up in sufficient concentrations to be observed spectroscopically because it is too photoreactive. Also note that the overlapping absorption bands of $Os_3(CO)_{12}$ and $Os_3(CO)_{12}Cl_2$ (Figure 1) preclude irradiation of $Os_3(CO)_{12}$ alone. Although we do not know the mechanism of formation of $Os(CO)_4Cl_2$, it is reasonable to propose that $Os_3(CO)_{12}Cl_2$ is an intermediate. In any case, it is clear both from the chlorocarbon reactions and from the experiments under CO pressure that $Os_3(CO)_{12}$ photofragmentation is a very inefficient process.

The observed photochemistry of $Os_3(CO)_{12}$ in the presence of PPh_3 is outlined in Scheme II.

Formation of $Os_3(CO)_{11}PPh_3$ presumably occurs by a mechanism involving photodissociation of $Os_3(CO)_{12}$ to give $Os_3(CO)_{11}$ + CO, followed by capture of PPh_3. The Os_3 unit fragments only *after* a PPh_3 binds at each Os atom, and even then the reaction is very inefficient. None of the infrared spectra of the $Os_3(CO)_{12}$–PPh_3 photolysis solutions exhibited bands attributable to $Os(CO)_4PPh_3$,[16] which should have formed had any $Os(CO)_4$ been extruded. Prolonged irradiation yielded only $Os(CO)_3(PPh_3)_2$, even at 420 nm, where $Os(CO)_4PPh_3$ does not absorb.

The observed photobehavior of $Os_3(CO)_{12}$ and $Os_3(CO)_{12-n}(PPh_3)_n$ complexes contrasts sharply with the finding[1] that Ru–Ru bond breaking is an efficient photoprocess in $Ru_3(CO)_{12}$ as well as in $Ru_3(CO)_{11}PPh_3$ (in fact, $Ru_3(CO)_{10}(PPh_3)_2$ and $Ru_3(CO)_9(PPh_3)_3$ never form in the photoreaction of $Ru_3(CO)_{12}$ with PPh_3 because photochemical fragmentation of $Ru_3(CO)_{11}PPh_3$ occurs so readily). One reason for the different photochemical behavior of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ is likely related to the relative M–M bond strengths in these species (Os–Os > Ru–Ru).[17] In our view, another important factor is the character of the lowest excited electronic state in each of the complexes. It is reasonable to expect that population of the lowest excited state ($\sigma \rightarrow \sigma^*$) of $Ru_3(CO)_{12}$ will lead to metal–metal bond cleavage and fragmentation. In the lowest excited state ($\sigma^{*\prime} \rightarrow \sigma^*$) of $Os_3(CO)_{12}$, however, the Os–Os bonds are probably not weakened appreciably. Internal conversion from the higher $\sigma \rightarrow \sigma^*$ state to $\sigma^{*\prime} \rightarrow \sigma^*$ must be very efficient, as irradiation at 313 nm gives a very small yield of fragmentation product (that is, Os–Os dissociation is not a principal decay pathway). From our observation that some Os–CO dissociation occurs upon $\sigma^{*\prime} \rightarrow \sigma^*$ excitation of $Os_3(CO)_{12}$, we infer that the $\sigma^{*\prime}\sigma^*$ state has partial Os–CO antibonding character.

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Eleven-Vertex Rhodium, Iridium, and Ruthenium Phosphinometallocarborane Complexes Formed from Sodium Undecahydro-5,6-dicarba-*nido*-decaborate(1−)

C. W. Jung and M. F. Hawthorne*

Contribution from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received November 19, 1979*

Abstract: Reactions of sodium undecahydro-5,6-dicarba-*nido*-decaborate(1−) ($NaC_2B_8H_{11}$) with $[IrClL_n]$ (n = 2, L = $P(CH_3)_2Ph$, $As(CH_3)_2Ph$; n = 3, L = PPh_3) afforded the 18e⁻ Ir^{III} complexes [*closo*-1,1-L_2-1-H-1,2,4-$IrC_2B_8H_{10}$], while reaction with $[RhClL_3]$ produced the 16e⁻ Rh^I complexes [*nido*-9,9-L_2-9,7,8-$RhC_2B_8H_{11}$] (L = PPh_3, $P(p\text{-tolyl})_3$) and the 18e⁻ Rh^I complexes [*nido*-9,9,9-L_3-9,7,8-$RhC_2B_8H_{11}$] (L = $As(CH_3)_2Ph$, $P(CH_3)_2Ph$, $P(CH_3)_3$, $As(CH_3)_3$, $Sb(CH_3)_3$, PEt_3). In solution, [*nido*-$Rh(PEt_3)_3(C_2B_8H_{11})$] dissociates triethylphosphine reversibly to form [*nido*-$Rh(PEt_3)_2(C_2B_8H_{11})$], which partially isomerizes to [*closo*-1,1-$(PEt_3)_2$-1-H-1,2,4-$RhC_2B_8H_{10}$] upon standing. The standard enthalpy and entropy of formation of $[RhH(PEt_3)_2(C_2B_8H_{10})]$ from $[Rh(PEt_3)_2(C_2B_8H_{11})]$ are -3.1 ± 0.1 kcal mol^{-1} and -10.5 ± 0.4 eu, respectively. The reaction of $NaC_2B_8H_{11}$ with $[RuHCl(PPh_3)_3]$ yielded [*closo*-1,1,3-$(PPh_3)_3$-1-H-1,2,4-$RuC_2B_8H_9$], in which a PPh_3 ligand has displaced a terminal B–H hydrogen atom of the carborane ligand.

Recently, a new synthetic route to *closo*-metallocarboranes was developed involving the formal oxidative addition of the acidic bridging hydrogens of *nido*-carboranes to 16-electron metal complexes.[1-3] Thus, reactions of 7,8- and 7,9-$C_2B_9H_{12}^-$ with $[MCl(PPh_3)_3]$ (M = Rh, Ir) and $[RuHCl(PPh_3)_3]$ afforded respectively the complexes $[MH(PPh_3)_2(C_2B_9H_{11})]$[1,4] and $[RuH_2(PPh_3)_2(C_2B_9H_{11})]$.[2] These complexes are active catalysts for the hydrogenation and isomerization of alkenes,[1,2] hydrosilylation of ketones,[1] and deuterium exchange at terminal B–H sites.[5]

We have extended this reaction to other *nido*-carborane moieties containing acidic bridging hydrogens,[3] and in this paper we describe the reactions of the $C_2B_8H_{11}^-$ anion derived[6] from 5,6-dicarba-*nido*-decaborane(12) with coordinatively unsaturated metal complexes. This anion resembles its $(C_2B_9H_{12})^-$ congener by forming catalytically active metal-

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locarboranes. However, the remaining bridging hydrogen in $(C_2B_8H_{11})^-$ is much less reactive than that of the $(C_2B_9H_{12})^-$ anion.[7] This difference allows intermediates along the oxidative-addition pathway to be isolated or detected. The synthesis of [*closo*-1,1-$(PPh_3)_2$-1-H-1,2,4-$IrC_2B_8H_{10}$] from $NaC_2B_8H_{11}$ and $[IrCl(PPh_3)_3]$ was reported in a preliminary communication.[3]

Direct spectroscopic evidence has been obtained showing a reversible metal abstraction of a B-H-B bridging hydrogen atom from the carborane cage in $[Rh(PEt_3)_2(C_2B_8H_{11})]$. This has been postulated as the mechanism of formation for $[MH(PPh_3)_2(C_2B_9H_{11})]$ (M = Rh, Ir).[9] The reverse pathway of metal-hydride transfer to a carborane cage forming a B-H-B bridge may provide an important aspect of metallocarborane catalysis, especially in the area of small-molecule reduction.

Results and Discussion

Iridacarboranes. The reaction of $NaC_2B_8H_{11}$ with $[IrCl(PPh_3)_3]$,[10] $[IrCl(P\{CH_3\}_2Ph)_2]$, or $[IrCl(As\{CH_3\}_2Ph)_2]$ produced the yellow, crystalline complexes formulated as [*closo*-1,1-L_2-1-H-1,2,4-$IrC_2B_8H_{10}$] (Ia-c; L = PPh_3, $P(CH_3)_2Ph$, and $As(CH_3)_2Ph$, respectively). The complexes $[IrCl(P\{CH_3\}_2Ph)_2]$ and $[IrCl(As\{CH_3\}_2Ph)_2]$ were generated in situ by reaction of $[IrCl(C_8H_{14})_2]_2$[11] with $P(CH_3)_2Ph$ and $As(CH_3)_2Ph$, respectively. The iridium-hydride stretching vibrations of Ia-c appeared as medium-intensity bands at about 2100 cm^{-1} (KBr pellet) in the infrared. The ^1H NMR spectra of Ia-c displayed two carboranyl C-H resonances, aryl and/or alkyl proton resonances, and a hydride resonance at approximately τ 17. For complexes Ia,b the hydride signals appeared as equal-intensity quartets, while that for complex Ic appeared as a singlet. The quartet pattern arises from spin coupling of the hydride to two inequivalent ^{31}P nuclei. The methyl proton NMR patterns of Ib showed four doublets while ^{31}P decoupling collapsed the hydride and methyl signals to singlets ($J_{P-C-H} = 10.0 \pm 0.5$ Hz for all four methyl groups). The ^1H NMR spectrum of Ic exhibited four methyl resonances in a triplet pattern, as coincidental overlap of two of the methyl resonances produced an unsymmetrical singlet at τ 8.40.

The ^1H NMR data for complexes Ia-c are consistent with bonding of the hydride and L ligands to an iridium atom which is asymmetric due to the absence of symmetry in the carboranyl ligand[12] (Figure 1). The ^{11}B NMR spectra of these compounds support this conclusion, and those of Ib,c each contain eight doublets. The spectrum of Ia consisted of very broad and poorly resolved peaks,[13] but ^1H decoupling showed the presence of seven unique resonances of approximate relative areas 1:1:1:1:1:2:1. The low-field resonances at about 50 ppm suggest that each of these complexes contains a low-coordinate boron atom next to the iridium atom.[14,15] The cage carbon vertices are therefore assigned to the 2,4 positions of the octadecahedron. Isomers with the carbons in the 2,5 or 2,10 positions are also consistent with the NMR data, but only the 2,3 and 2,4 isomers have been observed for closo-monometallic complexes of the $(C_2B_8H_{10})^{2-}$ ligand.[14] Attempts to isomerize Ia-c to the thermodynamically more stable 2,3 isomers by heating in refluxing toluene, or in the solid state at 150 °C, resulted only in partial decomposition of the complexes.

