Ten-Vertex *closo*- and *hyper-closo*-Phosphinometallocarborane Complexes Derived from Sodium Dodecahydro-1,3-dicarba-*arachno*-nonaborate(1−)

C. W. Jung, R. T. Baker, and M. F. Hawthorne*

Contribution from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received May 14, 1980*

Abstract: Reactions of $Na(1,3\text{-}C_2B_7H_{12})$ with $[RhCl(PR_3)_2]_2$ or $[RhCl(PR_3)_3]$ (R = Ph, *p*-tolyl) and of $Na(1,3\text{-}R'_2\text{-}1,3\text{-}C_2B_7H_{10})$ (R′ = H, CH_3) with $[IrCl(PPh_3)_3]$ afforded the complexes [*closo*-2,3-R'_2-6,6-$(PR_3)_2$-6-H-6,2,3-$MC_2B_7H_7$] (Ia–d). Complex Ia (M = Rh, R′ = H, R = Ph) is a catalyst precursor for the homogeneous hydrogenation of vinyltrimethylsilane under mild conditions. Reactions of $Na(1\text{-}R^1\text{-}3\text{-}R^2\text{-}1,3\text{-}C_2B_7H_{10})$ ($R^1 = R^2$ = H, CH_3; R^1 = H, R^2 = Ph) with $[RuHCl(PPh_3)_3]$ yielded the unsaturated complexes [*hyper-closo*-2-R^1-3-R^2-6,6-$(PPh_3)_2$-6,2,3-$RuC_2B_7H_7$] (IIa–c). Complex IIa ($R^1 = R^2$ = H) is the most effective ruthenacarborane catalyst yet studied for the homogeneous hydrogenation of terminal alkenes, and it reacts with carbon monoxide to form [*closo*-6,6-$(CO)_2$-6-(PPh_3)-6,2,3-$RuC_2B_7H_9$] (III). The addition of excess triethylphosphine to a dichloromethane solution of IIa results in a thermochromic solution which exhibits a remarkable equilibrium between {*hyper-closo*-6,6-$[P(C_2H_5)_3]_2$-6,2,3-$RuC_2B_7H_9$} (IV) and {*closo*-6,6,6-$[P(C_2H_5)_3]_3$-6,2,3-$RuC_2B_7H_9$} (V), the polyhedral structures of which are significantly different, as evidenced by multinuclear dynamic FT NMR. Complex IV reacts with carbon monoxide to form {*closo*-6,6-$[P(C_2H_5)_3]_2$-6-CO-6,2,3-$RuC_2B_7H_9$} (VI). Possible modes of formation of these species are discussed.

Introduction

We have reported the synthesis of the 12-vertex metallocarborane complexes [*closo*-$(PPh_3)_2HMC_2B_9H_{11}$] (VII; M = Rh[1,2] and Ir[1]) and [*closo*-$(PPh_3)_2H_2RuC_2B_9H_{11}$][3] (VIII) by the formal oxidative addition of the (*nido*-$C_2B_9H_{12}$)$^-$ anion[4,5] to $[MCl(PPh_3)_3]$ (M = Rh and Ir) and $[RuHCl(PPh_3)_3]$, respectively. More recently these reactions were extended[6,7] to the synthesis of analogous 11-vertex *nido*- and *closo*-metallocarborane complexes derived from the (*nido*-5,6-$C_2B_8H_{11}$)$^-$ anion.[8] Preliminary catalytic screening results indicated that the 11-vertex metallocarboranes possess significantly less activity as catalyst precursors for the homogeneous hydrogenation of vinyltrimethylsilane under mild conditions than do their 12-vertex analogues. This paper describes the synthesis, characterization, and preliminary catalytic screening results of 10-vertex *closo*- and *hyper-closo*-metallocarboranes derived from the addition of coordinatively unsaturated d^6 and d^8 transition-metal phosphine complexes to the (*arachno*-1-R^1-3-R^2-1,3-$C_2B_7H_{10}$)$^-$ anion.[9] Portions of this work have been described in a preliminary communication.[6]

While this investigation was in progress, Stone and co-workers reported[10] that the reactions of d^{10} nickel and platinum complexes with *arachno*-1,3-R_2-1,3-$C_2B_7H_{11}$ (R = H or CH_3) formed *nido*-metallocarboranes of the type $[L_2MC_2B_7H_9R_2]$, with the metal atom bonded to two borons and a carbon atom of the open face. It has been suggested that these complexes are formed via an initial oxidative addition of an axial C–H bond of the carborane to the d^{10} metal atom to form an intermediate metal hydride complex, which was detected by infrared and ^1H NMR spectroscopy for M = Pt and L = $P(C_2H_5)_3$.

Results

***closo*-Rhoda- and -Iridacarboranes.** Reaction of an ether solution of $Na(1,3\text{-}C_2B_7H_{12})$ with $[RhCl(PPh_3)_3]$ or $[RhCl(PPh_3)_2]_2$ at room temperature produced the complex [*closo*-6,6-$(PPh_3)_2$-6-H-6,2,3-$RhC_2B_7H_9$] (Ia) in 80% yield according to eq 1. One molar equivalent (based on rhodium) of hydrogen gas was found to be liberated.

$$[RhCl(PPh_3)_3] + NaC_2B_7H_{12} \rightarrow [RhH(PPh_3)_2(C_2B_7H_9)] + H_2 + PPh_3 + NaCl \quad (1)$$

The infrared spectrum of Ia exhibited a sharp, medium intensity ν_{Rh-H} absorption[11] at 2081 cm^{-1} along with bands due to coordinated triphenylphosphine and a neutral carborane moiety. No bands attributable[12] to B-H-B bridge vibrations could be observed in the regions of 1460–1500 or 1800–2050 cm^{-1}. The ^1H-decoupled 80.5-MHz ^{11}B NMR spectrum of Ia consisted of singlets of relative areas 1:2:2:1:1, suggesting the existence of a mirror plane in the complex. In spite of the absence of a resonance in the 40–80 ppm range, which is normally assigned[13-16] to a low-coordinate boron atom adjacent to a metal vertex, this spectrum suggests that the two polyhedral carbon atoms occupy the 2,3-positions of a 10-vertex closo-polyhedron as shown in Figure 1A. The rule cited above was suggested for first-row transition metals[16] and need not apply to second- and third-row transition-metal metallocarboranes.

The ^1H NMR spectrum of Ia contained only a broad singlet at τ 2.80 assigned to the phenyl protons. The lack of expected spin–spin coupling in the phenyl region and an upfield hydride signal is probably the result of fast triphenylphosphine exchange,[17] but the low solubility of Ia precluded measurement of the proton NMR at the low temperatures necessary to stop this exchange

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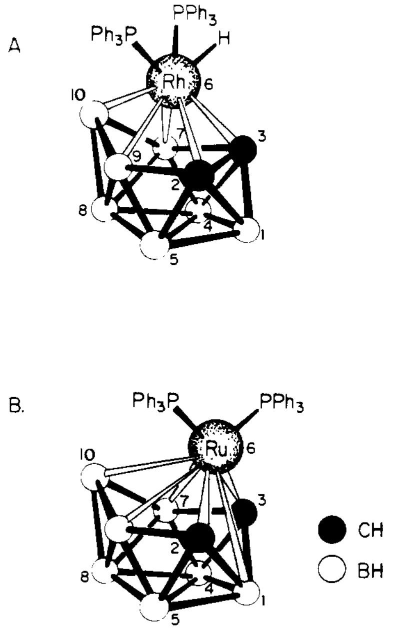

Figure 1. Proposed molecular structures for the metallocarborane complexes Ia (A) and IIa (B).

process. Addition of excess triphenylphosphine (1.0 M) to a solution of the complex (0.04 M) led to the observation of a broad "quartet" ($W_{1/2}$ = 10 Hz) at τ 23.45 due to the metal hydride. Phosphorus-31 decoupling collapsed the multiplet to a broad doublet ($|J_{Rh-H}|$ = 16 Hz). From these NMR data it appears that [*closo*-6,6-$(PPh_3)_2$-6-H-6,2,3-$RhC_2B_7H_9$] (Ia) dissociates triphenylphosphine more readily than its 12-vertex congener [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (VIIa), as all the expected spectral features were found in the latter complex without the addition of triphenylphosphine.

