Metallacarboranes in Catalysis. 3. Synthesis and Reactivity of *exo-nido*-Phosphinerhodacarboranes[1]

Judith A. Long,[2a] Todd B. Marder,[2b] Paul E. Behnken,[2c] and M. Frederick Hawthorne*

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. *Received June 29, 1983*

Abstract: The carbon-substituted *closo*-bis(triphenylphosphine)hydridorhodacarborane [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_9RR'$] [R, R′ = μ-1′,2′-$CH_2C_6H_4CH_2$– (IIa)], the carbon-substituted *exo-nido*-bis(triphenylphosphine)rhodacarborane complexes [$(PPh_3)_2Rh$(7,8-$C_2B_9H_{10}RR'$)] [R = Me, R′ = Ph (IIb); R = R′ = Me (IIc); R, R′ = μ-$(CH_2)_3$ (IId)], and the salt [$(PPh_3)_3Rh]^+$[*nido*-7-R-7,8-$C_2B_9H_{11}]^-$ [R = 1′-(*closo*-1′,2′-$C_2B_{10}H_{11}$) (IVe)] were prepared by the reaction of the carborane anions [*nido*-7-R-8-R′-7,8-$C_2B_9H_{10}]^-$ (Ia–e) with [$(PPh_3)_3RhCl$] in benzene. Complexes IIa,c exhibited a closo–exo-nido equilibrium in solution. The exo-nido complexes can be regarded as being composed of an $[L_2Rh]^+$ cation bound to a [*nido*-7-R-8-R′-7,8-$C_2B_9H_{10}]^-$ anion cage via two exo polyhedral three-center, two-electron interactions (Rh–H–B bridges) with terminal hydrogen atoms. The $[L_2Rh]^+$ moiety can apparently rotate with respect to and, in some cases, migrate about the polyhedral surface of the cage. Complex IIA reacted with 2 equiv of PCy_3 (Cy = cyclohexyl) to generate the mixed phosphine exo-nido complex [$(PPh_3)(PCy_3)Rh$-7,8-μ-(1′,2′-$CH_2C_6H_4CH_2$–)-7,8-$C_2B_9H_{10}$] (IIIa). Reaction of the *exo-nido*-bis(triphenylphosphine)rhodacarboranes with good σ donors or CO displaced the rhodium from the carborane cage to give cationic species of the form $[L_4Rh]^+$, $[L_3RhS]^+$, $[L_2Rh(CO)_3]^+$ (L = PPh_3, S = solvent); $[L_4Rh]^+$ (L = PEt_3); $[(L–L)_2Rh]^+$ (L–L = dppe); and $[(L–L–L)(L')Rh]^+$ (L–L–L = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$ = triphos, L′ = PPh_3). The $[(PEt_3)_4Rh]^+$ complexes (Va–e) reacted further to generate closo species of the general formula [*closo*-$(PEt_3)_2Rh(H)(C_2B_9H_9RR')$]. The 3,1,2-isomer was obtained when R = R′ = Me (VIIc), R, R′ = μ-$(CH_2)_3$– (VIId), and R, R′ = μ-(1′,2′-$CH_2C_6H_4CH_2$–) (VIIa); but in the cases of R = Ph, R′ = Me and R = 1′-(*closo*-1′,2′-$C_2B_{10}H_{11}$), R′ = H, a polytopal rearrangement occurred, resulting in the formation of [*closo*-1-R-8-R′-2,2-$(PEt_3)_2$-2-H-2,1,8-$RhC_2B_9H_9$], R = Me, R′ = Ph (VIb) and R = H, R′ = 1′-(*closo*-1′,2′-$C_2B_{10}H_{11}$) (VIe). The complexes IIa–d and IIIa underwent oxidative addition of H_2 to give dihydrido Rh(III) products in which the $[(PPh_3)_2Rh(H)_2]^+$ or $[(PPh_3)(PCy_3)Rh(H)_2]^+$ fragment remains bonded to the carborane cage through two three-center, two-electron Rh–H–B interactions. Molecular structures of two representative *exo-nido*-rhodacarboranes (IIb and IIIa) along with that of *closo*-rhodacarborane (IIa) have been determined and are formally presented in the following paper of this series.

The previous paper[1] in this series described the synthesis and reactivity of a series of 12-vertex *closo*-bis(triphenylphosphine)-hydridorhodacarborane complexes, many of which show catalytic activity in a variety of reactions including the hydrogenation and isomerization of alkenes. The *closo*-metallacarborane catalysts are unusual; in addition to being both electronically and coordinatively saturated species, the rhodium center is present in the formal +3 oxidation state. A catalytic hydrogenation mechanism could be envisaged in which a phosphine ligand is replaced by an alkene leading to an 18-e⁻ Rh(III) [*closo*-(PPh_3)(H)(alkene)-Rh(carborane)] complex, and indeed, two such complexes have recently been prepared and structurally characterized in this laboratory.[3] Migratory insertion of hydride would lead to the 16-e⁻ Rh(III) alkyl complex, and we have recently characterized a similar 18-e⁻ Rh(III) alkyl complex stabilized by a chelating carbonyl oxygen.[1] The critical problem concerns the potential mode of hydrogen activation by the 16-e⁻ alkyl complex. Oxidative addition of H_2 would require a transient Rh(V) species, and thus seems very unlikely, although heterolytic activation of H_2 would formally avoid this unusually high oxidation state. In addition, deuterium labeling studies[4] demonstrated that the original Rh–H(D) ligand is retained at rhodium after a catalytic hydrogenation experiment. Therefore, the migratory insertion reaction of the closo alkene–hydride complex does not play a role in the hydrogenation mechanism since such a process would result in the loss of identity of the original hydride ligand during the first turnover of Rh.[5] It seemed unlikely that any mechanism involving only closo species would suffice. An alternative pathway was considered involving an internal redox reaction accompanied by prototropy that transforms the 18-e⁻ Rh(III) *closo*-rhodacarboranes into 16-e⁻ Rh(I) nido tautomers. We previously reported an analogous tautomeric transformation in the 11-vertex C_2B_8 system.[6] Consequently, a similar coordinatively unsaturated and low-valent tautomer of the C_2B_9 species was an attractive candidate catalyst precursor. At this point in time no *nido*-RhC_2B_9 species had been isolated or even observed spectroscopically. However, continued efforts to prepare C,C′-disubstituted analogues of the closo 12-vertex complexes by the procedures described in the preceding paper[1] resulted in the synthesis and isolation of the unusual C,-C′-bridged *o*-xylylene derivative IIa. Although the solid-state structure[7] of this complex is analogous to that of the monosubstituted *closo*-rhodacarboranes discussed above, both $^{31}P\{^1H\}$ and ^1H NMR spectroscopy proved the closo complex to be in equilibrium with an exo-nido tautomer in solution. Subsequent development of an alternative synthesis for C,C′-disubstituted C_2B_9 phosphinerhodacarboranes resulted in the isolation of several of the elusive *exo-nido*-phosphinerhodacarboranes. These compounds proved to be active hydrogenation catalysts as expected. Kinetic

(1) Taken in part from the Ph.D. Thesis of T. B. Marder (1982) and J. A. Long (1981), University of California, Los Angeles. For part 2 of this series see: Baker, R. T.; Delaney, M. S.; King, R. E., III; Knobler, C. B.; Long, J. A.; Marder, T. B.; Paxson, T. E.; Teller, R. G.; Hawthorne, M. F. *J. Am. Chem. Soc.*, first of five papers in this issue.

(2) (a) University of California Chancellor's Intern Fellow 1977–1981. (b) University of California Regents' Intern Fellow 1976–1980. (c) University of California Regents' Fellow 1979–1980.

(3) Delaney, M. S.; Knobler, C. B.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1980**, 849; *Inorg. Chem.* **1981**, *20*, 1341. Delaney, M. S.; Teller, R. G.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 235.

(4) Behnken, P. E.; Belmont, J. A.; Busby, D. C.; King, R. E., III; Kreimendahl, C. W.; Marder, T. B.; Wilczynski, J. J.; Hawthorne, M. F. *J. Am. Chem. Soc.*, fifth of five papers in this issue.

(5) Insertion of the alkene into the Rh–D bond of specifically metal-deuterated catalyst followed by activation of H_2 would lead to alkane-*d* and catalyst containing Rh–H. There is some loss of the Rh–D label after many turnovers (under H_2), and there is a slow loss of the Rh–D label when Rh–D catalyst is equilibrated with alkene in the absence of H_2. However, loss of the label is slow with respect to either hydrogenation of isomerization of the alkene. See ref 4 for details of the mechanism of catalysis.

(6) Jung, C. W.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1980**, *102*, 3024.

(7) Knobler, C. B.; Marder, T. B.; Mizusawa, E. A.; Teller, R. G.; Long, J. A.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.*, third of five papers in this issue.

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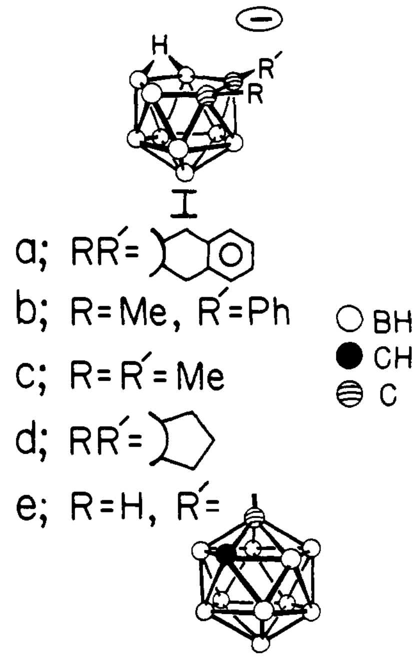

Figure 1. Schematic representations of the structures of the *nido*-carborane anions (Ia–e).

and mechanistic studies of catalysis by *closo*- and *exo-nido*-bis(phosphine)rhodacarborane catalyst precursors are reported in part 6 of this series.[4] In addition, since *exo-nido*-bis(phosphine)rhodacarboranes were believed to be important intermediates in the carborane cage exchange reaction,[8] isolation of these exo-nido complexes permitted a series of kinetic and mechanistic studies of that reaction which are described in part 5 of this series.[9] We have also determined by X-ray diffraction the solid-state structure of two of the new *exo-nido*-bis(phosphine)-rhodacarboranes (IIb and IIIa), [*closo*-1,2-μ-(1',2'-$CH_2C_6H_4CH_2$-)-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_9$] (IIa), the $[(PPh_3)_3Rh]^+$[*nido*-7-R-7,8-$C_2B_9H_{11}$]$^-$ (R = 1'-(*closo*-1',2'-$C_2B_{10}H_{11}$) salt (IVe), and the rearranged [*closo*-1-Me-2,2-$(PEt_3)_2$-2-H-8-Ph-2,1,8-$RhC_2B_9H_9$] (VIb). These structural studies are formally presented and discussed in part 4 of this series.[7] A detailed synthetic and spectroscopic study of the *exo-nido*-bis(phosphine)rhodacarboranes and their reactions with various ligands and small molecules comprises the subject of this contribution.

