Acknowledgment. We thank Susan Heytens for the illustrations and Dr. Su-Miau Wu Shih for data collection of III. Computing costs were supported, in part, by an intramural grant from the UCLA Office of Academic Computing. Other computations were performed on a Digital VAX-11/780 computer, National Science Foundation Grant CHE 79-10965. This research was supported by National Science Foundation Grant CHE 77-22910.

Registry No. I, 76287-19-9; I·$2CH_2Cl_2$, 89437-70-7; II, 89414-09-5; II·$1.5(C_6H_6)$, 89414-10-8; III, 89397-42-2; IV, 89302-17-0; V, 89397-43-3; V·CH_2Cl_2, 89397-44-4.

Supplementary Material Available: Tables of observed and calculated structure factors and tables (Tables VIII–XII) of final positional and thermal parameters for I–V (115 pages). Ordering information is given on any current masthead page.

Metallacarboranes in Catalysis. 5. Interconversion of *closo*-Bis(phosphine)hydridorhodacarboranes by Rhodium Transfer between η^5-*nido*-Carborane Anions[1]

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

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

Abstract: Both the hydride and dicarbollide ligands of a series of closo, formally six-coordinate Rh(III), bis(triphenylphosphine)hydrido η^5-(*nido*-$C_2B_9H_9RR'$) complexes were easily replaced by a series of [*nido*-$C_2B_9H_{12}$]$^-$ ligands using thermal reactions. The following trend for ease of displacement of the *nido*-carborane anion in cage-carbon-substituted [*closo*-$(PPh_3)_2Rh(H)(C_2RR'B_9H_9)$] complexes has been found: 7,8-disubstituted > 7,8-monosubstituted > 7,8-unsubstituted > 7,9-unsubstituted ~ 2,9-unsubstituted. Kinetic studies of the reaction of [*closo*-3,3-$(PPh_3)_2$-3-H-1-R-2-R'-3,1,2-$RhC_2B_9H_9$] (R = Me, R' = H) (IVd) with [*nido*-7,8-$C_2B_9H_{12}$]$^-$ (Ia) and [*nido*-2,9-$C_2B_9H_{12}$]$^-$ (III) in THF at 29 °C showed no anion concentration dependence and a common first-order rate constant for the two reactions although in the case of [*nido*-7,9-$C_2B_9H_{12}$]$^-$ (II), anion dependence was observed. Similar kinetic studies of the reaction of [*exo-nido*-$(PPh_3)_2$Rh-7-Me-8-Ph-7,8-$C_2B_9H_{10}$] (IVf) with anions Ia, II, and III in THF at −63 °C proved these exchanges with exo-nido substrates to be much faster than the reactions involving closo substrates. In the cases of Ia and II, the less stable kinetic product of the reaction, the exo-nido tautomer, was initially observed along with its conversion to the more stable closo tautomer. Analysis of the anion concentration dependence of the rates of these reactions suggested the existence of a spectroscopically invisible intermediate, presumably an isomer of the exo-nido starting complex. Formation of an analogous intermediate appears to be the rate-determining step in reactions of *closo*-IVd with anions Ia and III. In addition, the dissociation of either PPh_3 or *nido*-carborane anion does not appear to be involved in any of these cage exchange reactions. Anion III was found to be a more effective nucleophile than Ia which, in turn, was more nucleophilic than II.

One of the more fascinating mechanistic problems associated with organometallic chemistry is that of the occasionally observed displacement of η^6 or η^5 ligands by other ligands of high hapticity or by electron-pair donors. Such processes have an important bearing upon the mechanisms of reactions which employ η^6 or η^5 organometallics as homogeneous catalysts or catalyst precursors.

There have been a number of reports concerning thermal ligand exchange reactions of ferrocene and related complexes.[3] The conditions required were vigorous, and Lewis acid catalysis was necessary. Khan and Dormond have reported[4] facile thermal exchange of cyclopentadienyl rings in certain titanium complexes, and Brubaker has studied[5] photolytic exchanges using [$(\eta^5$-$C_5H_5)_2MCl_n$] (M = V, Ti, Zr, Hf; n = 0, 1, 2). A recent study[6] of the complex {$Ru(\eta^5$-$C_5H_5)[\eta^5$-$C_5(CO_2Me)_5]$} showed that the bonding between the $C_5(CO_2Me)_5$ group and the ruthenium is relatively weak and thus the $C_5(CO_2Me)_5$ ligand can be displaced by 2-e$^-$ donor ligands under mild conditions.

An interest in arene exchange reactions[7] has also developed, particularly in view of the discovery of homogeneous catalysts for the hydrogenation of aromatic hydrocarbons.[8] The experimental conditions required for the arene exchange reactions varied widely. For example, it was found[9] that reasonable rates for arene exchanges in [(arene)$Cr(CO)_3$] complexes could be obtained at temperatures of ca. 140 °C when promoted by electron donor solvents. In contrast to these rather vigorous conditions, the toluene ligand in [$(\eta^6$-$C_6H_5CH_3)Ni(C_6F_5)_2$] is so labile that it can be rapidly exchanged with other arene ligands at room temperature.[10]

The exact means by which the cyclopentadienyl or arene ligand is removed from the metal center is thus far unanswered. The assumption that dissociation is a stepwise process, perhaps of the type η^5–η^3–η^1–η^0 for cyclopentadienyl ligands and η^6–η^4–η^2–η^0 for arene ligands, is not at all unreasonable.

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(1) (a) A preliminary account of this work has been presented. Marder, T. B.; Long, J. A.; Hawthorne, M. F. "Abstracts of Papers", 181st National Meeting of the American Chemical Society, Atlanta, GA, 1981; American Chemical Society: Washington, DC, 1981; INOR 217. (b) For the previous paper in this series see: 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.

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

(3) (a) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N. *Tetrahedron Lett.* **1963**, 1725; *Dokl. Akad. Nauk. SSSR* **1963**, *149*, 615. (b) Morrison, W. H., Jr.; Ho, E. Y.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1974**, *96*, 3603. (c) Roman, E.; Astruc, D. *Nouv. J. Chim.* **1977**, *1*, 183. (d) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N.; Shul'pina, L. S. *J. Organomet. Chem.* **1979**, *182*, C36.

(4) (a) Khan, O.; Dormond, A. *Bull. Soc. Chim. Fr.* **1977**, 951. (b) Khan, O.; Dormond, A.; Letourneux, J. P. *J. Organomet. Chem.* **1977**, *132*, 149.