Replacement of triphenylphosphine with the more basic and less labile tri-*p*-tolylphosphine ligand should reduce the extent of phosphine dissociation and increase the solubility[18] of the resultant complex. The reaction of $\{RhCl[P(p\text{-tolyl})_3]_2\}_2$ with $NaC_2B_7H_{12}$ afforded the light yellow crystalline complex {*closo*-6,6-$[P(p\text{-tolyl})_3]_2$-6-H-6,2,3-$RhC_2B_7H_9$} (Ib). The 100-MHz ^1H NMR spectrum of Ib contained a hydride resonance at τ 22.24 as a triplet of doublets due to coupling of the hydride to ^{103}Rh and to two equivalent ^{31}P nuclei. This was the multiplet expected for the hydride resonance of Ia in the presence of excess triphenylphosphine which was obscured by the broad signal that was actually observed. The magnitude of the phosphorus-hydride coupling (25 Hz) was typical of hydride cis to a tertiary phosphine in octahedral Rh^{III} or Ir^{III} complexes.[19]

The activity of [*closo*-6,6-$(PPh_3)_2$-6-H-6,2,3-$RhC_2B_7H_9$] (Ia) as a catalyst for the hydrogenation of terminal alkenes has been investigated, and the initial rates observed at room temperature and 0.75 atm of H_2 show its 12-vertex congener VIIa to be greater than 20 times more active than Ia.[20]

Reactions of $[IrCl(PPh_3)_3]$ with Na(1,3-$C_2B_7H_{12}$) and Na-[1,3-$(CH_3)_2$-1,3-$C_2B_7H_{10}$] in diethyl ether afforded [*closo*-6,6-$(PPh_3)_2$-6-H-6,2,3-$IrC_2B_7H_9$] (Ic) and [*closo*-2,3-$(CH_3)_2$-6,6-$(PPh_3)_2$-6-H-6,2,3-$IrC_2B_7H_7$] (Id), respectively.

The 80.5-MHz ^{11}B NMR spectrum of Ic consisted of broad, weak signals[21] but indicated the presence of a symmetry plane in the molecule. Although the infrared spectra of Ia, Ic, and Id are similar, suggesting that they are isostructural, the metal-hydride stretching frequencies of the iridacarboranes are shifted about 120 cm^{-1} to higher frequencies from those of the rhodacarboranes. The hydride resonance of Ic (triplet at τ 24.47, $|^2J_{P-H}|$ = 25 Hz) was not broadened by phosphine exchange in contrast to Ia. The mass spectra of the iridacarboranes contained moderately strong parent peaks and intense mass envelopes assigned to the species $[IrH(PPh_3)(C_2B_7H_7R_2)]^+$ (R = H or CH_3). Due to its low solubility, complex Id was characterized by its elemental analysis and infrared and mass spectra only. Although complexes Ia–d are air stable in the solid state, the rhodacarborane complexes Ia,b are decomposed in dichloromethane solutions after several days of exposure to air. The iridacarborane complexes Ic,d are air stable in solution. The enhanced stability to oxidation of the iridacarboranes may be attributed, in part, to greater iridium bond strengths.[22,23] The iridium complexes Ic,d are virtually inactive as catalysts for alkene hydrogenation and isomerization under mild conditions.[20]

***closo*- and *hyper-closo*-Ruthenacarboranes.** The complexes [*hyper-closo*-2-R^1-3-R^2-6,6-$(PPh_3)_2$-6,2,3-$RuC_2B_7H_7$] (IIa–c) were obtained from the reactions of $[RuHCl(PPh_3)_3]$ with Na(1-R^1-3-R^2-1,3-$C_2B_7H_{10}$) in diethyl ether in 85% yield according to eq 2. Two molar equivalents (based on ruthenium) of hydrogen

$$[RuHCl(PPh_3)_3] + Na(C_2B_7H_{10}R^1R^2) \rightarrow [(PPh_3)_2RuC_2B_7H_7R^1R^2] + 2H_2 + PPh_3 + NaCl \quad (2)$$

gas were found to be liberated. The highest mass species observed in the mass spectra of the ruthenacarboranes correspond to the species $[(PPh_3)RuC_2B_7H_7R^1R^2]^+$, and no signals attributable to ruthenium-hydride or B–H–B bridges were observed in the infrared or ^1H NMR spectra. At 100 MHz, the ^1H NMR spectra of IIa ($R^1 = R^2$ = H) and IIb ($R^1 = R^2 = CH_3$) contained singlets due to the two equivalent carborane C–H and C-methyl groups, respectively. In addition, both spectra exhibited a broad resonance at low field (τ –0.5). The $^{11}B\{^1H\}$ NMR spectra of IIa,b consisted of broad, poorly resolved singlets[21] which were, however, consistent with a symmetrical carborane cage and included very low-field resonances at 108.0 and 105.2 ppm, respectively. As the ^1H NMR chemical shifts of boron-bound hydrogens generally correlate with the ^{11}B NMR chemical shifts of the borons to which they are bound,[24] we presumed that the terminal hydrogen responsible for the low-field ^1H NMR resonance was bound to the boron which is responsible for the very low-field ^{11}B NMR resonance. This was subsequently confirmed by variable-frequency proton decoupling of the ^{11}B NMR spectrum of IV (vide infra). The origin of these low-field resonances will be addressed in the discussion.

The $^{31}P\{^1H\}$ NMR spectrum of IIc (R^1 = H, R^2 = Ph) contained two doublets at 35.5 and 12.7 ppm ($|^2J_{P-P}|$ = 37 Hz) assigned to the two coordinated triphenylphosphine ligands which are inequivalent due to the asymmetric carborane ligand. The $^{11}B\{^1H\}$ NMR spectrum of IIc was too poorly resolved to show the asymmetry of the carborane cage, and the expected low-field resonance was not observed due to the low solubility of the complex. The addition of excess triethylphosphine to a solution of IIc, however, generated the bis(triethylphosphine) analogue of IIc which was more soluble and exhibited all the expected spectral features discussed above.[25]

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[20] Potential catalysts were screened by using a previously reported procedure and apparatus (R. T. Baker, R. E. King III, C. B. Knobler, C. A. O'Con, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **100**, 8266 (1978)). With use of an initial hydrogen pressure of 0.75 atm, an initial vinyltrimethylsilane concentration of 9.84 × 10^{-2} M, and catalyst concentrations of 2.72 × 10^{-3} M, the initial hydrogenation rates (±10%) at 24.60 °C for Ia, IIa, and VIIa were 1.68 × 10^{-8}, 6.70 × 10^{-8}, and 5.27 × 10^{-7} mol/s, respectively. The 12-vertex ruthenacarborane complex VIII was an ineffective catalyst under these mild conditions (rates reported in the above communication and ref 7 are erroneously large by a factor of 100). R. T. Baker and M. F. Hawthorne, to be submitted for publication.