Results and Discussion

Synthesis and Characterization of *exo-nido*-Phosphinerhodacarboranes. Complex IIa was originally prepared by heating $[(PPh_3)_3RhCl]$ and $[Me_3NH]^+$[*nido*-7,8-μ-(*o*-xylylene)-7,8-$C_2B_9H_{10}$]$^-$ (Ia) in ethanol. As this reaction required ca. 24 h to complete, several undesired side products (e.g., $[(PPh_3)_2RhCl]_2$ and *trans*-$[(PPh_3)_2Rh(CO)Cl]$) were formed as well as the closo complex (IIa). Attempts to prepare other CC'-disubstituted complexes by this route were unsuccessful although closo monosubstituted complexes were easily formed.[1] An alternative route was developed which involved the reaction of Cs^+ or Tl^+ salts of the disubstituted carborane monoanions (I) (Figure 1) with $[(PPh_3)_3RhCl]$ in benzene at room temperature. Since CsCl or TlCl was formed as an insoluble precipitate and no alcohols were present, formation of the side products was eliminated and the phosphinerhodacarboranes were isolated in good yields. The use of small quantities of ethanol to aid in the dissolution of the

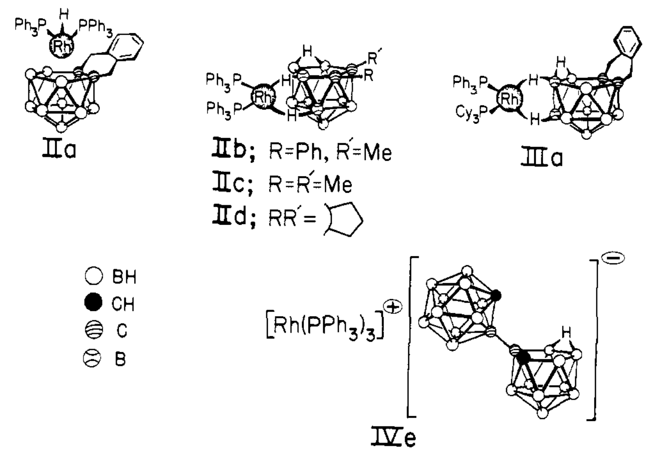

Figure 2. Schematic representations of the structures of the bis(triphenylphosphine)rhodacarborane complexes (IIa–d), the mixed phosphine complex (IIIa), and the $[(PPh_3)_3Rh]^+$[carborane]$^-$ salt (IVe).

carborane anion salts appeared to have little effect on the course of the reactions. Complex IIa was isolated as yellow needles, whereas complexes IIb (R = Ph, R' = Me), IIc (R = R' = Me), and IId (R, R' = μ-$(CH_2)_3$–) were all isolated as red crystals (see Figure 2).

Complexes IIb and IId reacted with PPh_3 and $Me_4N^+Cl^-$ in ethanol at room temperature to yield $[(PPh_3)_3RhCl]$ as a precipitate. Thus, complexes IIb and IId, for example, can be prepared from $[(PPh_3)_3RhCl]$ only by reactions which lead to the formation of an insoluble chloride salt (i.e., TlCl or CsCl) since the metathesis reaction leading to their formation is reversible.

The crystalline complex (IIa) was characterized as a member of the *closo*-bis(phosphine)hydridorhodacarborane series by the presence of a Rh–H stretching band at 2015 cm^{-1} in its IR (mull) spectrum. An X-ray diffraction study, reported elsewhere,[7] confirmed this conclusion and provided additional structural details. Reaction of IIa with 2 equiv of PCy_3 (Cy = cyclohexyl) exchanged one PPh_3 by PCy_3 and produced the red-orange species (IIIa). The compounds IIIa and IIb were the subjects of X-ray diffraction studies which are reported in detail in the following paper of this series.[7] Compounds IIb and IIIa are representative members of a new group of rhodacarboranes which we have classified as exo-nido species. The distinguishing feature associated with rhodacarboranes of this class is the presence of an $[L_2Rh]^+$ (L = phosphine) tightly held to a [*nido*-7,8-$C_2B_9H_{11}$]$^-$ through the agency of a pair of B–H–Rh three-center, two-electron bonds. It will be shown in a later paper[9] that the unsubstituted parent exo-nido species may be observed under special conditions. Since the carborane anion and the rhodium cation retain their formal charges in the exo-nido compounds, these species may be thought of as ion pairs whose Coulombic binding interaction is greatly augmented by the two cis B–H–Rh bridge bonds. We have recently reported[10] the structure of a related iridacarborane complex [*exo-nido*-$(H)_2(PPh_3)_2Ir(C_2B_9H_{12})$] in which the $[Ir(H)_2(PPh_3)_2]^+$ fragment is bonded to the carborane anion through two cis three-center two-electron B–H–Ir bridge linkages. In addition, the structure of the *exo-nido*-aluminacarborane $[Me_2Al(C_2B_9H_{12})]$ was reported in 1971.[11] The Me_2Al moiety present in this species was found to be bound to the edge of the open polyhedral face present in the *nido*-7,8-$C_2B_9H_{12}$ fragment by a pair of three-center two-electron bonds (Al–H–B) which originate from peripheral terminal B–H atoms. The aluminacarborane is fluxional in solution, and both this compound and the iridacarborane may be considered as members of the exo-nido class of metallacarboranes.

Closo–Exo-Nido Tautomerism and the Fluxional Behavior of

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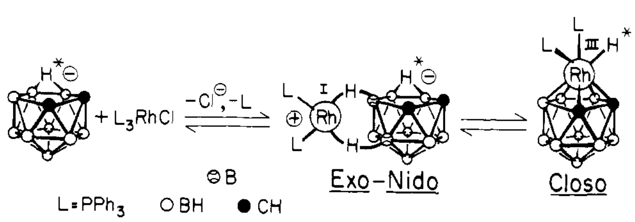
(9) Marder, T. B.; Long, J. A.; Hawthorne, M. F. *J. Am. Chem. Soc.*, fourth of five papers in this issue; "Abstracts of Papers", 181st National Meeting of the American Chemical Society, Atlanta, GA, April 1981; American Chemical Society: Washington, D.C.; INOR 217.

(10) Doi, J. A.; Teller, R. G.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1980**, 80.

(11) Churchill, M. R.; Reis, A. H., Jr.; Young, D. A. T.; Willey, G. R.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1971**, 298.

Exo-Nido Species. Complexes IIb and IId displayed one doublet (J_{Rh-P} = 185 Hz) in the $^{31}P\{^1H\}$ NMR spectrum and no signals attributable to a terminal metal hydride in the ^1H NMR or IR spectra. However, a broad resonance at ca. −2.5 ppm in the ^1H NMR spectra indicated the presence of a B–H–B bridge. A broad peak at ca. 2050 cm^{-1} in the IR spectra was tentatively assigned to M–H–B bridges, but could possibly be due to the B–H–B bridge (vide infra). Thus, in the cases of complexes IIb and IId only the exo-nido isomer was observed in solution or in the solid state. Complexes (IIa and IIc) however, displayed two doublets in the $^{31}P\{^1H\}$ NMR spectra (recorded in THF/C_6D_6 ca. 10:1) and both metal hydride and B–H–B resonances in the ^1H NMR spectra. In these two cases the larger of the two doublets in the $^{31}P\{^1H\}$ NMR spectra had similar chemical shifts and Rh–P coupling constants to those of IIb and IId and thus originated from the exo-nido tautomer. The smaller doublet (J_{Rh-P} = 144 Hz) must then be attributed to the corresponding closo species containing a $(PPh_3)_2Rh(H)$ vertex. Although complexes IIa and IIc showed an equilibrium mixture of closo and exo-nido tautomers in solution, IIa was isolated as the crystalline closo complex whereas IIc was isolated as the crystaline exo-nido complex.

The reversible formation of highly substituted *exo-nido*-phosphinerhodacarboranes from $(PPh_3)_3RhCl$ and [*nido*-7,8-disubstituted-7,8-$C_2B_9H_{10}$] anions coupled with the observation of closo–exo-nido equilibria suggests that the reaction scheme shown below is general for all phosphinerhodacarboranes derived from the isomeric *nido*-$C_2B_9H_{12}^-$ ions and their substituted derivatives.



The closo–exo-nido tautomerism reported here may be formally viewed as a reversible oxidative addition–reductive elimination equilibrium in which the 12-e^- $(PPh_3)_2Rh^+$ moiety oxidatively adds the B–H–B bridge system of the *nido*-carborane anion accompanied by η^5 bonding to the open face of the anion.

Previously reported observations[1] proved that the B–H–B bridge hydrogen atom present in the carborane anion is specifically transferred to the $(PPh_3)_2Rh$ moiety to produce the *closo*-$(PPh_3)_2RhH$ vertex. Similar experiments with B–D–B bridge-deuterated 7,8-disubstituted-7,8-$C_2B_9H_9D^-$ ions and $(PPh_3)_3RhCl$ produced the exo-nido tautomer with scrambling of the bridge deuterium in the exo-nido product. This result prevailed under a wide variety of experimental conditions and specifically B–D–B bridge-deuterated 7,8-disubstituted exo-nido species are not available for further study. This failure to observe regiospecific retention of B–D–B in the conversion of the carborane anion to the stabiized exo-nido species may reflect the presence of a rapid B–D–B/terminal B–H scrambling mechanism which is only important in the cases of sterically encumbered carborane anion systems. Such scrambling is not a rapid process in the case of the unsubstituted [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] even though it will be shown[4,9] later that a closo–exo-nido equilibrium of the same type plays a vital role in the overall chemistry of this compound. As expected, the closo–exo-nido equilibria reported here are both solvent and temperature dependent. Thus, complex IIc showed only peaks due to the exo-nido tautomer in C_6H_6/C_6D_6 (ca. 10:1) in the $^{31}P\{^1H\}$ NMR spectrum (compare with THF/C_6D_6 above) and the ratio of exo-nido to closo (IIa) was larger in benzene than in THF/C_6D_6 mixtures. Interconversion between tautomers appears to be slow on the NMR time scale. However, above room temperature, the exo-nido–closo equilibrium ratio for IIa, in benzene solution, increased with increasing temperature.

The exo-nido tautomers exhibited interesting behavior in their ^1H NMR spectra in the B–H–B and Rh–H–B bridging region (ca. −2 to −8 ppm). The B–H–B resonance, in general, sharpened with decreasing temperature, presumably due to thermal decoupling of the boron atoms.[12] There appears to be a dynamic process that serves to exchange the terminal B–H hydrogens with the Rh–H–B hydrogens. For example, complex IId displayed a broad quartet at ca. −4 ppm at 42 °C in addition to the broad doublet at −2.5 ppm assigned to the B–H–B bridge proton (see Figure 3).

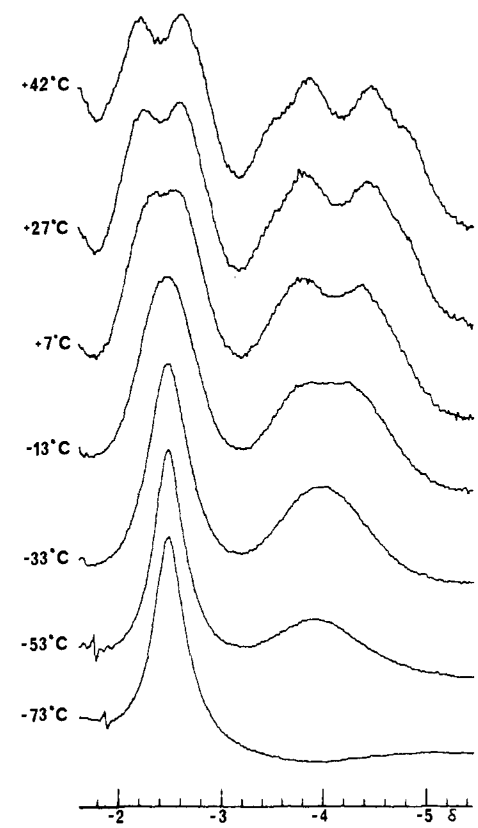


Figure 3. Variable-temperature ^1H NMR spectra of complex IId in THF-d_8. The B–H–B/Rh–H–B bridge region upfield from 0 ppm is displayed.

This resonance at −4 ppm appears to be due to a rapid exchange between M–H–B and terminal B–H hydrogens. Cooling the sample to −73 °C resulted in the expected sharpening of the B–H–B resonance as well as the disappearance of the resonance at −4 ppm into the base line.

The mixed PPh_3, PCy_3 exo-nido complex (IIIa) apparently has a larger barrier to the dynamic process described above. Thus at room temperature, the ^1H NMR spectrum of IIIa (see Figure 4) displayed broad resonances due to both B–H–B (−2.8 ppm) and exchanging M–H–B/B–H (−4.5 ppm) hydrogens. Upon cooling, the B–H–B resonance sharpened and then finally broadened into two peaks at −88 °C. It would appear that exchange between two preferred rotational isomers of the $[(PPh_3)(PCy_3)Rh]$ fragment (with respect to the carborane cage) was relatively slow on the NMR time scale at this temperature. In addition, the broad resonance at ca. −4.5 ppm broadened further with decreasing temperature and disappeared into the base line upon cooling to −33 °C. Further cooling to −88 °C produced a fairly sharp resonance at −7.0 ppm indicative of a relatively slow exchange between M–H–B and terminal B–H hydrogens since this signal is in the proper position for a "static" Rh–H–B hydrogen.[13-16]

(12) Beall, H.; Bushweller, C. H. *Chem. Rev.* **1973**, *73*, 465 and references contained therein.
(13) Baker, R. T.; King, R. E., III; Knobler, C. B.; O'Con, C. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1978**, *100*, 8266; **1979**, *101*, 1908 correction.
(14) Sneddon, L. G.; Grimes, R. N. *J. Am. Chem. Soc.* **1973**, *95*, 6623.
(15) Jones, C. J.; Francis, J. N.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 7633.
(16) Callahan, K. P.; Lo, F. Y.; Strouse, C. E.; Sims, A. L.; Hawthorne, M. F. *Inorg. Chem.* **1974**, *13*, 2842.

