formulation is based on the IR spectrum of this salt and the observation that this species reacts with $AgBF_4$ in CH_2Cl_2 to produce the analytically pure complex [*closo*-3-PPh_3-3-CO-3-CH_3-3,1,2-$RhC_2B_9H_{11}$] (**12a**). Interestingly, complex **12a** reacts with CO in acetone to produce **8a**. Thus, carbon monoxide insertion into alkylrhodacarboranes is quite facile, and in the absence of carbon monoxide the deinsertion of CO from acylrhodacarboranes is also quite favorable.

The aforementioned insertion of carbon monoxide into alkylrhodacarboranes suggests that these systems may function as homogeneous hydroformylation catalysts. The crucial step in hydroformylation, however, is aldehyde elimination, and the reactivity of the acyl complexes described above with molecular hydrogen remains to be explored.

While the simple alkylrhodacarboranes described above reacted immediately with carbon monoxide to produce acylrhodacarboranes, the π-allyl complex **2a** did not immediately react with carbon monoxide at room temperature in benzene. This is probably due to the stability of the η^3-allyl ligand with respect to rearrangement to the η^1-allyl ligand. Although it is possible that **2a** might react with CO at elevated temperatures and pressures, the appropriate experiments have not yet been performed.

Conclusions

A variety of alkyl- and acylrhodacarboranes have been prepared by reactions of alkylating agents with rhodacarborane anions, thus demonstrating the feasibility of carrying out selective chemical transformations at the metal vertex of a metallacarborane. The availability of these alkylrhodacarboranes has also allowed an examination of the reactivity of these species with molecular hydrogen. It is proposed that hydrogenolysis of closo Rh(III) alkylrhodacarboranes occurs via a transitory Rh(V) intermediate. Alkylrhodacarboranes also react with carbon monoxide to produce acylrhodacarboranes. The latter reaction represents the first example in metallacarborane chemistry of alkyl migration to coordinated carbon monoxide.

Experimental Section

General Methods. All reactions involving air-sensitive materials were performed under deoxygenated argon with Schlenk techniques or in a Vacuum Atmospheres inert-atmosphere glovebox. NMR solvents were dried, degassed, and vacuum-transferred into NMR tubes containing the solid samples at −196 °C and sealed in vacuo. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WP-200 spectrometer operating in the Fourier transform mode at 200.133 and 81.02 MHz, respectively. ^{11}B NMR spectra were recorded at 80.5, 111.80, and 127.01 MHz by using an instrument designed and constructed by Professor F. A. L. Anet and co-workers at UCLA. Proton chemical shifts were referenced to residual protons in the solvent (CD_2Cl_2 5.28 ppm, C_6D_6 7.25 ppm). Phosphorus chemical shifts were referenced to external 85% H_3PO_4 (0 ppm), with downfield shifts taken as positive. Boron chemical shifts were referenced to external $Et_2O{\cdot}BF_3$, with downfield shifts taken as positive. Infrared spectra were obtained as Nujol mulls by using a Perkin-Elmer 137 instrument.

Solvents were distilled from the following drying agents under a dry nitrogen atmosphere: benzene and tetrahydrofuran, potassium metal; heptane, sodium metal; dichloromethane, phosphorus pentoxide; acetonitrile, calcium hydride; acetone, 4-Å molecular sieves; methanol, magnesium methoxide.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Materials. All solvents were reagent grade (Mallinckrodt). The species [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (H(**1a**)) and [*closo*-2,2-$(PPh_3)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$] (H(**1b**)) were prepared by literature methods.[7] Allyl chloride and methallyl chloride (Aldrich) were distilled from calcium chloride prior to use. Trimethyloxonium tetrafluoroborate was prepared by a literature procedure.[23] Prior to its use, this salt was washed with anhydrous dichloromethane and diethyl ether and dried in a stream of nitrogen. Benzyl bromide, methyl iodide, and 18-crown-6 (Aldrich) were used as received. K-Selectride was available as a 1 M solution in THF (Aldrich). Carbon monoxide was obtained from Air Products and used directly from the cylinder.

