Metallacarboranes in Catalysis. 6. Kinetics and Mechanism of Alkene Hydrogenation and Isomerization Catalyzed by Rhodacarborane Clusters.[1] A Search for Cluster Catalysis

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Abstract: In a search for cluster-catalyzed reactions the rhodacarboranes [*closo*-3,3-(PPh$_3$)$_2$-3-H-3,1,2-RhC$_2$B$_9$H$_{11}$] (I), [*closo*-2,2-(PPh$_3$)$_2$-2-H-2,1,7-RhC$_2$B$_9$H$_{11}$] (II), [*closo*-2,2-(PPh$_3$)$_2$-2-H-2,1,12-RhC$_2$B$_9$H$_{11}$] (III), and [*exo-nido*-(PPh$_3$)$_2$Rh-μ-7,8-(CH$_2$)$_3$-C$_2$B$_9$H$_{10}$] (IV) were employed as catalyst precursors in a study of 1-hexene (B) isomerization. Precursors I, III, and IV were examined in the hydrogenation of 3-methyl-3-phenyl-1-butene (A). Complete rate laws were developed for isomerization and hydrogenation. Studies with D$_2$ demonstrated the presence of reversible alkylrhodium formation during hydrogenation. The use of D-labeled catalyst precursors, etc., proved that the Rh–H ligand of the closo precursors was not directly involved in either alkene isomerization or in hydrogenation. Competitive isomerization and hydrogenation of 1-hexene catalyzed by precursors I and IV suggested the presence of a common intermediate for these two reactions. Extensive intermolecular D scrambling was observed in equilibration experiments which employed propene-*1,1,1-d$_3$* and propene-*2-d* with precursor I and isotopically normal propene. The slow regiospecific transfer of deuterium from carbon in A to the 9, 10, and 12 boron vertices in I was observed and is believed to proceed via H–Rh–B bonded intermediates. The mechanistic implications of these and other observations are integrated into a mechanistic scheme which is based upon the prior equilibrium of Rh(3+) *closo*- and Rh(1+) *exo-nido*-rhodacarboranes which, in the presence of alkene, produce an equilibrium concentration of a key (phosphine)(alkene)Rh(1+) exo-nido intermediate regardless of the closo or exo-nido nature of the catalyst precursor used. Alkene isomerization is thought to involve η^3-allylic intermediates produced from the exo-nido alkene complex. Hydrogenation appears to proceed via oxidative addition of H$_2$ to this same complex followed by rate-determining decomposition of the hydridorhodium alkyl produced by this means. These kinetic characteristics may have their origin in the weak electron-donor properties of the chelated *exo-nido*-C$_2$B$_9$H$_{12}^-$ ligands which are attached to Rh(1+) or Rh(3+) in the exo-nido intermediates by a pair of B–H–Rh three-center, two-electron bonds.

In the four preceding papers of this series,[4–7] the chemistry of *closo*-bis(triphenylphosphine)hydridorhodacarboranes and *exo-nido*-bis(triphenylphosphine)rhodacarboranes was developed from the viewpoints of synthesis, molecular structure, reactivity, and the tautomeric interconversion of these two types of rhodacarboranes (Figure 1). In this paper we explore the mechanistic basis of the catalysis observed using these *closo*- and *exo-nido*-rhodacarboranes as catalyst precursors for alkene hydrogenation and isomerization reactions. Since the *closo*- and the *exo-nido*-rhodacarboranes utilized in this study are cluster species, it is clear that the results presented here describe not only metallacarborane catalysis in a specific sense but also one facet of the potentially broad area of cluster catalysis. Consequently, this contribution constitutes a search for cluster catalysis.

The discovery[8] that [*closo*-3,3-(PPh$_3$)$_2$-3-H-3,1,2-RhC$_2$B$_9$H$_{11}$] (I)[4] and [*closo*-2,2-(PPh$_3$)$_2$-2-H-2,1,7-RhC$_2$B$_9$H$_{11}$] (II)[4] were effective catalysts for the isomerization of alkenes was not, in itself, surprising since these formal 18-electron Rh(3+) species carried potentially dissociable PPh$_3$ ligands as well as a hydride ligand

at Rh. Accordingly, one might expect the reversible replacement of a PPh$_3$ ligand by terminal alkene followed by reversible alkyl formation to result in facile alkene isomerization.[9] It was surprising, however, to observe that the rapid homogeneous hydrogenation of simple terminal alkenes at room temperature with less than 1 atm of hydrogen partial pressure was catalyzed by I and II.[8] The iridium congeners[8] of I and II were also catalytically active, but gave lower turnover rates. In nearly every case examined, the catalyst could be quantitatively recovered from hydrogenation or alkene isomerization product solutions upon completion of the reaction. This characteristic catalyst stability is to be contrasted with much less robust homogeneous hydrogenation catalysts of somewhat greater reactivity such as (PPh$_3$)$_3$RhCl.[10]

The fact that hydrogenation was catalyzed by I and II was of great importance to us since the mechanism of these reactions, taken at face value, would require the activation of H$_2$ by electron- and orbital-precise formal Rh(3+) closo species. Aside from heterolysis[11] of H$_2$, one is hard pressed to suggest a viable mechanism for H$_2$ activation at a *closo*-Rh(3+) vertex. Consequently, we initially considered the possibility of reductive elimination of the Rh center present in I and II to produce an equilibrium concentration of a catalytically active *endo-nido*-rhodacarborane species which contained formal Rh(1+) and which would be similar to the *endo-nido*-Rh(1+) isomer derived from

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(4) 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.

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

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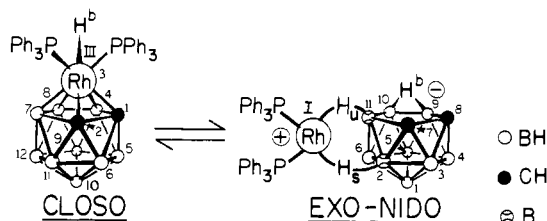3012 *J. Am. Chem. Soc., Vol. 106, No. 10, 1984*

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Figure 1. Rh(3+)-closo–Rh(1+)-exo-nido equilibrium using closo precursor (I) as an example illustrating numbering system and reversible regiospecific transfer of hydrogen atom H^b during tautomerization. The H-atoms in the two B–H–Rh bridge positions of the exo-nido tautomer are designated H_u and H_s since they originate at unsaturated and saturated B-atoms, respectively.

$(PPh_3)_2Rh(H)(C_2B_8H_{10})$.[12] An alternative, of course, was the possibility that the Rh center of the *closo*-rhodacarboranes was completely expelled from the closo cluster by reductive elimination to generate catalytically active $(PPh_3)_2Rh^+$[13] and the uncoordinated *nido*-$C_2B_9H_{12}^-$ ion. Both of these hypotheses were eventually shown to be incorrect, the former by stereoelectronic arguments derived from accurate calculations of interatomic distances[14] and the latter by noting the reactivity and rate-law differences between authentic $(PPh_3)_2Rh^+$ catalysts[13] and the rhodacarboranes. Somewhat later, the carbon-substituted *exo-nido*-bis(triphenylphosphine)rhodacarboranes containing Rh–H–B bridge-coordinated $(PPh_3)_2Rh^+$ centers were prepared and characterized[5] with regard to structure and reactivity, including their apparent catalytic activity. In view of this discovery, the corresponding exo-nido tautomers derived from the parent *closo*-I and II appeared to be superior candidates to fill the role of the invisible, but catalytically active, species involved in the catalytic reactions of *closo*-I and II. Following the accumulation of the results reported here, it became obvious that this hypothesis was essentially correct and novel modes of H_2 activation and terminal alkene isomerization peculiar to these catalyst systems were discovered. Below we develop the kinetic and mechanistic results which support these conclusions.

Results

Scope of the Investigation and Kinetic Methods. The investigation reported here includes kinetic, deuterium-labeling, and reaction product studies of representative terminal alkene hydrogenation and isomerization reactions. Previous experience had shown that nonterminal alkenes were sluggish in hydrogenation reactions carried out with our catalyst precursors in the presence of added PPh$_3$ and that 1-alkenes which were capable of double bond migration rearranged during hydrogenation to form much less reactive 2-alkenes. Consequently, the blocked 1-alkene, 3-methyl-3-phenyl-1-butene (A), was chosen for hydrogenation studies. Alkene isomerization, hydrogenation, and related reactions were studied in detail with 1-hexene (B) and specifically deuterated propenes were equilibrated with I in reactions related to alkene isomerization.