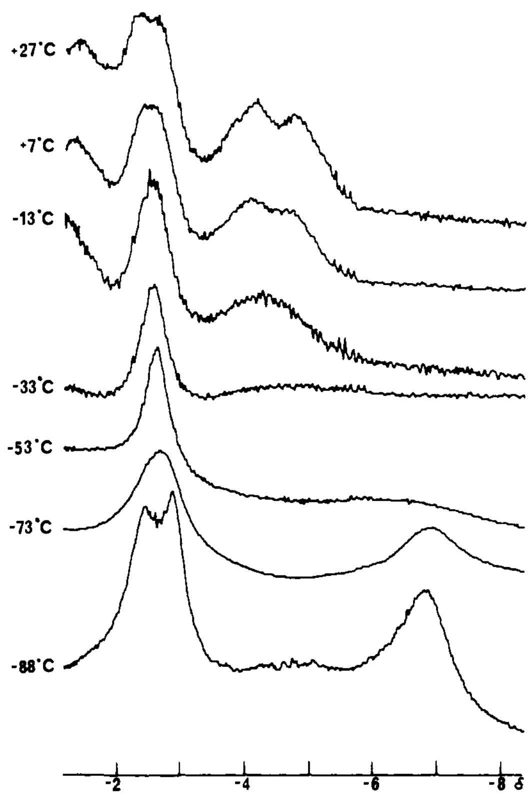


Figure 4. Variable-temperature ^1H NMR spectra of complex IIIa in CD_2Cl_2. The B–H–B/Rh–H–B bridge region upfield from 0 ppm is displayed.

We are thus far unable to determine the exact nature of this fluxional process. The ^{11}B and $^{11}B\{^1H\}$ NMR spectra of these compounds (even at 127 MHz) are all broad[12] and unresolved and are of no value in the assignment of the B–H groups involved. It has also proven impossible to assign the ^1H NMR resonances attributable to the terminal B–H protons in these complexes since the spectra often consist of large envelopes of broad overlapping peaks even at very high field strengths. However, the following points should be emphasized. The observation of a unique doublet in the $^{31}P\{^1H\}$ NMR spectra of the *exo-nido*-bis(triphenylphosphine)rhodacarboranes combined with the aforementioned observations in the ^1H NMR spectra minimally implies that the $[(PPh_3)_2Rh]$ fragment must rotate rapidly on the NMR time scale even at very low temperatures. The fluxional process appears to involve more than a simple rotation, however, and we believe that the $[L_2Rh]$ fragment may wander about a substantial number of sites on the polyhedral surface of the carborane cage. This hypothesis is supported by the fact that only one methyl resonance is observed (in the ^1H NMR spectrum) for the 7,8-Me_2 substituents on the exo-nido tautomer of complex IIc. Likewise, pseudo mirror symmetry is suggested by the pattern of resonances attributed to the cage-carbon substituents in symmetrically disubstituted complexes (IIa,d and IIIa). It is, of course, possible that additional substituent resonances were coincidentally overlapped with those observed or otherwise simply unresolved, but this seems unlikely.

Unexpectedly, the metal hydride resonance observed in the ^1H NMR spectra of the closo tautomers of IIa and IIc were triplets. Single-frequency ^{31}P decoupling studies collapsed these resonances to singlets (full width at half-height = 15 Hz). Thus, although coupling to two equivalent phosphorus atoms was observed ($^2J_{P-H}$ = 30 Hz), coupling to the ^{103}Rh ($I = {}^1/_2$) was apparently not resolved due to the inherent line width of the peak. We believe that this broadening may be due to partial coupling of the hydride to a boron atom on the pentagonal bonding face of the carborane cage trans to the hydride ligand. Consistent with this hypothesis, the crystal structure of complex IIa[7] demonstrated that in the solid state, the metal hydride lies over the C–C bond of the carborane ligand in a symmetric conformation which places it trans to the central boron atom on the C_2B_3 face of the cage. It would also appear that the barrier to metal vertex rotation with respect to the cage face is quite large.[17] Lowering the temperature has been shown to be an effective procedure for decoupling boron,[12] and thus it was expected that the Rh–H coupling might be observed at low temperature. This did not prove to be effective for either IIa or IIc although small Rh–H coupling constants were observed for two analogous triethylphosphine complexes (VIIc and VIId) (vide infra).

Reactions of *exo-nido*-Phosphinerhodacarboranes with Phosphines. In an attempt to prepare a novel exo-nido derivative having an icosahedral carborane substituent, $[(PPh_3)_3RhCl]$ was reacted with Tl^+ $\{nido\text{-}7\text{-}[1'\text{-}(closo\text{-}1',2'\text{-}C_2B_{10}H_{11})]\text{-}7,8\text{-}C_2B_9H_{11}\}^-$ in benzene. The product, isolated as red crystals, exhibited IR and ^1H NMR spectra similar to previously prepared *exo-nido*-phosphinerhodacarboranes, but was shown by elemental analysis and $^{31}P\{^1H\}$ NMR spectroscopy to contain three triphenylphosphine ligands per molecule. The new species, formulated as $[Rh(PPh_3)_3]^+\{7\text{-}[(1'\text{-}(closo\text{-}1',2'\text{-}C_2B_{10}H_{11})]\text{-}7,8\text{-}C_2B_9H_{11}\}^-$ (IVe), showed a broad doublet (J_{Rh-P} = 186 Hz) centered at 43.7 ppm and broad resonances at 35.3 and −5.7 ppm (free PPh_3) in the $^{31}P\{^1H\}$ NMR (10% C_6D_6/THF, 27 °C). At −73 °C, in the same solvent system, the $^{31}P\{^1H\}$ NMR spectrum exhibited resonances characteristic of two distinct $[Rh(PPh_3)_3]$ fragments. Occupation of the fourth coordination site of rhodium by either solvent or a carborane anion (hence two species) makes the phosphine ligands inequivalent. Thus, the phosphine trans to the fourth coordination site gives rise to a doublet of triplets (J_{Rh-P} = 195 Hz; $^2J_{P-P}$ = 40 Hz) due to coupling to ^{103}Rh and two equivalent cis phosphine ligands. Similarly, phosphines cis to the fourth coordination site give rise to a doublet of doublets (J_{Rh-P} = 145 Hz; $^2J_{P-P}$ = 40 Hz). Assignment of the two sets of resonances was based on the observation that below −73 °C, the doublet of doublets centered at 29.1 ppm broadened appreciably. This was interpreted as a consequence of hindered rotation of the $[Rh(PPh_3)_3]^+$ fragment with respect to the asymmetric carborane anion rendering the two cis phosphine ligands inequivalent. Consequently, the upfield set of resonances (50.1; 29.1 ppm) are assigned to the carborane anion bound $[Rh(PPh_3)_3]$ fragment and the downfield set (51.3; 32.0 ppm) are assigned to the solvent bound $[Rh(PPh_3)_3(THF)]^+$ ion.

In order to further elucidate the nature of these interactions, the known *exo-nido*-bis(triphenylphosphine)rhodacarboranes (IIb–d) and the closo complex (IIa) were reacted with excess triphenylphosphine and their variable-temperature $^{31}P\{^1H\}$ NMR spectra were recorded. Of interest is the observation that the less sterically hindered exo-nido complexes (IIc and IId) and the closo complex (IIa) in the presence of excess triphenylphosphine exhibited resonances due to both types of $[Rh(PPh_3)_3X]$ species (X = solvent or carborane anion) whereas the most sterically hindered exo-nido complex (IIb) exhibited only resonances due to $[Rh(PPh_3)_3(THF)]^+$ in the low-temperature $^{31}P\{^1H\}$ NMR spectra. At low temperatures, complexes IIa and IId exhibited an additional doublet at 31 ppm (J_{Rh-P} = 134 Hz) when reacted with 2 equiv of PPh_3 in 10% C_6D_6/THF (see Figure 5). In CH_2Cl_2/CD_2Cl_2 mixtures, complexes IIb–d and IVe reacted with 2–3 equiv of PPh_3 at −88 °C to display only the doublet at 31 ppm (J_{Rh-P} = 134 Hz) (see Figure 6). At intermediate temperatures, a broad doublet of doublets at 29.9 ppm (J_{Rh-P} = 134 Hz; $^2J_{P-P}$ = 32 Hz) and a broad doublet of triplets at 48.5 ppm (J_{Rh-P} = 244 Hz; $^2J_{P-P}$ = 32 Hz) were observed. There are several structures that could produce the latter pattern. However, as it appears impossible to confirm the exact nature of this species one can only propose likely candidates. It is most probable that the T-shape of the $[Rh(PPh_3)_3]$ fragment is maintained with two equivalent trans phosphines. The unusually large Rh–P coupling constant (244 Hz) for the unique phosphorus atom is probably due to the absence of a strong interaction with a trans ligand.[18] If the complex is

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

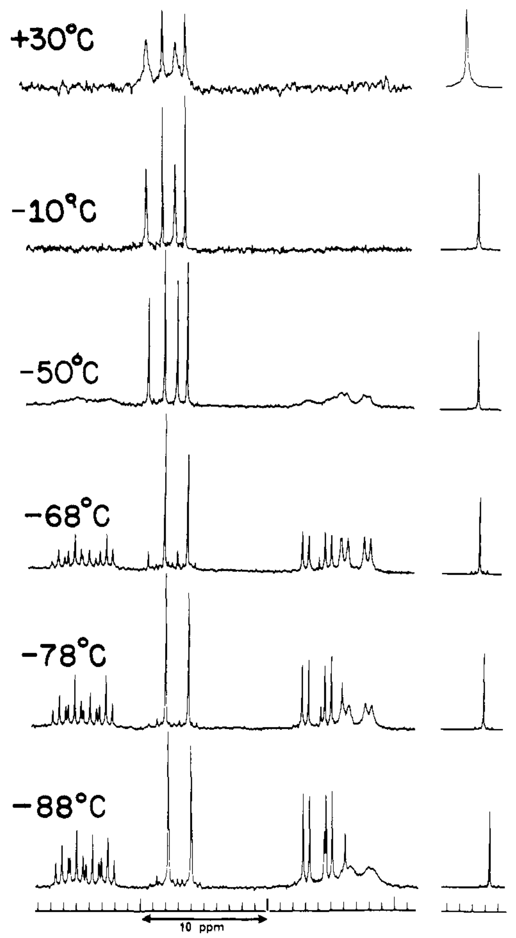


Figure 5. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of complex IIa in the presence of 2 molar equiv of PPh_3 in 10% C_6D_6/THF.