Like the complexes $[MH(PPh_3)_2(C_2B_9H_{11})]$ (M = Rh, Ir),[1,4] the above iridacarboranes can be considered as octahedral complexes of Ir^{III} with the $(C_2B_8H_{10})^{2-}$ ligand occupying three facial coordination sites. The magnitudes of the hydride-phosphorus coupling constants in Ia,b ($^2J_{P-H}$ = 14-32 Hz) are typical[16] of hydride cis to a tertiary phosphine in octahedral Ir^{III} complexes. Consistent with their formulation as coordinatively saturated Ir^{III} complexes, these compounds do not react with carbon monoxide (1 atm) at room temperature, appear to be air stable indefinitely, and are virtually inactive in alkene isomerization and hydrogenation (1 atm hydrogen) at ambient temperatures.

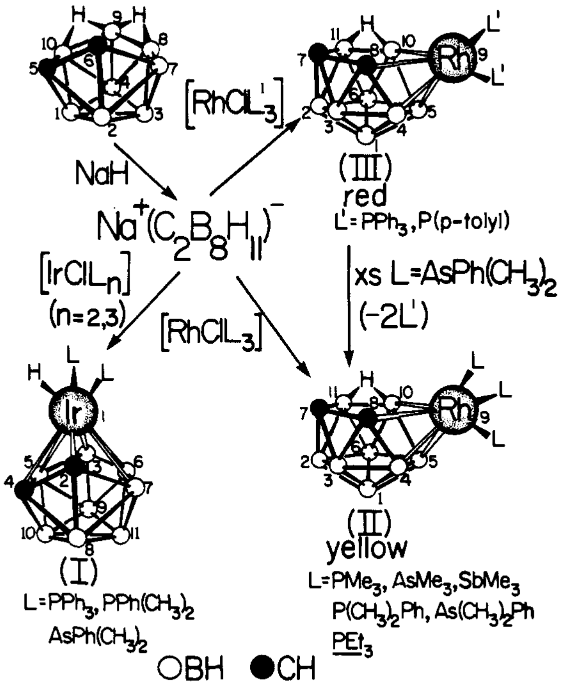

Figure 1. Synthesis of rhoda- and iridacarboranes from $(C_2B_8H_{11})^-$

Rhodacarboranes. Reactions of $NaC_2B_8H_{11}$ with $[RhClL_3]$[22] (L = $As(CH_3)_2Ph$, $P(CH_3)_2Ph$, $P(CH_3)_3$, $As(CH_3)_3$, and $Sb(CH_3)_3$) afforded yellow crystals of [*nido*-9,9,9-L_3-9,7,8-$RhC_2B_8H_{11}$] (IIa-e), respectively. Elemental analyses of IIa-e firmly established a ratio of three triorgano group 5A ligands to one carboranyl ligand per rhodium atom. No bands attributable to a rhodium-hydride stretching vibration were present in the infrared spectra.

The 80.5-MHz ^{11}B NMR spectra of complexes IIa,b were nearly identical. With ^1H decoupling they appeared as six singlets of intensities 2:1:2:1:1:1. The low-field singlets at about 13 ppm of relative area 2 are due to overlap of two singlets and this resonance appears unsymmetrical. With proton coupling this peak appears as an unresolved triplet instead of the expected two doublets. The ^{11}B NMR spectra of IIc-e were better resolved and consisted of eight doublets.

The ^1H NMR spectra of complexes IIa-d contained a broad resonance at τ 12.5-13.4 which may be assigned to a hydrogen atom bridging two boron atoms of the cage. A hydrogen atom bridging a cage boron and a rhodium atom would be expected[20,23-25] to appear above τ 15. The bridge hydrogen resonance of IIb appeared only upon ^{31}P decoupling and cooling to −20 °C, as cooling effects a degree of boron decoupling.[19] In all cases, cooling the sample solutions IIa-d to below −40 °C sharpened the B-H-B ^1H NMR resonance considerably.

The presence of the bridging hydrogen atom suggests that complexes IIa-e are *nido*-metallocarboranes.[24,26] The basic polyhedral structure of these complexes is most likely an 11-vertex icosahedral fragment with the metal atom bordering the open face,[18] as depicted in Figure 1. Assuming that no polyhedral rearrangement occurred upon complexation, the two polyhedral carbon atoms should occupy either the 4,8 or 7,8 vertices to form an asymmetric cage. Interactions of $\{RhL_3\}$ with the C(5)C(6)B(9)B(10) face of the $(C_2B_8H_{11})^-$ ligand should produce the 4,8 isomer, whereas bonding of the rhodium atom to the C(6)B(7)B(8)B(9) face will yield the 7,8 isomer. The ^1H-decoupled ^{13}C NMR spectrum of IIa in 20% CD_2Cl_2/CH_2Cl_2 at 26 °C contained two broad singlets (ca. 60 Hz half-widths) at 44.5 and 61.9 ppm downfield from

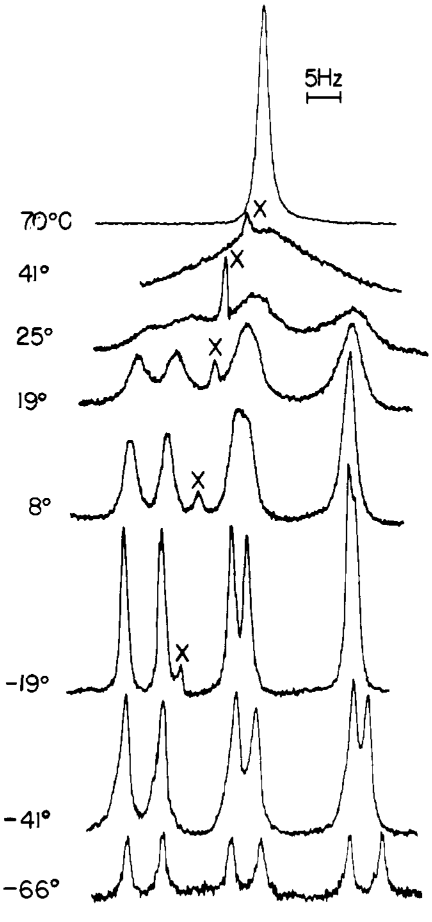

Figure 2. The variable-temperature 60-MHz ^{1}H NMR spectra of IIa in the methyl region (CD_2Cl_2); the −66 °C spectrum is in 20% CH_2Cl_2-CHF_2Cl. Traces of free $AsMe_2Ph$ are marked by an X. Removal of free ligand in other samples leaves the spectrum unchanged.

Me_4Si due to the two polyhedral carbon atoms. As expected, these peaks sharpened as the temperature was decreased because of more efficient ^{10}B and ^{11}B quadrupolar relaxation[19] and appeared as a singlet (44.4 ppm) and a doublet (62.7 ppm, $J_{Rh-C} = 22$ Hz) at −72 °C. The coupling of only one cage carbon to ^{103}Rh confirms the assignment of the carbon atoms to the 7,8 rather than the 4,8 cage positions.

Like its isoelectronic and isostructural borane analogue[18] $(B_{10}H_{12})^{2-}$, the $(C_2B_8H_{11})^-$ ligand can formally be considered to be a bidentate ligand. Therefore, these rhodacarboranes are formally five-coordinate Rh^I complexes. The coordination geometry about the metal is unknown but may be square pyramidal with the bidentate carborane ligand occupying two cis basal sites. This is precisely the arrangement of the ligands about the metal atom in [*nido*-8,8-$(PEt_3)_2$-8-H-8,7-$PtSB_9H_{10}$] (the phosphine ligands occupy an axial and a basal site).[27] The $(SB_9H_{10})^-$ ligand is isoelectronic with both $(B_{10}H_{12})^{2-}$ and $(C_2B_8H_{11})^-$

Owing to the asymmetry inherent in the carborane cage, the three triorgano group 5A ligands in complexes IIa–e are magnetically inequivalent. The ^{1}H NMR spectra of IIb,c contained six doublets and three doublets, respectively, in the methyl region at 35 °C consistent with this inequivalence. However, the ^{1}H NMR spectra of IIa, IId, and IIe showed only one signal in the methyl region indicating that some sort of exchange process was occurring.

A variable-temperature ^{1}H NMR study on complex IIa shown in Figure 2 confirmed this hypothesis. The fast exchange limiting spectrum was observed at 70 °C and the low-temperature limiting spectrum was obtained at about −70 °C. Cooling the sample resolved the spectrum into six equal-intensity singlets, and these spectral changes were reversible indefinitely with temperature. At −72 °C the ^{1}H-decoupled ^{13}C NMR spectrum of IIa contained six methyl singlets at 11.6, 12.3, 12.6, 13.0, 13.7, and 14.9 ppm. The methyl region at 26 °C consisted of broad, partially overlapped peaks at 13.8, 14.7, and 15.3 ppm. We believe (although a detailed NMR line-shape analysis[28] was not done) that this ligand exchange process is due to rotation of the $\{Rh(As(CH_3)_2Ph)_3\}$ moiety about the asymmetric carborane cage. This process would permute the six methyl groups, but would not affect the rhodium–carborane cage configuration. Arsine ligand dissociation could also effect the observed exchange but may be ruled out in this case because addition of 3 molar equiv of $As\{CH_3\}_2Ph$ leaves the ^{1}H NMR spectrum unchanged (where the spectrum is not obscured by free ligand).