(5) (a) Vitz, E.; Brubaker, C. H., Jr. *J. Organomet. Chem.* **1974**, *84*, C16; **1974**, *104*, C33. (b) Lee, J. G-S.; Brubaker, C. H., Jr. *Inorg. Chim. Acta* **1977**, *25*, 181.

(6) Bruce, M. I.; Skelton, B. W.; Wallis, R. C.; Walton, J. K.; White, A. H.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1981**, 428.

(7) (a) Sievert, A. C.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 489 and references therein. (b) Muetterties, E. L.; Bleeke, J. R.; Sievert, A. C. *J. Organomet. Chem.* **1979**, *178*, 197 and references therein.

(8) Muetterties, E. L.; Bleeke, J. R. *Acc. Chem. Res.* **1979**, *12*, 324.

(9) Mahaffy, C. A. L.; Pauson, P. L. *J. Chem. Res., Synop.* **1979**, 126.

(10) Klabunde, K. J.; Anderson, B. B.; Bader, M.; Radonovich, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 1313.

In the course of our studies[11a–e] on homogeneous alkene hydrogenation catalyzed by phosphinemetallacarboranes we have synthesized a variety of closo 18-electron, Rh(III) catalyst precursors of the general form $[(PPh_3)_2Rh(H)(R,R'C_2B_9H_9)]$. Reaction of $[(PPh_3)_3RhCl]$ in ethanol with the three isomeric *nido*-carborane anions $[7,8\text{-}C_2B_9H_{12}]^-$, $[7,9\text{-}C_2B_9H_{12}]^-$, and $[2,9\text{-}C_2B_9H_{12}]^-$[12] gives the parent closo-complexes $[3,3\text{-}(PPh_3)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$, $[2,2\text{-}(PPh_3)_2\text{-}2\text{-}H\text{-}2,1,7\text{-}RhC_2B_9H_{11}]$, and $[2,2\text{-}(PPh_3)_2\text{-}2\text{-}H\text{-}2,1,12\text{-}RhC_2B_9H_{11}]$, respectively. In addition, several carbon-substituted analogues of the [closo-3,1,2-] isomer have been prepared by analogous reactions where R = Me, Ph, R′ = H, and R = R′ = D.[11e] Furthermore, since nido isomers are believed to be key intermediates in the catalytic reduction of alkenes, several catalytically active *exo-nido*-phosphinerhodacarboranes were also synthesized by using C,C′-disubstituted carborane cages.[13] Since these exo-nido and closo complexes exhibited catalytic activity in the homogeneous hydrogenation and isomerization of alkenes, it was of importance to determine whether complexes of these two structural types could be interconverted and, if so, by what mechanism.

In a recent preliminary communication[14] we described a general and facile method for transferring the $\{(PPh_3)_2Rh\}$ vertex from one 11-vertex *nido*-carborane ligand to another in such a manner as to allow the interconversion of icosahedral *closo*-bis(phosphine)hydridorhodacarboranes. We now wish to report the results of a detailed study of this unprecedented η^5-dicarbollide exchange reaction and to propose a mechanism for this process which makes use of exo-nido intermediates.

Experimental Section

Materials. The *closo*-[11e] and *nido*-rhodacarborane[13] derivatives were synthesized by modifications of previously published procedures. Unless otherwise indicated, all reactions were conducted under prepurified argon or nitrogen, and solvents were dried, purified, and transferred by using standard inert atmosphere techniques. Anhydrous ethanol was saturated with argon or nitrogen prior to use. NMR solvents were obtained from the following suppliers: THF-d_8 (Stohler Isotope Chemicals), C_6D_6 (Aldrich), and CD_2Cl_2 (Merck Sharp and Dome Laboratories). $^{11}B\{^1H\}$ NMR spectra were recorded at 112.00 or 127.00 MHz on a Fourier transform spectrometer designed and built by Prof. F. A. L. Anet of this department. ^1H and $^{31}P\{^1H\}$ NMR spectrra 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 the B-VT-100 digital temperature controller by means of a thermocouple situated in the cooling gas a few centimeters below the sample.

Exchange Reactions Monitored by Proton NMR Spectra. The rhodium complex and the Cs salt[15] of the carborane anion were weighed on a Mettler microbalance and carefully transferred to a 5-mm NMR tube which was subsequently attached to a high-vacuum line. A measured volume of THF-d_8 was dried over activated alumina, freeze–pump–thaw degassed several times, and condensed onto the solid sample at −196 °C. The NMR tube was then sealed in vacuo. The sample was maintained at −196 °C and was warmed rapidly (ca. 1 min) to room temperature immediately before obtaining the series of spectra.

Exchange Reactions Monitored by Phosphorus NMR Spectra. The rhodium complex was weighed on an analytical balance and transferred to a 10-mm NMR tube which was then capped with a rubber septum. To this was added 1.2 mL of THF and 0.3 mL of C_6D_6 while an argon purge was maintained. The sample was then cooled to −78 °C and briefly purged by bubbling with argon. The Cs salt of the carborane anion(s) was weighed on an analytical balance and transferred to a test tube which was then capped with a rubber septum. To this was added 1.5 mL of THF and the sample was cooled to −78 °C and purged with argon. Immediately prior to obtaining the spectra, 1.0 mL of the THF solution of the anion was transferred to the NMR tube containing the solution of the rhodium complex and the sample was placed in the probe which had been equilibrated at −63 °C. The spectrometer was locked on the C_6D_6 deuterium resonance. The transfer and locking procedure were complete in ca. 1 min.