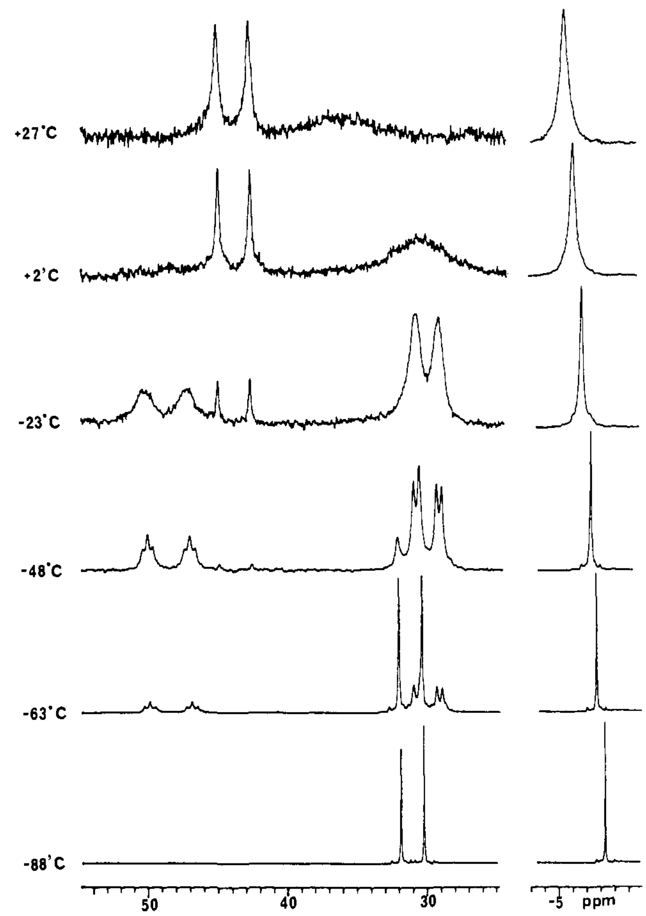


Figure 6. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of complex IIb in the presence of 2 molar equiv of PPh_3 in 10% CD_2Cl_2/CH_2Cl_2.

indeed square planar, any ligand trans to the unique phosphorus must be weakly bound, at best. Thus, either the carborane anion cage is coordinated weakly through a single terminal B–H group, the complex exists as a tight ion pair, or this coordination site is occupied by a dichloromethane molecule. Alternatively, the complex could be trigonal bipyramidal in which the two equivalent phosphines would be axial ligands and the unique phosphine and the carborane anion cage (coordinated through two B–H groups) would occupy equatorial sites. A rapid rotation of the $[Rh(PPh_3)_3]$ fragment with respect to the carborane anion cage or a migration of the rhodium about the polytopal surface of the carborane anion cage (similar to that observed with the $[Rh(PPh_3)_2]$ exo-nido species) would make the two mutually trans phosphine ligands equivalent on the NMR time scale. It seems unlikely that the $[Rh(PPh_3)_3]^+$ fragment exists as a free cation since a facile fluxional process would probably make all the phosphine ligands equivalent on the NMR time scale. Complex IVe in CH_2Cl_2/CD_2Cl_2 displayed only the expected doublet of doublets and doublet of triplets at −88 °C in the absence of added PPh_3. The doublet at 31 ppm, observed at low temperature in the presence of excess PPh_3, can be assigned to a $[Rh(PPh_3)_4]^+$ cation since all of the ligands are equivalent and it is only formed when the molar ratio of total PPh_3 to Rh is ≥4. Additionally, the $^{31}P\{^1H\}$ NMR spectrum of IVe in acetone was identical with that of $[Rh(PPh_3)_3(Me_2CO)]^+[ClO_4]^-$ in acetone,[19] confirming complete dissociation from the carborane anion cage. Unfortunately, the lack of solubility of $[Rh(PPh_3)_3]^+[ClO_4]^-$ in either THF or CH_2Cl_2 precluded further comparison. Additional resonances attributable to closo species were observed in those compounds (IIa and IIc) which exhibit a closo–exo-nido tautomerism in these solvents. Thus, the closo–exo-nido tautomerism is extremely slow at low temperature relative to the conversion of the exo-nido tautomers of IIa and IIc to other species.

In order to elucidate possibly bonding interactions between the $[Rh(PPh_3)_3]$ and carborane fragments, an X-ray crystallographic study of complex IVe was undertaken. The detailed results of this structural study are described in an accompanying manuscript.[7] However, the structure was only sufficiently refined to demonstrate that the environment of the rhodium is identical with that in a previously published structure of the unsolvated $[Rh(PPh_3)_3]^+[ClO_4]^-$ complex.[20]

Complexes IIa–d and IVe all reacted rapidly with excess PEt_3 to give $[(PEt_3)_4Rh]^+[cage]^-$ salts in quantitative yield as shown by $^{31}P\{^1H\}$ NMR spectroscopy (d, 8.3 ppm, J_{Rh-P} = 135 Hz). In addition, the $^{11}B\{^1H\}$ NMR spectra of these salts were identical with those of the respective carborane anions. Two of these salts, namely Vb and Vd derived from IIb and IId, respectively, have been isolated as crystalline solids, although they lose significant amounts of PEt_3 in the solid state over a 2-day period. When a sealed NMR tube containing complex Vb in 10% C_6D_6/THF was heated to 60 °C for several hours closo complex VIb was formed as well as free PEt_3. Integration of the $^{31}P\{^1H\}$ NMR spectrum at −73 °C[21] gave equal areas for complex VIb and the free PEt_3. Since complex VIb was shown to be a *closo*-bis(phosphine)-hydridorhodacarborane (vide infra), it was clear that Vb was an $[L_4Rh]^+[cage]^-$ salt. Analogous complexes (Va,c–e) could be

(18) For example, in the trigonal-bipyramidal complex $[Rh\{P(OMe)_3\}_5]$-BPh_4 the equatorial phosphite ligands show a significantly larger Rh–P coupling constant (J_{Rh-P} = 206 Hz) than the axial ones (J_{Rh-P} = 143 Hz). The equatorial ligands are not trans to a filled coordination site. Meakin, P.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 7272.

(19) The $^{31}P\{^1H\}$ NMR spectrum was recorded in this laboratory on a sample prepared by the literature procedure (ref 20).

(20) Yared, Y. W.; Miles, S. L.; Bau, R.; Reed, C. *J. Am. Chem. Soc.* **1977**, *99*, 7076.

(21) A relaxation delay (RD) of 5 s was used.

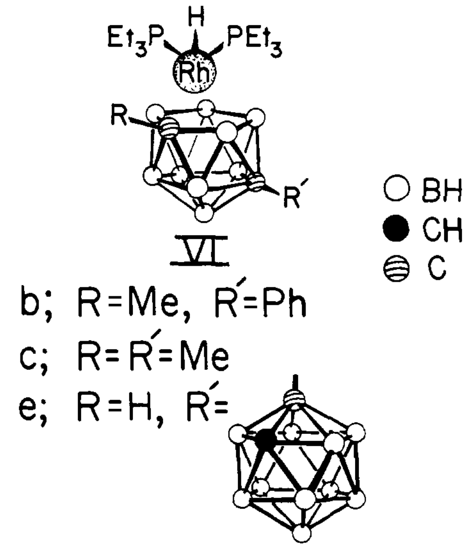


Figure 7. Schematic representation of the strucures of the rearranged *closo*-2,1,8-[$(PEt_3)_2Rh(H)$(carborane)] complexes (VIb,c,e).

converted to *closo*-bis(triethylphosphine)hydridorhodacarboranes in the same manner.

An examination of the $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of these closo complexes revealed two distinct structural classes. Complexes VIIa,c,d were shown by ^1H, $^{31}P\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectroscopy to be [*closo*-1-R-2-R′-3,3-$(PEt_3)_2$-3-H-3,1,2-$RhC_2B_9H_9$] carborane complexes. As discussed previously with respect to complexes IIa and IIc, the rhodium hydride resonance in the ^1H NMR spectra of complexes VIIa,c,d consisted of a triplet at room temperature ($^2J_{Rh-P}$ = 30 Hz) where the Rh–H coupling was unresolved. However, cooling VIIc,d to ca. −75 °C effected sufficient thermal decoupling of the boron nucleus *trans* to the metal hydride to allow Rh–H coupling to be observed (J_{Rh-H} = 6 Hz).[22] The Rh–H coupling was not resolved for VIIa even at −75 °C. Complexes VIb,e were believed to result from a polytopal migration of a carbon vertex in the carborane cage. Subsequently, it was found that complex VIIc, when heated to 60 °C in 10% C_6D_6/THF in a sealed NMR tube, would slowly rearrange in a similar fashion to give VIc. Analogous PPh_3 complexes have also been isolated from the rearrangement of [*closo*-1-R-3,3-$(PPh_3)_2$-3-H-3,1,2-$MC_2B_9H_{10}$] (M = Rh, R = *n*-Bu;[23] M = Ir, R = Ph, Me, 1-(*closo*-1,2-$C_2B_{10}H_{11}$][24,25]). The variable-temperature $^{31}P\{^1H\}$ NMR spectra of the rearranged closo complex (VIb) in 10% C_6D_6/THF exhibited marked second-order effects, although at −103 °C, the spectrum is virtually first order, with cis P–P coupling of 26 Hz clearly discernible. When the sample was warmed, the peaks broadened until at room temperature only three broad overlapping resonances were observed. Although simulation of the spectra was not undertaken, the dynamic behavior of the complex appears to be in accord with a simple hindered rotation of the [RhL_2H] fragment with respect to the pentagonal bonding face of the carborane cage.[17] When complexes VIIa,d, containing linked carborane carbon atoms, were heated to 60 °C in 10% C_6D_6/THF in sealed NMR tubes for ca. 6 weeks, there was no evidence of rearranged species in the $^{31}P\{^1H\}$ NMR spectra. Furthermore, there appeared to be no decomposition of either VIIa or VIId. Thus, it seemed likely that the carborane carbon atoms in the rearranged closo complexes were no longer adjacent. A comparison of the ^1H and $^{31}P\{^1H\}$ NMR spectra with those of [*closo*-1-R-2,2-$(PPh_3)_2$-2-H-2,1,7-$RhC_2B_9H_{10}$] (R = Me, Ph)[1] clearly demonstrated that the new complexes were not 1-R,7-R′ isomers, and thus it appeared that one of the carbon vertices had migrated away from both the other carbon vertex and the rhodium vertex to produce a new 2,1,8 series of isomers (Figure 7). This hypothesis was confirmed by an X-ray crystallographic study of complex VIb,[7] [*closo*-1-Me-2,2-$(PEt_3)_2$-2-H-8-Ph-2,1,8-$RhC_2B_9H_9$].

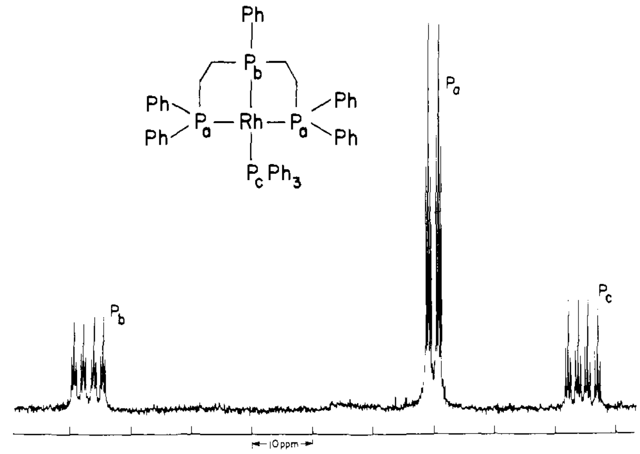


Figure 8. $^{31}P\{^1H\}$ NMR spectrum of the [(triphos)$(PPh_3)Rh]^+$ cation (VIII) in 10% C_6D_6/THF at −73 °C.

Complex IIa reacted with triphos [$(Ph_2PCH_2CH_2)_2PPh$] in 10% C_6D_6/THF in a sealed NMR tube to quantitatively yield [(triphos)$Rh(PPh_3)]^+$[*nido*-7,8-*μ*-(*o*-xylylene)-7,8-$C_2B_9H_{10}]^-$ (VIII) as determined by $^{31}P\{^1H\}$ NMR spectroscopy. Free PPh_3 was the only additional product of the reaction. The same cation could be generated by the analogous reaction of complex IVe, with triphos and an identical $^{31}P\{^1H\}$ NMR spectrum was obtained. (See Figure 8 for the $^{31}P\{^1H\}$ NMR spectrum of VIII.) The spectrum was assigned on the basis of chemical shift patterns of chelated phosphines as well as upon the basis of phosphorus–phosphorus coupling constants.[26] P_a appears as a doublet of triplets at 46.3 ppm (J_{Rh-P_a} = 141 Hz, $^2J_{P_b-P_a} = {}^2J_{P_c-P_a}$ = 31 Hz), P_b appears as a doublet of doublet of triplets at 103.3 ppm (J_{Rh-P_b} = 122 Hz, $^2J_{P_c-P_b}$ = 259 Hz, $^2J_{P_a-P_b}$ = 31 Hz), and P_c appears as a doublet of doublet of triplets at 21.7 ppm (J_{Rh-P_c} = 133 Hz, $^2J_{P_a-P_c}$ = 31 Hz, $^2J_{P_b-P_c}$ = 259 Hz). The ^{11}B NMR spectra of these salts are identical with those of various other non-transition-metal salts of the respective carborane anions.