Rotation of the $\{MHL_2\}$ moiety (M = Rh, Ir) in [*closo*-1,1-L_2-1-H-1,2,4-$MC_2B_8H_{10}$] (I) would not exchange the two nonequivalent L ligands owing to the inherent asymmetry of the carborane cage. Rotation about the metal–carborane axis may be a widespread phenomenon in metallocarborane complexes.[29]

Rotation of the $\{RhL_3\}$ group with respect to the $C_2B_8H_{11}^-$ ligand occurs in all of the complexes IIa–e. The methyl protons of IId appeared in the ^{1}H NMR as a broad, asymmetric singlet at 35 °C and as three singlets at 0 °C. Complex IIe displayed a sharp singlet at 35 °C but its low solubility precluded measurement of its ^{1}H NMR spectra at lower temperatures. Scrambling of the three phosphine ligands in IIb,c occurred at higher temperatures. Both complexes exhibit broad singlets in the methyl region at 70 °C. Rearrangement barriers appear to decrease ($P(CH_3)_3 < As(CH_3)_3 < Sb(CH_3)_3$ and $P(CH_3)_2Ph < As(CH_3)_2Ph$) with increasing ligand size as measured by the ligand cone angle.[30,31]

Reaction of $[RhCl(PR_3)_3]$ or $[RhCl(PR_3)_2]_2$ with $NaC_2B_8H_{11}$ in diethyl ether or tetrahydrofuran afforded the red, crystalline 16e$^-$ Rh^I complexes [*nido*-9,9-$(PR_3)_2$-9,7,8-$RhC_2B_8H_{11}$] (IIIa,b; R = Ph and *p*-tolyl), which may also be prepared from the reaction of $[RhCl(PPh_3)_3]$ with *nido*-5,6-$C_2B_8H_{12}$ in refluxing ethanol. Elemental analyses of IIa,b established a ratio of two triorganophosphine ligands to one carborane cage per rhodium atom and their infrared spectra contained no bands attributable to either a Rh–H or a B–H–B bridge vibration. The ^{11}B NMR spectra of IIIa,b were broad and poorly resolved, but the ^{1}H and ^{31}P NMR spectra were consistent with the proposed formulation, and display the expected magnetic inequivalence of the two tertiary phosphine ligands. The mass spectra of IIIa,b exhibited only $(PR_3)^+$ peaks.

Consistent with the formulation of IIIa,b as [*nido*-9,9-$(PR_3)_2$-9,7,8-$RhC_2B_8H_{11}$], these complexes are found to react with dimethylphenylarsine to quantitatively yield [*nido*-9,9,9-$(As\{CH_3\}_2Ph)_3$-9,7,8-$RhC_2B_8H_{11}$] (IIa). These rapid and facile reactions, accomplished at room temperature over a period of only a few seconds, suggest that complexes IIa–e and IIIa,b have identical cage configurations. An X-ray diffraction study[32] of [*nido*-9,9-$(P\{p\text{-tolyl}\}_3)_2$-9,7,8-$RhC_2B_8H_{11}$] is in progress and preliminary results support its suggested structure (Figure 1).

The formation of $[Rh(PR_3)_3(C_2B_8H_{11})]$ appears not to be possible with these phosphines because of the larger ligand cone angles[30] (ca. 145°) of PPh_3 and $P(p\text{-tolyl})_3$. The three phosphines of these pseudo-square-pyramidal complexes occupy the apical and two cis-basal positions. Examination of scale models clearly showed extreme steric crowding about the metal atom when three PPh_3 or $P(p\text{-tolyl})_3$ ligands are coordinated in such a manner. The position of the "extra" hydrogen has not been located, but it probably bridges either B(10) and B(11) or B(10) and Rh.[25,33] Both NMR and infrared data related to this point were lacking as no high-field signal in the ^{1}H NMR or B–H–B stretch in the infrared could be found.

Neglecting the bridging hydrogen atom, the Rh^1 atom of IIa,b contains only 16 valence electrons and can conceptually contribute one empty orbital to form a three-center, two-electron bond with the unlocated hydrogen and B(10).[20] This bonding is clearly not possible in the $[RhL_3(C_2B_8H_{11})]$ complexes. We favor a B–H–B bridge, however, as the "extra" hydrogen of IIIc (L = PEt_3) bridges two borons rather than boron and rhodium. In addition, coordinatively unsaturated complexes of the $(B_{10}H_{12})^{2-}$ ligand (cf. $(PPh_3)_2PtB_{10}H_{12}$) do not contain B–H–M bridges.[18]

The fact that reactions of $(C_2B_8H_{11})^-$ with $[IrClL_3]$ yielded the *closo*-iridacarboranes [*closo*-1,1-L_2-1-H-1,2,4-$IrC_2B_8H_{10}$] (Ia–c) while analogous reactions proceeding through presumably an analogous mechanism formed the *nido*-rhodacarboranes [*nido*-9,9,9-L_3-9,7,8-$RhC_2B_8H_{11}$] (IIa–f) or [*nido*-9,9-L_2-9,7,8-$RhC_2B_8H_{11}$] (IIIa–c) may be due to the greater propensity of 16-electron Ir^1 complexes to undergo oxidative addition.[34,35] This reactivity difference must be due to differences in the electronic properties of the two metal atoms as manifested by their ability (or lack thereof) to initially form 16-electron M^1 complexes, then to abstract the acidic B–H–B bridging hydrogen and undergo cage closure. The process may be viewed as an internal redox reaction and insertion of the metal into a B–H–B bond. Examination of molecular models of IIIa,b indicates that this nido to closo isomerization requires very little atomic motion.[36] Although complexes IIIa,b are models for intermediates in the formation of *closo*-iridacarboranes, attempts to effect their cage closure resulted only in decomposition. Increasing the electron density at the Rh^1 atom by use of more basic ligands should increase its tendency to undergo oxidative-addition reactions.[34,35] However, except for triethylphosphine (vide infra), only pseudopentacoordinate Rh^1 complexes were isolated when the triarylphosphines were replaced by more basic ligands.

While skeletal electron counting schemes[37–40] indicate that [*closo*-1,1-L_2-1-H-1,2,4-$MC_2B_8H_{10}$] (Ia–d) and [*nido*-9,9-L_2-9,7,8-$RhC_2B_8H_{11}$] (IIIa–c) both contain 12 skeletal electron pairs, a generalization of these skeletal electron counting schemes recently proposed by Colquhoun et al.[41] and, more formally, by Nishimura[42] takes account of the $16e^-$ metal vertex, making the $\{RhL_2\}$ moiety a three- rather than a one-skeletal-electron donor. Thus, [9,9-L_2-9,7,8-$RhC_2B_8H_{11}$] contains 13 skeletal electron pairs as predicted for an 11-vertex *nido*-metallocarborane.

Complexes IIa,b did not react with hydrogen (1 atm), but IIIb was found to be catalytically active in the hydrogenation of vinyltrimethylsilane in THF at 25 °C (0.75 atm hydrogen)[43] and the isomerization of 1-octene to internal octenes at 25 °C (ca. 20% conversion after 15 h; 9.4×10^{-4} M IIIb; 1.2×10^{-1} M 1-octene in benzene; *trans*-:*cis*-2-octene = 1.13).

Treatment of IIb in toluene with carbon monoxide instantly produced a yellow solution and yellow crystals of IV were formed upon addition of petroleum ether. The infrared spectrum (KBr) of IV contained a strong ν_{CO} band at 2014 cm^{-1}. Elemental analysis and NMR spectral data suggest that IV is the pseudopentacoordinate complex [*nido*-9-CO-9,9-$[P(p\text{-tolyl})_3]_2$-9,7,8-$RhC_2B_8H_{11}$], presumably isostructural with complexes IIa–e, and may be considered as a square-pyramidal molecule[44] with the carbon monoxide ligand occupying a basal site.

The ^1H and ^{13}C NMR spectra of IV indicated that exchange of the two magnetically inequivalent tertiary phosphine ligands occurs. The fast exchange limiting spectrum was reached at 75 °C. The solution at this temperature was red while upon cooling to room temperature the solution reverted slowly to its normal yellow color. Rotation of the $\{Rh(CO)(P[p\text{-tolyl}]_3)_2\}$ moiety about the carborane cage would not interconvert the two phosphine environments,[12] while retention of the ^{103}Rh–^{13}C coupling in the fast exchange limit rules out carbonyl dissociation.[45] The observed doublet pattern (192.73 ppm, J_{Rh-C} = 58 Hz) of the carbonyl carbon in the fast exchange limit suggests that phosphine dissociation is the operative method for interconversion.

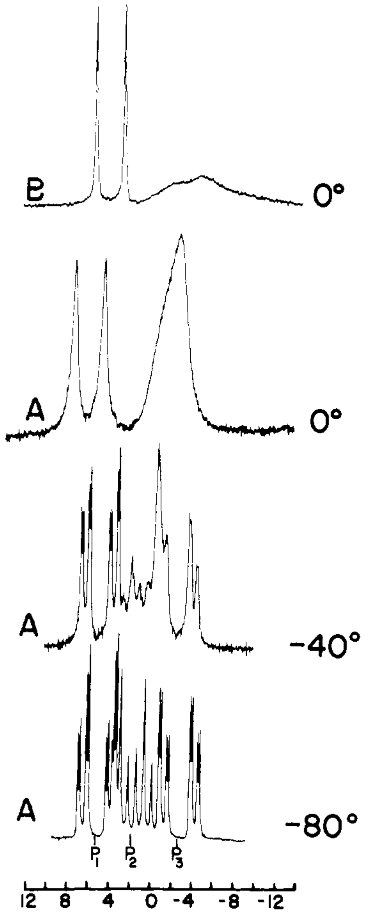

Figure 3. (A) The ^1H-decoupled 40.5-MHz ^{31}P NMR spectra of IIf (0.25 M) at various temperatures in CD_2Cl_2; (B) same in the presence of excess PEt_3(0.67 M; 0.27 M **12a**). The scale is in parts per million from external 85% H_3PO_4.

Addition of $NaC_2B_8H_{11}$ to an ether solution of $[RhCl(PEt_3)_3]$ instantly produced a yellow precipitate which was recrystallized at −15 °C affording yellow prisms of a compound analyzing as [*nido*-9,9,9-$(PEt_3)_3$-9,7,8-$RhC_2B_8H_{11}$] (IIf). Solutions of this compound were observed to be deep red at room temperature and yellow at ca. −10 °C. This transformation was reversible indefinitely. Solutions of IIf were also yellow in the presence of an eightfold molar excess of triethylphosphine.