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Complexes IIa–c are deep blue to blue-green in solution or as powders but almost black in the crystalline states. Large crystals of these complexes are decomposed by air over a period of several months to insoluble, uncharacterized black powders. The solutions are much more air sensitive and precipitate brown powders after a few minutes of exposure to air. The homologous dark blue crystalline complex[3] $[2,2\text{-}(PPh_3)_2\text{-}2,1,7\text{-}RuC_2B_9H_{11}]$ (IX) is much more air sensitive than IIa–c, and we have not yet obtained suitable crystals of IX for an X-ray structural study.[26] Complexes IIa–c and IX are formally 16-electron Ru^{II} species but, unlike IX, complex IIa does not oxidatively add hydrogen (at 1 atm) to form a dihydridoruthenium(IV) complex. Treatment of IIa in toluene or dichloromethane with concentrated hydrochloric acid or dry hydrogen chloride gas instantly produced dark yellow solutions; however, attempts to isolate the yellow compound, presumably [*closo*-$RuHCl(PPh_3)_2(C_2B_7H_9)$], were unsuccessful. These solutions reverted to the dark blue color of IIa upon dilution with petroleum ether, concentration under vacuum, or gentle warming. No ruthenium hydride resonance was detected in the ^1H NMR spectrum of the yellow solution. In contrast, IX reacts with hydrogen chloride to form yellow, crystalline $[RuHCl(PPh_3)_2\text{-}(1,7\text{-}C_2B_9H_{11})]$.[3] Apparently, complex IIa also oxidatively adds hydrogen chloride, but the resultant Ru^{IV} complex is thermodynamically unstable.

Complex IIa was found to be an active catalyst precursor for the hydrogenation of vinyltrimethylsilane and exhibited rates about 4 times greater than those observed for Ia.[20] In the presence of activated olefins IIa formed dark brown solutions in benzene or dichloromethane. With ethyl acrylate, the blue color of IIa reappeared upon removal of the alkene under vacuum or dilution with pentane. No tractable compounds were isolated from reactions of IIa with fumaronitrile, dimethylfumarate, or diphenylacetylene. Presumably, IIa formed weak π complexes with these alkenes and acetylene which dissociated upon attempted isolation, to yield IIa. Treatment of IIa with carbon monoxide in toluene was monitored by infrared and $^{31}P\{^1H\}$ NMR spectroscopy and shown to proceed stepwise as shown in eq 3 to form

$$Ru(PPh_3)_2C_2B_7H_9 \xrightarrow{CO} Ru(PPh_3)_2(CO)C_2B_7H_9 \xrightarrow[-PPh_3]{CO} Ru(PPh_3)(CO)_2C_2B_7H_9 \quad (3)$$

the air-stable, yellow, crystalline complex [*closo*-$6\text{-}(PPh_3)\text{-}6,6\text{-}(CO)_2\text{-}6,2,3\text{-}RuC_2B_7H_9$] (III) as supported by spectral and analytical data. No low-field resonances were observed in the ^{11}B or ^1H NMR spectra of III. Ruthenacarboranes IIa–c also reacted with *o*-styryldiphenylphosphine,[27] (*o*-allylphenyl)diphenylphosphine[28] and $Ph_{3-n}P(CH_2CH_2CH{=}CH_2)_n$ (n = 1, 2)[29] to form *closo*- and *hyper-closo*-ruthenacarborane complexes in which both the phosphine and alkenyl groups are coordinated to the metal atom.[30] In a recently completed X-ray diffraction study of the hyper-closo complex $\{\overline{Ru[PPh_2(C_6H_4CH{=}CH_2)]}[C_2B_7H_7\text{-}(CH_3)_2]\}$, the cage geometry was found to be distorted from the ten-vertex closo structure as depicted in Figure 1B for IIa.

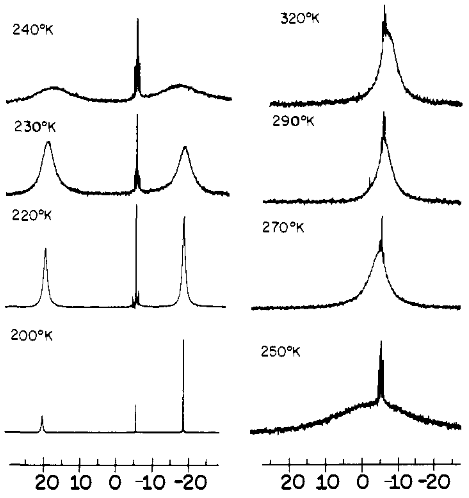

Figure 2. Dynamic 81.02-MHz $^{31}P\{^1H\}$ FT NMR spectra of IIa in the presence of excess triethylphosphine. The sharp resonance at ca. −6 ppm is due to uncoordinated triphenylphosphine.

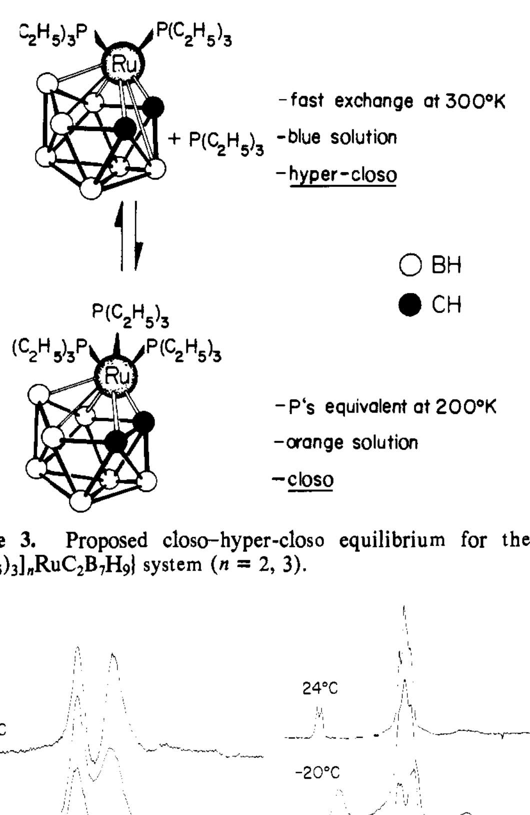

Figure 3. Proposed closo–hyper-closo equilibrium for the $\{[P(C_2H_5)_3]_nRuC_2B_7H_9\}$ system (n = 2, 3).

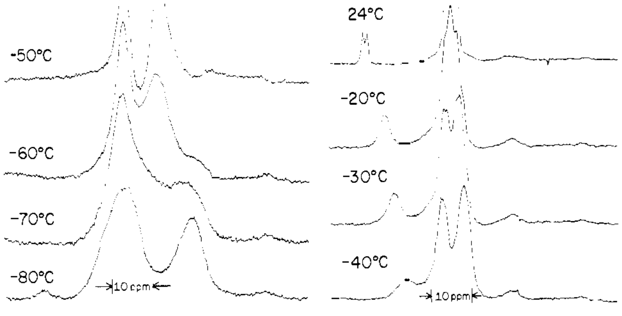

Figure 4. Dynamic 127.01-MHz ^{11}B NMR of IV in the presence of ca. 1 equiv of triethylphosphine. The low-field resonance at 105.6 ppm which is observed only in the 24 °C spectrum is not shown.

Treatment of a dichloromethane solution of IIa with excess triethylphosphine produces a blue solution which becomes orange upon cooling to −80 °C. The dynamic $^{31}P\{^1H\}$ FT NMR shown in Figure 2 indicated that the blue species {*hyper-closo*-$6,6\text{-}[P(C_2H_5)_3]_2\text{-}6,2,3\text{-}RuC_2B_7H_9$} (IV) is undergoing fairly rapid intermolecular triethylphosphine exchange at 47 °C. Intermediate exchange occurs in the region centered around −25 °C, and the process is slow at −73 °C, presumably due to the formation of {*closo*-$6,6,6\text{-}[P(C_2H_5)_3]_3\text{-}6,2,3\text{-}RuC_2B_7H_9$} (V) (Figure 3). The

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[25] NMR spectral data for {*hyper-closo*-$2\text{-}Ph\text{-}6,6\text{-}[P(C_2H_5)_3]_2\text{-}6,2,3\text{-}RuC_2B_7H_8$} follow: $^{31}P\{^1H\}$ FT NMR (10% CD_2Cl_2–CH_2Cl_2) 15.1 (d, $^2J_{P-P}$ = 37 Hz) and 11.8 (d) ppm; ^1H FT NMR (CD_2Cl_2) τ −0.63 (br m, 1 H), 2.54 (d, $^3J_{P-H}$ = 7 Hz, 2 H), 2.93 (m, 3 H), 6.78 (br s, 1 H), 8.37 (m, 6 H), 8.51 (m, 6 H), 8.95 (m, 18 H); $^{11}B\{^1H\}$ NMR (111.8 MHz, CH_2Cl_2) 110.5 (1), 15.5 (1), 1.3 (1), −4.8 (2), −6.9 (1), −7.5 (1) ppm.