Meek and co-workers have reported several studies[27-30] of rhodium complexes of the analogous tris-chelating phosphine $(Ph_2PCH_2CH_2CH_2)_2PPh$ (ttp), including the structure of the complex [Rh(ttp)$(PEt_3)]^+$.[30] They reported[27,28] difficulty in preparing monomeric complexes of the triphos ligand which contains one less methylene unit on each arm. However, King et al. reported[31] numerous complexes of triphos including the complexes [(triphos)RhCl] and [(triphos)$RhCl_3$].

When complex IId was reacted with 2 equiv of dppe ($Ph_2PCH_2CH_2PPh_2$) in 10% C_6D_6/THF in a sealed NMR tube the $^{31}P\{^1H\}$ NMR spectrum displayed two doublets at 57.0 (J_{Rh-P} = 132 Hz) and 64.6 ppm (J_{Rh-P} = 137 Hz) due to complexes IXd and Xd, respectively, and a singlet due to free PPh_3. However, reaction of complex IIb with 3 equiv of dppe in THF at room temperature followed by addition of heptane resulted in the isolation of a new complex (IXb) as yellow crystals in virtually quantitative yield. This complex displayed only one doublet at

(22) Preliminary $^1H\{^{11}B\}$ NMR spectra at 395 MHz substantiate the hypothesis that the source of the broadening is coupling to ^{11}B.

(23) Delaney, M. S. Ph.D. Dissertation, University of California, Los Angeles, 1980.
(24) Doi, J. A.; Mizusawa, E. A.; Hawthorne, M. F., unpublished results.
(25) Doi, J. A. Ph.D. Dissertation, University of California, Los Angeles, 1980.
(26) Pregosin, P. S.; Kunz, R. W. "^{31}P and ^{13}C NMR Spectra of Transition Metal Phosphine Complexes"; Springer-Verlag: Berlin, 1979.
(27) Nappier, T. E., Jr.; Meek, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 306.
(28) Nappier, T. E., Jr.; Meek, D. W.; Kirchner, R. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 4194.
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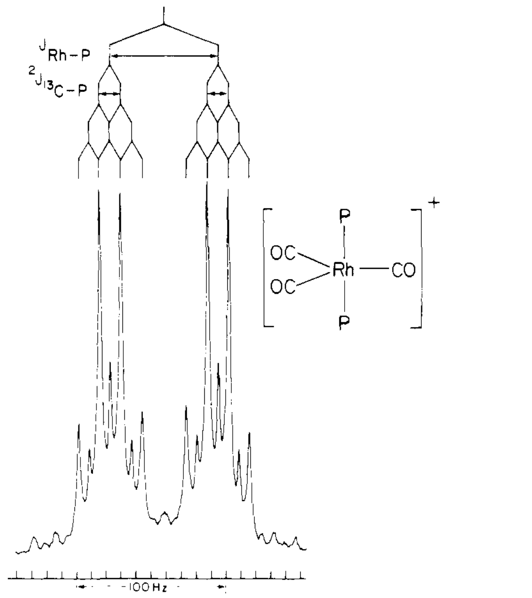

Figure 9. $^{31}P\{^1H\}$ NMR spectrum of complex IId in the presence of excess ca. 91% ^{13}C-enriched CO in 10% C_6D_6/THF at −78 °C.

57.0 ppm (J_{Rh-P} = 132 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. ^1H NMR spectroscopy revealed the presence of coordinated dppe as well as a resonance due to a B–H–B bridge proton. The ^{11}B NMR spectrum was identical with that of the carborane anion (Ib), and no metal hydride stretch was visible in the IR spectrum. Therefore it seemed likely that this species was $[(dppe)_2Rh]^+[$*nido*-7-Me-8-Ph-7,8-$C_2B_9H_{10}]^-$, and this hypothesis was confirmed by elemental analysis. Thus, an analogous complex (IXd) was formed in the in situ reaction of IId with dppe as well as a species which appears to be [*closo*-1,2-μ-$(CH_2)_3$-3,3-DPPE-3-H-3,1,2-$RhC_2B_9H_9$] (Xd) as shown by the observation of a Rh–H stretch at 1945 cm^{-1} in the IR spectrum (Nujol mull) and a metal hydride resonance at −8.81 ppm, doublet of triplets (J_{Rh-H} = 4 Hz, $^2J_{P-H}$ = 13 Hz) in the ^1H NMR spectrum of an isolated sample of a mixture of IXd and Xd. Salts of the $[(dppe)_2Rh]^+$ cation are known,[32-36] and indeed, the crystal structure of the $[ClO_4]^-$ salt has been reported.[35] Our ^{31}P NMR data are consistent with a literature report for the chloride salt.[36]

Reactions of *exo-nido*-Phosphinerhodacarboranes with Carbon Monoxide. Complexes IIa–d all reacted instantaneously with carbon monoxide in 10% C_6D_6/THF to yield yellow solutions of complexes XIa–d, respectively. Although pale yellow crystals could be isolated from CO-saturated solvents, removal of the CO atmosphere led to loss of coordinated CO and produced a mixture of products which was difficult to characterize. When the reaction was performed in NMR tubes with excess CO, the low-temperature $^{31}P\{^1H\}$ NMR spectra exhibited a doublet at 32.2 ppm (J_{Rh-P} = 72 Hz). As the temperature was raised from −63 °C the peaks broadened and at room temperature one broad resonance was observed. No free PPh_3 was observed at any temperature, and this suggested that CO exchange gave rise to the observed dynamic behavior. Additional $^{31}P\{^1H\}$ NMR spectra of IIb and IId at −78 °C in the presence of ca. 91% ^{13}C-enriched CO exhibited a doublet of quartets and a less intense doublet of triplets both centered at 32.2 ppm (J_{Rh-P} = 72, $^2J_{C-P}$ = 15 Hz) (see Figure 9). A trigonal-bipyramidal $[(PPh_3)_2(CO)_3Rh]^+$ cation with trans PPh_3 groups would account for the observed spectra. Thus, coupling of the equivalent phosphorus atoms to three equivalent CO groups (probability = 75%)[37] would give rise to the quartets, and coupling to two ^{13}CO groups (probability = 22%) would account for the observed triplets. Consistent with this hypothesis, the $^{13}C\{^1H\}$ NMR spectrum of IId, in the presence of ca. 91% ^{13}C-enriched CO at −63 °C, exhibited a doublet of triplets at 186.6 ppm (J_{Rh-C} = 67 Hz, $^2J_{P-C}$ = 15 Hz) as shown in Figure 10. Schrock and Osborn reported[38] the preparation of salts of the $[(PPh_3)_2(CO)_3Rh]^+$ cation and, in keeping with our observations, they found that this cation rapidly dissociates CO in solution. The Fourier transform IR spectra of CO-saturated CH_2Cl_2 solutions of complexes XIb,d exhibited one carbonyl absorption at 2029 cm^{-1}, consistent with D_{3h} symmetry. Schrock and Osborn were unable to obtain satisfactory IR spectra in solution but reported[38] two carbonyl absorptions at 2037 and 2023 cm^{-1} in the mull spectrum, which they attributed to cation–anion interactions in the crystal.

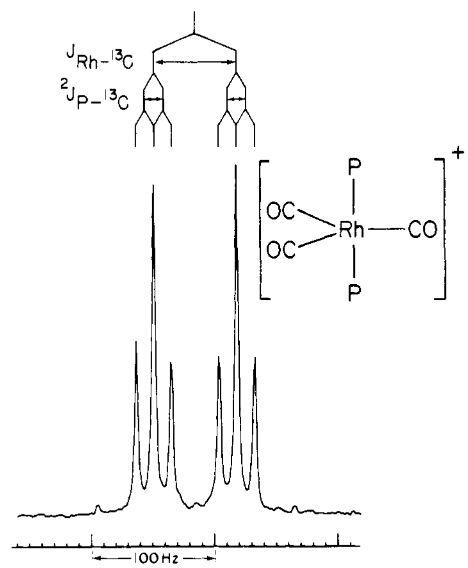

Figure 10. $^{13}C\{^1H\}$ NMR spectrum of complex IId in the presence of excess ca. 91% ^{13}C-enriched CO in 10% C_6D_6/THF at −63 °C.

The ^{11}B NMR spectra of complexes XIa–d were identical with those of the respective carborane anions from which the starting complexes were derived. The ^1H NMR spectra exhibited resonances due to coordinated PPh_3, substituents on the carborane anion cage, and a B–H–B bridging proton. Occasionally, a weak doublet of doublets was observed in the metal hydride region (e.g., for the complex derived from IId this signal appears at ca. −8.43 ppm, J_{Rh-H} = $^2J_{P-H}$ = 25 Hz). We attribute this resonance to the presence of trace quantities of [*closo*-3-PPh_3-3-CO-3H-3,1,2-$RhC_2B_9H_9RR'$] (R, R′ = μ-$(CH_2)_3$–).

Reactions of *exo-nido*-Phosphinerhodacarboranes with Dihydrogen. The exo-nido species derived from complexes IIa–d and IIIa all bind molecular hydrogen at 1 atm and room temperature in CD_2Cl_2, although the equilibrium constant for dihydride formation is small. The ^1H NMR spectra obtained under these conditions typically display a broad hydride signal in the region of ca. −16 ppm. Cooling a sample of IIb which had been exposed to H_2 at ambient conditions to −103 °C resulted in the observation of two broad hydride resonances at −15.14 and −15.67 ppm, as well as a broad resonance at −4.37 ppm, indicative of Rh–H–B bridging hydrogens. Complexes IIa,c,d, under an H_2 atmosphere, exhibited three broad and partially overlapped rhodium hydride resonances at low temperature in the ^1H NMR spectrum (e.g., for IIa, broad peaks were observed at −15.3, −15.9, and −16.7 ppm). Complex IIIa, however, displayed a sharp metal

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(33) Mague, J. T.; Mitchner, J. P. *Inorg. Chem.* **1969**, *8*, 119.
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(36) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 120. Note: Sanger's ^{31}P chemical shifts are referenced to the upfield side of P_4O_6 whereas the chemical shifts given here are reported downfield from 85% H_3PO_4 (ref 17). P_4O_6 resonates 112.5 ppm lower in field than 85% H_3PO_4 (ref 47).

(37) The probability that all three CO ligands contain ^{13}C is $0.91^3 = 0.75$ and the probability that exactly two of the CO ligands are ^{13}CO is $3 \times (0.91)^2 \times 0.09 = 0.22$.
(38) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397.