The yellow complex IIf exhibited NMR spectra consistent with its formulation. The ^1H NMR contained a carboranyl C–H resonance at τ 7.31, a B–H–B peak at τ 12.6 (at −50 °C), and alkyl resonances centered at τ 8.37 and 8.88. The low-temperature ^{11}B NMR exhibited a pattern very similar to those of the other complexes IIa–e discussed previously.

At 60 °C no peaks assignable to the yellow complex were present in the ^{11}B NMR. A pattern strikingly similar to that observed in spectra of the complexes IIIa,b was found. These data suggest that the red complex is isostructural with IIIa,b and may be formulated as [*nido*-9,9-$(PEt_3)_2$-9,7,8-$RhC_2B_8H_{11}$]. At 38 °C the degree of dissociation (obtained from the ^{11}B NMR spectrum) is approximately 45%. The ^1H-decoupled ^{31}P NMR spectra of IIf were obtained at several temperatures below 0 °C and showed (see Figure 3) loss of spin coupling of two of the three ^{31}P nuclei to ^{103}Rh and the other ^{31}P nucleus, providing conclusive proof[45] that the exchange process involves rapid, reversible dissociation of two of the

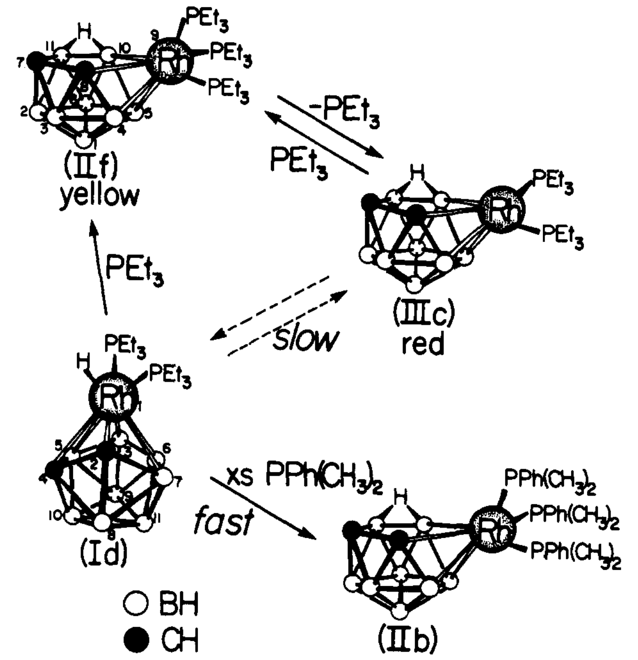

Figure 4. Reactions of the $[Rh(PEt_3)_n(7,8\text{-}C_2B_8H_{11})]$-$[RhH(PEt_3)_2(2,4\text{-}C_2B_8H_{10})]$ system.

coordinated triethylphosphines.[30,46] The presence of excess triethylphosphine increases the phosphine exchange rate and decouples the bound phosphine ^{31}P resonance from the other phosphines. The two dissociable PEt_3 ligands may be labilized by a trans influence of the carborane cage.[47]

Although attempts to isolate the red complex [*nido*-9,9-$(PEt_3)_2$-9,7,8-$RhC_2B_8H_{11}$] (IIIc) were unsuccessful, addition of petroleum ether to dilute dichloromethane solutions of this complex slowly deposited yellow crystals of a compound with a rhodium hydride stretching vibration at 2044 cm^{-1} and analyzing as [*closo*-1,1-$(PEt_3)_2$-1-H-1,2,4-$RhC_2B_8H_{10}$] (Id). Neither [*nido*-9,9,9-$(PEt_3)_3$-9,7,8-$RhC_2B_8H_{11}$] (IIf) nor (*nido*-9,9-$(PEt_3)_2$-9,7,8-$RhC_2B_8H_{11}$] (IIIc) was present in solid samples of [*closo*-1,1-$(PEt_3)_3$-1-H-1,2,4-$RhC_2B_8H_{10}$] (Id).

A broad resonance was observed at τ 15.5 (ca. 80 Hz $W_{1/2}$) in the ^1H NMR of complex Id at 35 °C which sharpened with decreasing temperature to a broad multiplet at −45 °C. Simultaneously, another broad resonance appeared at τ 12.7. Both of these sets of spectral changes were reversible, although no high-field resonances were observed over the temperature range of 40–80 °C. These data suggested that a hydrogen atom was exchanging between a B–H–B bridge and a terminal site on the rhodium atom (Figure 4).

A study of the proton-decoupled ^{11}B and ^{31}P NMR spectra over a range of temperatures revealed the presence of the two complexes Id and IIIc and permitted spectral assignments and the ratios of complex Id/complex IIIc to be measured. The plot of $\Delta G°$ of the reaction IIIc $\rightleftharpoons$ Id vs. temperature is linear over the range −60 to 50 °C and yields $\Delta H° = -3.1 \pm 0.1$ kcal mol^{-1} and $\Delta S° = -10.5 \pm 0.4$ eu. The corresponding activation parameters were not determined. The ^{11}B resonances of IIIc and Id were not resolved sufficiently below approximately 0 °C to yield accurate equilibrium data. These determinations were more accurately obtained from integration of the ^{31}P NMR spectra. Above 60 °C (in 1,2-dichloroethane), the rate of exchange between IIIc and Id increases to the point where separate resonances of these isomers were not observed (intermediate exchange region). At 75 °C, the ^1H-decoupled ^{11}B NMR spectrum consisted of a broad hump at 7.5 ppm and two sharp lines at −21.9 and −25.2 ppm. Lack of a suitable high-boiling solvent precluded measurement of the high-temperature limiting spectrum. The absence of high-field peaks in the ^1H NMR spectra of Id at 50–80 °C is attributable to lower concentrations of Id and faster Id–IIIc interconversion in this temperature range. The intramolecular exchange process is frozen out at about −60 °C.

Addition of small amounts of triethylphosphine to solutions of Id lightened the deep red color. The ^1H NMR spectrum of Id (0.35 M) in 10% triethylphosphine–dichloromethane showed only the presence of IIf (91%) and IIIc (9%). Pure IIf can be obtained in essentially quantitative yields by addition of petroleum ether to solutions of Id containing excess triethylphosphine (ca. 0.5 M). Similarly, treatment of Id in toluene with dimethylphenylphosphine (ca. fourfold molar excess) afforded complex IIb. Even though triethylphosphine is more basic than dimethylphenylphosphine, this phosphine exchange reaction is favored by the smaller cone angle of the latter (123°).[30] These reactions complement the NMR spectral data in supporting the proposed reversible isomerization of IIf to Id.

Ruthenacarboranes. Reaction of $NaC_2B_8H_{11}$ with $[RuHCl(PPh_3)_3]$ produced the red, air-stable, crystalline complex [*closo*-1,1,3-$(PPh_3)_3$-1-H-1,2,4-$RuC_2B_8H_9$] (V). The ruthenium hydride stretching vibration was observed at 1951 cm^{-1} (w, br).

The ^1H NMR spectrum displayed an octet at τ 13.39 assignable to a metal hydride spin-coupled to three nonequivalent ^{31}P nuclei. The phenyl region of the ^1H NMR contains resonances at τ 2.12, 2.59, and 3.07 of relative areas 6:9:30, respectively, suggesting that one triphenylphosphine is in an environment differing from that of the other two phosphines. The phenyl resonances may be assigned[48] to the ortho protons (τ 2.12) and the meta, para protons (τ 2.59) of the unique PPh_3 and to the protons (τ 3.07) of the two similar PPh_3 ligands. The proton-decoupled ^{11}B NMR spectrum contained a low-field doublet at 35.5 ppm indicative of coupling to a ^{31}P nucleus (J_{B-P} = 130 Hz). Furthermore, only two phosphines were detected in the ^1H-decoupled ^{31}P NMR spectrum, suggesting that the third ^{31}P nucleus is boron coupled and too broad to detect.

The data support the formulation of V as a closo pseudooctahedral Ru^{II} complex isostructural to complex Id, but containing a $(C_2B_8H_9\{PPh_3\})^-$ ligand instead of a $(C_2B_8H_{10})^{2-}$ as in Id. Although comparative data are scarce,[49] it is reasonable to assume that the cage substitution occurred at a boron atom directly bonded to the metal atom. In addition, we believe that the cage-bonded triphenylphosphine is attached to B(3) because it is the low-field resonance at 35.5 ppm, normally assigned to a low-coordinate boron adjacent to the metal vertex, which is split into a doublet by the cage-bonded phosphorus.

Complex V was probably formed intermolecularly via attack of free triphenylphosphine at B(3) of an intermediate complex [1,1-$(PPh_3)_2$-1,2,4-$RuC_2B_8H_{10}$] to yield a nido complex [*nido*-9,9,10-$(PPh_3)_3$-9,7,8-$RuC_2B_8H_{10}$]. This nido complex then rapidly tautomerizes to the observed product V (Figure 5). Similar reaction sequences were proposed[24] to produce the closo complexes [*closo*-1-(η^5-C_5H_5)-5-L-1,2,4-$CoC_2B_8H_9^+$] (L = pyridine or piperidine) from [*closo*-1-(η^5-C_5H_5)-1,2,4-$CoC_2B_8H_{10}$] and were advanced[49] for the formation of [*closo*-3,8-$(PPh_3)_2$-3-H-3,1,2-$NiC_2B_9H_{10}$] from [*closo*-3,3-$(PPh_3)_2$-$NiC_2B_9H_{11}$].