The catalyst precursors selected (Figure 2) for study were I,[4,8] II,[4,8] [*closo*-2,2-(PPh$_3$)$_2$-2-H-2,1,12-RhC$_2$B$_9$H$_{11}$] (III),[4] and [*exo-nido*-(PPh$_3$)$_2$Rh-μ-7,8-(CH$_2$)$_3$-7,8-C$_2$B$_9$H$_{10}$] (IV)[5] with major emphasis placed upon I and IV. Attempts to obtain meaningful kinetic data for the hydrogenation of A with catalyst precursor II were unsuccessful due to the apparent instability and poor reproducibility of this particular system. In contrast to these observations, II gave reproducible alkene isomerization kinetics
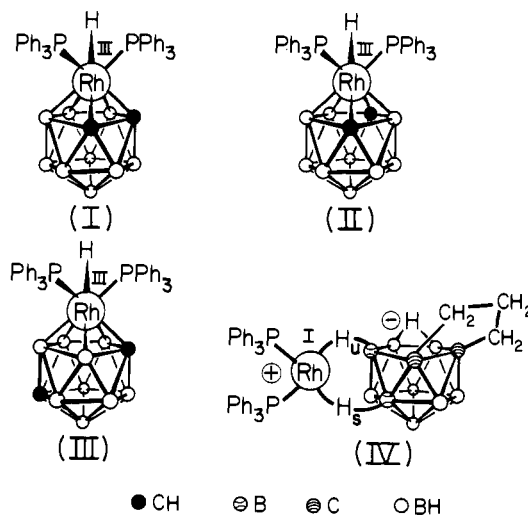

Figure 2. Structures of rhodacarboranes I–IV which were employed in catalytic alkene isomerization and hydrogenation reactions.

with B. Reproducibility of all catalyst precursor reactivities, from one preparation of precursor to another, was quite acceptable and generally gave reaction rates within ±3% of the mean hydrogenation and isomerization rates. All kinetic measurements of alkene hydrogenation and isomerization were carried out in the presence of known concentrations of added PPh$_3$. Tetrahydrofuran (THF) was employed as the reaction solvent throughout these studies, and 40.8 °C was utilized as the standard temperature for all quantitative measurements. This choice of solvent and reaction temperature was dictated by the limited solubilities of I, II, and III in other solvents and at lower temperatures in THF. Thermodynamic activation parameters were not sought due to the complexity of the catalytic systems under study and the resulting uncertainty in interpretation.

Hydrogen uptake at constant pressure was monitored to determine hydrogenation rates with the use of a recording, manometrically controlled, automatic hydrogen titrator[1,15] with an available H_2 partial pressure range of from approximately 0.13 to 1.6 atm. Alkene isomerization reactions were monitored by quantitative GLC.

Reactions of Catalyst Precursors I and IV with Hydrogen and Deuterium. Early in the present investigation it was discovered that while I gave no apparent reaction with H_2, autocatalyzed BH/D_2 exchange as well as RhD formation occurred when I was exposed to D_2 in toluene[16] at temperatures of 65–100 °C. Further study[17] of this system revealed that autocatalyzed exchange of I and D_2 was facile and regiospecific in THF solution at temperatures of 25–40 °C. While this deuterium exchange process has not been defined with respect to molecularity, the ordering of the reactivity of the various BH vertices in I with respect to exchange was determined[18] by ^{11}B FTNMR studies coupled with the complete assignment of the ^{11}B resonances of I.[19] From these results the ordering of relative exchange rates 9,12 > 10 > 5,11 > 6 ≫ 8 ca. 4,7 (see Figure 1) was observed, a result which suggests that the exchange process is electrophilic in nature and favors electron-rich BH vertices[18] farthest removed from the carborane C atoms. That the hydrogen of the RhH vertex of I is not involved in the autocatalyzed BH/D_2 exchange process is amply illustrated by the observation that exchange of I with D_2 in THF at 25 °C for 70 h produced I containing at least 90% BD

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(14) We are indebted to Dr. Michael Thompson for carrying out interatomic distance calculations using the SHELX76 program coupled with bond distances previously measured in other molecules and geometries assumed for logical *endo-nido*-Rh(1+) species. In no case could an attractive model be generated without bringing the Rh(1+) vertex to within bonding distance of the bridge H-atom present in the face of the $C_2B_9H_{12}^-$ ligand. Consequently, we conclude that no viable *endo-nido*-Rh(1+) tautomer based upon a dicarbollide ligand of variable facial hapticity can exist in other than the guise of a transition state for closo–exo-nido tautomerization.

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at all boron vertices and no detectable RhD.[18] Furthermore, the BH/D_2 exchange process is markedly inhibited by added PPh_3. The stability of RhD with respect to terminal hydrogen exchange with all available BH vertices is relatively high since the half-life (^{1}H FTNMR) of autoexchange at 40.8 °C in THF containing 5×10^{-3} M rhodium-deuterated I, I-*3-d*, was roughly 20 h. A more carefully monitored experiment containing 5×10^{-3} M I-*3-d* and 2.4×10^{-4} M PPh_3 at 40.8 °C gave a first-order rate constant of $\approx 8 \times 10^{-6}$ s^{-1} (from initial rate) and $t_{1/2}$ = ca. 24 h. From these results one concludes that RhH exchange with D_2 and/or BD is much slower than BH exchange with D_2 at low temperatures and that although the rhodium present in I must provide the catalytic exchange site, the hydride ligand attached to Rh in I is protected in some manner from entering the catalytic BH/D_2 reaction. Although the reactions of II and III with D_2 were not investigated in detail, BH exchange reactions with D_2 similar to those observed with I were observed.

In a previous paper of this series we described[5] the reactions of several *exo-nido*-bis(triphenylphosphine)rhodacarboranes, including IV, with hydrogen in THF solution. At low temperatures Rh(3+) *exo-nido*-bis(triphenylphosphine) dihydrides were evident in FTNMR experiments which are most likely isostructural with the structurally characterized Ir(3+) *exo-nido*-bis(triphenylphosphine) *cis*-dihydride reported previously.[20] One may conclude that a small, but undetected, equilibrium quantity of the *cis*-dihydride derived from IV and H_2 is present at 40.8 °C, as well. However, no evidence has developed which would suggest that these dihydrides play a significant role in the chemistry described here.

The reaction of D_2 with IV provides a rapid autocatalyzed BH/D_2 exchange process similar in nature to that observed with I and inhibited by added PPh_3. Regiospecific deuterium exchange at BH vertices and the B–H–B bridge in IV was evident in THF at 40.8 °C although the positional assignment of the BH vertices which were preferentially exchanged is not available at this time. Related to these results is the observation of deuterium scrambling during the preparation of IV from the reaction of specifically bridge-deuterated (B–D–B) [*nido-μ*-7,8-$(CH_2)_3$-7,8-$C_2B_9H_{10}$]$^-$ with $(PPh_3)_3RhCl$. Consequently, no IV species containing deuterium specifically in its B–H–B bridge position could be prepared for further study by this or several less obvious routes. Thus, the B–H–B bridge hydrogen of IV easily equilibrates with terminal BH positions also present in IV. As in the case of I, the mechanisms of these autocatalyzed exchange and D-scrambling reactions are under investigation with IV.

Kinetics of 1-Hexene (B) Isomerization. The kinetics of the isomerization of B to a mixture of *cis*- and *trans*-2-hexenes was examined in THF at 40.8 °C using catalyst precursors I–IV. No 3-hexenes were observed and the concentrations of B and the reaction products were monitored by GLC. All kinetic runs contained a known concentration of added PPh_3 which was varied to determine the dependence of rate upon PPh_3 concentration. The concentrations of the precursors I, II, III, and IV were varied, as well. Reactions were followed to 75% completion and the pseudo-first-order rate constants (k_{obsd}) obtained with all systems were fit to the rate expression 1, where [Rh]$_t$ represents the total concentration of Rh derived from catalyst precursor. In order

$$-\frac{d[\text{Hexene-1}]}{dt} = k_{obs}[\text{B}] = \frac{k_i[\text{B}][\text{Rh}]_t}{[\text{PPh}_3]} \qquad (1)$$

to determine the importance, if any, of reversible dissociation of $(PPh_3)_2Rh^+$ from the *nido*-carborane anion ligands, 4.0 equiv (based on the concentration of catalyst precursor) of the corresponding Cs^+ *nido*-carborane anion salts was added to rate runs which employed II and IV. No large rate effect was observed in either case although the isomerization rate with II, $k_i = 1.26 \times 10^{-4}$ s^{-1}, was slightly enhanced and the isomerization rate with IV, $k_i = 1.54 \times 10^{-5}$ s^{-1}, was slightly depressed. These relatively small effects do not support the existence of a mass-action effect.

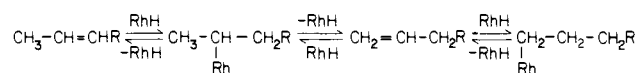(20) Doi, J. A.; Teller, R. G.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1980**, 80.