[26] A crystal structure of the isoelectronic $[2\text{-}Cl\text{-}2\text{-}PPh_3\text{-}2,1,7\text{-}RhC_2B_9H_{11}]$ complex has recently been completed and establishes the 16-electron closo structure[43] with no significant distortion of the carborane cage ligand relative to the 18-electron closo complex VIII (R. E. King, R. G. Teller, and M. F. Hawthorne, to be submitted for publication).

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[30] C. W. Jung, R. T. Baker, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **102**, 5782 (1980). The term "hyper-closo" defines an n vertex cluster which possesses less than n + 1 skeletal electron pairs *and* is significantly distorted from the idealized closo structure.

single resonance due to V broadens at −88 °C relative to the free triphenyl- and triethylphosphine resonances, but the fluxional process responsible for the equivalence of the three coordinated triethylphosphine resonances could not be arrested, due to the lack of solubility of V in suitable low-temperature solvents. Although attempts to isolate V by crystallization at −80 °C were unsuccessful, the dynamic $^{11}B\{^1H\}$ FT NMR of an equimolar solution of IV (vide infra) and triethylphosphine in dichloromethane-d_2 presented in Figure 4 indicated that the polyhedral structures of IV and V are quite different, and the very low-field resonance of IV at 105.6 ppm, which is observed at 24 °C, is absent at −50 °C. The weak resonance at 15.4 ppm at −80 °C is due to the presence of a small amount of IV, indicating that the intermolecular exchange process is slow, and the broad, symmetric resonances[31] due to V also reflect its fluxional nature at −80 °C. In addition, the dynamic ^1H FT NMR of the above solution exhibits a low-field resonance at τ −0.1 which is absent at −20 °C. At −88 °C only one carborane C–H resonance is observed for V at τ 6.87, as well as broad resonances due to the coordinated triethylphosphine ligands at τ 8.20 and 9.05.

Complex IV was isolated as large blue-black or small, bright green crystals, and the analytical data were consistent with the proposed formulation. Grinding the large blue-black crystals under argon yielded a bright green powder. The spectral data for IV were similar to those for IIa,b, with the exception of an additional strong, broad absorption at 2275 cm^{-1} in the infrared spectrum of the green solid. This absorption was absent in the infrared spectrum of the blue solution obtained by dissolving the green solid in dichloromethane. The origin of this absorption is referred to the discussion.

Crystals of IV decompose rapidly in moist air to insoluble, uncharacterized powders containing ν_{O-H} absorptions in the infrared. Unlike IIa, IV did not react with activated olefins and was inactive as a catalyst for the hydrogenation of vinyltrimethylsilane under mild conditions.[20] The extended reaction of IV with triethylphosphine and the reaction of IV with hydrogen chloride both yielded phosphinoruthenacarboranes containing metal–hydrogen and boron–phosphorus bonds and will be described elsewhere.[32] Solutions of IV reacted rapidly with carbon monoxide to afford the yellow, crystalline complex {*closo*-6-(CO)-6,6-$[P(C_2H_5)_3]_2$-6,2,3-$RuC_2B_7H_9$} (VI) as supported by spectral and analytical data. Like the analogous *closo*-ruthenacarborane II, the ^{11}B and ^1H FT NMR spectra of VI exhibited no very low-field resonances.

Discussion

The low-field ^{11}B and ^1H NMR resonances observed for IIa–c and IV are a general feature of hyper-closo 10-vertex ruthenacarborane complexes in which only four electrons are formally donated to the ruthenium vertex by the exopolyhedral ligands[30] and *are not observed* for closo 10-vertex metallocarborane complexes of second- and third-row transition metals which contain $n + 1$ skeletal electron pairs[33] (i.e., Ia–d, III and VI). The structure of the 10-vertex *hyper-closo*-metallocarborane complexes was first established for $\{[(\eta^5\text{-}C_5H_5)Fe]_2C_2B_6H_8\}$[34,35] and, more recently, for $\{Ru[PPh_2(C_6H_4CH{=}CH_2)][C_2B_7H_7(CH_3)_2]\}$[30] and is shown in Figure 1B for complex IIa. A very low-field ^{11}B NMR resonance (103.8 ppm) has also been observed for the bis(dicarboranyl)cobalt anion[36,37] and was assigned to the boron atoms which are bound to both carbon atoms and interact with the cobalt atom through fluxional Co–H–B bridges. As a similar withdrawal of electron density from B(1) by the ruthenium atom in IIa–c and IV seems likely, the low field ^{11}B and ^1H NMR resonances are tentatively assigned to B(1) and H(1), respectively (see Figure 1B).

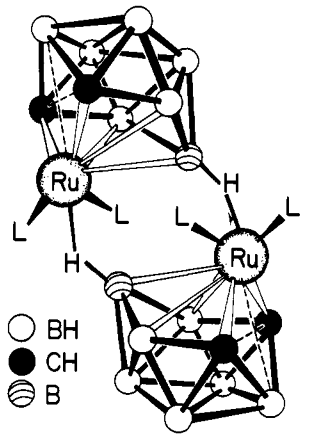

Figure 5. Proposed dimeric structure of IV in the solid state (L = $P(C_2H_5)_3$).

The strong infrared absorption at 2270 cm^{-1} observed in the solid-state spectrum of the green crystals of IV suggests that IV is associated in the solid state via the formation of intermolecular Ru–H–B bridge bonds. Similar M–H–B absorptions have been observed at 2100–2300 cm^{-1} for $[Cu_2B_{10}H_{10}]$,[38] and, recently, Wallbridge et al. have reported the molecular structure of the dimeric, 11-vertex *arachno*-argentacarborane complex $[PPh_3AgC_2B_8H_{11}]_2$, which exhibits a strong infrared absorption between 2300 and 2350 cm^{-1} in the solid state, resulting from the interaction of the 16-e Ag^{I} vertex with a terminal boron–hydrogen bond of the neighboring enantiomeric argentacarborane molecule.[39] As the interacting hydrogen atom is bound to the boron atom which is closest to the metal and furthest from the carbon atoms (site of greatest electron density), we tentatively propose the dimeric structure shown in Figure 5 for IV in the solid state. Complexes IIa–c are presumably unable to associate in this manner as a result of steric crowding in the vicinity of the transition-metal vertex.

The presence of a single, broad resonance in the $^{31}P\{^1H\}$ FT NMR spectrum and a single carborane C–H resonance in the ^1H FT NMR spectrum of V indicates that this pseudo-octahedral *closo*-ruthenacarborane complex is fluxional in solution at −88 °C. As the $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ FT NMR spectra of V demonstrate that the intermolecular triethylphosphine exchange process is slow at −80 °C, the fluxionality of V is probably the result of hindered rotation of the $\{RuL_3\}$ vertex with respect to the five-membered face of the carborane cage. Such a process has recently been proposed for a series of five-coordinate 11-vertex rhodacarborane complexes,[7] [*nido*-$L_3RhC_2B_8H_{11}$] (L = tertiary phosphine or arsine ligand), and for several pseudo-octahedral *closo*-metallocarborane complexes,[40] including [2,2-$(PPh_3)_2$-2-H-2,1,7-$MC_2B_9H_{11}$] (M = Rh, Ir), on the basis of multinuclear dynamic FT NMR studies. In an attempt to obtain a measurable rotational barrier for a 10-vertex *closo*-ruthenacarborane complex, we monitored the reaction of IIc with excess triethylphosphine by $^{31}P\{^1H\}$ FT NMR spectroscopy. Only the C-phenyl analogue

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(35) E. Nishimura has recently suggested (*J. Chem. Soc., Chem. Commun.*, 858 (1978)) that distortion from the idealized bicapped Archimedean antiprismatic structure is a result of "hyperpolyhedral" metal–metal bonding which relieves the electronic unsaturation at the iron atoms. While the distortion observed for $\{Ru[PPh_2(C_6H_4CH{=}CH_2)][(C_2B_7H_7(CH_3)_2]\}$ may be similarly explained by a two-electron B→Ru coordinate bond, we believe this approach to be limited and to favor an approach which involves three-dimensional delocalization of the electron unsaturation.