Conclusion

Reactions of $NaC_2B_8H_{11}$ with $[IrClL_n]$ (n = 3, L = PPh_3; n = 2, L = $P(CH_3)_2Ph$, $As(CH_3)_2Ph$) yielded only the closo complexes [*closo*-1,1,L-1-H-1,2,4-$IrC_2B_8H_{10}$] (Ia–c). In contrast, reactions of $[RhClL_3]$ yielded the nido complexes [*nido*-9,9,9-L_3-9,7,8-$RhC_2B_8H_{11}$] (IIa–f) (L = $P(CH_3)_3$, $As(CH_3)_3$, $Sb(CH_3)_3$, $P(CH_3)_2Ph$, $As(CH_3)_2Ph$, and PEt_3)

and [*nido*-9,9-L_2-9,7,8-$RhC_2B_8H_{11}$] (IIIa-c) (L = PPh_3, P(*p*-tolyl)$_3$, and PEt_3). The mechanism of formation of these complexes was rationalized as an oxidative-addition reaction. Reactivity differences between the rhodium system and the iridium system may be explained in terms of the ability of Rh^I or Ir^I (based on the metal's basicity) to abstract the acidic B-H-B bridge hydrogen atom. Formation of complexes IIIa-c was rationalized on the basis of the bulky ligands employed.

[*nido*-9,9,9-$(PEt_3)_3$-9,7,8-$RhC_2B_8H_{11}$] (IIf) was found in the absence of excess phosphine to dissociate triethylphosphine to form [*nido*-9,9-$(PEt_3)_2$-9,7,8-$RhC_2B_8H_{11}$] (IIIc). Triethylphosphine contains internal degrees of freedom which allow its cone angle to vary over about a 15° range with comparatively small changes in its strain energy.[30] Thus, at low temperatures three triethylphosphines can coordinate to the rhodium atom, while at higher temperatures extensive triethylphosphine dissociation occurs.[50] The degree of dissociation was approximately 45% at 38 °C (0.25 M, IIf). Complex IIf partially isomerizes in solution to [*closo*-1,1-$(PEt_3)_2$-1-H-1,2,4-$RhC_2B_8H_{10}$] (Id) and an equilibrium exists between these two complexes for which K_{eq} = 1.0 at 22 °C, $\Delta H°$(IIIc $\rightleftharpoons$ Id) = −3.1 ± 0.1 kcal/mol, and $\Delta S°$ = −10.5 ± 0.4 eu. With a bulky phosphine less basic than triethylphosphine the Rh^I atom cannot be oxidized as readily, so that the equilibrium favors the nido complexes IIIa,b.

The equilibrium between IIIc and Id represents the first documented example of facile, reversible cage opening and reversible hydride transfer. The possibility of utilizing this feature in catalytic reactions is being currently investigated. This dynamic process may also be present[51] in [*nido*-8,8-$(P\{CH_3\}_3)_2$-8,7,10-$PtC_2B_8H_{10}$], which is isoelectronic with complex IIIc.

The complex [*closo*-1,1,3-$(PPh_3)_3$-1-H-1,2,4-$RuC_2B_8H_9$] (V) was isolated from the reaction of [$RuHCl(PPh_3)_3$] with $NaC_2B_8H_{11}$. This ruthenacarborane was remarkably air stable, unlike other Ru(II) carborane complexes,[2,3] but was inactive in catalyzing alkene hydrogenation[43] and isomerization under ambient conditions.

Experimental Section

Unless otherwise indicated, all reactions were conducted under purified argon or nitrogen and solvents were dried and purified using standard inert atmosphere techniques.[52,53]

Infrared spectra were recorded on a Perkin-Elmer 421 dual-grating spectrometer or on a Beckman IR-4 spectrometer as KBr pellets unless otherwise indicated. ^1H NMR spectra (s = singlet, d = doublet, t = triplet, q = quartet, m = complex multiplet, and br = broad) were measured with a Varian A-60D (60 MHz) or HA 100D (100 MHz) spectrometer. Sample temperatures were determined using methanol and ethylene glycol temperature standards.[54] ^{13}C NMR spectra (20 MHz) were obtained on a Varian CFT-20 spectrometer. A copper-constantan thermocouple immersed in an NMR tube containing dichloromethane or 1,2-dichloroethane was used to monitor the sample temperature. ^{31}P NMR spectra were obtained as ^1H-decoupled spectra using Bruker HFX-10 and Varian XL100 spectrometers operating at 36.4 and 40.5 MHz, respectively. A superconducting, Fourier-transform instrument designed and constructed by Professor F. A. L. Anet (University of California, Los Angeles) was used to obtain the 80.5-MHz ^{11}B NMR spectra. The chemical shifts for ^{11}B and ^{31}P NMR were referenced to external $BF_3{\cdot}OEt_2$ and 85% H_3PO_4, respectively, where positive shifts refer to lower field. Mass spectra were obtained using an AEI MS-9 spectrometer.

Alkene isomerization experiments were conducted using a previously described procedure.[55] All alkenes used were passed through activated alumina and distilled from calcium hydride prior to use.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Melting points were determined in open capillaries and are uncorrected.

Literature methods were used to prepare [$RhCl(PPh_3)_3$],[56] [$RuHCl(PPh_3){\cdot}PhCH_3$],[57,58] [$IrCl(PPh_3)_3$],[10] [$RhCl(C_2H_4)_2]_2$,[59] [$IrCl(C_8H_{14})_2]_2$,[60] and *nido*-5,6-$C_2B_8H_{12}$.[6] Solutions of $NaC_2B_8H_{11}$ were prepared by stirring 5,6-$C_2B_8H_{12}$ in a suspension of excess sodium hydride in diethyl ether or tetrahydrofuran for about 5 min. After filtration, the clear solutions were used immediately. Tertiary phosphines and arsines were obtained from commercial sources or prepared by literature methods.[61,62] Trimethylstibine was prepared by the method of Morgan and Yarsley.[63]

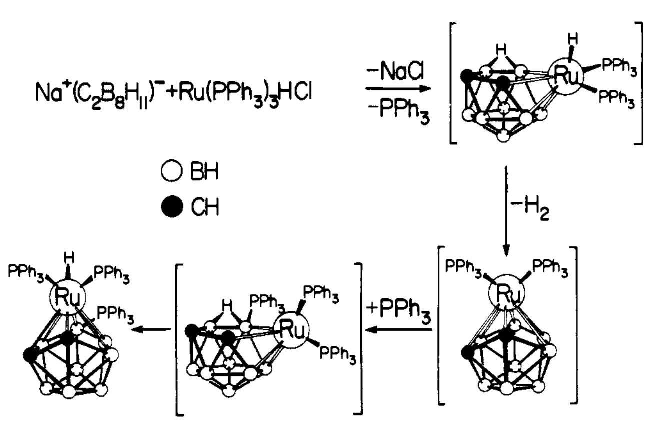

Figure 5. Proposed mode of formation of V.

Preparation of [*closo*-1,1-$(PPh_3)_2$-1-H-1,2,4-$IrC_2B_8H_{10}$] (Ia). A diethyl ether (30 mL) solution of [$IrCl(PPh_3)_3$] (1.86 g, 1.83 mmol) and $NaC_2B_8H_{11}$ (2.58 mmol) was stirred for 24 h at room temperature. The resulting light green powder was filtered in air, washed with diethyl ether, and dissolved in dichloromethane (25 mL). Addition of absolute ethanol or heptane (50 mL) followed by slow evaporation of the mixed solvent system with a nitrogen stream yielded needles of [*closo*-1,1-$(PPh_3)_2$-1-H-1,2,4-$IrC_2B_8H_{10}$] (Ia, 1.05 g, 67%), mp 250–253 °C dec. Anal. Calcd for $C_{38}H_{41}B_8P_2Ir$: C, 54.44; H, 4.93; B, 10.32; P, 7.38; Ir, 22.93. Found: C, 54.47; H, 5.10; B, 10.06; P, 7.26; Ir, 23.81. ^1H NMR data (100 MHz, CD_2Cl_2 solution): τ 2.90 (m, 30 H), 6.88 (br, s, 1 H), 7.60 (br, s, 1 H), 16.30 (q, $^2J_{P-H}$ = 14.0 and 32.0 Hz, 1 H). $^{11}B\{^1H\}$ NMR data (CH_2Cl_2 solution): 55.2 (1), 10.1 (1), 2.7 (1), −6.0 (1), −11.2 (1), −24.8 (2), −45.0 ppm (1). Infrared spectrum: 3081 (m), 3061 (m), 2540 (s, br), 2150 (m), 1479 (s), 1432 (s), 1310 (m), 1280 (m), 1184 (m), 1156 (m), 1088 (s), 1073 (m), 1025 (m), 1019 (m, sh), 998 (m), 972 (s), 929 (m), 899 cm^{-1} (m).

Preparation of [*closo*-1,1-$(P(CH_3)_2Ph)_2$-1-H-1,2,4-$IrC_2B_8H_{10}$] (Ib). Addition of $NaC_2B_8H_{11}$ (1.06 mmol) in diethyl ether (25 mL) to a solution of [$IrCl(P(CH_3)_2Ph)_2$], prepared by reacting [$IrCl(\eta^2$-$C_8H_{14})_2]_2$[11] (0.350 g, 0.390 mmol) with dimethylphenylphosphine (0.25 mL, 1.75 mmol) in diethyl ether (30 mL), produced a yellow powder instantly. After stirring for 8 h at room temperature the crude product was filtered onto Celite, washed with diethyl ether, dissolved in CH_2Cl_2, and crystallized from petroleum ether-CH_2Cl_2 at −15 °C for 2 days, yielding yellow crystals of [*closo*-1,1-$(PMe_2Ph)_2$-1-H-1,2,4-$IrC_2B_8H_{10}$] (Ib, 0.87 g, 81%), mp 176–178 °C. Anal. Calcd for $C_{18}H_{33}B_8P_2Ir$: C, 36.64; H, 5.64; P, 10.49. Found: C, 36.77; H, 5.62; P, 10.28. ^1H NMR data (100 MHz, $CDCl_2$): τ 2.63 (m, 10 H), 6.14 (br, 1 H), 6.50 (br, 1 H), 8.42, 8.47, 8.56, and 8.72 (d, $^2J_{PH}$ = 10.0 ± 0.5 Hz, 3 H), and 17.31 (q, $^2J_{PH}$ = 16.0 and 28.4 Hz, 1 H). ^{11}B NMR data (CD_2Cl_2): 53.6 (1), 8.56 (1), 1.40 (1), −8.34 (1), −13.9 (1), −22.8 (1), −28.2 (1), and −46.5 ppm (1). Infrared spectrum: ν_{IrH} 2145 (w).