Table I. Collected Rate Data for the Isomerization of 0.18 M 1-Hexene (B) in THF at 40.8 °C

catalyst precursor	[Rh]$_t$	[PPh$_3$]	k_{obsd}, s^{-1}	k_i, s^{-1}
I[a]	5.18×10^{-3}	5.82×10^{-4}	7.89×10^{-5}	8.86×10^{-6}
	1.04×10^{-2}	5.82×10^{-4}	1.60×10^{-4}	8.95×10^{-6}
	2.71×10^{-3}	5.82×10^{-4}	3.87×10^{-5}	8.30×10^{-6}
	4.90×10^{-3}	2.91×10^{-4}	1.40×10^{-4}	8.31×10^{-6}
II[b]	5.12×10^{-3}	2.69×10^{-3}	2.03×10^{-4}	1.07×10^{-4}
	2.59×10^{-3}	4.83×10^{-3}	6.04×10^{-4}	1.13×10^{-4}
	1.01×10^{-2}	5.17×10^{-3}	2.14×10^{-4}	1.10×10^{-4}
	5.53×10^{-3}	5.24×10^{-3}	1.20×10^{-4}	1.14×10^{-4}
	5.13×10^{-3}	1.12×10^{-2}	5.39×10^{-5}	1.17×10^{-4}
III[c]	5.22×10^{-3}	5.44×10^{-3}	6.80×10^{-5}	7.09×10^{-5}
	5.10×10^{-3}	9.90×10^{-3}	3.43×10^{-5}	6.65×10^{-5}
	5.12×10^{-3}	2.91×10^{-3}	1.13×10^{-4}	6.44×10^{-5}
	2.75×10^{-3}	5.69×10^{-3}	3.33×10^{-5}	6.88×10^{-5}
	1.02×10^{-2}	6.11×10^{-3}	1.12×10^{-4}	6.76×10^{-5}
IV[d]	4.49×10^{-3}	5.82×10^{-4}	1.63×10^{-4}	2.11×10^{-5}
	4.48×10^{-3}	1.16×10^{-3}	8.08×10^{-5}	2.11×10^{-5}
	4.49×10^{-3}	2.91×10^{-4}	3.55×10^{-4}	2.30×10^{-5}
	2.30×10^{-3}	5.82×10^{-4}	7.97×10^{-5}	2.01×10^{-5}
	8.77×10^{-3}	1.16×10^{-4}	1.83×10^{-4}	2.43×10^{-5}

[a] Average k_i^I = 0.861×10^{-5} s^{-1}.   [b] Average k_i^{II} = 11.2×10^{-5} s^{-1}.   [c] Average k_i^{III} = 6.76×10^{-5} s^{-1}.   [d] Average k_i^{IV} = 2.19×10^{-5} s^{-1}.

Table I presents the collected rate data and the calculated k_i values obtained with precursors I–IV. Product distributions obtained with the *closo* catalyst precursors I, II, and III were virtually identical with each other and gave a *cis*- to *trans*-2-hexene ratio of about 0.5, which is essentially the equilibrium isomer ratio.[21] Control experiments proved that under the same conditions with I, *cis*-2-hexene was converted to its trans isomer at a greater rate than B was converted to the mixed 2-hexene isomer mixture. The *nido* catalyst precursor (IV) produced a much higher *cis*- to *trans*-2-hexene ratio of ca. 5:1 as a result of kinetic control.

Deuterium-Labeling Experiments Pertinent to the Alkene Isomerization Mechanism. In order to explore the possible role of the hydride ligand attached to the formal Rh(3+) of the *closo* catalyst precursors in alkene isomerization (MH addition–elimination mechanism[9,10,11,13]), the rate of deuterium exchange of I-*3-d*

$$CH_3-CH=CHR \underset{-RhH}{\overset{RhH}{\rightleftharpoons}} CH_3-\underset{\underset{Rh}{|}}{CH}-CH_2R \underset{RhH}{\overset{-RhH}{\rightleftharpoons}} CH_2=CH-CH_2R \underset{-RhH}{\overset{RhH}{\rightleftharpoons}} \underset{\underset{Rh}{|}}{CH_2}-CH_2-CH_2R$$

with B was determined by ^{1}H FTNMR analysis of developing RhH in recovered catalyst precursor as a function of time in THF containing 2.4×10^{-4} M PPh_3 at 40.8 °C. In another series of identical experiments, a 68:32 *cis*-2-hexene:*trans*-2-hexene mixture was similarly examined with I-*3-d*. In both series of experiments initial concentrations of alkene and I-*3-d* were 0.21 and 5.2×10^{-3} M, respectively. The initial RhD exchange rate observed with the 2-hexene system was indistinguishable from the rate of autoexchange ($k = 8 \times 10^{-6}$ s^{-1}) observed in the absence of alkenes. This result suggests that the 2-hexenes are kinetically stable toward the rhodium hydride ligand of I. In contrast to these results, the initial rate of exchange of B with I-*3-d* was much more rapid, giving a first-order rate constant estimated from initial rate data of approximately 1.2×10^{-4} s^{-1}. In addition, after 58 min, the calculated half-life of B isomerization under these conditions, only 35% RhD exchange was observed. Thus, 5.2×10^{-3} mol of I-*3-d* catalyzed the conversion of 0.1 mol of B to 2-hexenes while suffering only 1.8×10^{-3} mol of deuterium loss from available RhD or, stated another way, approximately one RhD exchange occurred per 55 mol of B isomerization. After seven isomerization half-lives the recovered catalyst precursor contained approximately 65% RhH and the isomerization of B was virtually complete. As

(21) The equilibrium ratio of *cis*- to *trans*-2-hexene is approximately 0.45 at 41 °C. Calculated from data taken from: "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds"; Carnegie Press: Pittsburgh, PA, 1953.

in the case of autocatalyzed BH/D$_2$ exchange of I, the predominant terminal alkene isomerization reaction catalyzed by precursor I proceeds without significant direct involvement of the hydride ligand attached to the rhodium vertex.

The alkene (A) was also exained for deuterium exchange with I-*3-d* under exactly the same conditions outlined above for B and the 2-hexenes. While A is structurally incapable of isomerization, it was important to evaluate the reactivity of the RhH hydride ligand present in I toward this alkene since A was the alkene employed in the hydrogenation studies to be described below.

The initial rate of RhD exchange in I-*3-d* with A was found to be identical, within experimental error, with the autocatalyzed exchange rate for I-*3-d* under the same conditions and reactant concentrations ([A] = 0.21 M, [I-*3-d*]$_0$ = 5.2 × 10^{-3} M and [PPh$_3$] = 2.4 × 10^{-4} M). This result suggests that A, like the 2-hexenes, is essentially inert with respect to reaction with the RhH present in I.

Having shown that RhD in I-*3-d* was not rapidly exchanged with alkene during B isomerization and that A was essentially inert in this exchange process, it was important to establish the integrity of terminal B–H bonds toward the possible oxidative addition of Rh(1+). The B–Rh–H species which would result from such a reaction could provide a source of RhH which might account for alkene isomerization without RhD exchange in I-*3-d*. Thus [*closo*-3,3-(PPh$_3$)$_2$-3-H-3,1,2-Rh(C$_2$H$_2$B$_9$D$_9$)] (I-*d*$_9$) (5.2 × 10^{-3} M) was employed in 1-hexene (0.32 M) isomerization with 5.2 × 10^{-4} M PPh$_3$ and the isotopic purity of the catalyst precursor was monitored by using 160-MHz ^{11}B NMR spectra. After 13 turnovers of Rh under kinetic conditions the ^{11}B spectrum of (I-*d*$_9$) remained unchanged. It is estimated that as little as 5% exchange of BD for BH would have been easily detected by the appearance of line broadening due to ^{11}B–^{1}H spin coupling. An identical experiment carried out using A instead of B as the alkene gave the same result after 5 h of equilibration. Thus it may be concluded that terminal BH bonds do not become involved in alkene isomerization under the conditions employed in the kinetic experiments.

The results reported above prove that alkene isomerization does not proceed via the agency of the RhH centers associated with closo precursors or from RhH centers possibly produced by oxidative addition of a B–H vertex to Rh(1+). Other reactions carried out with A and I which contained ortho-deuterated triphenylphosphine ligands gave no evidence of deuterium loss in I recovered after 20 turnovers. Consequently, the search for evidence to support an alkene isomerization mechanism shifted from the metal hydride addition–elimination mechanism[9,10,11,13] to a mechanism which employs η^3-allylic intermediates.[9,11,13]

In this study use was made of the specifically deuterated propenes CD$_3$CH=CH$_2$ and CH$_3$CD=CH$_2$ and their equilibration with I in THF-*d*$_8$ at 41 °C. These and related experiments which follow were monitored by ^{1}H FTNMR with 4.8 × 10^{-3} M (I), 2 × 10^{-4} M PPh$_3$, and 8 × 10^{-2} M total alkene. If the isomerization of terminal alkenes observed with catalyst precursors I–IV simply involved η^3-allylic intermediates, formed as shown below, with deuterated propenes as reactant, one would observe
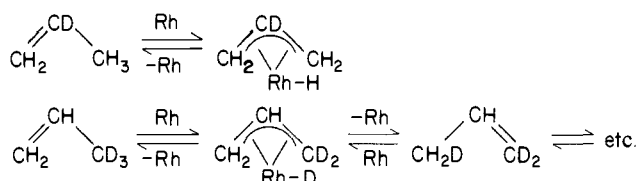
no equilibration of hydrogen isotopes between the 2- and the flanking 1- and 3-positions. However, deuterium should be distributed between the 1- and 3-positions using CD$_3$CH=CH$_2$ as the initial reactant. In fact, CH$_3$CD=CH$_2$ rapidly loses deuterium from the 2-position ($t_{1/2}$ = ca. 80 min) and CD$_3$CH=CH$_2$ loses its proton from the 2-position ($t_{1/2}$ = ca. 50 min) as well as scrambling deuterium between positions 1 and 3 ($t_{1/2}$ = ca. 50 min). In all of these reactions which involve deuterated propenes, no RhD was seen to develop by exchange since the ^{1}H FTNMR