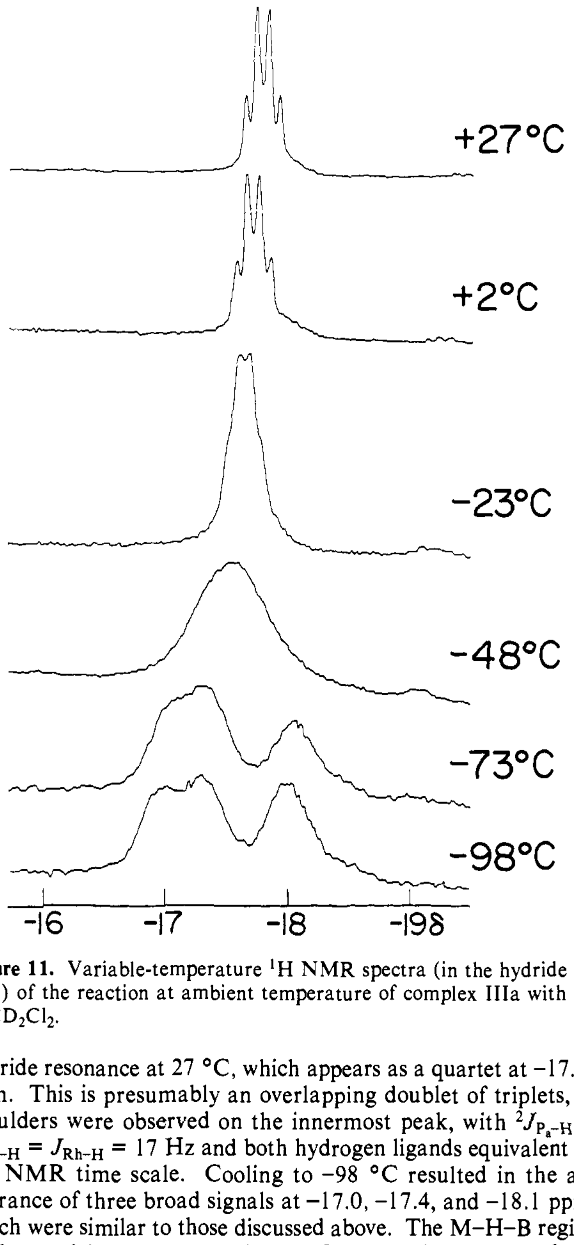

Figure 11. Variable-temperature ^{1}H NMR spectra (in the hydride region) of the reaction at ambient temperature of complex IIIa with H_2 in CD_2Cl_2.

hydride resonance at 27 °C, which appears as a quartet at −17.87 ppm. This is presumably an overlapping doublet of triplets, as shoulders were observed on the innermost peak, with $^2J_{P_a-H}$ = $^2J_{P_b-H}$ = J_{Rh-H} = 17 Hz and both hydrogen ligands equivalent on the NMR time scale. Cooling to −98 °C resulted in the appearance of three broad signals at −17.0, −17.4, and −18.1 ppm, which were similar to those discussed above. The M–H–B region is obscured by resonances due to IIIa as well as those of the product. (See Figure 11 for the variable-temperature ^{1}H NMR spectra of IIIa + H_2 in CD_2Cl_2.) The ^{31}P{^{1}H} NMR spectra of the reactions of IIb–d with H_2 in 10% C_6D_6/THF displayed only resonances due to starting material at 27 °C. At low temperature, the doublet due to starting material broadened considerably with the appearance of a new doublet at ca. 43 ppm (J_{Rh-P} = 120 Hz) (e.g., complex IId gave rise to a doublet at 43.4 ppm, J_{Rh-P} = 120 Hz, at −98 °C, in addition to resonances due to trace quantities of other species). Complex IIIa, when reacted with H_2 in 10% C_6D_6/THF, displayed a pair of doublets of doublets at 54.6 (J_{Rh-P} = 110 Hz, $^2J_{P-P}$ = 366 Hz) and 33.7 ppm (J_{Rh-P} = 110 Hz, $^2J_{P-P}$ = 366 Hz) and a doublet of significantly lower intensity at 47.0 ppm (J_{Rh-P} = 107 Hz), as well as intense resonances due to starting material in the ^{31}P{^{1}H} NMR spectrum at 27 °C. The large value of $^2J_{P-P}$ for the species giving rise to the two doublets of doublets is consistent with a mutually trans arrangement of the two phosphine ligands. The doublet of lower intensity may be due to traces of a monophosphine dihydrido species, although a $(PCy_3)_2(H)_2Rh$ species, formed by disproportionation, cannot be excluded.[39] Cooling the sample resulted in broadening of all the resonances in a fashion similar to that observed when samples of the pure starting material are cooled. The main species, in all cases a bis(phosphine) dihydride complex, appears to be analogous to the *exo-nido* iridium complex[10] synthesized and structurally characterized in this laboratory. The variable-temperature ^{1}H and ^{31}P{^{1}H} NMR spectra of the iridium complex[10,25] indicate that the $[(PPh_3)_2(H)_2Ir]$ fragment may well be fixed to the same cage positions in solution as found in the solid state. However, both ^{1}H and ^{31}P{^{1}H} NMR spectra of the bis(triphenylphosphine)-rhodium analogues suggest that exchange with hydrogen and rotation and/or polytopal migration of the $[(PPh_3)_2(H)_2Rh]$ fragment are occurring in solution.

The mixed $(PCy_3)(PPh_3)$ complex (IIIa) binds H_2 more effectively than the $(PPh_3)_2$ complexes at ambient temperatures. This is probably due to the increased basicity of the PCy_3 ligand in addition to its added steric demands. Both of these properties of PCy_3 should enhance the stability of a Rh(III) *cis*-H_2–*trans*-P_2 complex.

It is of interest to note the similarities of these dihydrides with the iridium and rhodium hydroborate complexes [*cis*-$(H)_2$-*trans*-$(PMe(t\text{-}Bu)_2)_2M(BH_4)$] (M = Rh, Ir) which contain the bidentate BH_4 ligand.[40] It was found[40] that the iridium complex was *not* fluxional in solution but that the rhodium analogue exhibited a complex terminal Rh–H resonance pattern in the ^{1}H NMR spectrum which was temperature dependent, suggesting fluxional behavior. The reported ^{1}H NMR resonances at −16.85 (terminal Rh–H), −4.53 (bridging RhH_2B), and 3.9 ppm (terminal B–H) are very similar to those observed for the *exo-nido*-carborane complexes discussed above. Recently, Van Gaal reported[41] the synthesis of the complex $[(PCy_3)_2(H)_2Rh(BH_4)]$. In the ^{1}H NMR spectrum, the BH_4 protons are equivalent on the NMR time scale at room temperature and appear as a broad resonance centered at −3 ppm. The terminal Rh–H resonance appears at −16.7 ppm (J_{Rh-H} = $^2J_{P-H}$ = 15 Hz).[41] It is not obvious, at this time, why the iridium complexes, unlike their rhodium analogues, are apparently static in solution. It is also not yet clear whether there is intramolecular exchange of terminal rhodium hydride ligands with bridging Rh–H–B hydrogens. However, a series of ^{1}H{^{11}B} and ^{11}B NMR spectra of complex IId which had previously been treated with deuterium gas in THF exhibited extensive incorporation of deuterium into terminal B–H sites as well as a decrease in intensity of the resonance due to the B–H–B bridge in the ^{1}H NMR spectrum. This BH/D_2 exchange appears to be somewhat selective; some terminal B–H sites exchange faster than others and the B–H–B site exchanges fairly slowly. It should be noted that the closo complex $[3,3\text{-}(PPh_3)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$ is an active catalyst for BH/D_2 exchange[42–44] and indeed undergoes autocatalyzed deuteration when exposed to D_2. In addition, the rhodium hydride exchanges much more slowly than the terminal B–H sites and there is also selectivity at the B–H sites. The exact mechanism by which these BH/D_2 exchange reactions proceed is not yet clearly understood, but is under continued investigation.

Conclusions

The isolation of *exo-nido*-bis(phosphine)rhodacarboranes which contain the 11-vertex icosahedral fragment, C_2B_9, and the demonstration of a facile equilibrium between the fluxional exo-nido species (exo-nido tautomers of IIa and IIc) and the corresponding

(39) In samples which had been treated with hydrogen at ca. 40 °C, an additional six line pattern of lower intensity, centered at −19.3 ppm was occasionally observed in the room-temperature ^{1}H NMR spectrum. This pattern, presumably a doublet of triplets (J_{Rh-H} = 22 Hz, $^2J_{P-H}$ = 17 Hz), possibly results from a rapidly rotating $(PCy_3)_2(H)_2Rh$ species with cis hydrides and trans phosphines (vide infra). Since spectra of complex IIa under similar conditions did not display these signals, a $(PPh_3)_2$ species seems unlikely. We cannot exclude the possibility of a mono PCy_3 species with inequivalent hydrides which give rise to overlapping resonances.

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closo tautomers provide the second example of closo-nido tautomerism. The first example involved closo-nido equilibria in the C_2B_8 phosphinerhodacarborane series[6] and differed from the present case in that the nido species was shown to be of the endo type in which the rhodium atomic orbitals contribute to the skeletal molecular orbitals of an 11-vertex nido cluster. It will be shown in the following contributions to this series that the closo-exo-nido tautomerism described here is a general phenomena for all [*closo*-$(PPh_3)_2(H)Rh(C_2B_9H_{11})$] isomers and their carbon-substituted derivatives. Indeed, the existence of the parent unsubstituted exo-nido species [*exo-nido*-$(PPh_3)_2Rh(7,8\text{-}C_2B_9H_{12})$] has been demonstrated[9] and its rearrangement to the closo tautomer observed in situ by $^{31}P\{^1H\}$ at low temperatures. With these observations in hand, the unusual mechanisms of alkene isomerization and hydrogenation by [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] and related species were elucidated and are described in a companion paper.[4]

Although not specifically pointed out in this paper, the exo-nido species reported here are excellent and easily recoverable catalysts for the isomerization and hydrogenation of terminal alkenes. In common with the known closo species described previously,[1] they are unique in that they provide a catalytic pathway for alkenyl carboxylate hydrogenolysis,[45] the details of which will be published elsewhere.

Aside from the obvious importance of the exo-nido compounds to catalysis mechanisms, the exo-nido species are convenient reagents for the introduction of $[L_2Rh]^+$ (L = phosphine) into reaction schemes not directly involved in metallacarborane chemistry. An example of this utility is provided by the simple preparation of $(PPh_3)_2Rh(CO)_3^+$ and $[L_4Rh]^+$ (L = phosphine) species reported here.

The following contribution to this series describes the X-ray diffraction studies upon which the structural information employed in this paper was based.

Experimental Section

All operations were performed under an atmosphere of dry nitrogen or argon, unless otherwise indicated, using standard inert atmosphere techniques.[46]

Physical Measurements. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WP-200 spectrometer operating in the Fourier transform mode at 200.133 and 81.02 MHz, respectively. Sample temperatures were measured with a B-VT-1000 digital temperature controller by means of a thermocouple situated in the cooling gas a few centimeters below the sample. The ^{11}B NMR spectra were recorded at 112.0 or 127.0 MHz on a Fourier transform instrument designed and built by Professor F. A. L. Anet of this department. Proton chemical shifts were referenced to residual protons in the solvent (CD_2Cl_2 5.28, THF-d_8 3.58; C_6D_6 7.25 ppm with respect to tetramethylsilane). Phosphorus chemical shifts were referenced to external 85% H_3PO_4 as previously described, with downfield shifts taken as positive.[17] ^{11}B chemical shifts were referenced to external $Et_2O{\cdot}BF_3$, with downfield shifts taken as positive (numbers appearing in parentheses refer to the number of boron atoms giving rise to that resonance). Infrared spectra were recorded as Nujol mulls or KBr pellets on a Perkin-Elmer 137 spectrometer or in solution on a Nicolet MX-1 Fourier transform instrument. Melting points were determined in open capillaries and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Materials. Unless otherwise noted all solvents (Mallinckrodt) were reagent grade. Benzene and tetrahydrofuran (THF) were distilled from potassium metal. Diethyl ether was pretreated with activity I alumina (Merck) to remove peroxides. Heptane was distilled from sodium metal. Dichloromethane was purified according to a literature procedure[47] and distilled from P_2O_5. All other solvents were deoxygenated by bubbling with argon or nitrogen and used without further purification. Triethylphosphine, tricyclohexylphosphine, triphos (Strem), 1,2-bis(diphenylphosphino)ethane (Pressure Chemical Co.), triphenylphosphine, tetramethylammonium chloride (Aldrich), rhodium trichloride trihydrate (Matthey Bishop), and ca. 91% ^{13}C-enriched carbon monoxide (Prochem) were purchased from commercial sources and used as received. Tris(triphenylphosphine)rhodium chloride,[48] salts of the [*nido*-7-Me-8-Ph-7,8-$C_2B_9H_{10}$]$^-$ (Ib), [*nido*-7,8-Me_2-7,8-$C_2B_9H_{10}$]$^-$ (Ic),[49,50] and [*nido*-7,8-μ-$(CH_2)_3$-7,8-$C_2B_9H_{10}$]$^-$ (Id)[51] anions, 1,2-μ-(1′,2′-xylylene)-1,2-$C_2B_{10}H_{10}$ (μ-1,2-xylylenecarborane)[52-54] and biscarborane[55,56] were prepared according to the literature methods. Degradation of μ-1,2-xylylenecarborane to give anion Ia was accomplished via a procedure similar to that used to prepare the other carborane anions.