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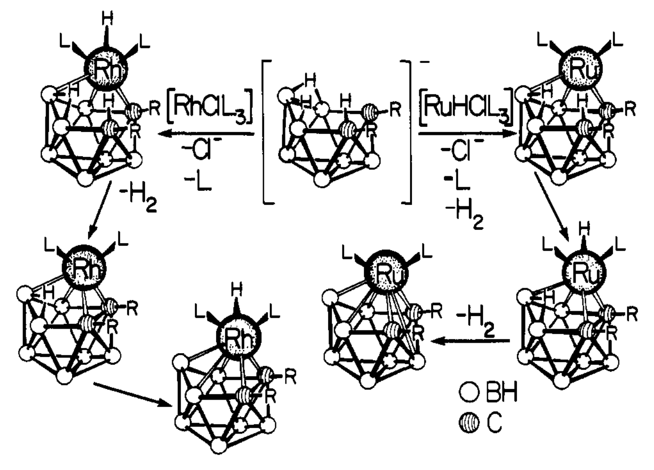

Figure 6. Proposed mechanism for the formation of Ia and IIa (R = H; L = PPh_3).

of IV was observed from −90 °C to 30 °C, however, as the increased steric crowding of the metal vertex (relative to IV) presumably precluded the formation of the C-phenyl analogue of V.

The reaction scheme proposed by Stone and co-workers[10] for the syntheses of [*nido*-5,9-$(CH_3)_2$-6,6-L_2-6,5,9-$MC_2B_7H_9$] (M = Ni, Pt; L = tertiary phosphine) from the reactions of *arachno*-1,3-$(CH_3)_2$-1,3-$C_2B_7H_{11}$ with zero-valent nickel and platinum complexes involved initial insertion of the d^{10} metal atom into an axial C–H bond to form an intermediate metal hydride complex. The formation of Ia–d, however, probably involves initial nucleophilic attack on the $\{ML_3Cl\}$ moiety by the $(C_2B_7H_{10}R_2)^-$ (R = H, CH_3) anion, followed by insertion of the d^8 metal atom into a B–H–B bridge to yield a 16-e M^{III}[*arachno*-$L_2HMC_2B_7H_9R_2$] intermediate which is isoelectronic to Stone's "nido" complexes,[41] which contain a six-membered open face. This arachno intermediate may then undergo reductive elimination of hydrogen and formation of metal–carbon and carbon–carbon bonds to produce a 16-e M^I[*nido*-$L_2MC_2B_7H_8R_2$] intermediate, which is isoelectronic to another 10-vertex platinacarborane prepared by Stone et al., {*nido*-Pt$[P(C_2H_5)_3]_2[C_2B_7H_7(CH_3)_2]$},[45] which contains a four-membered open face. Subsequent insertion of the d^8 metal atom into the remaining B–H–B bond of the carborane ligand then generates the 18-e M^{III} closo complexes $[L_2HMC_2B_7H_7R_2]$ as shown in Figure 6. *hyper-closo*-Ruthenacarborane complexes IIa–c were probably formed in the same manner by the reductive elimination of a second mole of hydrogen. Although the arachno and nido intermediates were not observed, the nido to closo tautomerism, with concomitant increase in formal oxidation state (i.e., $Rh^I \rightarrow Rh^{III}$), has been observed for the 16-e Rh^I complex {*nido*-9,9-$[P(C_2H_5)_3]_2$-9,7,8-$RhC_2B_8H_{11}$}.[7]

The remarkable closo–hyper-closo equilibrium which exists between IV and V (Figure 3) is reminiscent of the familiar diamond–square–diamond rearrangement process originally proposed by Lipscomb[46] and can be rationalized in a qualitative manner by assuming that the lowest unoccupied molecular orbital of the *hyper-closo*-ruthenacarborane is delocalized over the ruthenium, two carbon and boron(1) atoms (Figure 1B). The addition of a two-electron donor ligand, then, results in cleavage of the Ru–B(1) bond, with concomitant formation of a carbon–carbon bond. Conversely, the removal of a two-electron donor ligand from the *closo*-ruthenacarborane results in cleavage of the carbon–carbon bond and formation of the Ru–B(1) bond. This closo–hyper-closo equilibrium has also been recently demonstrated for the alkenylphosphine ruthenacarborane complexes $[RuL_2C_2B_7H_9]$, where L = $Ph_{3-n}P(CH_2CH_2CH{=}CH_2)_n$ (*n* = 1, 2).[30]

The stability of the 10-vertex hyper-closo structure is likely to be enhanced by the reduction of the coordination number of the carbon atoms[43,46] from six in the closo structure to five in the hyper-closo structure. The 11-vertex hyper-closo complex $[(PPh_3)_2RuC_2B_8H_{10}]$ exists only as a postulated intermediate[7] which succumbs to nucleophilic attack on the activated ruthenacarborane cage by a free triphenylphosphine ligand, affording the closo complex [1,1,3-$(PPh_3)_3$-1-H-1,2,4-$RuC_2B_8H_9$]. The postulated 12-vertex hyper-closo intermediate $[(PPh_3)NiC_2B_9H_{11}]$ reacts similarly to yield the closo complex [3,8-$(PPh_3)_2$-3-H-3,1,2-$NiC_2B_9H_{10}$].[48] Complexes IIa and IV, however, did not react with triphenylphosphine at 100 °C in toluene, and IV reacted only slowly with triethylphosphine at 80 °C in benzene, producing several isomeric *closo*-ruthenacarborane complexes which contain ruthenium–hydrogen and boron–phosphorus bonds and comprise the body of a future publication.[32]

While the rhodacarborane complex Ia is an active catalyst precursor for the homogeneous hydrogenation of vinyltrimethylsilane, the observed catalytic activity parallels that of the 11-vertex rhodacarboranes[7] and is significantly less than that of the 12-vertex rhodacarborane complex VIIa. The 10-vertex ruthenacarborane complex IIa, however, is the most active ruthenacarborane catalyst yet studied under the mild conditions employed,[20] and further catalytic studies will be necessary to elucidate the catalytic mechanism using *hyper-closo*-ruthenacarborane catalyst precursors.

Conclusions

Reactions of Na(1,3-R'_2-1,3-$C_2B_7H_{10}$) with $[RhCl(PR_3)_3]$, $[RhCl(PR_3)_2]_2$, or $[IrCl(PPh_3)_3]$ yielded the 18-e metallocarborane complexes [*closo*-2,3-R'_2-6,6-$(PR_3)_2$-6-H-6,2,3-$MC_2B_7H_7$] (Ia–d). Reactions of Na(1-R^1-3-R^2-1,3-$C_2B_7H_{10}$) with $[RuHCl(PPh_3)_3]$, however, yielded the 16-e ruthenacarborane complexes [*hyper-closo*-2-R^1-3-R^2-6,6-$(PPh_3)_2$-6,2,3-$RuC_2B_7H_7$] (IIa–c). Complex IIa reacted with carbon monoxide to produce the 18-e ruthenacarborane complex [*closo*-6,6-$(CO)_2$-6-PPh_3-6,2,3-$RuC_2B_7H_9$] (III). The reaction of complex IIa with $P(C_2H_5)_3$ yielded {*hyper-closo*-6,6-$[P(C_2H_5)_3]_2$-6,2,3-$RuC_2B_7H_9$} (IV), which, in the presence of additional $P(C_2H_5)_3$, was converted to {*closo*-6,6,6-$[P(C_2H_5)_3]_3$-6,2,3-$RuC_2B_7H_9$} (V) at low temperatures. This facile, reversible polyhedral rearrangement is thought to be a result of the perturbation of the skeletal bonding induced by the 16-e Ru^{II} vertex. Complex IV also reacted with carbon monoxide to form {*closo*-6,6-$[P(C_2H_5)_3]_2$-6-CO-6,2,3-$RuC_2B_7H_9$} (VI). Studies are presently underway in this laboratory to isolate and structurally characterize 11- and 12-vertex *hyper-closo*-metallocarborane complexes.