Scheme I
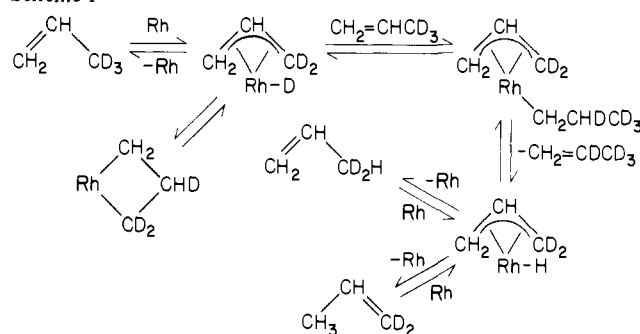
spectra showed no changes in the RhH region. Clearly, processes other than simple η^3-allylic isomerization are in operation. These observed interconversions of deuterated propenes could be explained on the basis of a composite η^3-allylic–RhH alkene addition sequence and/or the operation of a metallacyclobutane or a similar obscure mechanism.[11c] The former sequence, a portion of which is illustrated in Scheme I, would be expected to redistribute deuterium intermolecularly among all available alkene molecules present in the reaction mixture. Thus, a 50:50 mixture of CH$_2$=CHCH$_3$ (*m/e* 42) and CH$_2$=CHCD$_3$ (*m/e* 45) was equilibrated by using the I and PPh$_3$ concentrations described above and observed to rapidly produce a mixture of propene-*d*$_n$ (*n* = 0–6) the relative abundances of which were monitored as a function of time by GC/MS ($t_{1/2}$ = 280 min). If these deuterium redistribution reactions truly involved the simultaneous interaction of two alkene molecules with a Rh center, then such reactions would be expected to be sensitive to the bulk of the constituent alkenes and alkenes such as A or 3,3-dimethyl-1-butene should enter such exchange reactions with difficulty, if at all. The equilibration of I with A-*2-d*, either by itself or in the presence of equal quantities of propene or 3,3-dimethyl-1-butene, gave only very slow appearance of A (=CH—) ($t_{1/2}$ = ca. 62 h). These very slow exchange processes are probably unrelated to the alkene isomerization reactions normally observed under kinetic conditions and arise instead via slow side reactions which involve oxidative addition of Rh(1+) to B–H bonds to produce reactive B–Rh–H centers. Such reactions are delineated below.

In experiments carried out in the *absence of added PPh*$_3$, it was shown that A-*1,1,2-d*$_3$ would slowly undergo a regiospecific deuterium exchange reaction with isotopically normal I. As an example, equilibration of 0.11 M A-*1,1,2-d*$_3$ (81% isotopically pure) with 3.76 × 10^{-2} M (I) in THF-*d*$_8$ at 40 °C for 31 h was monitored by ^{1}H FTNMR. Isolation of the resulting I and A and analysis (IR) of the I produced indicated a BD content of approximately 28% and only a trace of RhD. The recovered A was shown (GC/MS) to have a total D content of 56% of the three exchange sites. The ^{11}B NMR spectrum of recovered I was examined after its in situ conversion[19] to [*closo*-3,3-(PEt$_3$)$_2$-3-H-3,1,2-RhC$_2$B$_9$H$_{11}$]. While quantitatively imprecise, the loss of ^{1}H–^{11}B coupling in the resonances assigned[19] to BH vertices 9, 10, and 12 (see Figure 1) due to D substitution proves that the BH/CD exchange reaction is regiospecific. Calculated D analyses based upon three exchangeable BH sites among a total of nine give calculated equilibrium values of 20% BD in I and 60% CD in recovered A. These values are within the experimental error of the observed D analyses and make no allowance for isotope effects.

Hydrogenation of 3-Methyl-3-phenyl-1-butene (A) with the Closo Catalyst Precursors I and III. The kinetics of the hydrogenation of A with the closo catalyst precursors I and III were studied at 40.8 °C in THF solution, and similar results were obtained in both cases. In all rate runs the initial concentration of A was 0.16 M and concentrations of PPh$_3$, catalyst precursor ([Rh]$_t$), and hydrogen were varied from run to run. Each kinetic run with I or III was nicely first order in A with the pseudo-first-order rate constant k_{obsd}. Collected rate data proved that k_{obsd} was first order in [Rh]$_t$ and reciprocal first order in [PPh$_3$] at any fixed H$_2$ pressure, and this relationship was employed to

Table II. Collected Rate Data for the Hydrogenation of 0.18 M 3-Methyl-3-phenyl-1-butene (A) with Catalyst Precursors 1 and III in THF at 40.8 °C

catalyst precursor	$[Rh]_t$	$[PPh_3]$	$[H_2]$	k_{obsd}, s^{-1}	k_h^A, s^{-1}
I	1.50×10^{-2}	1.75×10^{-3}	9.86×10^{-4}	1.28×10^{-5}	1.48×10^{-6} [f]
	1.50×10^{-2}	8.73×10^{-4}	9.89×10^{-4}	2.56×10^{-5}	1.49×10^{-6} [f]
	1.50×10^{-2}	4.37×10^{-4}	9.91×10^{-4}	5.34×10^{-5}	1.55×10^{-6} [f]
	1.50×10^{-2}	2.18×10^{-4}	2.53×10^{-4}	4.03×10^{-5}	5.84×10^{-7}
	1.50×10^{-2}	2.18×10^{-4}	6.38×10^{-4}	8.06×10^{-5}	1.17×10^{-6}
	1.50×10^{-2}	2.18×10^{-4}	3.18×10^{-4}	4.90×10^{-5}	7.10×10^{-7}
	1.50×10^{-2}	2.18×10^{-4}	1.48×10^{-3}	1.27×10^{-4}	1.84×10^{-6}
	1.50×10^{-2}	2.18×10^{-4}	4.65×10^{-4}	6.37×10^{-5}	9.25×10^{-7}
	1.50×10^{-2}	6.55×10^{-4}	7.69×10^{-4}	3.07×10^{-5}	1.34×10^{-6}
	1.50×10^{-2}	6.55×10^{-4}	2.25×10^{-3}	4.97×10^{-5}	2.16×10^{-6}
	1.50×10^{-2}	8.73×10^{-4}	1.96×10^{-3}	3.57×10^{-5}	2.07×10^{-6}
	1.50×10^{-2}	1.75×10^{-3}	2.23×10^{-3}	1.87×10^{-5}	2.17×10^{-6}
	9.98×10^{-3}	2.88×10^{-4}	9.88×10^{-4}	5.69×10^{-5}	1.64×10^{-6} [f]
	2.01×10^{-2}	2.91×10^{-4}	9.88×10^{-4}	1.13×10^{-4}	1.64×10^{-6} [f]
	1.19×10^{-2}	1.72×10^{-4}	9.86×10^{-4}	1.32×10^{-4}	1.91×10^{-6} [a]
	1.19×10^{-2}	1.72×10^{-4}	9.86×10^{-4}	1.26×10^{-4}	1.83×10^{-6} [b]
	7.93×10^{-3}	1.15×10^{-4}	9.86×10^{-4}	1.05×10^{-4}	1.52×10^{-6} [c]
	8.00×10^{-3}	1.16×10^{-4}	9.86×10^{-4}	1.22×10^{-4}	1.80×10^{-6} [d]
	8.00×10^{-3}	9.3×10^{-5}	9.86×10^{-4}	1.07×10^{-4}	1.24×10^{-6} [e]
III	6.95×10^{-3}	1.46×10^{-4}	6.29×10^{-4}	1.79×10^{-4}	3.75×10^{-6}
	8.21×10^{-3}	1.46×10^{-4}	3.89×10^{-4}	1.44×10^{-4}	2.54×10^{-6}
	6.38×10^{-3}	1.46×10^{-4}	2.52×10^{-3}	3.98×10^{-4}	9.08×10^{-6}
	1.61×10^{-2}	2.33×10^{-4}	1.13×10^{-3}	4.07	5.91×10^{-6}

[a] D_2 replaced H_2. [b] D_2 replaced H_2, preequilibrated 4h with D_2. [c] 3.1×10^{-2} M Cs[7,8-$C_2B_9H_{12}$] added. [d] With 3.1×10^{-5} M 4-methoxyphenol. [e] With 3.1×10^{-5} M diisopropylethylamine. [f] This k_h^A value averaged with others determined at some pressure to give plotted (Figure 3) value of 1.56×10^{-6} s^{-1}.

compute k_h^A for I and III (k_h^{IA} and k_h^{IIIA}, respectively) as defined by eq 2. The dependence of k_h^{IA} and k_h^{IIIA} upon hydrogen

$$-\frac{d[H_2]}{dt} = k_{obs}[A] = \frac{k_h^A[A][Rh]_t}{[PPh_3]} \qquad (2)$$

concentration was revealed by the fact that plots of $(k_h^{IA})^{-1}$ and $(k_h^{IIIA})^{-1}$ vs. $[H_2]^{-1}$ (Figure 3) were linear with positive slopes m^I (3.6×10^2 M s) and m^{III} (1.3×10^2 M s) and intercepts C^I (2.9×10^5 s) and C^{III} (0.55×10^5 s), respectively (eq 3). Table II

$$1/k_h^A = \frac{m}{[H_2]} + C \quad \text{and} \quad k_h^A = \frac{[H_2]}{m + C[H_2]} = k_{obs}\frac{[PPh_3]}{[Rh]_t}$$

$$k_{obs} = \frac{[Rh]_t[H_2]}{[PPh_3](m + C[H_2])} \qquad (3)$$

$$-\frac{d[H_2]}{dt} = \frac{[Rh]_t[A][H_2]}{[PPh_3](m + C[H_2])}$$

presents collected kinetic data and k_h^A values for precursors I and III. The solubility of H_2 in THF[22] at 40.8 °C is $1.7 \pm 0.1 \times 10^{-3}$ M atm^{-1}.