[*closo*-3-PPh_3-3-(η^3-C_3H_5)-3,1,2-$RhC_2B_9H_{11}$] (2a). By the procedure described elsewhere,[4] as a first step 1.00 g (1.31 mmol) of complex H(**1a**) was converted to Li^+[*closo*-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{11}$]$^-$ (Li(**1a**)) with butyllithium. The salt so obtained was then reacted with 30 mL of neat, or a benzene solution of, allyl chloride in a Schlenk flask for 3 h, producing an orange-yellow solution and a colorless precipitate. The allyl chloride (and solvent) was removed in vacuo, leaving an orange-yellow oil. This oil was then vigorously stirred with deaerated distilled water for 1 h, producing a yellow solid. This solid was isolated and thoroughly dried in vacuo. Yield: 0.60 g (85%). An analytically pure sample was obtained after several recrystallizations of the reaction product from dichloromethane–heptane. ^1H NMR (CD_2Cl_2, 25 °C): 7.59–7.27 (envelope, 15 H, phenyl rings), 4.97 (m, 1 H, H_aH_sC–CH_c–CH_aH_s), 4.10 (d, 2 H, H_s, $J_{H_s-H_c}$ = 8 Hz), 2.85 (s, br, 2 H, carboranyl C–H), 2.53 ppm (t, 2 H, H_a, spacing = 2 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 45.0 ppm (d, J_{Rh-P} = 142 Hz). Anal. Calcd for $C_{23}H_{31}B_9RhP$: C, 51.28; H, 5.80; B, 18.06; Rh, 19.11; P, 5.75. Found: C, 51.33; H, 5.91; B, 18.06; Rh, 19.10; P, 5.73.

An alternative route to **2a** consisted of adding 1.1 mol equiv of allyl acetate to a tetrahydrofuran solution of Li(**1a**) at room temperature. After 3 h of reaction, the volatile components were removed in vacuo. The brown residue was pulverized and placed at the top of a silica gel column. Elution of the various components was carried out in air, using the solvent sequence heptane–benzene (1:1) (eluting purple dimer [*closo*-3-PPh_3-3,1,2-$RhC_2B_9H_{11}$]$_2$;[8,9] then benzene eluting **2a**). A dark brown residue remains at the top of the column. The stability of **2a** when exposed to air, even when in solution, was proved by thin-layer chromatography where only one spot was observed (visible, UV short, I_2). The yield of **2a** was 60–65%.

[*closo*-3-PPh_3-3-(η^3-C_4H_7)-3,1,2-$RhC_2B_9H_{11}$] (3a). This complex was produced by a procedure analogous to that used for complex **2a** using Li(**1a**) and methallyl chloride. The reaction product was purified by dissolving the mixture in 100 mL of benzene, filtering the solution, and then gently layering 300 mL of heptane onto the benzene solution. After 2 days, small orange blocks of [*closo*-3,3-$(PPh_3)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$] and large yellow needles of **3a** had formed. The solvent was then decanted, and the crystals were dried in a stream of nitrogen. The large yellow crystals were mechanically separated from the smaller orange crystals and were then recrystallized from dichloromethane–heptane to produce yellow microcrystals, which were found to contain approximately 1 CH_2Cl_2 solvate molecule per molecule of complex. Yield: 22%. ^1H NMR (CD_2Cl_2, 25 °C): 7.58–7.33 (envelope, 15 H, phenyl rings), 3.73 (s, 2 H, H_s, H_aH_sC–$C(CH_3)$–CH_aH_s), 2.82 (s, br, 2 H, carboranyl C–*H*), 2.46 (d, 2 H, H_a, J_{P-H_a} = 12 Hz), 1.81 ppm (s, 3 H, CH_3). $^{31}P\{^1H\}$ NMR (10% C_6D_6–THF, 25 °C): 45.1 ppm (d, J_{Rh-P} = 154 Hz). Anal. Calcd for $C_{25}H_{35}B_9RhPCl_2$: C, 47.09; H, 5.53; B, 15.26; Rh, 16.14; P, 4.86; Cl, 11.12. Found: C, 47.41; H, 5.85; B, 15.83; Rh, 15.86; P, 4.97; Cl, 9.11.