Preparation of [*closo*-1,1-$(As\{CH_3\}_2Ph)_2$-1-H-1,2,4-$IrC_2B_8H_{10}$] (Ic). The dimethylphenylarsine complex Ic was prepared similarly to Ib discussed above using $NaC_2B_8H_{11}$ (0.697 mmol), [$IrCl(\eta^2$-$C_8H_{14})_2]_2$ (0.281 g, 0.314 mmol), and dimethylphenylarsine (0.25 mL, 1.7 mmol). After recrystallization, 0.17 g (40%) of [*closo*-1,1-$(As\{CH_3\}_2Ph)_2$-1-H-$IrC_2B_8H_{10}$] (Ic) was obtained, mp 156–158 °C. Anal. Calcd for $C_{18}H_{33}B_8As_2Ir$: C, 31.89; H, 4.91; As, 22.09. Found: C, 31.95; H, 4.79; As, 22.21. ^1H NMR data (100 MHz, CD_2Cl_2): τ 2.70 (m, 10 H), 5.80 (br, 1 H), 6.20 (br, 1 H), 8.40 (s, 6 H), 8.55 (s, 3 H), 8.68 (s, 3 H), and 16.77 (s, 1 H). ^{11}B NMR data (CD_2Cl_2): 51.9 (1), 9.39 (1), −0.35 (1), −7.60 (1), −13.6 (1), −23.7 (1), −28.5 (1), and −47.8 ppm (1). Infrared spectrum: ν_{IrH} 2102 (m, sh) and 2087 cm^{-1} (m).

Perparation of [*nido*-9,9,9-$(As\{CH_3\}_2Ph)_3$-9,7,8-$RhC_2B_8H_{11}$] (IIa). Dimethylphenylarsine (0.45 mL, 3.1 mmol) was added to a suspension of [$RhCl(C_2H_4)_2]_2$ (0.194 g, 0.499 mmol) in diethyl ether (30 mL), and the mixture was stirred for 10 min. A solution of $NaC_2B_8H_{11}$ (1.22 mmol) in diethyl ether (50 mL) was added to the resultant brown slurry of $[RhCl(As\{CH_3\}_2Ph)_3]$.[22] A yellow powder precipitated instantly, and all of the $[RhCl(As\{CH_3\}_2Ph)_3]$ disappeared within 2–3 min. After 30 min the crude product was filtered on Celite and washed with diethyl ether (3 × 20 mL). It was then dissolved in dichloromethane (30 mL) and filtered through the Celite. A small amount (ca. 0.1 g) of a fine, gray powder remained on the Celite (presumably NaCl and Rh metal). Petroleum ether (60 mL) was quickly stirred into the yellow filtrate. The turbid solution slowly deposited large, yellow prisms upon standing undisturbed at room temperature. The mixture was cooled to −15 °C for several hours, filtered quickly in air, washed with methanol and petroleum ether, and vacuum dried, yielding [*nido*-9,9,9-$(As\{CH_3\}_2Ph)_3$-9,7,8-$RhC_2B_8H_{11}$] (IIa, 0.63 g, 82%), mp 204–206 °C dec. Anal. Calcd for $C_{26}H_{44}B_8As_3Rh$: C, 40.52; H, 5.75; B, 11.22; As, 29.16; Rh, 13.36. Found: C, 40.37; H, 5.58; B, 11.27; As, 28.93; Rh, 12.78. $^{13}C\{^1H\}$ NMR (20.0 MHz, 20% CD_2Cl_2–CH_2Cl_2, −72 °C): 138.2; 137.7, 137.3, 130.4, 130.2, 129.9, 128.9, 128.5, 128.1, 127.8 (s, phenyl carbons), 62.7 (d, $J_{Rh-C} = 22$ Hz), 44.4 (s) (carborane carbons), 14.9, 13.7, 13.0, 12.6, 12.3, and 11.6 ppm (s, methyl carbons). At 26 °C: 131.1, 129.1, 128.7 (s, phenyl carbons), 61.9, 44.5 (br, s, $W_{1/2} \approx 60$ Hz, carborane carbons), 13.8, 14.7, and 15.3 ppm (br, methyl carbons). ^1H NMR (60.0 MHz, CD_2Cl_2, 70 °C): τ 2.65 (br, s, 15 H) and 8.54 (br, s, 18 H). At −66 °C in 20% CH_2Cl_2–CHF_2Cl: τ 2.52–2.80 (complex multiplet, 15 H), 7.70 (br, 1 H), 7.99 (br, 1 H), 8.19, 8.30, 8.51, 8.58, 8.86, 8.93 (s, 3 H), and 12.5 (br, 1 H). ^{11}B NMR (CD_2Cl_2, 26 °C): 13.2 (2), −3.29 (1), −13.1 (2), −18.4 (1), −22.6 (1), and −25.2 ppm (1).

Preparation of Complexes IIb–e (L = $P(CH_3)_2Ph$, $P(CH_3)_3$, $As(CH_3)_3$, and $Sb(CH_3)_3$). These complexes were prepared as above for IIa using the following quantities of reagents. **[*nido*-9,9,9-$(P\{CH_3\}_2Ph)_3$-9,7,8-$RhC_2B_8H_{11}$](IIb) (86%)**; $[RhCl(C_2H_4)_2]_2$ (0.265 g, 0.680 mmol), $P(CH_3)_2Ph$ (0.65 mL, 4.5 mmol), $NaC_2B_8H_{11}$ (1.48 mmol), mp 196–215 °C dec. Anal. Calcd for $C_{26}H_{44}B_8P_3Rh$: C, 48.95; H, 6.79; P, 14.56. Found: C, 49.21; H, 7.03; P, 14.36. ^1H NMR (100 MHz, CD_2Cl_2, 35 °C): τ 2.65 (m, 15 H), 8.69 (br, s, 2 H, at −30 °C with ^{31}P decoupling), 7.95, 8.08, 8.17, 8.36, 8.55, 8.81 (d, $^2J_{PH} = 6.8 \pm 0.8$ Hz, 3 H), 13.4 (br, s, 1 H, at −20 °C). ^{11}B NMR (CD_2Cl_2): 12.2 (2), −3.89 (1), −12.8 (2), −18.5 (1), −22.4 (1), −25.2 ppm (1). **[*nido*-9,9,9-$[P\{CH_3\}_3]_3$-9,7,8-$RhC_2B_8H_{11}$] (IIc, 60%)**; $[RhCl(C_2H_4)_2]_2$ (0.242 g, 0.625 mmol), $P(CH_3)_3$ (0.641 L, 0.145 atm, 25 °C, 3.80 mmol), $NaC_2B_8H_{11}$ (1.49 mmol), mp 247–248 °C dec (darkens at 235 °C). Anal. Calcd for $C_{11}H_{38}B_8P_3Rh$: C, 29.18; H, 8.46; P, 20.52. Found: C, 29.03; H, 8.51; P, 20.48. ^1H NMR (100 MHz, CD_2Cl_2, 35 °C): τ 7.43 (br, s, 2 H), 8.41 (d, $^2J_{PH} = 6.7$ Hz, 9 H), 8.60 (d, $^2J_{PH} = 8.4$ Hz, 9 H), 8.63 (d, $^2J_{PH} = 8.4$ Hz, 9 H), 13.2 (br, s, 1 H, at −70 °C). ^{11}B NMR (CD_2Cl_2): 12.6 (1), 9.32 (1), −5.07 (1), −13.4 (1), −15.2 (1), −18.1 (1), −22.2 (1), −27.2 ppm (1). Infrared spectrum: 2970 (m), 2910 (m), 2510 (s, br), 1426 (m, sh), 1412 (s), 1300 (m, sh), 1294 (s), 1275 (s), 1066 (m), 1018 (m), 1010 (m), 995 (s, br), 930 (s, br), 898 (m), 873 (m), 843 (m), 767 (m), 755 (m), 715 (s), 673 (s), 665 (s), 621 cm^{-1} (m). **[*nido*-9,9,9-$(As\{CH_3\}_3)_3$-9,7,8-$RhC_2B_8H_{11}$] (IId, 28%)**; $[RhCl(C_2H_4)_2]_2$ (0.400 g, 1.03 mmol), $As(CH_3)_3$ (0.70 mL, 6.65 mmol), $NaC_2B_8H_{11}$ (4.33 mmol), mp >300 °C (darkens at 240 °C). Anal. Calcd for $C_{11}H_{38}B_8As_3Rh$: C, 22.60; H, 6.55; As, 38.45. Found: C, 22.87; H, 6.62; As, 38.38. ^1H NMR (60 MHz, CD_2Cl_2, 30 °C): τ 7.38 (br, s, 2 H), 2.70 (asymmetric, s, 27 H), 12.3 (br, s, 1 H, at −20 °C). At 0 °C in methyl region: τ 8.53, 8.74, and 8.76 (s, 9 H). ^{11}B NMR (CD_2Cl_2): 12.5 (1), 10.2 (1), −4.60 (1), −14.6 (2), −18.6 (1), −23.1 (1), −27.1 ppm (1). **[*nido*-9,9,9-$(Sb\{CH_3\}_3)_3$-9,7,8-$RhC_2B_8H_{11}$] (IIe, 31%)**; $[RhCl(C_2H_4)_2]_2$ (0.190 g, 0.490 mmol), $Sb(CH_3)_3$ (0.35 mL, 3.18 mmol), $NaC_2B_8H_{11}$ (1.00 mmol), mp 225–230 °C dec (darkens at 190 °C). Anal. Calcd for $C_{11}H_{38}B_8Sb_3Rh$: C, 18.22; H, 5.28; Sb, 50.38. Found: C, 18.22; H, 4.94; Sb, 50.00. ^1H NMR (100 MHz, CD_2Cl_2, 35 °C): τ 6.90 (br, s, 1 H), 7.40 (br, s, 1 H), 8.94 (s, 27 H). ^{11}B NMR (CH_2Cl_2): 10.7 (1), 9.56 (1), −6.34 (1), −12.9 (1), −15.1 (1), −18.7 (1), −22.7 (1), −26.5 ppm (1).