In order to further probe the nature of the hydrogenation of A with I, a series of kinetic experiments were carried out at 0.58 atm H_2 pressure in which a base (i-Pr_2NEt), a radical scavenger (4-methoxyphenol), and Cs$^+$[7,8-$C_2B_9H_{12}$]$^-$ were separately employed as addends. The i-Pr_2NEt and the 4-hydroxyanisole concentrations were approximately 15% that of I present in their respective experiments. The common-ion experiment utilized a Cs$^+$[7,8-$C_2B_9H_{12}$]$^-$ concentration equal to four times the concentration of I present. The values of k_h^{IA} observed in these rate runs (see Table II) are not sufficiently different from the k_h^{IA} values observed in the absence of addends to warrant interpretation.

In another kinetic experiment I, deuterated at both carborane carbon vertices (I-$1,2$-d_2),[4] was employed as the catalyst precursor in the presence of 1 equiv of isotopically normal Cs$^+$[7,8-$C_2B_9H_{12}$]$^-$ at 0.58 atm of H_2. The observed $k_h^{IA} = 1.64 \times 10^{-6}$ s^{-1} was in the normal range. Recovery of I present at the conclusion of the rate run and examination of its ^1H FTNMR proved that appre-
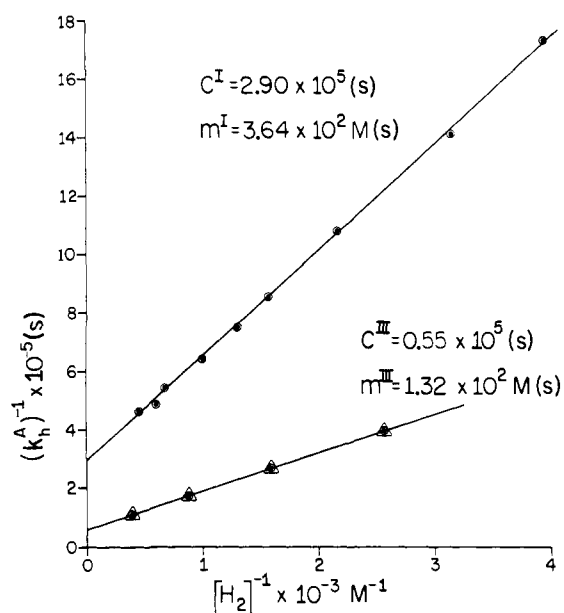
(22) We are indebted to Professor Brian James and his co-workers for this solubility determination.

Figure 3. Plot of $(k_h^{IA})^{-1}$ and $(k_h^{IIIA})^{-1}$ vs. $[H_2]^{-1}$ in accord with eq 3 and the data of Table II.

ciable exchange of the deuterated ligand originally present in I-$1,2$-d_2 had occurred as evidenced by the appearance of the characteristic resonance[4] of the protons present at the 1 and 2 positions of isotopically normal I. As expected, this result demonstrates that ligand exchange, which presumably proceeds via an exo-nido intermediate,[7] occurs independently without alteration of the observed rate of hydrogenation. Thus, exchange of [7,8-$C_2B_9H_{12}$]$^-$ ligand between I and free anion does occur, but no mass-action effect is evident in the observed hydrogenation rate as would be expected if free solvated (PPh$_3$)$_2$Rh$^+$ or similar cationic species were involved in hydrogenation catalysis.

Deuterium was substituted for H_2 (see Table II) and $(k_h^{IA})_H/(k_h^{IA})_D$ values of about 0.85 were observed at H_2 and D_2 partial pressures of 0.58 atm. Due to the fact that some conversion of BH to BD vertices occurs when I is treated with D_2 in the presence of A the identification of the origin of this kinetic isotope

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Table III. Isotopic Analyses of Products Resulting from the Reduction of 0.47 M 3-Methyl-3-phenyl-1-butene (A) with D_2 (9.8×10^{-4}) Using 1 (3.94×10^{-3} M) and Triphenylphosphine (7.9×10^{-5} M) at 40.8 °C in THF

% reaction	turnovers of total Rh^a	alkene, %			alkane, %				D balance, Δ^b	recovered % RhH^c	(I) % BD^c
		d_0	d_1	d_2	d_0	d_1	d_2	d_3			
3	4	99	1		1	61	41		0.88	93	3.3
9	11	96	4		0	56	45		0.94	95	4.1
16	19	93	7		2	54	44	1	0.91	96	5.1
21	25	89	11		1	53	46	1	0.93	98	6.2
30	36	84	16		1	48	50	2	0.95	96	8.1
47	56	74	24	2	2	41	48	9	0.96	89	11.4

^{a} 100% reaction corresponds to 119 turnovers. ^{b} Calculated by using eq 4. ^{c} Determined by IR spectroscopy.

effect as primary, secondary, or a composite of effects is uncertain.

The possible direct involvement of the RhH vertex of I in the hydrogenation mechanism was excluded by carrying out the hydrogenation of A at 0.58 atm of H_2 with I-*3-d* and determining the extent of conversion of RhD to RhH under these conditions. If the RhD vertex were directly involved, the deuterium should be completely exchanged for hydrogen after one catalyst turnover. The results obtained in two different experiments showed 90% retention of the D label after 7 Rh turnovers and 60% retention of deuterium after 14 turnovers. The I-*3-d* and PPh_3 concentrations present in both of these reactions were 1.3×10^{-2} and 1.9×10^{-4} M, respectively. The loss of RhD observed may be largely accounted for by the slow autoexchange reaction, discussed above, in which the deuterium present in RhD is exchanged for terminal hydrogen on boron vertices, thereby generating an RhH vertex. It is obvious, however, that RhH does not participate in the hydrogenation sequence.

In another experiment designed to indicate the possible involvement of B–H bonds in hydrogenation, 5.2×10^{-3} M I-d_9, 5.2×10^{-4} M PPh_3, and 0.52 M A were carried through 10 hydrogenation catalyst turnovers (0.58 atm of H_2). Examination of the ^{11}B FTNMR of the recovered I revealed no loss of deuterium, thus proving that B–H vertices do not become involved in the hydrogenation mechanism.

In a search for the reversible formation of an Rh(alkyl) intermediate during hydrogenation, the isotopic composition of the products of the reaction of A with D_2 (0.58 atm) catalyzed by the precursor I in a flow system at 40.8 °C in THF were determined as a function of time by periodically withdrawing samples of reaction mixture and separating the I present from A and 2-methyl-2-phenylbutane by flash evaporation. The reaction mixture was constantly supplied with solvent-saturated D_2 by passing the latter through the solution at a rate of ca. 2 mL min^{-1}. The recovered organic fraction was analyzed by GC/MS and the deuterium content of I at the RhH and BH vertices was estimated by IR spectroscopy. The initial concentration of A was 0.47 M and the I and PPh_3 concentrations were 3.9×10^{-3} and 7.9×10^{-5} M, respectively. Table III presents the results with reference to the percent of A consumed (1% reaction corresponds to 1.2 turnovers of I). Also included in Table III as a function of % reaction is the calculated deuterium balance parameter, Δ, which is expressed as the ratio of moles of total deuterium present in all organic species present to the deuterium content calculated on the basis of the introduction of 1 mol of D_2 per mol of reduction.

$$\Delta = \frac{\sum_{n=1}^{n=3} n[\text{alkene} - d_n] + \sum_{n=1}^{n=5} n[\text{alkane} - d_n]}{2\sum_{n=0}^{n=5}[\text{alkane} - d_n]} \quad (4)$$