[*closo*-3-PPh_3-3-CH_3-3-CH_3COCH_3-3,1,2-$RhC_2B_9H_{11}$] (4a). By previously described procedure,[4] 0.500 g (0.65 mmol) of complex H(**1a**) was converted to K(**1a**) with K-Selectride. The salt so obtained was dissolved in 40 mL of dry acetonitrile, and to this solution 0.22 g (1.48 mmol) of freshly prepared[23] Me_3OBF_4 was added at 0 °C. After 1.5 h, the solution was orange-yellow and an orange precipitate was present. A 70% ethanol–water solution was slowly added to the reaction to precipitate the product completely. The orange-yellow solid was isolated by filtration and dried in a stream of nitrogen. Further purification of this product

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was achieved by dissolving this solid with acetonitrile and passing this solution through a 20 × 2 cm column packed with Florisil, in the absence of air. Dropwise addition of deaerated 70% ethanol–water to the eluant produced orange-yellow plates. After isolation of the crystalline product and drying in vacuo, the solid was recrystallized twice from acetone–heptane at 0 °C, producing 0.26 g (70%) of **4a**. Mp: 150–155 °C dec. ^{1}H NMR (acetone-d_6, −73 °C): 7.46 (s, br, 15 H, phenyl rings), 4.04 (s, br, 1 H, carboranyl C–*H*), 2.23 (s, br, 1 H, carboranyl C–*H*), 1.95 (m, 6 H, CH_3COCH_3), 1.51 ppm (dd, 3 H, CH_3, J_{Rh-P} = 6 Hz). ^{31}P{^{1}H} NMR (10% acetone-d_6–acetone, 25 °C): 47.3 ppm (d, J_{Rh-P} = 133 Hz). Anal. Calcd for $C_{24}H_{35}B_9RhPO$: C, 50.50; H, 6.18; B, 17.05; Rh, 18.03; P, 5.43; O, 2.80. Found: C, 50.58; H, 6.00; B, 16.88; Rh, 17.94; P, 5.46.

[*closo*-2-PPh$_3$-2-CH$_3$-2-CH$_3$COCH$_3$-2,1,7-RhC$_2$B$_9$H$_{11}$] (4b). This complex was obtained in 70% yield as lemon yellow crystals by reacting K(**1b**)[4] (from H(**1b**), see above) and Me_3OBF_4 with use of a procedure analogous to that used for complex **4a**. Mp: 115–120 °C dec. ^{1}H NMR (acetone-d_6, −23 °C): 7.59–7.34 (envelope, 15 H, phenyl rings), 2.00 (m, 6 H, CH_3COCH_3), 1.67 (s, br, 1 H, carboranyl C–*H*), 1.23 (dd, 3 H, CH_3, J_{Rh-H} = 1.7 Hz, J_{P-H} = 5.0 Hz), 1.07 ppm (s, br, 1 H, carboranyl C–*H*). ^{31}P{^{1}H} NMR (10% acetone-d_6–acetone, −23 °C): 47.8 ppm (d, J_{Rh-P} = 155 Hz). Anal. Found (isomer of **4a**): C, 50.52; H, 5.86; B, 16.75; Rh, 17.04; P, 5.47.

[*closo*-3,3-(PPh$_3$)$_2$-3-CH$_3$-3,1,2-RhC$_2$B$_9$H$_{11}$] (5a). To a homogeneous solution of 0.175 g (0.31 mmol) of complex **4a** in 20 mL of dry acetone 0.107 g (0.41 mmol) of triphenylphosphine was added at 0 °C. After 1 h, the orange precipitate that formed was isolated by filtration and then washed with 2 × 10 mL of acetone, 2 × 10 mL of diethyl ether, and finally 2 × 20 mL of pentane and dried in vacuo, producing 0.20 g (85%) of **5a**. Mp: 155–165 °C dec. Anal. Calcd for $C_{39}H_{44}B_9RhP_2$: C, 60.45; H, 5.72; B, 12.56; Rh, 13.28; P, 7.99. Found: C, 60.33; H, 5.83; B, 12.83; Rh, 12.59; P, 7.64.

[*closo*-2,2-(PPh$_3$)$_2$-2-CH$_3$-2,1,7-RhC$_2$B$_9$H$_{11}$] (5b). By a procedure analogous to the one used for the preparation of **5a**, complex **5b** was prepared from **4b** and PPh_3 in 85% yield. Infrared analysis of the dried product indicated the presence of acetone in the crystal lattice, which was verified by elemental analysis. Mp: 165–170 °C dec. Anal. Calcd for $C_{24}H_{50}B_9RhP_2O$: C, 60.56; H, 6.05; B, 11.68; Rh, 12.36; P, 7.43; O, 1.92. Found: C, 60.75; H, 5.90; B, 12.29; Rh, 12.41; P, 7.00.