Preparation of [*nido*-9,9-$(PPh_3)_2$-9,7,8-$RhC_2B_8H_{11}$] (IIIa). Triphenylphosphine (1.9 g, 7.2 mmol) was added to a stirred suspension of $[RhCl(C_2H_4)_2]_2$ (0.615 g, 1.58 mmol). After 10 min, a solution of $NaC_2B_8H_{11}$ (3.62 mmol) in 100 mL of diethyl ether was added to the resultant bright orange slurry of $[RhCl(PPh_3)_2]_2$. Upon stirring overnight, a dark red-brown powder was obtained. The crude product was filtered, washed with diethyl ether (2 × 25 mL), and extracted with dichloromethane (5 × 25 mL). Ethanol (750 mL) was then layered on top of the red filtrate. The mixture was allowed to stand undisturbed for 2 days at room temperature, then cooled to 0 °C for several hours. The red crystals were filtered in air, washed with ethanol and petroleum ether, and dried overnight under vacuum yielding [*nido*-9,9-$(PPh_3)_2$-9,7,8-$RhC_2B_8H_{11}$] (IIIa, 1.8 g, 76%), mp 256–257 °C dec (darkens at 250 °C). Anal. Calcd for $C_{38}H_{41}B_8P_2Rh$: C, 60.93; H, 5.52; B, 11.54; P, 8.27; Rh, 13.74. Found: C, 60.69; H, 5.43; B, 11.47; P, 8.27; Rh, 13.38. ^1H NMR (CD_2Cl_2, 35 °C): τ 2.85 (m). $^{11}B\{^1H\}$ NMR (CH_2Cl_2): 12.9, 1.4, −17.9, and −20.5 ppm. Infrared spectrum (Nujol mull): 2551 (m), 2500 (s, sh), 2488 (s), 2469 (m), 1466 (m), 1422 (s), 1179 (m), 1156 (m), 1090 (s), 1073 (m), 1027 (m), 990 (m), 981 (m), 935 (m), 875 (m), 847 (m), 752 (s), 746 (s), 743 (s, sh), 705 (s, sh), and 696 cm^{-1} (s). The product can be purified further by recrystallization from tetrahydrofuran–methanol or tetrahydrofuran–cyclohexane solutions. Complex IIIa can also be prepared by reacting $[RhCl(PPh_3)_3]$ (0.50 g, 0.54 mmol) and *nido*-5,6-$C_2B_8H_{12}$ (0.076 g, 0.62 mmol) in 50 mL of refluxing ethanol for 2.5 h. After cooling to room temperature, the red-brown, microcrystalline product was filtered, washed with ethanol, and recrystallized from dichloromethane–methanol, affording IIIa (0.17 g, 42%).

Complex IIIb was prepared by the same method as complex IIIa discussed above. Successive additions of P(*p*-tolyl)$_3$ (0.838 g, 2.75 mmol) and $NaC_2B_8H_{11}$ (1.72 mmol) in 45 mL of diethyl ether to $[RhCl(C_2H_4)_2]_2$ (0.261 g, 0.671 mmol) in 30 mL of diethyl ether yielded **[*nido*-9,9-(P{*p*-tolyl}$_3$)$_2$-9,7,8-$RhC_2B_8H_{11}$] (IIIb)** (0.52 g, 46%) upon workup, mp 239–240 °C dec. Anal. Calcd for $C_{44}H_{53}B_8P_2Rh$: C, 63.42; H, 6.41; P, 7.43. Found: C, 63.43; H, 6.40; P, 7.44. ^1H NMR (100 MHz, CD_2Cl_2, 35 °C): τ 2.92 (m, 24 H), 6.35 (br, 2 H), and 7.72 (s, 18 H). $^{11}B\{^1H\}$ NMR (CH_2Cl_2): 13.3, 1.0, −18.3, and −20.8 ppm. $^{31}P\{^1H\}$ NMR (40.5 MHz, CD_2Cl_2, 30 °C): 49.49 (q, P_1 $\{J_{RhP} = 147.7$ and $^2J_{P_1P_2} = 33.4$ Hz$\}$), and 35.82 ppm (q, P_2 $\{J_{RhP} = 135.6$ Hz$\}$).

Reactions of [*nido*-9,9-$(PR_3)_2$-9,7,8-$RhC_2B_8H_{11}$] (IIIa,b) with Dimethylphenylarsine. Dimethylphenylarsine (0.10 mL, 0.66 mmol) was added using a gas-tight syringe to a solution of IIIb (51.0 mg, 0.0612 mmol) in toluene (2 mL). The deep red solution turned yellow within approximately 3 s, and after 10 min petroleum ether (15 mL) was gently layered above the yellow solution. The mixture was allowed to stand overnight at room temperature, then cooled to −15 °C for several hours. The yellow prisms were filtered in air, washed with petroleum ether, and vacuum dried, yielding complex IIa (42 mg, 89%) as identified by its infrared and ^{11}B and ^1H NMR spectra.

Similarly, complex IIIa (0.134 g, 0.179 mmol) reacted with dimethylphenylarsine (0.20 mL, 1.32 mmol) in toluene (5 mL) to yield complex IIa (100 mg, 73%). The reaction time was much longer than that of $As(CH_3)_2Ph$ with IIIb, probably because IIIa was almost insoluble in toluene.

Reaction of [*nido*-9,9-(P{*p*-tolyl}$_3$)$_2$-9,7,8-$RhC_2B_8H_{11}$] (IIIb) with Carbon Monoxide. Bubbling carbon monoxide through a toluene (3 mL) solution of IIIb (0.152 g, 0.182 mmol) instantly produced a yellow solution. After 2 min, the reaction was stopped and petroleum ether was added to the yellow solution, which then deposited yellow crystals upon standing overnight at room temperature. The mixture was subsequently cooled to −15 °C for several hours and filtered quickly in air. The yellow product was washed with petroleum ether and vacuum dried, yielding **[*nido*-9,9-(P{*p*-tolyl}$_3$)$_2$-9-CO-9,7,8-$RhC_2B_8H_{11}$] (IV)** (0.12 g, 76%), mp 218–220 °C dec. Anal. Calcd for $C_{45}H_{53}B_8P_2ORh$: C, 62.76; H, 6.20; P, 7.19. Found: C, 62.71; H, 6.40; P, 7.12. ^1H NMR (100 MHz, CD_2Cl_2, 35 °C): τ 2.95 (m, 24 H), 7.69 (br, s, 18 H), and 12.6 (br, s). $^{11}B\{^1H\}$ NMR (CH_2Cl_2): 13.7 (2), 0.8 (1), −10.8 (2), −18.1 (1), −21.3 (1), and −22.7 ppm (1). Infrared spectrum: ν_{CO} 2014 (s).

A sample of IV enriched with roughly 20% ^{13}CO was prepared by stirring a solution of IIIb (0.300 g, 0.360 mmol) in 5 mL of toluene under a blanket of 20% ^{13}C-enriched carbon monoxide (ca. 25 Torr) for 1 h. The resultant yellow solution was worked up as described above. After two recrystallizations from dichloromethane–petroleum ether, 0.159 g (51%) of IV was obtained. Infrared spectrum: 1969 cm^{-1} (s). $^{13}C\{^1H\}$ NMR (20.0 MHz, C_6D_6, 75 °C): 192.73 ppm (d, $J_{Rh-C} = 58.0$ Hz).

Preparation of [*nido*-9,9,9-$(PEt_3)_3$-9,7,8-$RhC_2B_8H_{11}$] (IIf). An ethereal slurry of $[RhCl(PEt_3)_3]$ was prepared by reacting $[RhCl(C_2H_4)_2]_2$ (0.486 g, 1.25 mmol) and triethylphosphine (1.20 mL, 8.13 mmol) in 25 mL of diethyl ether for 15 min. To this red-brown mixture was added $NaC_2B_8H_{11}$ (2.95 mmol) in diethyl ether (25 mL). A yellow precipitate formed immediately. After stirring for 10 min, the crude product was filtered on Celite, washed with diethyl ether, dissolved in dichloromethane (50 mL), and filtered through the

Celite into a flask immersed in an ice–water bath. The red filtrate was concentrated quickly under vacuum to about 40 mL. Petroleum ether was rapidly stirred in to produce a cloudy red solution, which was then cooled to −15 °C for 3 days. The resultant orange-yellow crystals were filtered in air, washed with methanol and petroleum ether, and vacuum dried, yielding [*nido*-9,9,9-(PEt$_3$)$_3$-9,7,8-RhC$_2$B$_8$H$_{11}$] (IIf, 0.756 g, 52%), mp 94–108 °C (melts to deep-red liquid). Anal. Calcd for C$_{20}$H$_{56}$B$_8$P$_3$Ph: C, 41.49; H, 9.75; P, 16.05. Found: C, 41.33; H, 9.64; P, 16.03. ^{1}H NMR (100 MHz, CD$_2$Cl$_2$, −30 °C): τ 7.42 (br, s, 2 H), 8.30 (m, 18 H), 8.90 (m, 27 H), and 12.6 (br, s, 1 H). ^{11}B NMR (CD$_2$Cl$_2$, −10 °C): 9.35 (2), −7.34 (1), −13.7 (1), −18.5 (2), −22.6 (1), and −27.4 ppm (1). (10% PEt$_3$–CH$_2$Cl$_2$, 25 °C, 0.35 M in IIf, contained ca. 9 % IIIc): 11.5 (2), −4.77 (1), −13.2 (1), −15.2 (1), −18.2 (1), −21.4 (1), and −26.1 ppm (1). ^{31}P{^{1}H} NMR (40.5 MHz, CD$_2$Cl$_2$, −80 °C): 5.39 (octet, P$_1$, $J_{RhP_1} = 109.9$, $^2J_{P_1P_2} = 31.3$, $^2J_{P_1P_3} = 8.5$ Hz), 2.01 (d of t, P$_2$, $J_{RhP_2} = 92.8$, $^2J_{P_2P_3} = 30.5$ Hz), and −2.52 ppm (octet, P$_3$, $J_{RhP_3} = 121.4$ Hz). Infrared spectrum: 3008 (m), 2961 (s), 2932 (s), 2905 (m, sh), 2875 (s), 2510 (s, br), 1447 (s), 1408 (s), 1369 (s), 1256 (m, sh), 1246 (s), 1237 (m, sh), 1157 (m), 1065 (m), 1039 (s, sh), 1020 (s), 1008 (s, sh), 980 (s, sh), 955 (m, sh), 939 (m), 865 (m), 760 (s, sh), 753 (s), 737 (s), 696 (m), 682 (m, sh), 677 (s), 652 (m), 623 (m), and 595 cm^{-1} (m). Complex IIf appeared to be air stable in the solid state but slowly developed the odor of triethylphosphine upon exposure to air, and therefore was stored under nitrogen. In solution, IIf (or IIf–IIIc mixtures) decomposed rapidly in air.