This ratio would be equal to unity if hydrogen in the organic species present did not exchange into the gas phase or, put another way, if each mole of D_2 which was taken up by the system accomplished a mole of reduction, but became scrambled between alkene and alkane in so doing. The values reported for Δ in Table III are actually close to unity, thus indicating the condition described above accompanied by extensive scrambling of deuterium between alkane product and alkene reactant, a manifestation of reversible Rh(alkyl) formation. Interestingly, RhH/D_2 and BH/D_2 exchange was not extensive in recovered I even after 56 turnovers (47% reaction) although the ubiquitous BH exchange
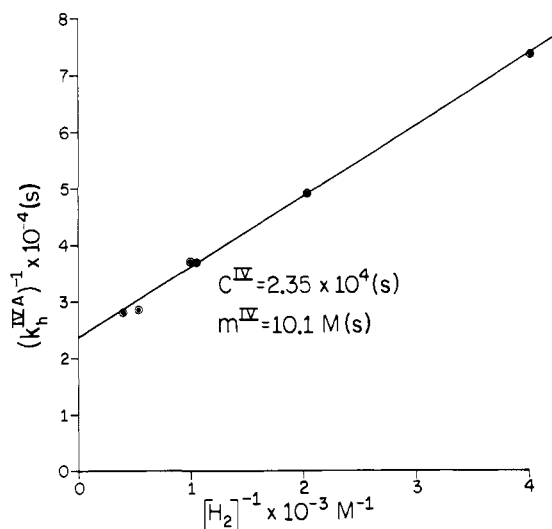

Figure 4. Plot of $(k_h^{IVA})^{-1}$ vs. $[H_2]^{-1}$ in accord with eq 3 and the data of Table IV.

with D_2 is apparently available as well as RhH autoexchange with BD. The latter result strongly suggests that BH/D_2 exchange is inhibited by A.

Hydrogenation of A with the Exo-Nido Catalyst Precursor IV. The kinetic study of the hydrogenation of A with the exo-nido catalyst precursor IV closely paralleled the similar study of A hydrogenation with the closo catalyst precursors I and III described above. As before, rate runs were conducted at 40.8 °C in THF with variable concentrations of IV, PPh_3, and hydrogen while $[A]_0$ = 0.16 M. Each kinetic run was first order in A with an observed pseudo-first-order rate constant, k_{obsd}. As in the cases of precursors I and III the data proved that k_{obsd} was first order in catalyst precursor $[Rh]_t$, and reciprocal first order in $[PPh_3]$ at any fixed H_2 pressure. The dependence of rate upon $[H_2]$ was identical in form with that found for the *closo*-I and III catalyst precursors and eq 3 provides a complete description of the prevailing rate law. Figure 4 is a plot of the $(k_h^{IVA})^{-1}$ vs. $[H_2]^{-1}$ values of Table IV from which the slope m^{IV} (10.1 M s) and intercept C^{IV} (2.4 $\times 10^4$ s) were evaluated.

Table IV contains data for a rate run carried out at 0.58 atm of H_2 using 4.3×10^{-3} M IV and in the presence of 1.7×10^{-2} M $Cs^+[\mu\text{-}7,8\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$. As before, the effect of added ligand anion is negligible and no common-ion effect is apparent. This observation supports the conclusion that catalysis is not due to the presence of low equilibrium concentrations of solvated $(PPh_3)_2Rh^+$ or related species.

As seen in Table IV substitution of D_2 for H_2 produced a small inverse kinetic isotope effect, $(k_h^{IVA})_H/(k_h^{IVA})_D$, of about 0.9 at H_2 and D_2 pressures of 0.58 atm. Again, complicating BH/BD exchange is simultaneous with the reduction of A, and the origin of this small kinetic isotope effect cannot be assigned. However, the near identity of the $(k_h^{IVA})_H/(k_h^{IVA})_D$ ratio observed in this exo-nido system and the corresponding ratio in the *closo*-I precursor system suggests a similarity of mechanism.

Table V presents the results of periodic analysis of the organic components seen in THF at 40.8 °C in the reduction of A with

Table IV. Collected Rate Data for the Hydrogenation of 0.1 M 3-Methyl-3-phenyl-1-butene (A) with Catalyst Precursor (IV) in THF at 40.8 °C

$[Rh]_t$	$[PPh_3]$	$[H_2]$	k_{obsd}, s^{-1}	$k_h{}^A$, s^{-1}
4.39×10^{-3}	5.82×10^{-4}	1.01×10^{-3}	2.06×10^{-4}	2.72×10^{-5} [c]
4.34×10^{-3}	1.16×10^{-4}	1.00×10^{-3}	1.035×10^{-4}	2.77×10^{-5} [c]
4.45×10^{-3}	1.75×10^{-3}	9.93×10^{-4}	7.13×10^{-5}	2.80×10^{-5} [c]
4.39×10^{-3}	3.49×10^{-3}	9.98×10^{-4}	3.35×10^{-5}	2.66×10^{-5} [c]
2.17×10^{-3}	1.16×10^{-3}	9.84×10^{-4}	5.10×10^{-5}	2.73×10^{-5} [d]
4.31×10^{-3}	1.16×10^{-3}	2.48×10^{-4}	5.13×10^{-5}	1.39×10^{-5} [e]
4.40×10^{-3}	1.16×10^{-3}	4.91×10^{-4}	7.61×10^{-5}	2.01×10^{-5} [f]
4.36×10^{-3}	1.16×10^{-3}	1.96×10^{-3}	1.30×10^{-4}	3.47×10^{-5}
4.45×10^{-3}	5.82×10^{-4}	2.47×10^{-4}	1.01×10^{-4}	1.32×10^{-5} [e]
4.33×10^{-3}	5.82×10^{-4}	4.90×10^{-4}	1.54×10^{-4}	2.07×10^{-5} [f]
4.48×10^{-3}	1.75×10^{-3}	2.47×10^{-3}	9.12×10^{-5}	3.56×10^{-5}
2.28×10^{-3}	1.16×10^{-3}	9.98×10^{-4}	5.22×10^{-5}	2.66×10^{-5} [c]
2.31×10^{-3}	5.82×10^{-4}	9.83×10^{-4}	1.08×10^{-4}	2.72×10^{-5} [d]
4.34×10^{-3}	1.15×10^{-3}	9.83×10^{-4}	7.18×10^{-6}	2.71×10^{-5} [a]
2.23×10^{-3}	5.76×10^{-4}	9.86×10^{-4}	7.49×10^{-6}	2.90×10^{-5} [b]
2.23×10^{-3}	1.15×10^{-3}	9.84×10^{-4}	1.58×10^{-5}	3.08×10^{-5} [b]

[a] In presence of 1.7×10^{-2} M Cs[7,8-(CH$_2$)$_3$C$_2$B$_9$H$_{10}$]. [b] D$_2$ replaced H$_2$. [c] This $k_h{}^A$ value averaged with others determined at same H$_2$ pressure to give plotted (Figure 4) value of 2.72×10^{-5} s^{-1}. [d] Same as c, average $k_h{}^A = 2.72 \times 10^{-5}$ s^{-1}. [e] Same as c, average $k_h{}^A = 1.36 \times 10^{-5}$ s^{-1}. [f] Same as c, average $k_h{}^A = 2.04 \times 10^{-5}$ s^{-1}.

Table V. Isotopic Analyses of Products Resulting from the Reduction of 0.52 M 3-Methyl-3-phenyl-1-butene (A) with D$_2$ (9.8×10^{-4} M) Using IV (3.63×10^{-3} M) and Triphenylphosphine (7.6×10^{-4} M) at 40.8 °C in THF

% reaction	turnovers of total Rh[a]	alkene, %		alkane, %					D balance, Δ[b]
		d_0	d_1	d_0	d_1	d_2	d_3	d_4	
12	17	89	11	14	50	36			1.00
20	29	88	12	14	52	33	1		0.85
44	63	68	32	11	44	38	7		0.91
75	107	54	46	6	17	34	38	4	1.15

[a] 100% reaction corresponds to 143 turnovers. [b] Calculated by using eq 4.

D$_2$ using 3.6×10^{-3} M IV and 7.6×10^{-4} M PPh$_3$. The initial concentration of A was 0.52 M and the D$_2$ (0.58 atm) was supplied as before to the flow system at a rate of ca. 2 mL min^{-1}. Each percent reaction corresponds to 1.43 precursor turnovers. As in the case of I, the entering deuterium is extensively scrambled between alkene reactant and alkane product. However, significant quantities of 2-methyl-2-phenylbutane-d_0 are produced, as well. The deuterium balance parameter, Δ, is near unity although these data inadvertently contain some scatter. Thus, each mole of alkene reduction results in the distribution of 1 mol of deuterium between the alkene remaining and the alkane product. Recovered IV was not examined for BD content.

Competitive Isomerization and Hydrogenation of 1-Hexene (B) with Catalyst Precursor I. Since one of the important mechanistic points to be established in these studies was the relationship of the alkene hydrogenation and isomerization reactions, a detailed study of competitive B hydrogenation and isomerization was carried out by using the representative closo and exo-nido catalyst precursors I and IV, respectively.