Table I. Results of Preparative-Scale Cage Exchange Reactions[a]

rhodium complex	carborane anion[b]	reaction time[c]	rhodium product	remarks
IVa	II (1.1)	36	V	85–90% yield; product contained traces of IVa
IVa	II (2.0)	48	V	10 molar equiv of PPh_3 added; product contained traces of IVa
IVa	III (1.0)	8	VI	74% yield; ca. 8:1 ratio of VI:IVa
V	Ia (2.0)	48	V	product contained traces of IVa
V	III (1.0)	72	V	60% recovery of V
VI	II (1.1)	48	VI	89% recovery of VI
IVb	none	168	IVb	no loss of D label, i.e., no IVa formed
IVb	Ia (2.0)	168	IVa	predominantly IVa
IVc	Ia (1.1)	2	IVa	92% yield
IVc	Ia (1.1)	2	IVa	5 molar equiv of PPh_3 added; 95% yield
IVc	Ia (1.1)	4	IVa	73% yield; reaction in THF at 25 °C using Cs salt of Ia
IVc	Ia (1.1)	9.5	IVa	Ia used was specifically deuterated at the bridge; IVa recovered contained 100% Rh–D
IVc	Id (2.0)	3	IVd	70% yield
IVd	Ia (0.9)	2	IVa	some IVd remains; 80% yield of Id
IVe	Ia (1.25)	24	IVa	77% yield
IVe	Ic (1.5)	5	IVc	40% yield; ca. 8:1 ratio of IVc:IVe

[a] Reactions in ethanol at the reflux temperature unless otherwise specified. Rhodacarboranes were not soluble in ethanol and reaction mixtures contained a solid rhodacarborane phase. [b] Molar equivalents of reactant anion are in parentheses. [c] Reaction times are in hours.

Kinetic Method. The NMR spectra were obtained at preselected time intervals by means of a simple computer program placing the spectrometer under automation. The spectra (as free induction decays) were automatically stored sequentially on disk. At the completion of the automation sequence, the spectra were all Fourier transformed and the integrals were plotted on graph paper. The reaction times (taken as the elapsed time from mixing to the middle of each spectral acquisition), crude integrals, and initial reactant concentration data were used as input to a locally written Fortran program CAGEXG which produced plots for first- and second-order kinetic analyses, percent composition vs. time, and generated rate constants by unweighted linear least-squares fitting of the data.

Preparative Scale Reactions. General Procedure. The rhodium complex and the carborane anion were placed in a Schlenk flask equipped with a magnetic stir bar and a reflux condenser. To this was added anhydrous ethanol (in which the rhodacarboranes have low solubilities), and the reaction mixture was brought to reflux. Reaction times and yields are reported in Table I. The reaction mixture was filtered while hot and the resulting solid was washed with anhydrous ethanol and dried in vacuo, yielding the pure rhodium complex. The carborane anion was recovered from the filtrate by removal of the solvent in vacuo followed by a benzene wash to remove any remaining metal complex. The resulting white solid was dried in vacuo. The purity of the rhodium complex was determined by ^1H or $^{31}P\{^1H\}$ NMR spectroscopy; the purity of the anion was determined by $^{11}B\{^1H\}$ NMR spectroscopy. To ensure recovery of pure metal complex, a minimum of 10% excess anion was used, whereas in order to isolate pure anion, a 10% deficiency of reactant anion was used.

Results

The set of three isomeric $[nido\text{-}C_2B_9H_{12}]^-$ and the $[nido\text{-}7\text{-}R\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_{10}]^-$ ions used as nucleophiles in this work are

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(11) (a) Paxson, T. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1974**, *96*, 2674. (b) Jung, C. W.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1977**, 499. (c) Sosinsky, B. A.; Kalb, W. C.; Grey, R. A.; Uski, V. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1977**, *99*, 6768. (d) Wong, E. H. S.; Hawthorne, M. F. *Inorg. Chem.* **1978**, *17*, 2863. (e) 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.

(12) Busby, D. C.; Hawthorne, M. F. *Inorg. Chem.* **1982**, *21*, 4101.

(13) Long, J. A.; Marder, T. B.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.*, second of five papers in this issue.

(14) Marder, T. B.; Long, J. A.; Hawthorne, M. F. *J. Chem. Soc. Chem. Commun.* **1980**, 677.

(15) The Cs salts of the carborane anions are sufficiently soluble in THF to allow low-temperature studies.

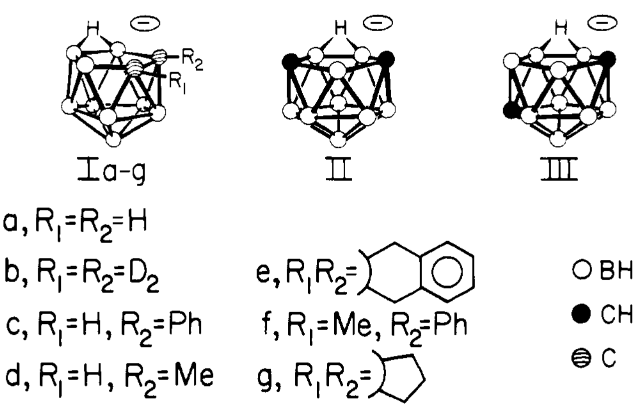

Figure 1. *nido*-Carborane anions employed in the cage exchange study.

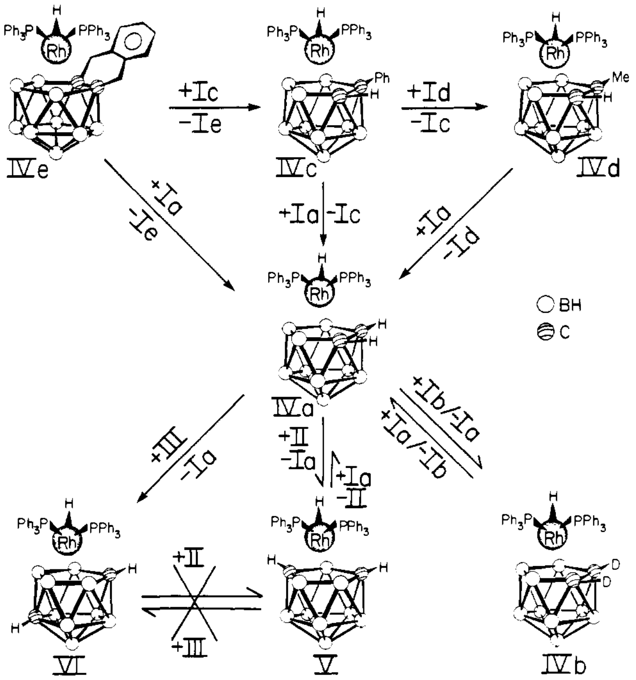

Figure 2. Schematic representation of cage exchange reactions employing *closo*-bis(triphenylphosphine)hydridorhodacarboranes.

illustrated in Figure 1. The a–g designation of substituents shown in Figure 1 for the nido anions also applies to the correspondingly substituted [*closo*-3,1,2] series of rhodacarboranes. The results of preparative scale reactions are summarized in Table I and the reaction sequences are shown in Figure 2. Under the conditions employed, the majority of the ligand exchange reactions were complete in a few hours. However, in the reaction of IVa with III, ca. 10% of IVa was present even after 3.5 days, and in the reaction of IVa with II, trace quantities of IVa were present after 2 days. After heating complex V with 10 equiv of Ia for 6 days, the resulting ratio of V to IVa was ca. 7:1. No exchange was observed in the reactions of either V with III or VI with II. In all cases so examined, the addition of up to 10 equiv of PPh_3 had no effect upon either the apparent reaction rate or product composition.