K[18-crown-6][*closo*-3-PPh$_3$-3-C$_6$H$_5$CH$_2$-3-Br-3,1,2-RhC$_2$B$_9$H$_{11}$] (6a). The golden crystalline salt K[18-crown-6](**1a**), prepared[4] from 0.500 g (0.657 mmol) of complex H(**1a**), was suspended in 50 mL of dry benzene. Benzyl bromide (80 μL, 0.12 g, 0.67 mmol) was added, and the mixture was stirred under nitrogen for 1.5 h. A red precipitate formed, which was isolated by decantation, washed repeatedly with diethyl ether, and dried in vacuo. Analytically pure material was obtained by recrystallizing the reaction product once from tetrahydrofuran–heptane and twice from dichloromethane–heptane. Yield: 0.35 g (55%). Mp: 115 °C dec. ^{1}H NMR (CD_2Cl_2, 25 °C): 7.90–7.28 (envelope, 15 H, phenyl rings), 3.61 (m, 1 H, H_aH_b–C–Rh), 3.55 (s, 24 H, crown ether), 2.85 (s, 1 H, carboranyl C–*H*), 1.76 (m, 1 H, H_b), 1.58 ppm (s, 1 H, carboranyl C–*H*). ^{31}P{^{1}H} NMR (20% CD_2Cl_2–CH_2Cl_2, 25 °C): 40.3 ppm (d, J_{Rh-P} = 149 Hz). Anal. Calcd for $C_{39}H_{57}B_9PKBrO_6$: C, 48.19; H, 5.91; B, 10.00; Rh, 10.59; P, 3.19; K, 4.02; Br, 8.22; O, 9.88. Found: C, 48.30; H, 5.98; B, 9.80; Rh, 10.18; P, 3.12; K, 3.98; Br, 8.08.

[*closo*-3-PPh$_3$-3-CO-3-COCH$_3$-3,1,2-RhC$_2$B$_9$H$_{11}$] (8a). A suspension of 0.400 g (0.48 mmol) of K[18-crown-6](**9a**)[4] in 30 mL of methanol under a CO atmosphere was combined with 2 mL of methyl iodide and over a period of 6 h produced an orange precipitate that was isolated and dried. Yield: 0.21 g (79%). An analytically pure sample was obtained by recrystallizing the reaction product from dichloromethane–methanol under a CO blanket. ^{1}H NMR (CD_2Cl_2, 25 °C): 7.61–7.41 (envelope, 15 H, phenyl rings), 2.69 (s, 3 H, CH_3), 2.25 (s, br, 1 H, carboranyl CO*H*), 2.06 ppm (s, br, 1 H, carboranyl C–*H*). ^{31}P{^{1}H} NMR (20% CD_2Cl_2–CH_2Cl_2, 25 °C): 31.2 ppm (d, J_{Rh-P} = 111 Hz). Infrared (Nujol): ν(CO) 2020 (vs), 1700 cm^{-1} (vs). Anal. Calcd for $C_{23}H_{29}B_9RhPO_2$: C, 48.58; H, 5.14; B, 17.11; Rh, 18.10; P, 5.44; O, 5.46. Found: C, 48.65; H, 5.11; B, 16.75; Rh, 18.21; P, 5.46.

[*closo*-2-PPh$_3$-2-CO-2-COCH$_3$-2,1,7-RhC$_2$B$_9$H$_{11}$] (8b). This complex was prepared from K[18-crown-6](**9b**),[4] methyl iodide, and CO in methanol in 80% yield by a procedure analogous to that used for the preparation of **8a**. ^{1}H NMR (CD_2Cl_2, 25 °C): 7.51–7.32 (envelope, 15 H, phenyl rings), 1.94 (s, br, 1 H, carboranyl C–*H*), 1.51 (s, 3 H, CH_3), 1.13 ppm (s, br, 1 H, carboranyl C–*H*). ^{31}P{^{1}H} NMR (20% CD_2Cl_2–CH_2Cl_2, 25 °C): 27.1 ppm (d, J_{Rh-P} = 115 Hz). Infrared (Nujol): ν(CO) 2015 (s), 1695 cm^{-1} (s). Anal. Found: C, 48.47; H, 5.40; B, 16.70; Rh, 17.78; P, 5.51.