Experimental Section

Unless otherwise indicated all operations were conducted under purified nitrogen or argon by using standard inert atmosphere techniques.[49] Infrared spectra[50] were determined as Nujol mulls

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[41] According to the recent extension of the skeletal electron counting schemes by Wallbridge et al.[42] and, more formally, by Nishimura,[43] the 16-e $\{ML_2\}$ vertex (M = Ni, Pt) in Stone's $[L_2MC_2B_7H_9R_2]$ complexes[10] *formally* contributes *four* electrons to the skeletal bonding and these complexes are, therefore, *arachno*-metallocarboranes. It is well-known that 10-vertex *nido*- and *arachno*-boranes and *nido*- and *arachno*-carboranes are isostructural,[44] although an alternative 10-vertex nido structure has been found for {*nido*-Pt$[P(C_2H_5)_3]_2[C_2B_7H_7(CH_3)_2]$}.[45]

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[43] E. Nishimura, private communication. This generalization of the skeletal electron-counting schemes simply takes account of metal-based unsaturation by introducing the variable *m* into the equation for the number of skeletal electrons donated by a transition metal vertex (i.e., $e = v + x - m + 6$, where $m \leq 18$ and refers to the EAN of the metal vertex). When $m \geq 18$, $e = v + x - 12$ which is, of course, the equation commonly used for skeletal electron counting schemes.[33]

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or KBr pellets on a Perkin-Elmer 421 dual grating spectrometer. Proton NMR[50] spectra were measured at 35 °C by using Varian HA100D spectrometers. A Varian C-1024 Computer of Average Transients was used to record low-intensity NMR resonances. The 200.133-MHz ^1H and 81.02-MHz $^{31}P\{^1H\}$ FT NMR were recorded on a Bruker WP-200 spectrometer equipped with a B-V-T-1000 variable-temperature unit, and all reported coupling constants are absolute values. The ^{11}B NMR spectra were obtained at 80.5, 111.80, and 127.01 MHz by using a Fourier transform instrument designed and constructed by Professor F. A. L. Anet and co-workers at UCLA. ^{11}B chemical shifts were referenced to external $BF_3 \cdot OEt_2$ where positive shifts refer to lower field. ^{31}P chemical shifts were referenced to external 85% H_3PO_4 and were calculated as in ref 40. All NMR solvents were vacuum distilled from P_2O_5 or CaH_2 into the NMR sample tube prior to sealing under vacuum ($<5 \times 10^{-5}$ torr). Mass spectra were obtained on an Associated Electrical Industries MS9 spectrometer.

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

Hydrated $RhCl_3$ and $RuCl_3$ were obtained from commercial sources. Literature methods were used to prepare $[RhCl(PPh_3)_3]$,[51] $[RuHCl(PPh_3)_3] \cdot C_6H_5CH_3$,[52,53] $[IrCl(PPh_3)_3]$,[22] $[RhCl(C_2H_4)_2]_2$,[54] $[IrCl(C_8H_{14})_2]_2$[55] (C_8H_{14} = cyclooctene), and *arachno*-1,3-$C_2B_7H_{13}$ and its carbon-substituted derivatives.[9] Solutions of $NaC_2B_7H_{10}R_2$ were prepared by stirring the parent carborane in a suspension of excess sodium hydride in diethyl ether for approximately 5 min. After filtration, the clear solutions were used immediately. Triethylphosphine (Strem) was used without further purification, and triphenylphosphine (Aldrich) was recrystallized from benzene–methanol prior to use. Tri-*p*-tolylphosphine was prepared by the Grignard method[56] and recrystallized several times from benzene–methanol. All alkenes used were vacuum distilled from calcium hydride before use. Florisil (60–100 mesh) for column chromatography was heated to approximately 120 °C under vacuum ($<1 \times 10^{-4}$ torr) overnight to removed adsorbed oxygen.

Preparation of [*closo*-6,6-$(PPh_3)_2$-6-H-6,2,3-$RhC_2B_7H_9$] (Ia). A solution of $NaC_2B_7H_{12}$ (1.42 mmol) in diethyl ether (25 mL) was placed in a 100-mL Schlenk flask connected to a gas buret. A small Schlenk addition tube containing $[RhCl(PPh_3)_3]$ (0.925 g, 1.00 mmol) was connected to the flask, and the system was then sealed and allowed to equilibrate for 10 min. The two reactants were mixed and stirred magnetically at room temperature. The initial red color of the suspension gradually lightened, and after about 5 min a yellow powder precipitated. All of the $[RhCl(PPh_3)_3]$ disappeared within 15 min, and hydrogen gas (0.86 mmol) was evolved over about 30 min. After 2 h, the crude yellow product was filtered off, washed with diethyl ether, and chromatographed on a 2 × 25 cm Florisil column, eluting with dichloromethane. A small dark brown band remained near the top of the column but was not characterized. The yellow eluate was concentrated under vacuum to about 20 mL and rechromatographed. Addition of octane (50 mL) to the resultant eluate followed by slow concentration under vacuum yielded 0.581 g (79%) of yellow microcrystalline [*closo*-6,6-$(PPh_3)_2$-6-H-6,2,3-$RhC_2B_7H_9$] (Ia): mp 191–192 °C (darkens at 180 °C); ^1H NMR data (100 MHz, CD_2Cl_2 solution) τ 2.80 (br s, $W_{1/2}$ = 15 Hz), 6.35 (br s), 23.5 (br q, J_{Rh-H} = 16 Hz; in presence of 1.0 M free PPh_3); $^{11}B\{^1H\}$ NMR data (CH_2Cl_2 solution) 23.6 (1), −5.9 (2), −19.5 (2), −22.1 (1), −33.6 (1) ppm; infrared spectrum (Nujol mull) 2586 (s), 2546 (s), 2516 (s), 2081 (m), 1581 (w), 1567 (w), 1474 (s), 1429 (s), 1309 (m), 1177 (m), 1151 (m), 1087 (s), 1068 (m), 1060 (m), 1022 (m), 993 (m), 754 (m), 749 (s), 738 (s), 731 (s), 708 (s), 692 (s), 679 (s, sh) cm^{-1}.

Anal. Calcd for $C_{38}H_{40}B_7P_2Rh$: C, 61.91; H, 5.47; B, 10.26; P, 8.40; Rh, 13.96. Found: C, 60.97; H, 5.95; B, 9.82; P, 8.27; Rh, 14.43.