The reaction of the carbon-deuterated analogue of IVa, namely IVb, with 2 equiv of the isotopically normal anion Ia showed a significant amount of carborane C–H (by ^{1}H NMR spectroscopy) incorporation into the *closo*-bis(triphenylphosphine)rhodacarborane after 1 week. In a control experiment, a sample of IVb that had been heated to reflux in ethanol for 1 week showed no carborane C–H in the ^{1}H NMR spectrum. Thus, the expected degenerate exchange of Ia with its corresponding *closo*-bis(phosphine)rhodacarborane was confirmed as a viable reaction under the experimental conditions employed here. When IVc was allowed to react with anion Ia which had been specifically deuterated at the B–H–B bridge position (Ib),[16] the exchange product (IVa) contained Rh–D and no Rh–H.[17] The source of the Rh–H in the exchange reaction product (Figure 3) is therefore the B–H–B bridge of the incoming carborane anion. This source of Rh–H was similarly identified in the reaction of Ia with $[(PPh_3)_3RhCl]$ to produce IVa.[13]

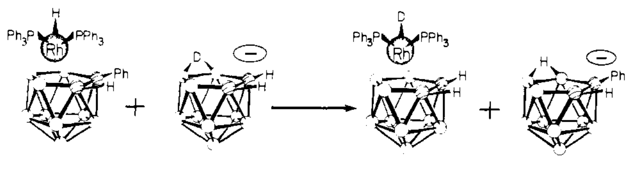

Figure 3. Cage exchange reaction of *closo*-IVc with bridge-deuterated anion Ia.

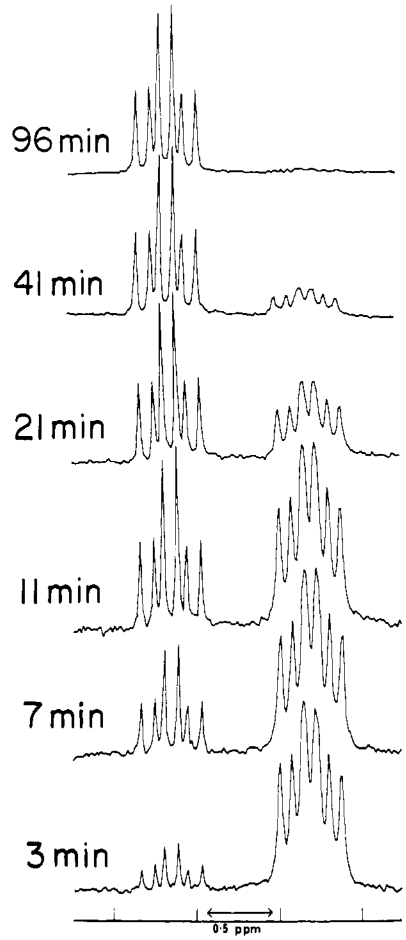

Figure 4. 200.133-MHz ^{1}H NMR spectra at 29 °C, in the metal hydride region, of the exchange between *closo*-IVd and Ia.

Exchange reactions carried out under kinetic conditions and monitored by NMR spectroscopy are summarized in Table II. Reactions of the closo complex IVd with anion Ia at 29 °C were monitored by ^{1}H NMR spectroscopy in the metal hydride region. A representative series of spectra is shown in Figure 4. When a 1:3 molar ratio of IVd to Ia was employed, the same observed first-order rate constant, ca. 5.3×10^{-4} s^{-1}, was obtained regardless of the initial concentrations of the reactants. A ratio of 1:0.6 gave k_{obsd} of 4.8×10^{-4} s^{-1}, only slightly slower than the reaction at 1:3 molar ratio, and a ratio of 1:6 gave k_{obsd} of 5.0×10^{-4} s^{-1}. Addition of 1 or 10 equiv of PPh_3 (per rhodium) had no effect on the first-order rate constant. Reaction of IVd with anion III also gave an identical k_{obsd} of 5.4×10^{-4} s^{-1}. However, when anion II was employed as the nucleophile, k_{obsd} was dependent upon anion concentration and the reaction was between first and second order overall.

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[16] Howe, D. V.; Jones, C. J.; Wiersema, R. J.; Hawthorne, M. F. *Inorg. Chem.* **1971**, *10*, 2516.

[17] Determined by ^{1}H NMR (δ_{Rh-H} −8.40, CD_2Cl_2) and IR (ν_{Rh-H} 2080 and 2120 cm^{-1}; ν_{Rh-D} 1520 cm^{-1}) spectroscopy.

Table II

carborane anion	[rhodium complex], M	[anion], M	k_{obsd}, s^{-1}
(a) Kinetic Data for Cage Exchange Reactions of *closo*-IVd with Carborane Anions[a]			
Ia	3.9×10^{-2}	1.03×10^{-1}	5.3×10^{-4}
Ia	1.63×10^{-2}	5.16×10^{-2}	5.4×10^{-4}
Ia	3.26×10^{-2}	2.01×10^{-2}	4.8×10^{-4}
Ia	3.26×10^{-2}	2.05×10^{-1}	5.0×10^{-4}
Ia[b]	3.26×10^{-2}	1.04×10^{-1}	5.3×10^{-4}
Ia[c]	3.28×10^{-2}	9.84×10^{-2}	5.4×10^{-4}
III	3.26×10^{-2}	1.03×10^{-1}	5.4×10^{-4}
II	3.27×10^{-2}	1.03×10^{-1}	3.5×10^{-4}
II	1.64×10^{-2}	5.14×10^{-2}	3.0×10^{-4}
II	3.29×10^{-2}	1.66×10^{-2}	0.2×10^{-5}
(b) Kinetic Data for Cage Exchange Reactions of *exo-nido*-IVf with Carborane Anions[d]			
Ia	9.87×10^{-3}	3.00×10^{-1}	1.3×10^{-3}
Ia	9.87×10^{-3}	2.00×10^{-1}	1.1×10^{-3}
Ia	9.87×10^{-3}	1.00×10^{-1}	8.4×10^{-4}
Ia	9.87×10^{-3}	5.01×10^{-2}	6.0×10^{-4}
III	1.50×10^{-2}	5.01×10^{-2}	3.2×10^{-3}

[a] Reactions at 29 °C in THF-d_8. k_{obsd} is the pseudo first-order rate constant. [b] In the presence of 1 molar equiv of $\mathrm{PPh_3/Rh}$. [c] In the presence of 10 molar equiv of $\mathrm{PPh_3/Rh}$. [d] Reactions at −63 °C in $\mathrm{THF/C_6D_6}$ (see Experimental Section). Constant ionic strength of 3.00×10^{-1} M maintained by addition of II (see text).