[*closo*-2-PPh$_3$-2-CO-2-COCH$_2$C$_6$H$_5$-2,1,7-RhC$_2$B$_9$H$_{11}$] (10b). This complex was prepared from K[18-crown-6](**9a**),[4] benzyl bromide, and CO in methanol in 75% yield by a procedure analogous to that used for complex **8a**. ^{1}H NMR (CD_2Cl_2, −33 °C): 7.48–6.69 (envelope, 20 H, phenyl rings), 4.68 (d, 1 H, H_aH_b–C(C_6H_5), $J_{H_a-H_b}$ = 9 Hz), 3.64 (d, 1 H, H_b $J_{H_a-H_b}$ = 9 Hz), 1.84 (s, br, 1 H, carboranyl C–*H*), 1.39 ppm (s, br, 1 H, carboranyl C–*H*). ^{31}P{^{1}H} NMR (10% $CDCl_3$–CH_2Cl_2, 25 °C): 27.1 ppm (d, J_{Rh-P} = 115 Hz). Infrared (Nujol): ν(CO) 2030 (vs), 1700 cm^{-1} (vs). Anal. Calcd for $C_{29}H_{33}B_9RhPO_2$: C, 54.03; H, 5.15; B, 15.09; Rh, 15.96; P, 4.80; O, 4.96. Found: C, 53.99; H, 4.84; B, 14.26; Rh, 15.90; P, 4.82.

[*closo*-3-PPh$_3$-3-CO-3-CH$_3$-3,1,2-RhC$_2$B$_9$H$_{11}$] (12a). To a suspension of 0.400 g (0.48 mmol) of K[18-crown-6](**9a**)[4] in 30 mL of methanol was added 2 mL of methyl iodide. After the reaction was stirred for 30 min, a yellow-orange solution was produced. Deaerated distilled water was added to this solution, producing an orange-yellow solid, which was isolated and dried. An analytically pure sample was obtained by recrystallizing the reaction product from ether–pentane and dichloromethane–methanol (−20 °C). ^{1}H NMR (CD_2Cl_2, 25 °C): 7.51–7.23 (envelope, 15 H, phenyl rings), 2.71 (s, br, 1 H, carboranyl C–*H*), 1.81 (s, br, 1 H, carboranyl C–*H*), 1.24 ppm (dd, 3 H, CH_3, J_{P-H} = 5 Hz, J_{Rh-H} = 1.7 Hz). Infrared (Nujol): ν(CO) 2050 cm^{-1} (vs). Anal. Calcd for $C_{22}H_{29}RhPO$: C, 48.88; H, 5.40; B, 18.00; Rh, 19.07; P, 5.73. Found: C, 48.81; H, 5.37; B, 17.71; Rh, 18.68; P, 5.68.

Reaction of 2a with Hydrogen. A 100-mL Schlenk flask was loaded with 100 mg (0.18 mmol) of **2a** and a magnetic stirring bar and then fitted with a vacuum adapter. The flask was then evacuated on the high-vacuum line. Benzene (30 mL) was freeze–pump–thaw degassed on the high-vacuum line and then distilled into the liquid nitrogen cooled Schlenk flask. After the mixture warmed to room temperature, hydrogen was admitted into the reaction flask (600 Torr). After 12 h, the solution had turned dark purple. The solvent was removed in vacuo, leaving a purple residue, which was dissolved in CH_2Cl_2 and then filtered through a short column of silica gel. The addition of hexane to the purple solution, followed by evaporation of the CH_2Cl_2 produced a purple solid, which was identified as [*closo*-3-PPh$_3$-3,1,2-RhC$_2$B$_9$H$_{11}$]$_2$[8,9] by its IR and ^{31}P{^{1}H} NMR spectra. Yield: 76 mg (85%).

Reaction of 2b with Hydrogen. Complex **2b** was treated with hydrogen by using the procedure described above for the reaction of complex **2a** with hydrogen, yielding a red solution. The addition of heptane to this solution precipitates a brick red solid. The ^{1}H NMR spectrum of this solid in benzene-d_6 exhibits four rhodium hydride resonances at −7.19 (t), −9.87 (dd), −10.72 (six-line multiplet), and −12.71 ppm (m). Further purification of this mixture was unsuccessful.