Preparation of {*closo*-6,6-[P(*p*-tolyl)$_3$]$_2$-6-H-6,2,3-$RhC_2B_7H_9$} (Ib). Tri-*p*-tolylphosphine (0.624 g, 2.05 mmol) was added to a stirred suspension of $[RhCl(C_2H_4)_2]_2$ (0.200 g, 0.514 mmol) in 75 mL of diethyl ether. After 15 min, the resultant yellow slurry of {RhCl[P(*p*-tolyl)$_3$]$_2$}$_2$[18] was added to a solution of $NaC_2B_7H_{12}$ (1.27 mmol) in 25 mL of diethyl ether and stirred at room temperature for 3 h. The mixture was worked up as described above, yielding yellow crystals of {*closo*-6,6-[P(*p*-tolyl)$_3$]$_2$-6-H-6,2,3-$RhC_2B_7H_9$} (Ib) (0.51 g, 60%): mp 240–260 °C (darkens at 120 °C); ^1H NMR data (100 MHz, CD_2Cl_2) τ 2.90 (br m, 24 H), 7.68 (s, 18 H), 8.73 (br s, 2 H), 22.4 (d of t, J_{Rh-H} = 16 Hz, $^2J_{P-H}$ = 25 Hz, 1 H); $^{11}B\{^1H\}$ NMR data (CH_2Cl_2) 22.9 (1), −7.25 (2), −20.5 (3), −34.0 (1) ppm; infrared spectrum (Nujol mull) ν_{Rh-H} at 2075 (m) cm^{-1}.

Anal. Calcd for $C_{44}H_{52}B_7P_2Rh$: C, 64.34; H, 6.38; P, 7.54. Found: C, 64.26; H, 6.52; P, 7.07.

Preparation of [*closo*-6,6-$(PPh_3)_2$-6-H-6,2,3-$IrC_2B_7H_9$] (Ic). The complex $[IrCl(PPh_3)_3]$ (3.10 g, 3.0 mmol) was stirred at room temperature overnight with $NaC_2B_7H_{12}$ (3.66 mmol) in diethyl ether (ca. 20 mL). The yellow precipitate was filtered in air and washed with diethyl ether. Recrystallization from dichloromethane–ethanol and dichloromethane–octane afforded light yellow crystals of [*closo*-6,6-$(PPh_3)_2$-6-H-6,2,3-$IrC_2B_7H_9$] (Ic) (0.70 g, 28%): mp 261–262 °C (darkens at 255 °C); ^1H NMR data (100 MHz, CD_2Cl_2) τ 2.79 (m, 30 H), 6.72 (br s, 2 H), 24.47 (t, $^2J_{P-H}$ = 24.5 Hz, 1 H); $^{11}B\{^1H\}$ NMR data (CH_2Cl_2) −8.46, −22.0, −24.4 ppm; infrared spectrum (KBr) ν_{Ir-H} = 2201 (m) cm^{-1}. Complex Ic can also be purified by prolonged Soxhlet extraction of the crude product with diethyl ether.

Anal. Calcd for $C_{38}H_{40}B_7P_2Ir$: C, 55.22; H, 4.88; B, 9.16; P, 7.49; Ir, 23.25. Found: C, 55.19; H, 5.03; B, 9.23; P, 7.21; Ir, 22.91.

Preparation of [*closo*-2,3-$(CH_3)_2$-6,6-$(PPh_3)_2$-6-H-6,2,3-$IrC_2B_7H_7$] (Id). The yellow, crystalline [*closo*-2,3-$(CH_3)_2$-6,6-$(PPh_3)_2$-6-H-6,2,3-$IrC_2B_7H_7$] (Id) was prepared by reaction of $[IrCl(PPh_3)_3]$ (1.40 g, 1.38 mmol) and $Na[C_2B_7H_{10}(CH_3)_2]$ (1.56 mmol) in diethyl ether (40 mL) and worked up as described above: yield 0.27 g (25%); *mp* 241–244 °C (darkens at 235 °C); infrared spectrum (Nujol mull) ν_{Ir-H} at 2210 (m) cm^{-1}.

Anal. Calcd for $C_{40}H_{44}B_7P_2Ir$: C, 56.21; H, 5.20. Found: C, 56.27; H, 5.27.

Preparation of [*hyper-closo*-6,6-$(PPh_3)_2$-6-2,3-$RuC_2B_7H_9$] (IIa). The complex $[RuHCl(PPh_3)_3] \cdot C_6H_5CH_3$ (2.90 g, 2.89 mmol) was suspended in a solution of $NaC_2B_7H_{12}$ (2.90 mmol) in 20 mL of diethyl ether, as per the preparation of Ia. The solution became deep blue after 30 min, and the purple crystals of $[RuHCl(PPh_3)_3]$ were gradually replaced by a blue powder. After the solution was stirred overnight, the evolved hydrogen gas amounted to 5.04 mmol. The reaction mixture was filtered through Celite, washed with diethyl ether (5 × 10 mL) and extracted with 50 mL of dichloromethane. Ethanol (absolute, 800 mL) was gently layered on top of the blue dichloromethane solution, and when the solution was left standing at −15 °C for 1 day, shiny black needles of [*hyper-closo*-6,6-$(PPh_3)_2$-6,2,3-$RuC_2B_7H_9$] (IIa) were obtained, washed with ethanol and petroleum ether, and vacuum dried. Additional purification was effected by similar recrystallization from tetrahydrofuran–methanol: yield 1.80 g (84.5%); mp 209–212 °C (darkens at 190 °C); ^1H NMR data (100 MHz, CD_2Cl_2) τ −0.47 (m, 1 H), 2.75 (m, 30 H), 6.19 (br s, 2 H); ^{11}B NMR data (CH_2Cl_2) 108.0 (1), 16.4 (1), −4.17 and −5.86 (5, overlapping peaks) ppm; $^{31}P\{^1H\}$ FT NMR (10% CD_2Cl_2–CH_2Cl_2) 35.1 (s) ppm.

Anal. Calcd for $C_{38}H_{39}B_7P_2Ru$: C, 62.15; H, 5.35; B, 10.30; P, 8.43; Ru, 13.76. Found: C, 61.77; H, 5.49; B, 10.26; P, 8.04; Ru, 13.90.

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(50) For NMR, abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, br = broad. For IR, abbreviations: s = strong, m = medium, w = weak, and sh = shoulder.

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Occasionally, the light blue dichloromethane–ethanol filtrate from the recrystallization of IIa turned purple upon standing at room temperature for several days. A purple solid was isolated but was not characterized due to its low and irreproducible yields.

Preparation of [*hyper-closo*-2,3-$(CH_3)_2$-6,6-$(PPh_3)_2$-6,2,3-$RuC_2B_7H_7$] (IIb) and [*hyper-closo*-2-Ph-6,6-$(PPh_3)_2$-6,2,3-$RuC_2B_7H_8$] (IIc). The cage-substituted analogues of IIa were prepared as described above. The complex [*hyper-closo*-2,3-$(CH_3)_2$-6,6-$(PPh_3)_2$-6,2,3-$RuC_2B_7H_7$] (IIb) was obtained in 82% yield from the reaction of [$RuHCl(PPh_3)_3$]·$C_6H_5CH_3$ (1.80 g, 1.77 mmol) with Na[1,3-$(CH_3)_2$-1,3-$C_2B_7H_{10}$] (1.94 mmol) in diethyl ether (40–50 mL): mp 220–230 °C (darkens at 115 °C); ^1H NMR data (100 MHz, CD_2Cl_2) τ −0.21 (m, 1 H), 2.80 (m, 30 H), 8.79 (s, 6 H); ^{11}B NMR data (CD_2Cl_2) 105.2 (1), 15.4 (1), 0.38 and −1.20 (4, overlapping peaks), −5.78 (1) ppm; infrared spectrum (KBr) 2540 (s), 2500 (s), 1578 (w), 1564 (w), 1473 (m), 1426 (s), 1329 (m), 1303 (m), 1177 (m), 744 (s), 737 (s), 719 (m), 692 (s), 680 (s), 620 (m) cm^{-1}.

Anal. Calcd for $C_{40}H_{43}B_7P_2Ru$: C, 63.01; H, 5.68; B, 9.92; P, 8.12. Found: C, 62.54; H, 5.77; B, 9.54; P, 8.59.