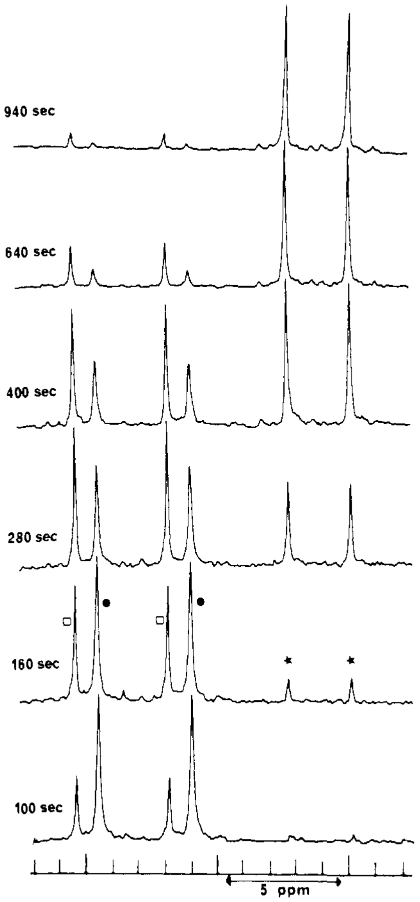

Figure 5. 81.02-MHz $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra at −63 °C of the exchange reaction between *exo-nido*-IVf and Ia. (□) *exo-nido*-IVa, (·) *exo-nido*-IVf, and (*) (*closo*-IVa.

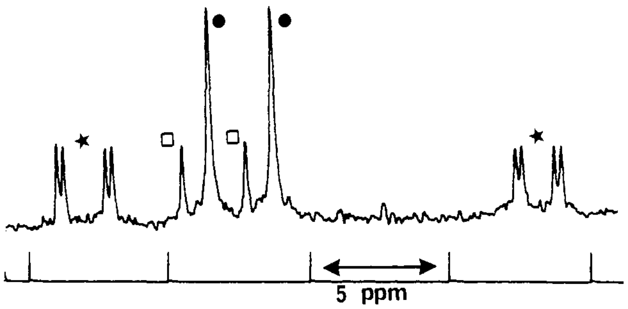

Figure 6. Representative 81.02-MHz $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum at −63 °C of the exchange reaction between *exo-nido*-IVf and II. (●) (*exo-nido*-IVf, (□) *exo-nido*-V, and (*) *closo*-V. *closo*-(V) appears as an 8-line pattern due to nonequivalence of the P atoms at this temperature. See ref 18.

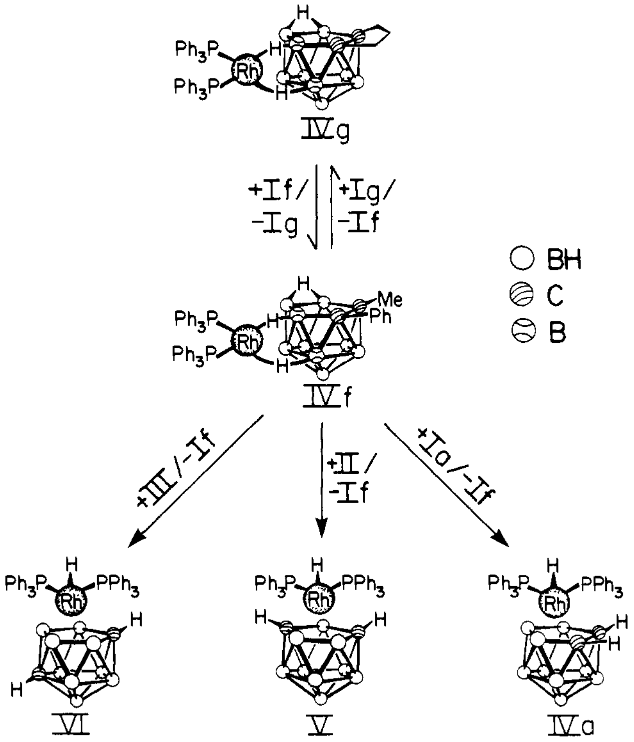

Figure 7. Schematic representation of cage exchange reactions employing *exo-nido*-bis(triphenylphosphine)rhodacarboranes.

Similar kinetic behavior was observed by $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy at −63 °C for the reaction of the structurally characterized[1] exo-nido complex IVf with Ia at several different initial reactant ratios and concentrations. At 29 °C exchanges of *exo-nido*-IVf with Ia were complete in less than 1 min, thus making it necessary to perform the kinetic study on complex IVf at low temperature (−63 °C) where reactions were virtually complete in ca. 0.5 h. Reaction of IVf with II, however, proceeded very slowly at −63 °C. This result allowed anion II to be added to exchange reactions of IVf with anion Ia in order to maintain constant ionic strength without otherwise affecting the course of the reaction; i.e., no V is formed during the period of interest. In addition, during the reaction of IVf with Ia an unstable intermediate is initially formed which we believe to be the exo-nido tautomer of IVa, the unsubstituted analogue of *exo-nido*-IVf ($^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR doublet,[19] 44.4 ppm, $J_{\mathrm{Rh-P}} = 186$ Hz (see Figure 5)).

A similar intermediate was observed ($^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR doublet, 44.9 ppm, $J_{\mathrm{Rh-P}} = 188$ Hz (see Figure 6 for a representative $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum)) when IVf was reacted with II although the reaction is between 1 and 2 orders of magnitude slower. When anion III was employed as the nucleophile no intermediate was detected and the observed first-order rate constant was ca. 5 times that for anion Ia at the same initial anion concentration. Reactions of the exo-nido complexes are depicted in Figure 7.