Reaction of 4a with Hydrogen. A 5-mm NMR tube was loaded with 5 mg of **4a**, and 0.30 mL of acetone-d_6 (freeze–pump–thaw degassed) was vacuum transferred into it. The vacuum line and the NMR tube were then filled with hydrogen (ca. 600 Torr). The tube was then sealed, and the mixture was warmed rapidly to −78 °C, producing a colorless solution (−73 °C) that displayed a rhodium hydride resonance at −6.84

Table III. Details of Crystallographic Data Collection for *closo*-3-PPh$_3$-3-η^3-C$_3$H$_5$-3,1,2-RhC$_2$B$_9$H$_{11}$

crystal size/mm	0.3 × 0.3 × 0.325
normal to faces	100, 0$\bar{1}$1, 101
appearance	yellow parallelepiped
diffractometer	Syntex P$\bar{1}$
radiation	Mo Kα (graphite monochromator)
wavelength/Å	0.7107
temp/°C	−163
2θ max/deg	50
data collcd	$h,k,\pm l$
scan width	1° below Kα$_1$, 1° above Kα$_2$
scan rate/deg min^{-1}	4.0
space group	$P2_1/c$
a/Å	12.678 (3)
b/Å	15.391 (4)
c/Å	15.454 (2)
β/deg	121.26 (1)
V/Å^3	2586
Z	4
ρ(calcd)/g cm^{-3}	1.30
μ/cm^{-1}	6.50
range of transmission factors	0.9093–0.9321; av 0.9254
no. of unique reflns	4573
no. of reflns obsd[a]	3851
no. of params refined	195
R[b]	0.041
R_w[c]	0.056
GOF[d]	2.15

[a] $I > 3\sigma(I)$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [(\sum w(|F_o| - |F_c|))^2/\sum w|F_o|^2]^{1/2}$; $w = [1/\sigma(F_o)]^2$. [d] GOF = $[\sum w(|F_o| - |F_c|)^2/N_o - N_v)]^{1/2}$; N_o = 3851; N_v = 195.

Table IV. Positional and Thermal Parameters

atom	x	y	z	10^4U, Å^2
Rh	−0.97641 (3)	0.23610 (2)	−0.22941 (2)	240
P	−0.7770 (1)	0.2287 (1)	−0.0854 (1)	250
B(4)	−1.0275 (5)	0.2629 (3)	−0.1173 (4)	336 (10)
B(5)	−1.1272 (5)	0.3521 (3)	−0.1318 (4)	394 (11)
B(6)	−1.1942 (5)	0.3948 (4)	−0.2555 (4)	447 (12)
B(7)	−1.1824 (5)	0.2225 (3)	−0.3265 (4)	369 (11)
B(8)	−1.1221 (4)	0.1775 (3)	−0.2028 (4)	359 (11)
B(9)	−1.1799 (5)	0.2432 (3)	−0.1411 (4)	416 (12)
B(10)	−1.2794 (5)	0.3238 (4)	−0.2261 (4)	454 (13)
B(11)	−1.2805 (5)	0.3121 (4)	−0.3418 (4)	434 (12)
B(12)	−1.2760 (5)	0.2188 (4)	−0.2718 (4)	429 (12)
C(1)	−1.0460 (4)	0.3531 (3)	−0.1916 (3)	343 (9)
C(2)	−1.1326 (4)	0.3292 (3)	−0.3090 (3)	379 (10)
C(01)	−0.8864 (5)	0.2700 (4)	−0.3179 (4)	516 (13)
C(02)	−0.9647 (5)	0.1994 (4)	−0.3570 (4)	518 (12)
C(03)	−0.9437 (5)	0.1248 (4)	−0.2993 (4)	546 (13)
C(11)	−0.7367 (3)	0.3382 (3)	−0.0318 (3)	305 (9)
C(12)	−0.7154 (4)	0.3593 (3)	0.0639 (3)	438 (11)
C(13)	−0.6950 (5)	0.4457 (4)	0.0967 (4)	599 (14)
C(14)	−0.6925 (5)	0.5104 (4)	0.0359 (4)	603 (14)
C(15)	−0.7155 (4)	0.4898 (3)	−0.0607 (4)	487 (11)
C(16)	−0.7388 (4)	0.4052 (3)	−0.0939 (3)	366 (9)
C(21)	−0.7544 (3)	0.1537 (2)	0.0145 (3)	285 (8)
C(22)	−0.6454 (4)	0.1545 (3)	0.1091 (3)	328 (9)
C(23)	−0.6267 (4)	0.0938 (3)	0.1823 (3)	387 (10)
C(24)	−0.7155 (4)	0.0315 (3)	0.1617 (3)	410 (10)
C(25)	−0.8216 (4)	0.0287 (3)	0.0675 (3)	436 (11)
C(26)	−0.8415 (4)	0.0895 (3)	−0.0057 (3)	373 (10)
C(31)	−0.6473 (4)	0.1943 (3)	−0.0986 (3)	300 (8)
C(32)	−0.6274 (4)	0.1058 (3)	−0.1004 (3)	377 (10)
C(33)	−0.5356 (4)	0.0759 (3)	−0.1172 (4)	479 (11)
C(34)	−0.4642 (5)	0.1337 (3)	−0.1318 (4)	512 (12)
C(35)	−0.4804 (5)	0.2217 (3)	−0.1275 (4)	521 (12)
C(36)	−0.5723 (4)	0.2527 (3)	−0.1112 (4)	430 (11)