Treatment of [$RuHCl(PPh_3)_3$]·$C_6H_5CH_3$ (1.30 g, 1.28 mmol) with Na[1-Ph-1,3-$C_2B_7H_{11}$] (1.42 mmol) in diethyl ether (45 mL) gave [*hyper-closo*-2-Ph-6,6-$(PPh_3)_2$-6,2,3-$RuC_2B_7H_8$] (IIc) in 77% yield: mp >300 °C (darkens at 170 °C); ^1H NMR data (CD_2Cl_2) τ 2.80 (m), 6.88 (br s); $^{31}P\{^1H\}$ FT NMR (10% CD_2Cl_2–CH_2Cl_2) 35.5 (d, $^2J_{P-P} = 37$ Hz), 12.7 (d) ppm; $^{11}B\{^1H\}$ NMR data (CD_2Cl_2) 13.5 (1), 4.36 (1), −5.18 (2, overlapping peaks), −7.97 (2, overlapping peaks) ppm. The expected low field peak (ca. 100 ppm) was not observed due to the low solubility of IIc, but the addition of ca. 4 equiv of $P(C_2H_5)_3$ generated {*hyper-closo*-2-Ph-6,6-[$P(C_2H_5)_3$]-6,2,3-$RuC_2B_7H_8$}, which was more soluble and exhibited a low-field ^{11}B NMR resonance at 110.5 ppm. Complete NMR spectral data for this complex are listed in ref 25.

Anal. Calcd for $C_{44}H_{43}B_7P_2Ru$: C, 65.21; H, 5.35; B, 9.34; P, 7.65. Found: C, 63.02; H, 5.40; B, 9.09; P, 7.12.

Reaction of [*hyper-closo*-6,6-$(PPh_3)_2$-6,2,3-$RuC_2B_7H_9$] (IIa) with Carbon Monoxide. Carbon monoxide was bubbled through a suspension of IIa (0.505 g, 0.688 mmol) in 4 mL of toluene at room temperature for 30 s. The blue solution instantly turned brown. The reaction mixture was stirred under a CO atmosphere for an additional 30 min. Addition of pentane to the resultant clear brown solution precipitated a yellow powder, which was filtered off in air and washed with pentane. Recrystallization from benzene–pentane afforded yellow crystals of [*closo*-6,6-$(CO)_2$-6-PPh_3-6,2,3-$RuC_2B_7H_9$] (III): ^1H NMR data (60 MHz, CD_2Cl_2) τ 2.49 (m, 15 H), 6.59 (br s, 2 H); $^{11}B\{^1H\}$ NMR data (CH_2Cl_2) 1.04 (2), −9.11 (1), −20.6 and −23.6 (4, overlapping peaks) ppm; $^{31}P\{^1H\}$ FT NMR (C_6D_6) 46.5 (s) ppm; infrared spectrum (Nujol mull) ν_{CO} at 2035 (s) and 1975 (s) cm^{-1}. Monitoring this reaction by infrared and $^{31}P\{^1H\}$ FT NMR spectroscopy demonstrated the initial formation of the intermediate complex [*closo*-6,6-$(PPh_3)_2$-6-CO-6,2,3-$RuC_2B_7H_9$]: infrared spectrum (Nujol mull) ν_{CO} at 1935 (s) cm^{-1}; $^{31}P\{^1H\}$ FT NMR (C_6D_6) 26.6 (s) ppm.

Anal. Calcd for $C_{22}H_{24}B_7PO_2Ru$: C, 50.03; H, 4.58; P, 5.86. Found: C, 50.26; H, 4.60; P, 5.91.

Preparation of {*hyper-closo*-6,6-[$P(C_2H_5)_3$]$_2$-6,2,3-$RuC_2B_7H_9$} (IV). A slurry of [$(PPh_3)_2RuC_2B_7H_9$] (734 mg, 1.00 mmol) and $P(C_2H_5)_3$ (365 mg, 3.09 mmol) in 50 mL of toluene was stirred for 12 h, layered with 100 mL of pentane, and cooled to −15 °C for 2 days. The resulting blue-black blocks and small green crystals were filtered off, washed with cold pentane (6 × 20 mL), and dried in vacuo to yield 380 mg of {*hyper-closo*-6,6-[$P(C_2H_5)_3$]$_2$-6,2,3-$RuC_2B_7H_9$} (IV) (85%): mp 145–150 °C; ^1H FT NMR (CD_2Cl_2) τ −0.27 (m, 1 H), 6.31 (br s, 2 H), 8.41 (m, 12 H), 9.05 (m, 18 H); $^{31}P\{^1H\}$ FT NMR (10% CD_2Cl_2–CH_2Cl_2) 15.1 (s) ppm; $^{11}B\{^1H\}$ NMR (127.01 MHz, CD_2Cl_2) 105.5 (1), 15.4 (1), −5.7 (2), 7.8 (3) ppm; infrared spectrum (Nujol) 2500 (vs), 2270 (vs), 1410 (s), 1260 (m), 1130 (m), 1040 (vs, br), 1010 (m, br), 955 (s), 918 (m), 840 (w, br), 820 (m), 805 (w), 770 (vs), 740 (vs, br), 725 (m), 708 (s, br), 690 (s) cm^{-1}.

Anal. Calcd for $C_{14}H_{39}B_7P_2Ru$: C, 37.69; H, 8.81; B, 16.96; P, 13.89; Ru, 22.65. Found: C, 37.44; H, 8.83; B, 16.70; P, 14.05; Ru, 23.32.

Spectral data for {*closo*-6,6,6-[$P(C_2H_5)_3$]$_3$-6,2,3-$RuC_2B_7H_9$} (V): ^1H FT NMR (CD_2Cl_2, −88 °C) τ 6.87 (br s, 2 H), 8.20 (m, 18 H) and 9.05 (m, 27 H); $^{31}P\{^1H\}$ FT NMR (10% CD_2Cl_2–CH_2Cl_2, −88 °C) 17.1 (br s) ppm; $^{11}B\{^1H\}$ NMR (127.01 MHz, CD_2Cl_2, −79 °C) −8.1 (4), −24.2 (3) ppm.

Preparation of {*closo*-6,6-[$P(C_2H_5)_3$]$_2$-6-CO-6,2,3-$RuC_2B_7H_9$} (VI). A blue solution of {[$P(C_2H_5)_3$]$_2RuC_2B_7H_9$} (445 mg, 1.00 mmol) in 30 mL of toluene was bubbled with carbon monoxide for 5 s, stirred for 5 min, and purged with nitrogen. The solution was layered with 100 mL of pentane, and, after the mixture was cooled at −15 °C for 1 day, the resulting yellow crystals were filtered off, washed with 2 × 20 mL of pentane, and dried in vacuo to yield 380 mg of {*closo*-6,6-[$P(C_2H_5)_3$]$_2$-6-CO-6,2,3-$RuC_2B_7H_9$} (VI) (80%); mp 151–154 °C; ^1H FT NMR ($CDCl_3$) τ 6.72 (br s, 2 H), 8.09 (m, 12 H), 8.87 (m, 18 H); $^{31}P\{^1H\}$ FT NMR (C_6D_6) 31.7 (s) ppm; $^{11}B\{^1H\}$ NMR (127.01 MHz, $CDCl_3$) 14.3 (1), −4.9 (1), −10.3 (1), −21.4 (2), −24.4 (2) ppm; infrared spectrum (Nujol mull) 2560 (s), 2500 (vs), 1925 (vs), 1410 (m), 1260 (m), 1240 (w), 1110 (w), 1040 (vs, br), 995 (w), 945 (w), 912 (m), 875 (w), 770 (vs), 742 (s), 718 (s), 696 (s) cm^{-1}.

Anal. Calcd for $C_{15}H_{39}B_7OP_2Ru$: C, 37.98; H, 8.29; B, 15.96; P, 13.07; Ru, 21.32. Found: C, 38.22; H, 8.33; B, 15.93; P, 12.92; Ru, 20.87.

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