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

(19) Referenced to external 85% $\mathrm{H_3PO_4}$ as previously described: Marder, T. B.; Baker, R. T.; Long, J. A.; Doi, J. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1981**, *103*, 2988.

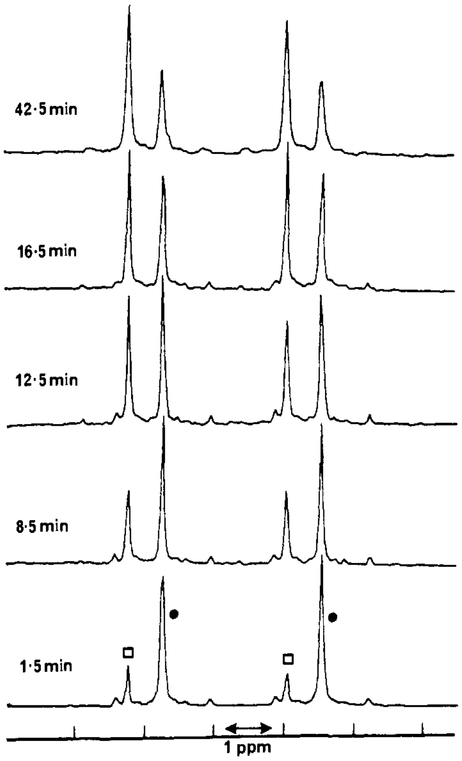

Figure 8. 81.02-MHz $^{31}P\{^1H\}$ NMR spectra at −33 °C of the exchange reaction between *exo-nido*-IVf and Ig and the resulting equilibrium mixture of products. (□) *exo-nido*-IVf and (●) *exo-nido*-IVg.

The exchange reactions of IVf with Ig and IVg with If were also followed by $^{31}P\{^1H\}$ NMR spectroscopy (as shown in Figure 8) and the same equilibrium mixture of ca. 61:39 IVg:IVf resulted from the two experiments at −33 °C.

Discussion

An examination of the results depicted in Table I and Figure 2 established the following order for the ease of displacement of the *nido*-carborane anion leaving group: Ie > Ic > Id > Ia > II ~ III. In the case of the [*closo*-3,1,2-] isomer series the thermodynamic stabilities of the rhodium complexes are inversely related to the degree of substitution at the cage-carbon atoms. The fact that complexes V and VI are more stable than complex IVa is consistent with the well-documented increase in stability of both carboranes and metallacarboranes obtained upon migration of the carbon atoms away from each other on the polyhedral surface.[20]

The deuterium labeling study using IVc and bridge-deuterated Ia depicted in Figure 3 suggested that in the reactions of the closo complexes the first step in the cage exchange mechanism is an intramolecular proton transfer which places the "hydride" ligand on the periphery of the carborane cage as a bridging B–H–B *proton*. This tautomerism represents a formal two-electron redox reaction which generates a 16-electron $[(PPh_3)_2Rh]^+$ fragment coordinated to the carborane anion cage in a manner similar to that shown in the confirmed[1] exo-nido structure of complex IVf (Figure 7). This allows the $[(PPh_3)_2Rh]^+$ fragment to be transferred from one closo cage to another in such a manner that the source of the metal hydride is the B–H–B proton from the cage which is bound to the metal atom when collapse to a closo tautomer occurs. A dynamic tautomeric equilibrium of this sort has been observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy for complex IVe.[13] The mode of bonding present in the exo-nido tautomers suggests that these or closely related species have both the electronic and coordinative unsaturation necessary to undergo nucleophilic attack by the incoming carborane anion. The kinetic study (Table II) of the reaction of IVd with Ia and IVd with III supported this hypothesis and is consistent with the conversion of *closo*-IVd to *exo-nido*-IVd or closely related intermediates as the rate-determining step since there was no dependence upon either the concentration or identity of the anion. Figure 9 presents a representative first-order kinetic plot for the reaction of 3.3×10^{-2} M IVd with 0.21 M Ia, and Figure 10 illustrates the corresponding variation in reaction mixture composition as a function of time. The fact that the addition of up to 10 equiv of PPh_3 had no effect on the observed first-order rate constant suggests that PPh_3 dissociation is not involved in the cage exchange mechanism. In order to address the possibility that the nondiscriminating $[(PPh_3)_2Rh]^+$ ion simply dissociated from an exo-nido intermediate (S_N1 type reaction), anions II and III were reacted with IVd under identical conditions. Anion III gave a k_{obsd} identical with that observed with anion Ia. However, reactions with anion II showed a less than first-order anion dependence and the overall reaction was neither strictly first nor second order, thus eliminating the possibility of a strict S_N1 mechanism. The following simple mechanism in which [Rh*] is a reactive intermediate (vide infra) is consistent with these results, but does not in itself conclusively eliminate $[(PPh_3)_2Rh]^+$ as Rh*.

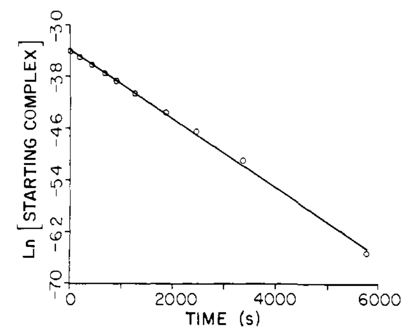

Figure 9. First-order kinetic plot for the exchange reaction of 3.3×10^{-2} M *closo*-IVd and 0.21 M Ia.

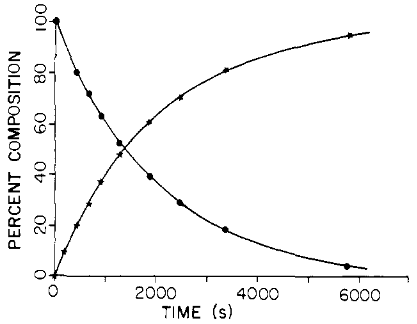

Figure 10. Plot of material balance vs. time for the exchange reaction between *closo*-IVd and Ia. (·) *closo*-IVd and (*) *closo*-IVa.

$$\mathrm{Rh}(closo) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Rh}^*] \xrightarrow{k_2[\mathrm{A}'^-]} \text{products}$$

Thus, for the reaction of IVd with anions Ia or III which are good nucleophiles, $k_2[A'^-] \gg k_{-1}$ and simple first-order kinetics are observed. Anion II, however, is a poor nucleophile, even though complex V is thermodynamically more stable than IVa, and thus the values of $k_2[A'^-]$ and k_{-1} may be comparable and give rise to a more complex rate law as observed.