The reaction of 0.30 M B, 5.05×10^{-3} M I, 7.2×10^{-4} M PPh$_3$, and 0.58 atm of H$_2$ in THF at 40.8 °C was monitored by GLC. A first-order rate constant for B consumption, 5.8×10^{-5} s^{-1}, was observed. The reaction products were hexane (4.5%) and a 2:1 equilibrium mixture of *trans*-2-hexene:*cis*-2-hexene (95.5%). Repetition of this experiment at twice the hydrogen pressure (1.16 atm) produced a first-order rate constant for B consumption of 7.8×10^{-5} s^{-1}. The reaction products from this reaction were identical with those observed at the lower H$_2$ pressure except that the proportion of hexane produced was doubled to 9.0%, a fact which demonstrates approximate first-order dependence of hexane formation upon H$_2$ pressure. Calculation of the first-order rate constants for the formation of the mixed 2-hexenes gave values of 5.5 and 7.1×10^{-5} s^{-1} for the lower and higher pressure experiments, respectively. When the value of $k_i{}^1$ reported in Table I (8.6×10^{-6} s^{-1}) was used, a k_{obsd} of 5.8×10^{-5} s^{-1} was calculated for the isomerization of B in the absence of H$_2$ and using the reagent concentrations employed in the two competition experiments reported here. Thus, it appears that the presence of H$_2$ (1.16 atm) may slightly increase the rate of B isomerization above that expected in the absence of H$_2$. The similar effect of 0.58 atm of H$_2$ in this respect is indistinguishable from experimental scatter.

The results of product analyses made during the reduction of B with D$_2$ (0.58 atm) in the presence of 4.9×10^{-3} M I and 7.1×10^{-4} M PPh$_3$ are presented in Table VI. These deuteration results are in agreement with the results of the product analyses of the rate runs described above. In addition, it is seen that the *cis*- and *trans*-2-hexenes produced during the deuteration of B each contain approximately 4–5% alkene-d_1, the small amount of alkane coproduct is 90–100% hexane-d_1, while unreacted B is apparently free of all deuterium. From these results one may conclude that B isomerization under these conditions is essentially independent of D$_2$ participation and that the reduction of B to

Table VI. Isotopic Analyses of Products Resulting from the Reduction of 0.59 M 1-Hexene (B) with D$_2$ (9.8×10^{-4} M) Using I (4.9×10^{-3} M) and Triphenylphosphine (7.1×10^{-4} M) at 40.8 °C in THF

1-hexene (B)				hexane				*trans*-2-hexene				*cis*-2-hexene				D balance, Δ[a]
%	d_0	d_1	d_2	%	d_0	d_1	d_2	%	d_0	d_1	d_2	%	d_0	d_1	d_2	
100	100															
90.5	100							5.4	100			3.4	100			
81.9	100			0.74	0	100	0	10.2	98.2	1.8	0	6.3	98.0	2.0	0	0.71
74.1	100			1.0	0	100	0	14.7	98.4	1.6	0	8.9	98.5	1.5	0	0.68
60.7	100			1.6	0	100	0	22.8	96.8	3.2	0	13.3	96.8	3.2	0	0.86
49.7	100			2.0	0	100	0	29.1	96.8	3.2	0	16.2	97.0	3.0	0	0.85
40.7	100			2.4	6	94	0	34.9	96.5	3.5	0	18.6	96.5	3.5	0	0.86
33.3	100			2.8	1.9	98.1	0	40.4	96.0	4.0	0	20.6	96.0	4.0	0	0.93
27.3	99.8	0.2	0	3.1	7.5	92.5	0	44.7	96.0	4.0	0	21.8	96.1	3.9	0	0.90
18.3	99.3	0.7	0	3.5	9.4	90.6	0	52.0	95.4	4.6	0	22.8	95.5	4.5	0	0.96

[a] Calculated by using eq 4.

Table VII. Isotopic Analyses of Products Resulting from the Reduction of 0.62 M 1-Hexene (B) with D_2 (9.8×10^{-4} M) Using IV (4.15×10^{-3} M) and Triphenylphosphine (2.6×10^{-3} M) at 40.8 °C in THF

1-hexene (B)					hexane							*trans*-2-hexene					*cis*-2-hexene					D balance,
%	d_0	d_1	d_2	d_3	%	d_0	d_1	d_2	d_3	d_4	d_5	%	d_0	d_1	d_2	d_3	%	d_0	d_1	d_2	d_3	Δ^a
94	87	13			5	34	50	16									1	88	12			1.64
82	54	44	1		16	39	36	21	4			1	64	27	9		2	66	29	5		1.67
62	23	65	10	2	31	21	26	35	18	1		2	41	39	16	4	5	42	41	16	1	1.75
35	4	65	25	6	55	13	21	26	32	7	1	2	34	37	24	5	8	26	34	34	7	1.55
25	4	60	27	9	62	10	18	24	33	12	3	3	29	34	28	9	9	23	32	36	8	1.55

^{a} Calculated by using eq 4.

hexane is accompanied by the formation of an equivalent amount of 2-hexenes-d_1. The presence of B-d_1 is not detected until very late in the reaction at which time a trace of hexane-d_0 is observed. The concentration of 2-hexenes-d_1 in the 2-hexenes product apparently increases throughout the reaction. These unusual observations may in part be due to experimental error resulting from low concentrations of deuterated products since the deuterium balance parameter, Δ, was less than unity during the initial stages of reaction.

Competitive Hydrogenation and Isomerization of 1-Hexene (B) with the Exo-Nido Catalyst Precursor IV. As shown above, the closo catalyst precursor I is not useful in a practical sense for the hydrogenation of terminal alkenes, such as B, since isomerization to internal alkenes easily occurs and the latter species are not rapidly hydrogenated by I or III under the conditions utilized in this study (THF, 40.8 °C, 0.58 atm of H_2, and the presence of added PPh_3). Although the exo-nido precursor IV provides an efficient terminal alkene isomerization catalyst, it was shown in the experiments to be described that the hydrogenation of B with IV was the predominant reaction at 40.8 °C in THF and at 0.58 atm of H_2 pressure by a factor of 11.5:1. Assuming that eq 3 describes the hydrogenation rate law for B, as well as for A, a rate constant, k_h^{IVB}, which corresponds to k_h^{IVA} in eq 3, having a value of 5.9×10^{-5} s^{-1} was measured with 2.3×10^{-3} M [Rh]$_t$, 5.8×10^{-4} M [PPh_3], and 0.58 atm of H_2. Analysis of the products of this experiment indicated the presence of 92% hexane and 8% 2-hexenes. Comparison of values of k_h^{IVB} at 0.58 atm of hydrogen with k_i^{IV} provides a ratio of 5.9×10^{-5}:2.2×10^{-5} = 2.7 for hydrogenation/isomerization. The disparity between the observed ratio of hydrogenation/isomerization of 11.5 seen in internal competition experiments and the calculated ratio of hydrogenation/isomerization of 2.7 from separate measurements suggests that the hydrogenation and isomerization reactions proceed through a common intermediate whose fate is determined by [H_2] with increasing [H_2] favoring hydrogenation at the expense of isomerization. The results of the competitive hydrogenation and isomerization experiments carried out at variable H_2 pressures with B and I, above, may be interpreted in a like manner.

The reaction of 0.63 M B with D_2 (0.58 atm) in the presence of 4.15×10^{-3} M catalyst precursor IV and 2.6×10^{-3} M PPh_3 was subjected to analysis at intervals using the flow system mentioned previously. These results are presented in Table VII.

Each percent reaction is equivalent to 1.51 turnovers of catalyst precursor. In this experiment the observed ratio of hydrogenation to isomerization was only about 5:1 with a *cis*- to *trans*-2-hexene product ratio of about 3:1, in approximate agreement with the results of the corresponding 1-hexene isomerization study described above. The isotopic analyses of the separated reactant and products revealed extensive D scrambling and a deuterium balance parameter, Δ, equal to approximately 1.6. Thus, extra deuterium entered the organic components of the system by a process which did not involve alkene reduction. This feature was not clearly observed in the similar study of IV with A and is presumably the result of the ability of a catalytic intermediate to directly exchange complexed hydrogen (derived from C–H) with D_2. In addition, a large proportion of hexane-d_0 is produced. These points will be developed below.
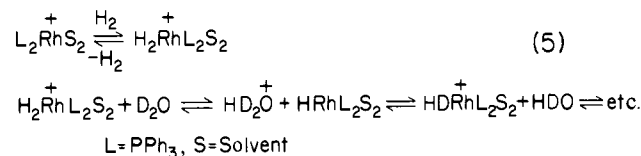
Another interesting feature seen in Table VII is the fact that B becomes extensively deuterated at the expense of rearrangement to *cis*- and *trans*-2-hexenes which are comparatively less deuterated

than their B precursor. These results suggest that the 2-hexenes, once formed, do not enter into further reaction to any great extent and that the preponderance of hexane results from B hydrogenation.

In separate experiments carried out with IV at 0.58 atm of H_2 in THF at 40.8 °C it was found that *trans*-2-hexene was essentially inert toward hydrogenation while simultaneous rearrangement to *cis*-2-hexene was quite slow. Under the same conditions, *cis*-2-hexene gave approximately equal amounts of hexane and *trans*-2-hexene.