Preparation of [*closo*-1,2-μ-(1′,2′-$CH_2C_6H_4CH_2$-)-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_9$] (IIa). A 1-L Schlenk flask was charged with [$(PPh_3)_3RhCl$] (10.00 g, 10.81 mmol) and Cs^+-Ia (5.00 g, 13.57 mmol). Absolute ethanol (40 mL) was added followed by benzene (450 mL), and the reaction mixture was stirred for 3 days at room temperature and filtered. The resulting yellow solid was washed in air with absolute ethanol (3 × 200 mL), a mixture of ethanol/water, ca. 1:1 (350 mL), 95% ethanol (150 mL), absolute ethanol (250 mL), and diethyl ether (250 mL) and then dried by suction. This procedure was used to remove excess PPh_3, Cs^+(Ia), and most of the CsCl. The resulting yellow solid was further purified as follows: A 1-L Schlenk flask containing absolute ethanol (ca. 375 mL) and THF (275 mL) was attached to a Soxhlet extraction apparatus, and the crude solid was loaded into the Soxhlet thimble. Extraction was continued until the eluent was colorless and the flask was then allowed to cool to room temperature. The resulting crystalline solid was collected by filtration and washed with absolute ethanol (2 × 50 mL). A second crop of crystals was obtained by concentration of the filtrate in vacuo followed by filtration. The total yield of IIa was 7.57 g (81%). The product could also be prepared from the Tl^+ salt of Ia by a similar procedure or from the Me_3NH^+ salt in refluxing ethanol. Due to the toxicity of Tl^+ compounds and the formation of side products (i.e., [$(PPh_3)_2RhCl$]$_2$ and [*trans*-$(PPh_3)_2Rh(CO)Cl$]) from the Me_3NH^+ salt, use of the Cs^+ salt is recommended. The product was not subjected to elemental analysis, but a sample recrystallized from CH_2Cl_2/heptane was studied by X-ray crystallography[7] and shown to contain two molecules of CH_2Cl_2 per molecule of IIa. It should also be noted that upon grinding the yellow crystals for an IR spectrum, the color of the sample changes to reddish, suggesting a thermal transformation of some of the material to the *exo-nido* tautomer in the solid state. IR (nujol): ν_{Rh-H} = 2015 cm^{-1}. ^1H NMR (CD_2Cl_2, −63 °C): −9.08 (t, J_{Rh-H} is unobserved, $^2J_{P-H}$ = 30 Hz, rhodium hydride); −2.71 (broad, B–H–B); AB pattern centered at 2.94 ppm (J_{Ha-Hb} = 15 Hz, $\Delta\nu = \nu_{Ha} - \nu_{Hb}$ = 55 Hz, methylene groups of xylylene substituent). It is not clear whether this AB pattern is due to the closo or the exo-nido tautomer; peaks observed at 2.05 and 1.95 ppm may be due to the other AB pattern, half of which is obscured by other resonances. $^{31}P\{^1H\}$ NMR (10% C_6D_6/THF): 44.4 (d, J_{Rh-P} = 186 Hz, nido), 43.3 ppm (d, J_{Rh-P} = 146 Hz, closo).

Preparation of [*exo-nido*-$(PPh_3)_2Rh(7\text{-}Me\text{-}8\text{-}Ph\text{-}7,8\text{-}C_2B_9H_{10})$] (IIb). To a solution of Cs^+[*nido*-7-Me-8-Ph-7,8-$C_2B_9H_{10}$]$^-$ (Ib) (4.28 g, 12.0 mmol) in benzene (550 mL)/ethanol (40 mL) was added [$(PPh_3)_3RhCl$] (7.40 g, 5.0 mmol). The solution was stirred at room temperature for 48 h, during which time a precipitate of CsCl formed. This was removed by filtration, the red filtrate was concentrated in vacuo to 150 mL, and ethanol (100 mL) was added. The resulting dark red crystals were isolated by filtration, washed with ethanol (2 × 50 mL), and dried in vacuo, yielding 4.79 g (70%) of IId. Anal. Calcd for $C_{45}H_{48}B_9P_2Rh$: C, 63.51; H, 5.68; B, 11.43; P, 7.28; Rh, 12.09. Found: C, 63.05; H, 5.60; B, 11.36; P, 7.42; Rh, 12.60.

Preparation of [*exo-nido*-$(PPh_3)_2Rh(7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_{10})$] (IIc). A method similar to the one described for the preparation of IIb was employed. A solution of Tl^+[*nido*-7,8-Me_2-7,8-$C_2B_9H_{10}$]$^-$ (Ib) (400 mg, 1.1 mmol) and [$(PPh_3)_3RhCl$] (925 mg, 1.0 mmol) in benzene (50 mL)/ethanol (10 mL) was stirred at room temperature for 18 h. After fil-

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tration to remove TlCl formed, the red solution was concentrated in vacuo to 25 mL and ethanol (25 mL) was added, affording dark red crystals of IIc (640 mg, 81%). Anal. Calcd for $C_{40}H_{46}B_9P_2Rh$: C, 60.90; H, 5.88; B, 12.33; P, 7.85; Rh, 13.04. Found: C, 60.96; H, 5.80; B, 12.48; P, 7.96; Rh, 12.94.

Preparation of [*exo-nido*-$(PPh_3)_2Rh(7,8\text{-}\mu\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10})$] (IId). A 1-L Schlenk flask was charged with [$(PPh_3)_3RhCl$] (8.00 g, 8.64 mmol) and the Cs^+ salt of anion Id (4.00 g, 12.96 mmol). Ethanol (70 mL) followed by benzene (350 mL) was added, and the mixture was stirred at room temperature for 24 h. The mixture was then gently refluxed for 2.5 h, allowed to cool to room temperature, and then filtered. Addition of ethanol (400 mL) to the filtrate followed by concentration in vacuo precipitated the product as red-orange microcrystals which were collected by filtration, washed with ethanol (100 mL), and dried in vacuo to give the monobenzene solvate of IId (5.1 g, 67%). Concentration of the filtrate followed by filtration yielded a second crop of crystals (1.1 g, 14%), giving a total yield of 6.2 g (81%). Similar yields were obtained by using a 36% molar excess of Cs^+-Id (instead of 50% excess) and omitting the heating step. Material thus obtained was of sufficient chemical purity for most applications; however, the analytical sample and samples for catalytic applications were further recrystallized from benzene/ethanol. Anal. Calcd for $C_{47}H_{52}B_9P_2Rh$: C, 64.22; H, 5.96; B, 11.07; P, 7.05; Rh, 11.71. Found: C, 63.80; H, 5.85; B, 11.63; P, 7.15; Rh, 12.14.

Reaction of Complex IIa with Tricyclohexylphosphine. Preparation of IIIa. A 100-mL Schlenk flask was charged with IIa (300 mg, 0.35 mmol) and tricyclohexylphosphine (223 mg, 0.80 mmol). Benzene (45 mL) was added, and the mixture was warmed (ca. 45 °C) to dissolve the solids and then stirred for 20 h at room temperature. Removal of the solvent in vacuo to a volume of ca. 15 mL followed by layering with ethanol (40 mL) precipitated the product as bright red-orange crystals which were collected by decanting the solvent. The crystals were dried in vacuo, yielding [*exo-nido*-$(PPh_3)(PCy_3)Rh(7,8\text{-}\mu\text{-}(1',2'\text{-}CH_2C_6H_4CH_2)\text{-}7,8\text{-}C_2B_9H_{10}]\cdot 1.5C_6H_6$ (IIIa) (269 mg, 78%). The analytical sample was recrystallized from benzene/ethanol. $^{31}P\{^1H\}$ NMR (10% C_6D_6/THF): 59.2 (dd, J_{Rh-P} = 173 Hz, $^2J_{P-P}$ = 36 Hz, PCy_3), 40.3 ppm (dd, J_{Rh-P} = 196 Hz, $^2J_{P-P}$ = 36 Hz, PPh_3). ^1H NMR (CD_2Cl_2): AB pattern centered at 3.08 ppm, (J_{Ha-Hb} = 15 Hz, $\Delta\nu = \nu_{Ha} - \nu_{Hb}$ = 57 Hz, CH_2 groups on xylylene substituent). Anal. Calcd for $C_{55}H_{75}B_9P_2Rh$: C, 66.17; H, 7.57; B, 9.75; P, 6.20; Rh, 10.31. Found: C, 65.62; H, 7.49; B, 10.35; P, 6.33; Rh, 10.23. The presence of $1.5C_6H_6$ was confirmed by an X-ray crystallographic study.[7]

Preparation of Tl[*nido*-7-[(1'-(*closo*-1',2'-$C_2B_{10}H_{11}$)]-7,8-$C_2B_9H_{11}$] (Ie).[56] To a solution of KOH (1.40 g, 25.0 mmol) in ethanol (200 mL) was added bis(carborane)[55] (2.90 g, 10.1 mmol), and the reaction was stirred and heated to reflux for 1.5 h. The solution was then cooled to room temperature, and the solvent was removed on a rotary evaporator. The resulting clear oil was dissolved in H_2O (100 mL), and the product was precipitated by addition of TlOAc (2.93 g, 11.1 mmol) which had been dissolved in a small amount of H_2O. The precipitate was collected by filtration, dried in vacuo, and then recrystallized twice by dissolution in glacial acetic acid (25 mL) followed by addition of benzene (200 mL). The clear white crystals were washed with benzene (3 × 20 mL) and dried in vacuo to give Tl(Ie)·$1.25C_6H_6$ (3.02 g, 52%). Anal. Calcd for $C_{11.5}H_{29.5}B_{19}Tl$: C, 23.91; H, 5.15; B, 35.56; Tl, 35.38. Found: C, 24.22; H, 5.46; B, 35.61; Tl, 35.25.

Preparation of $[Rh(PPh_3)_3]^+$[*nido*-7-(1'-(*closo*-1',2'-$C_2B_{10}H_{11}$))-7,8-$C_2B_9H_{11}]^-$ (IVe). A 250-mL Schlenk flask was charged with the Tl^+ salt of Ie (2.50 g, 5.21 mmol), [$(PPh_3)_3RhCl$] (4.38 g, 4.74 mmol), and benzene (80 mL). The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was then filtered through Celite, giving a clear, deep red solution which was reduced to a small volume (ca. 30 mL) in vacuo. Layering the concentrate with ethanol (100 mL) produced dark red crystals which were isolated by filtration, washed with ethanol (2 × 20 mL), and dried in vacuo, yielding IVe (5.03 g, 91%). Anal. Calcd for $C_{58}H_{67}B_{19}P_3Rh$: C, 59.78; H, 5.79; B, 17.63; P, 7.97; Rh, 8.83. Found: C, 58.69; H, 5.93; B, 18.07; P, 7.60; Rh, 8.52.

Formation of [$(PPh_3)_3RhCl$] from IIb. Complex IIb (213 mg, 0.25 mmol) was stirred in ethanol (30 mL) at room temperature for 2 h in the presence of PPh_3 (66 mg, 0.25 mmol) and $Me_4N^+Cl^-$ (54 mg, 0.50 mmol). An orange precipitate formed which was isolated by filtration, washed with ethanol and diethyl ether, and identified as [$(PPh_3)_3RhCl$] by $^{31}P\{^1H\}$ NMR spectroscopy; yield, 205 mg (85%).

Formation of [$(PPh_3)_3RhCl$] from IId. A 100-mL Schlenk flask was charged with complex IId (200 mg, 0.25 mmol), PPh_3 (133 mg, 0.50 mmol), and $Me_4N^+Cl^-$ (54 mg, 0.50 mmol). Ethanol (40 mL) was added, and the resulting mixture was stirred for 3.5 h and then filtered, washed with ethanol (25 mL), and dried to give [$(PPh_3)_3RhCl$] (191 mg, 83%), identified by its IR and $^{31}P\{^1H\}$ NMR spectra. Resonances apparently due to $[(PPh_3)_2RhCl]_2$ were also visible in the $^{31}P\{^1H\}$ NMR spectrum.