Since an exo-nido complex was assumed to be closely related to the key intermediate in the cage exchange reaction, a series of kinetic experiments were conducted at −63 °C and constant ionic strength with the very reactive exo-nido complex IVf as the bis(phosphine)rhodacarborane substrate and Ia as the nucleophile. The observed pseudo-first-order rate constant varied with anion concentration, but the reaction was not strictly second order overall (i.e., first order in phosphinerhodacarborane and first order in carborane anion) over a wide range of anion concentrations. These results are summarized in Table II. A typical pseudo first-order plot of a reaction involving 9.9×10^{-3} M complex IVf and 0.30 M anion Ia is shown in Figure 11, and a representative graph of

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[20] Hawthorne, M. F.; Callahan, K. P.; Wiersema, R. J. *Tetrahedron* **1974**, *30*, 1795.

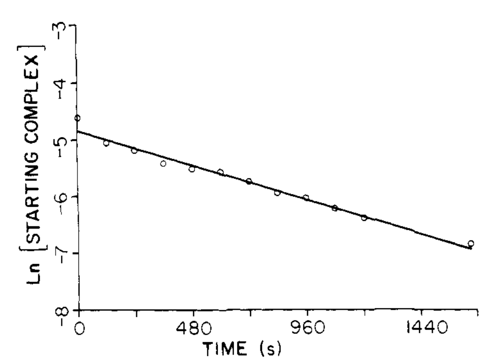

Figure 11. First-order kinetic plot for the exchange reaction between 9.9 × 10^{-3} M *exo-nido*-IV and 0.30 M Ia.

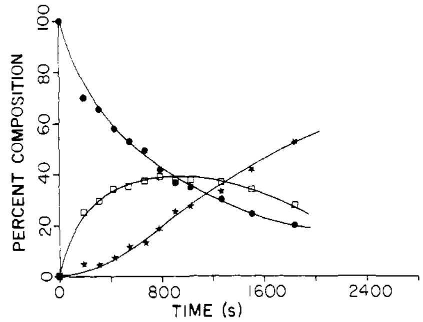

Figure 12. Plot of material balance vs. time for the exchange reaction between *exo-nido*-IVf and Ia. (●) *exo-nido*-IVf, (□) *exo-nido*-IVa, and (*) *closo*-IVa.

reaction mixture composition vs. time for a similar experiment is shown in Figure 12.

Analyses of the results (Table II) of a series of reactions of IVf with Ia suggest the following mechanism, which again incorporates the existence of an unobserved intermediate, [Rh*]:

$$\mathrm{Rh}(nido) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Rh}^*] \xrightarrow{k_2[\mathrm{A}'^-]} \text{products}$$

The use of large ratios of anion to rhodium exo-nido complex allowed the observed rates to be approximated by $k_{\mathrm{obsd}}[nido]$. Thus

$$\text{rate} = k_{\mathrm{obsd}}[\text{nido}] = k_1[\text{nido}]\,\frac{k_2[\mathrm{A}'^-]}{k_2[\mathrm{A}'^-] + k_{-1}}$$

which can be rearranged to give

$$\frac{1}{k_{\mathrm{obsd}}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_2[\mathrm{A}'^-]}$$

A linear plot of $1/k_{\mathrm{obsd}}$ vs. $1/[\mathrm{A}'^-]$ with a slope of k_{-1}/k_1k_2 and an intercept of $1/k_1$ is presented in Figure 13. The intercept of 650 s gives k_1 equal to 1.5 × 10^{-3} s^{-1} and therefore from the slope of 51 mol s L^{-1} a value of ca. 13 L mol^{-1} is obtained for the ratio of $k_2{:}k_{-1}$. Thus, at the anion concentrations employed (0.05–0.30 M) $k_2[\mathrm{A}'^-]$ is approximately equal to k_{-1}, which is consistent with the observed kinetics. In preliminary experiments conducted at −53 °C, in which constant ionic strength was not maintained, a common ion effect was not observed since there was no significant drop in k_{obsd} when 1 or 2 equiv of anion If was added to the exchange reaction of *exo-nido*-IVf with anion Ia. This strongly suggests that the $[(\mathrm{PPh_3})_2\mathrm{Rh}]^+$ ion does not dissociate from the carborane cage in IVf prior to attack by incoming anion. In addition, if there were a rapid and reversible preequilibrium involving the dissociation of either the $[(\mathrm{PPh_3})_2\mathrm{Rh}]^+$ ion or a $\mathrm{PPh_3}$ ligand, the reaction would show a half-order dependence on the exo-nido species rather than the observed first-order dependence. The mechanistic scheme shown in Figure 14 is therefore proposed which includes a possible structure for [Rh*], the reactive intermediate in nucleophilic cage exchange. The depicted [Rh*] species may well be an intermediate in the tautomerism between closo and nido geometries, and it is likely that this singly bridged exo-nido intermediate is indeed the reactive species which undergoes nucleophilic attack by the incoming *nido*-carborane anion when the starting material is a *closo*-bis(phosphine)hydridorhodacarborane. The proposed structure of [Rh*] is appealing because the movement of the phosphine ligands from a cis geometry in the exo-nido species toward a mutually trans arrangement by enlarging the P–Rh–P angle in [Rh*] would allow close approach of the relatively bulky *nido*-carborane anion to rhodium as well as diminishing the interaction between the $[(\mathrm{PPh_3})_2\mathrm{Rh}]^+$ fragment and the original carborane cage. Clearly, this proposed intermediate is more easily accessible from the exo-nido reactant complex than from the closo complexes since this transformation only requires the rupture of a single B–H–Rh linkage. Thus, although the final product of an exchange using IVf and Ia is a closo complex, namely IVa, an unstable exo-nido isomer is initially observed which is presumably similar in structure to IVf. For this system, at least, the qualitative energy diagram shown in Figure 15 is proposed. A similar energy ordering probably exists for complex V. As previously mentioned, no exo-nido isomer of VI was observed in the reaction of IVf with

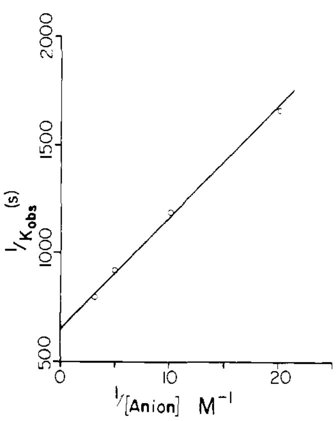

Figure 13. Plot of 1/[anion] vs. $1/k_{\mathrm{obsd}}$ for the exchange reaction between *exo-nido*-IVf and Ia.