ppm (dd), while the room-temperature spectrum displayed two rhodium hydride resonances at −6.84 (dd) and −7.61 ppm (dd); the higher field resonance predominates (ca. 85%). After the tube was removed from the NMR probe, a slight discoloration of the solution was noted.

Reaction of 4b with Hydrogen. A homogeneous solution of **4b** in acetone was exposed to an atmosphere of hydrogen for 15 min at 0 °C, producing a nearly colorless solution. The addition of precooled heptane (0 °C) precipitated white microcrystals. ^{1}H NMR (acetone-d_6, 25 °C): −8.18 ppm (dd).

Collection and Reduction of X-ray Data. A yellow crystal, obtained from vapor diffusion of pentane into a 10% acetone–benzene solution of [*closo*-3-PPh_3-3-(η^3-C_3H_5)-3,1,2-$RhC_2B_9H_{11}$] (**2a**) as a parallelepiped with faces (100), (0$\bar{1}$1), (010), ($\bar{1}$00), (01$\bar{1}$), and (0$\bar{1}$0), approximately 0.3 × 0.3 × 0.325 mm, was mounted along the c axis on a glass fiber. Unit cell dimensions were determined from a least-squares fit of 15 accurately centered reflections. These, and other parameters, including conditions of data collection, are summarized in Table III. Data were collected on a Syntex P$\bar{1}$ diffractometer equipped with a graphite monochromator (Mo Kα radiation, λ = 0.71069 Å); the θ–2θ scan mode was used, to a limit in 2θ of 50°. Three reflections, $\bar{2}$44, 02$\bar{2}$, and 132, were measured every 100 reflections to check stability. Intensities of these reflections fluctuated only slightly, a maximum of ±3% during the course of the experiment. A scan rate of 4°/min and a scan range of 1.0° below Kα_1 to 1.0° above Kα_2 were employed. A total of 4573 unique reflections were measured. Of these, 3851 were considered observed ($I > 3\sigma(I)$) and were used in subsequent structure analysis. Data were corrected for Lorentz, polarization, and absorption effects.[24]

Solution and Refinement of the Structure. Atoms were located by use of the heavy-atom method. In the course of refinement, all cage C and B atoms were assigned boron scattering factors, and full-matrix least-squares refinement of positional and vibrational parameters for these atoms led to identification of the carbon atoms. All calculations were performed on the VAX 11/780 of the chemistry department. All cage and allyl hydrogen atoms were located and included in the structure factor calculation. All hydrogen atoms of phenyl groups were included in calculated positions, C–H = 0.95 Å. A total of 195 parameters were refined, including positional and anisotropic thermal parameters for Rh and P, positional and isotropic thermal parameters for all other non-hydrogen atoms, and positional parameters for all cage and allyl hydrogen atoms. All hydrogen atoms of the allyl group were assigned a thermal parameter of 4.5. All hydrogen atoms of the icosahedron were assigned a thermal parameter of 4.0. All hydrogen atoms of the phenyl groups were assigned thermal parameters according to the carbon atoms to which they are attached. Scattering factors for H were obtained from Stewart et al.,[25] and those for other atoms were taken from ref 26. Anomalous dispersion terms were applied to scattering of Rh and P. Least-squares refinement converged to final agreement factors R = 0.041, R_w = 0.056, and GOF = 2.15. Final positional and thermal parameters are given in Table IV. A table of structure factors is available as supplementary material.

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Supplementary Material Available: Tables of anisotropic thermal parameters, parameters for hydrogen atoms, and complete listings of interatomic angles and distances (6 pages); a listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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