Preparaton of [*closo*-1,2-μ-(1',2'-$CH_2C_6H_4CH_2$-)-3,3-$(PEt_3)_2$-3-H-3,1,2-$RhC_2B_9H_9$] (VIIa) from IIa and PEt_3. A 250-mL Schlenk flask was charged with IIa (862 mg, 1.00 mmol) and a 25-mL dropping funnel was attached. THF (90 mL) was added to the flask, and the mixture was stirred to partially dissolve the solid. THF (15–20 mL) was added to the dropping funnel followed by PEt_3 (0.32 mL, 2.17 mmol). The solution of PEt_3 was added slowly to the reaction mixture over a period of 25 min which gradually lightened the color of the solution from red to yellow. The dropping funnel was washed with THF (25 mL) which was then added to the reaction mixture. Stirring was continued for ca. 2.5 h, the solution was concentrated in vacuo, and absolute ethanol (75 mL) was added. The solution was gradually concentrated in vacuo to a volume of ca. 40 mL. The resulting precipitate was isolated by filtration and washed with absolute ethanol (25 mL). Recrystallization from THF/ethanol yielded VIIa (377 mg, 66%) as fluffy light yellow microcrystals. IR (Nujol): ν_{Rh-H} = 1995, 1970 cm^{-1}. (This sample was recrystallized from THF/ethanol. A waxy sample precipitated from benzene/ethanol which displayed an identical $^{31}P\{^1H\}$ NMR spectrum and only a single Rh–H stretch at ca. 1980 cm^{-1} in its Nujol IR spectrum.) ^1H NMR (CD_2Cl_2): −10.07 (t, J_{Rh-H} is unobserved, $^2J_{P-H}$ = 29 Hz, rhodium hydride), AB pattern centered at 3.40 ppm (J_{Ha-Hb} = 19 Hz, $\Delta\nu = \nu_{Ha} - \nu_{Hb}$ = 62 Hz, CH_2 groups of xylylene substituent). $^{31}P\{^1H\}$ NMR (10% C_6D_6/THF, −48 °C): 33.0 ppm (d, J_{Rh-P} = 134 Hz). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): −15.8 (2), −9.2 (3), −5.5 (3), −2.0 (1) ppm. Two samples of complex VIIa were submitted for elemental analysis; sample A was recrystallized from THF/heptane and sample B was recrystallized from THF/ethanol. Each sample was dried under high vacuum for several hours at room temperature. In each case, the analytical data were consistent with the presence of 0.5 molecule of THF per molecule of VIIa. Anal. Calcd for $C_{24}H_{52}B_9P_2RhO_{0.5}$: C, 47.19; H, 8.58; B, 15.93; P, 10.14; Rh, 16.85. Found (sample A): C, 47.10; H, 8.59; B, 16.28; P, 10.26; Rh, 17.35. Found (sample B): C, 47.25; H, 8.65; B, 15.36; P, 10.27; Rh, 16.48.

Preparation of $[(PPh_3)_4Rh]^+$[*nido*-7-Me-8-Ph-7,8-$C_2B_9H_{10}]^-$ (Vb) and [*closo*-1-Me-2,2-$(PEt_3)_2$-2-H-8-Ph-2,1,8-$RhC_2B_9H_9$]2 (VIb) from IIb and PEt_3. (a) Addition of PEt_3 (0.18 mL, 1.2 mmol) to a stirred solution of IIb (255 mg, 0.3 mmol) in THF (30 mL) resulted in an immediate color change from red to orange. The solution was stirred at room temperature for 1.5 h, heptane (25 mL) was added, and the solution was concentrated in vacuo to 40 mL to induce crystallization. Orange crystals of Vb $[(PEt_3)_4Rh]^+$[*nido*-7-Me-8-Ph-7,8-$C_2B_9H_{10}]^-$ formed overnight (175 mg, 73%). We were unable to obtain a satisfactory analysis on this compound, and thus it was characterized spectroscopically.

(b) A solution containing IIb (750 mg, 0.98 mmol) and PEt_3 (0.33 mL, 2.20 mmol) in THF (75 mL) was heated to reflux for 24 h. The orange color produced on addition of PEt_3 gradually faded and the solution became pale yellow. Addition of heptane (50 mL) resulted in the formation of pale yellow crystals of VIb, [*closo*-1-Me-2,2-$(PEt_3)_2$-2-H-8-Ph-2,1,8-$RhC_2B_9H_9$]$_2$ (430 mg, 87%). IR (Nujol): ν_{Rh-H} = 2040 cm^{-1}. ^1H NMR (CD_2Cl_2): −11.69 ppm (dt, J_{Rh-H} = 17 Hz, $^2J_{P-H}$ = 32 Hz, rhodium hydride). $^{31}P\{^1H\}$ NMR (10% C_6D_6/THF): +27 °C, broad overlapping resonances are observed at 19.6, 18.0, and 16.7 ppm; −103 °C, an ABM pattern is observed centered at 19.2 ppm which is virtually first order, $^2J_{P-P}$ = 26 Hz. $^{11}B\{^1H\}$ NMR (CD_2Cl_2): −0.7 (1), −3.0 (1), −4.9 (1), −7.1 (1), −8.4 (1), −9.7 (1), −14.5 (1), −15.1 (1), −18.0 (1) ppm. Anal. Calcd for $C_{21}H_{48}B_9P_2Rh$: C, 44.82; H, 8.60; B, 17.29; P, 11.01; Rh, 18.29. Found: C, 44.72; H, 8.64; B, 17.37; B, 11.18; Rh, 17.89.

(c) When less than 4 equiv of PEt_3 was used and the reaction carried out at room temperature, a mixture of Vb and VIb was isolated. This could be converted to pure VIb by heating a THF or benzene solution of the mixture to reflux for a few hours.

Preparation of [*closo*-1,2-Me_2-3,3-$(PEt_3)_2$-3-H-3,1,2-RhC_2B_9] (VIIc) from IIc and PEt_3. When PEt_3 (0.15 mL, 1.0 mmol) was syringed into a benzene (50 mL) solution of IIc (316 mg, 0.4 mmol) the color immediately turned orange. After the solution was stirred overnight at room temperature it became yellow. Reduction of solution volume in vacuo followed by addition of ethanol (20 mL) produced bright yellow crystals. These were isolated by filtration and washed with ethanol (30 mL) and diethyl ether (30 mL) to yield 140 mg (70%) of VIIc. IR (Nujol): ν_{Rh-H} = 1970 cm^{-1}. ^1H NMR (CD_2Cl_2, −78 °C): 2.31 ($C-CH_3$), −9.84 ppm (dt, J_{Rh-H} = 7 Hz, $^2J_{P-H}$ = 31 Hz, rhodium hydride). $^{31}P\{^1H\}$ NMR (10% C_6D_6/THF) 32.0 ppm (d, J_{Rh-P} = 134 Hz). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): −3.2 (1), −5.9 (3), −8.3 (3), −14.8 (2) ppm. Anal. Calcd for $C_{16}H_{46}B_9P_2Rh$: C, 38.38; H, 926; B, 19.43; P, 12.37; Rh, 20.55. Found: C, 38.52; H, 9.39; B, 19.07; P, 12.54; Rh, 20.83.

Preparation of [*closo*-1,2-μ-$(CH_2)_3$-3,3-$(PEt_3)_2$-3-H-3,1,2-$RhC_2B_9H_9$] (VIId) from IId and PEt_3. Complex VIId was prepared by a procedure similar to that used for the preparation of VIIa. When IId (801 mg, 0.91 mmol) and PEt_3 (0.32 mL, 2.17 mmol) are reacted in THF, 322 mg (69%) of complex VIId was obtained after recrystallization from THF/ethanol. IR (Nujol): ν_{Rh-H} = 1990 cm^{-1}. ^1H NMR (CD_2Cl_2, −78

°C): −9.88 ppm (dt, J_{Rh-H} = 5 Hz, $^2J_{P-H}$ = 32 Hz, rhodium hydride). $^{31}P\{^1H\}$ NMR (10% C_6D_6/THF): 33.3 ppm (d, J_{Rh-P} = 137 Hz). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): −15.9 (2), −10.2 (2), −7.93 (3), −3.1 (1), +0.1 (1) ppm. Anal. Calcd for $C_{17}H_{46}B_9P_2Rh$: C, 39.83; H, 9.04; B, 18.98; P, 12.08; Rh, 20.07. Found: C, 39.91; H, 9.20; B, 18.72; P, 11.87; Rh, 19.74.

Preparation of [*closo*-2,2-$(PEt_3)_2$-2-H-8-(1′-(*closo*-1′,2′-$C_2B_{10}H_{11}$))-2,1,8-$RhC_2B_9H_{10}$] (VIe) from IVe and PEt_3. To a solution of IVe (500 mg, 0.429 mmol) in benzene (50 mL) was added PEt_3 (0.16 mL, 1.1 mmol) and the reaction was heated to reflux for 2 h. The resulting light yellow solution was cooled and the solvent removed in vacuo. The solid residue was extracted with heptane (25 mL) to remove PPh_3, and the remaining white powder was recrystallized from benzene/heptane to give [*closo*-2,2-$(PEt_3)_2$-2-H-8-(1′-(*closo*-1′,2′-$C_2B_{10}H_{11}$))-2,1,8-$RhC_2B_9H_{10}$] 0.5C_6H_6 (VIe) (172 mg, 65%). IR (Nujol): ν_{Rh-H} = 2060 cm^{-1}. ^1H NMR (CD_2Cl_2): −10.37 ppm (dt, J_{Rh-H} = 17 Hz, $^2J_{P-H}$ = 29 Hz, rhodium hydride). $^{31}P\{^1H\}$ NMR (10% C_6D_6/THF): 23.8 ppm (d, J_{Rh-P} = 107 Hz). Anal. Calcd for $C_{19}H_{55}B_{19}P_2Rh$: C, 34.90; H, 8.48; B, 31.41; P, 9.47; Rh, 15.74. Found: C, 34.50; H, 8.45; B, 32.02; P, 9.72; Rh, 15.99.

Reaction of Complexes IIa and IVe with Triphos. These reactions were monitored by $^{31}P\{^1H\}$ NMR spectroscopy. When reactions were conducted on a preparative scale it proved impossible to obtain crystalline samples of the products with any of several carborane anions.

Reaction of Complex IIb with dppe To Produce $[(dppe)_2Rh]^+$[*nido*-7-Me-8-Ph-7,8-$C_2B_9H_{10}]^-$ (IXb). A 100-mL Schlenk flask was charged with IIb (250 mg, 0.29 mmol) and $Ph_2PCH_2CH_2PPh_2$ (dppe) (350 mg, 0.88 mmol), and THF (25 mL) was added. The resulting solution became light yellow within seconds and was stirred for 1.75 h. Heptane (20 mL) was added in two portions to precipitate the product as yellow microcrystals which were isolated by filtration in air, washed with heptane (20 mL), and dried, yielding $[(dppe)_2Rh]^+$ [*nido*-7-Me-8-Ph-7,8-$C_2B_9H_{10}]^-$ (IXb) (305 mg, 92%), which was pure by $^{31}P\{^1H\}$ NMR spectroscopy. The analytical sample was recrystallized from THF/heptane. Anal. Calcd for $C_{61}H_{66}B_9P_4Rh$: C, 65.22; H, 5.92; B, 8.66; P, 11.03; Rh, 9.16. Found: C, 65.30; H, 6.15; B, 8.47; P, 10.70; Rh, 8.75.

Reactions with Carbon Monoxide. Carbon monoxide was bubbled through a solution of IIb (200 mg, 0.24 mmol) in dichloromethane (25 mL), and the solution turned pale yellow immediately. After the solution was stirred at room temperature for 15 min, ethanol (15 mL) was added maintaining a CO atmosphere. Pale yellow crystals formed which after filtration and removal of the CO atmosphere turned brighter yellow. Attempts to recrystallize the product from CO-saturated dichloromethane/ethanol regenerated the pale yellow color of the solution and again produced pale yellow crystals. When argon saturated solvents were used, the solution turned bright yellow and then orange, and no tractable product could be isolated. Thus reactions of the exo-nido complexes with CO were monitored spectroscopically.

Reactions with PPh_3 and with H_2. Since the exo-nido complexes would only bind PPh_3 at low temperature and the reactions with H_2 were not complete at any temperature, these reactions were monitored by NMR spectroscopy only.

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