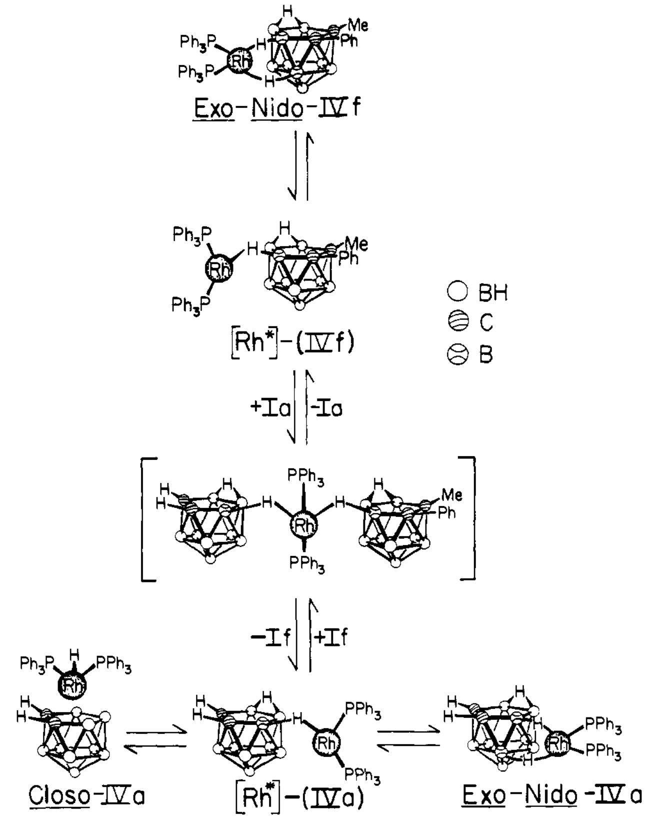

Figure 14. Proposed mechanistic scheme for the cage exchange reactions showing intermediate Rh*.

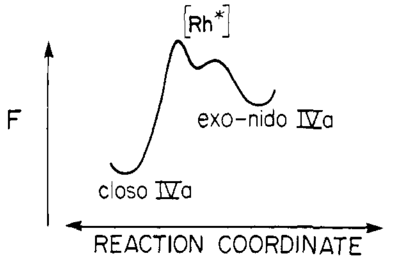

Figure 15. Proposed energy diagram for IVa showing relationship of closo and exo-nido tautomers to the high-energy intermediate Rh* which is subject to nucleophilic attack by incoming carborane anion.

III, a fact which undoubtedly reflects a very favorable pathway for conversion of the exo-nido species to its closo counterpart.

The reactions of equimolar quantities of IVf with Ig and IVg with If allowed the relative stabilities of two isolable *exo-nido*-bis(phosphine)rhodacarborane complexes to be examined. The resulting ratio of IVg to IVf at equilibrium at −33 °C was 61:39. Therefore, the equilibrium constant $K_{eq} = (61/39)^2 = 2.45$ and $\Delta F = -0.43$ kcal/mol at −33 °C. This value of ΔF might be ascribed to the fact that the cage-carbon substituents in complex IVf are more sterically demanding than those in IVg.

It is interesting to consider the relative nucleophilicites of the isomeric [*nido*-$C_2B_9H_{12}$]$^-$ ions Ia, II, and III. The order III > Ia > II is apparent from their relative rates of exchange with nido complex IVf as well as with closo complex IVd. This nucleophilicity sequence for the isomeric [*nido*-$C_2B_9H_{12}$]$^-$ ions may be rationalized on the basis of their respective charge distributions which, in turn, is perhaps best examined by viewing these nido anions as the monoprotonated dicarbollide dianions. The carbon atoms in carborane structures are known to be positively charged with respect to the boron atoms.[21] In the isomeric [*nido*-$C_2B_9H_{12}$]$^-$ ions the bridge proton resides on adjacent boron atoms on the open face of the cage and thus renders those particular atoms less nucleophilic than nonbridged (unprotonated) boron atoms. In the case of anion Ia, there is an unprotonated boron atom that is between a protonated boron atom and a carbon atom. However, in anion II, the unprotonated boron atom resides *between* the two carbon atoms and is less anionic in character than the unprotonated boron in Ia. This suggests that II should be a poorer nucleophile than Ia. Anion III has four boron atoms and a single carbon atom in the open face, and protonation of a B–B bond leaves *two* unprotonated boron atoms, thus placing more negative charge in the atoms in the open face of the cage. Thus, the negative charge is delocalized to the greatest extent in II, to a lesser extent in Ia, and to the smallest extent in III.

In conclusion, it should be pointed out that the hypothetical singly B–H–Rh bridged exo-nido intermediate [Rh*] is quite closely related to singly bridged, *exo-nido*- and *trans*-(PPh_3)-(alkene)Rh(1+) complexes proposed[22] as key intermediates in the alkene hydrogenation and isomerization reactions catalyzed by both closo and exo-nido precursors.

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Registry No. Ia·Cs, 63748-65-2; Ib·Cs, 89462-07-7; Ic·Cs, 89462-08-8; Id·Cs, 89462-09-9; Ie·Cs, 89462-10-2; If·Cs, 89486-20-4; Ig·Cs, 89462-13-5; II·Cs, 12305-33-8; III·Cs, 89486-21-5; IVa (closo isomer), 53687-46-0; IVa (exo–nido isomer), 89462-11-3; IVb, 76270-74-1; IVc, 65337-89-5; IVd, 76287-17-7; IVe, 76287-19-9; IVf, 89397-42-2; IVg, 89462-12-4; V, 53754-45-3; VI, 76287-18-8.

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(21) Lipscomb, W. N. "Boron Hydrides"; W. A. Benjamin: New York, 1963. Grimes, R. N. "Carboranes"; Academic Press: New York, 1970. Dixon, D. A.; Kleier, D. A.; Halgren, T. A.; Hall, J. H.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1977**, *99*, 6226.

(22) 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.