Preparation of [*closo*-1,1-(PEt$_3$)$_2$-1-H-1,2,4-RhC$_2$B$_8$H$_{10}$] (Id). Complex IIf (0.300 g, 0.518 mmol) was dissolved in dichloromethane (5 mL). Petroleum ether (30 mL) was gently layered on top of the red solution. Upon standing at room temperature for 2 days, yellow crystals of Id formed and were filtered off, washed with pentane, and vacuum dried, yielding [*closo*-1,1-(PEt$_3$)$_2$-1-H-1,2,4-RhC$_2$B$_8$H$_{10}$] (Id, 0.174 g, 77%), mp 113–115 °C dec. Anal. Calcd for C$_{14}$H$_{41}$B$_8$P$_2$Rh: C, 36.49; H, 8.97; B, 18.77; P, 13.44; Rh, 22.33. Found: C, 36.45; H, 9.02; B, 18.58; P, 13.78; Rh, 22.07. ^{1}H NMR (100 MHz, CD$_2$Cl$_2$, −45 °C): same as that of IIIc (see below) plus a resonance at τ 15.5 (br, m). ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$, 40 °C, 42% Id–58% IIIc): 44.2, 9.39, −2.93, −15.4, −18.2, −22.0, and −27.0 ppm. ^{31}P{^{1}H} NMR (40.5 MHz, CD$_2$Cl$_2$, −60 °C, 87.5% Id–12.5% IIIc): 39.70 (q, P$_1$, $J_{RhP_1} = 108.6$ Hz), 35.85 ppm (q, P$_2$, $J_{RhP_2} = 107.7$, $^2J_{P_1P_2} = 29.3$ Hz). Infrared spectrum (Nujol): 2600 (s), 2551 (s), 2500 (s, br), 2044 (m), 1411 (m), 1249 (m), 1065 (m), 1032 (s), 1021 (s), 995 (m), 957 (s), 942 (s), 906 (m), 894 (m), 753 (s), 741 (m, sh), 716 (s), 710 (s), 683 (m), 649 (m), 620 (m), 618 (m), and 598 cm^{-1}. (KBr): 2975 (m), 2935 (m), 2878 (m), 1449 (m), 1410 (m), and 1367 cm^{-1} (m).

Spectral Properties of [*nido*-9,9-(PEt$_3$)$_2$-9,7,8-RhC$_2$B$_8$H$_{11}$] (IIIc). ^{1}H NMR (100 MHz, CD$_2$Cl$_2$, −45 °C, Id–IIIc equilibrium mixture): τ 5.63 (br, s, 1 H), 6.26 (br, s, 1 H), 8.30 (m, 12 H), 8.90 (m, 18 H), and 12.7 (br, 1 H). ^{11}B{^{1}H} NMR (1,2-C$_2$H$_4$Cl$_2$, 60 °C): 10.9, 3.79, −6.55, −20.1, −25.4, and −41.3 ppm. (CD$_2$Cl$_2$, 40 °C): 10.6, 3.03, −6.51, −20.6, −24.2, and −41.5 ppm. ^{31}P{^{1}H} NMR (40.5 MHz, CD$_2$Cl$_2$, −60 °C, Id–IIIc equilibrium mixture): 37.28 (q, P$_3$, J_{RhP_3} 136.4, $^2J_{P_3P_4} = 36.6$ Hz) and 25.66 ppm (q, P$_4$, $J_{RhP_4} = 135.8$ Hz).

Reaction of [*closo*-1,1-(PEt$_3$)$_2$-1-H-1,2,4-RhC$_2$B$_8$H$_{10}$] (Id) with Triethylphosphine. Complex Id (0.101 g, 0.219 mmol) was dissolved in dichloromethane (1.5 mL) and triethylphosphine (0.5 mL) was added, yielding a yellow solution. Upon addition of petroleum ether (15 mL), yellow crystals were formed. The ^{11}B and ^{1}H NMR and infrared spectra of this product were identical with those of IIf (0.094 g, 73%).

Reaction of [*closo*-1,1-(PEt$_3$)$_2$-1-H-1,2,4-RhC$_2$B$_8$H$_{10}$] (Id) with Dimethylphenylphosphine. Complex Id (0.175 g, 0.380 mmol) dissolved in toluene (20 mL) was treated with dimethylphenylphosphine (0.35 mL, 2.4 mmol). The color of the solution instantly changed from red to yellow and after approximately 5 min a yellow powder precipitated from solution. The reaction mixture was heated to reflux for 1 h, slowly cooled to room temperature, mixed with 50 mL of petroleum ether, and filtered quickly through Celite. The filtrate was concentrated and cooled to −15 °C, depositing yellow crystals of IIb (0.196 g, 81%) as identified by its infrared and ^{1}H and ^{11}B NMR spectra.

Preparation of [*closo*-1,1,3-(PPh$_3$)$_3$-1-H-1,2,4-RuC$_2$B$_8$H$_9$] (V). The complex [RuHCl(PPh$_3$)$_3$·PhMe] (0.70 g, 0.70 mmol) was added to a solution of NaC$_2$B$_8$H$_{11}$ (0.79 mmol) in diethyl ether (20 mL) with stirring. After 30 min all the purple crystals of the Ru(II) complex were consumed and a pink powder was deposited. The mixture was stirred for 12 h, then filtered, washed with diethyl ether (3 × 25 mL) and methanol (2 × 25 mL), and recrystallized from a layered solution of tetrahydrofuran–methanol. After standing overnight and cooling at −15 °C for 1 day, the solution was filtered, washed with methanol and petroleum ether, and dried under vacuum to yield red, crystalline [*closo*-1,1,3-(PPh$_3$)$_3$-1-H-RuC$_2$B$_8$H$_9$] (V, 0.50 g, 70%), mp 210–212 °C. Anal. Calcd for C$_{56}$H$_{55}$B$_8$P$_3$Ru: C, 66.69; H, 5.50; B, 8.58; P, 9.21; Ru, 10.02. Found: C, 67.12; H, 5.64; B, 9.04; P, 9.06; Ru, 9.79. ^{1}H NMR (100 MHz, CD$_2$Cl$_2$, 35 °C): τ 2.12 (m, 6 H), 2.59 (m, 9 H), 3.07 (m, 30 H), 6.97 (br, s, 1 H), 8.48 (br, s, 1 H), and 13.39 (octet, 1 H, $^2J_{PH} = 30.0$ and 38.0, $^3J_{PH} = 22.5$ Hz). ^{11}B{^{1}H} NMR (CH$_2$Cl$_2$, 25 °C): 35.5 (d, $^1J_{BP} = 130$ Hz), 6.12, 0.56 −5.20, −18.5, −22.7, −27.13, and −42.0 ppm. ^{31}P{^{1}H} NMR (36.4 MHz, CD$_2$Cl$_2$, 30 °C): −0.30 (d, P$_1$, $^2J_{P_1P_2} = 22.0$ Hz) and −12.49 ppm (d, P$_2$). Infrared spectrum: 3045 (m), 2512 (s), 1951 (w, br), 1473 (s), 1426 (s), 1179 (m), 1068 (m, sh), and 688 cm^{-1} (s). The product may also be recrystallized from dichloromethane–methanol.

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Influence of Steric and Electronic Effects on the Binding of Arenediazonium Cations to 18-Crown-6 in Methanol at 25 °C[1a]

R. M. Izatt,*[1b] J. D. Lamb,[1b] C. S. Swain,[1b] J. J. Christensen,[1b] and Barry L. Haymore[1c]

Contribution from the Departments of Chemistry and Chemical Engineering and No. 183 from the Thermochemical Institute, Brigham Young University, Provo, Utah 84602, and the Department of Chemistry, Indiana University, Bloomington, Indiana 47405. Received October 24, 1979

Abstract: Log K, ΔH, and $T\Delta S$ values for the interaction of several arenediazonium salts with 18-crown-6 were determined in methanol at 25 °C by the calorimetric titration technique. The complex of benzenediazonium cation with 18-crown-6 is enthalpy stabilized with $\log K = 2.50$. Substitution of a methyl group onto the ortho position(s) of benzenediazonium cation results in a total loss of complex stability. Substitution of various groups onto the para position results in changes in complex stability according to the electronic effect exerted in the diazonium moiety. A linear Hammett relationship ($\rho = 0.65$) was found between log K and σ_p^+ values associated with the para substituent.

Introduction

Macrocyclic ligands are known to bind many metal cations by sequestering them within the macrocyclic ligand cavity.[2] In similar fashion, 18-crown-6 was shown first by Gokel and Cram[3] and subsequently by Haymore et al.[4] and by Kyba et al.[5] to complex benzenediazonium cation ($PhNN^+$) in solution with the insertion of the diazonium moiety into the ligand cavity. The formation of such complexes has been exploited by Bartsch and his co-workers[6] to enhance the stability of arenediazonium cations against decomposition. These workers found that the rate of thermal decomposition of p-t-$BuC_6H_4NN^+$ ion in organic solvents and of photochemical decomposition of diazonium ions in the solid phase are significantly reduced by addition of crown ethers. The ligand 18-crown-6 (18C6) was more effective in stabilizing these cations than 15-crown-5.

We reported in a previous communication[7] that the value of the stability constant of the 18C6 complex of benzenediazonium cation is very sensitive to steric interference from substituent groups in the ortho positions as was demonstrated qualitatively by Gokel and Cram[3] and by Kyba et al.[5] We here report the details of this study and the effect on complex stability of substituents in the para position which exert varying electronic influence on the diazonium moiety.

Experimental Section

Materials. The 18C6 (Parish Chemical) was used without further

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