Hydrogenation of A with Precursor I in the Presence of D_2O. Among the many a priori mechanistic pathways of the rhodacarborane-catalyzed alkene hydrogenation reaction is the possibility that the exo-nido tautomers of the catalyst precursors investigated in this study function via dissociation to produce the corresponding $C_2B_9H_{12}^-$ ion and catalytically active, solvated $(PPh_3)_2Rh^+$. If this cation or a related species participated as a hydrogenation catalyst, the established mechanism[13] of this process suggests that $(PPh_3)_2Rh^+H_2$ would be formed. Furthermore, it has been shown[13] that the $(PPh_3)_2Rh^+H_2$ ion is sufficiently acidic to exchange with D_2O, thus producing $(PPh_3)_2Rh^+D_2$, $(PPh_3)_2Rh^+(H)D$, and $(PPh_3)_2RhD$, as shown in eq 5. Each of these deuterated species could be involved as alkene

$$L_2RhS_2 \underset{-H_2}{\overset{H_2}{\rightleftharpoons}} H_2RhL_2S_2 \tag{5}$$

$$H_2\overset{+}{Rh}L_2S_2 + D_2O \rightleftharpoons HD_2\overset{+}{O} + H\overset{+}{Rh}L_2S_2 \rightleftharpoons HD\overset{+}{Rh}L_2S_2 + HDO \rightleftharpoons etc.$$

$$L = PPh_3, \quad S = Solvent$$

hydrogenation intermediates[13] and signal their presence by producing at least some partially deuterated alkane. The hydrogenation of 0.54 M A using 3.9×10^{-3} M I in the presence of 1.5×10^{-4} M PPh_3, 2.2 M D_2O, and 0.58 atm of H_2 at 40.8 °C in THF gave no detectable deuterated alkane (GC/MS) in the recovered products. In agreement with this demonstration of the apparent absence of free $(PPh_3)_2Rh^+$ as an intermediate is the fact that relatively large quantities of added carborane ligand anions do not markedly alter the observed rates of hydrogenation or isomerization catalyzed with the corresponding precursors. Thus no identifiable common-ion effect manifests itself in relatively sensitive kinetic measurements, and $(PPh_3)_2Rh^+$ is not responsible for the observed catalysis using the catalyst precursors described in this study. In contrast to these results, it was demonstrated in a previous paper of this series[5] that the $(PPh_3)_2Rh^+$ moiety was easily removed from IV and similar 7,8-disubstituted exo-nido species by displacement with CO, the product of this reaction with IV being $[(PPh_3)_2Rh(CO)_3]^+$ $[nido-\mu-7,8-(CH_2)_3-7,8-C_2B_9H_{10}]^-$.

Discussion

The results presented above contain several facts which will serve as focal points for discussion of the mechanisms of catalytic alkene isomerization and hydrogenation using the catalyst precursors I–IV. These items include the following topics: (1) The hydride ligand of the RhH vertex of the closo catalyst precursor I is not directly involved in catalysis. (2) The fact that very similar rate laws prevail for isomerization and hydrogenation. (3) Reversible Rh(alkyl) formation is observed by D scrambling during alkene reductions using D_2. (4) The stereoelectronic characteristics of the η^2-exo-nido-carborane cage ligands and their relationship to the reaction mechanisms observed. (5) The origin of the small

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inverse kinetic deuterium isotope effects observed with D_2 in the reduction of A using I and IV. (6) Unusual intermolecular D scrambling reactions which are observed with deuterated propenes and their relationship to isomerization. Item 1 is addressed below.

Catalysis with Nido Intermediates. In previous papers of this series[4,5,7] evidence was presented which proved that *closo*-bis-(triphenylphosphine)hydridoorhodacarboranes, containing formal Rh(3+), were in rapid equilibrium with their corresponding Rh(1+) exo-nito tuatomers as shown in Figure 1. On the basis of kinetic arguments developed during carborane cage exchange studies, an intermediate in these exo-nido–closo interconversions was proposed[7] in which a single pivotal BH_u-Rh(1+) three-center bond interaction on the periphery of the open face of the carborane ligand provided the only covalent bonding of the $(PPh_3)_2Rh^+$ center with the $C_2B_9H_{12}^-$ cage. Also illustrated in Figure 1 is the fact that the hydride ligand of the *closo*-RhH vertex is in regiospecific equilibrium with the B–H–B bridge hydrogen of the corresponding exo-nido tautomer, as observed through D-labeling experiments.[4,7] Substitution of the carbon vertices of these systems by alkyl and/or aryl groups favors the stabilization of the exo-nido tautomer with respect to the corresponding closo tautomer[5] and often allows the isolation of the exo-nido species. In certain cases, both the closo and the exo-nido tautomers may be simultaneously observed[5] in $^{31}P\{^1H\}$ FTNMR spectra of solutions prepared from either pure crystalline exo-nido or closo tautomer. Thus, one may conclude that this closo–exo-nido equilibrium, acompanied by a two-electron change in Rh oxidation state, is a characteristic reaction of all of the catalyst precursors employed in this study. The supposition that spectroscopically invisible *exo-nido* Rh(1+) species may be reversibly generated from the more stable Rh(3+) closo tautomers of the unsubstituted systems (I–III) strongly suggests that these exo-nido species are closely related to the key intermediates of the catalytic BH/D_2 exchange, alkene isomerization, and hydrogenation reactions. Plausible mechanisms for these same catalytic reactions may be devised which employ only Rh(3+) closo intermediates, but in each case the hydride ligand of the *closo*-RhH vertex would become directly involved in the reaction mechanism and its identity lost after one turnover in the catalytic cycle. Determination of the fate of isotopic H or D labels at rhodium in I or I-*3-d* in the BH/D_2 exchange, alkene isomerization, and hydrogenation reactions provided a direct test of these mechanistic possibilities.

As shown above, the autocatalyzed BH/D_2 exchange reaction with precursor I rapidly leads to the selective conversion of certain BH to BD vertices at low temperatures without extensive conversion of the RhH vertex to RhD. This result supports the belief that the intermediate in this exchange process which activates D_2 and B–H is an exo-nido or similar species in which the hydride ligand of the RhH vertex originally present in the closo tautomer of I is sequestered in the B–H–B bridge array of the exo-nido intermediate. In agreement with this idea is the observation that A apparently inhibits BH/D_2 exchange, presumably by interception of a Rh(1+) exo-nido intermediate. Thus, the RhH vertex would not be directly involved in the exchange process. At temperatures of 65 °C or higher[16] the BH/D_2 exchange reaction is accompanied by the formation of RhD. This apparent equilibration of *nido*-B–H–B bridge or *closo*-RhH with terminal BD or D_2 may actually involve the direct intramolecular interchange of terminal BD with the B–H–B bridge in an exo-nido species since I-*3-d* very slowly loses deuterium at the RhD vertex (presumably to form terminal BD) with an apparent first-order rate constant of 8×10^{-6} s^{-1} at 40.8 °C in THF solution containing 2.4×10^{-4} M PPh_3. The failure to prepare B–D–B bridge-labeled IV from B–D–B bridge-labeled $[nido-\mu-7,8-(CH_2)_3-7,8-C_2B_9H_{10}]^-$ and $(PPh_3)_3RhCl$ (and by other means) suggests that the apparent ease of deuterium leakage from the B–D–B bridge of IV to neighboring BH vertices is accentuated by the fact that IV is an exo-nido complex and, unlike the case of *closo*-I, the required formation of an exo-nido tautomer in an unfavorable equilibrium prior to deuterium migration is not involved.
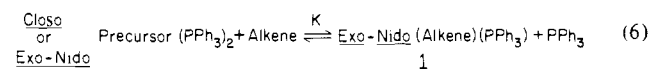
The ability of catalyst precursor I-*3-d* to rapidly isomerize B to a 2:1 mixture of *trans*-2-hexene:*cis*-2-hexene with the conversion

Scheme II
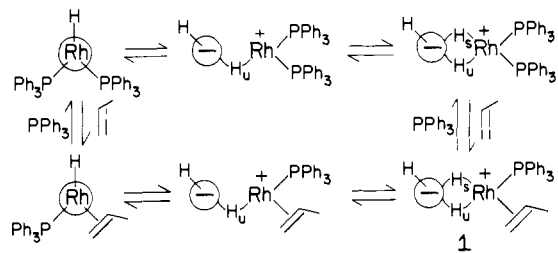
of only one RhD to RhH per approximately 55 mol of double bond migration suggests that the major pathway for this isomerization reaction involves exo-nido intermediates containing a B–D–B bridge. That similar, or perhaps identical, types of exo-nido intermediates must be involved in the hydrogenation reactions using precursor I was demonstrated by the fact that A hydrogenation could be carried through several turnovers with only a minimal loss of RhD from I-*3-d*. The operation of alkene isomerization and hydrogenation mechanisms which contain *closo*-Rh(alkyl) intermediates derived directly from I-*3-d* and alkene would have resulted in the essentially complete conversion of RhD to RhH after one turnover of catalyst.

Rh(1+) *Exo-Nido*-(Alkene)(PPh₃) Species as Intermediates. The elimination of closo species derived directly from I as important intermediates in alkene isomerization and hydrogenation suggests that the catalyst precursors I–IV function by providing Rh(1+) *exo-nido*-(alkene)(PPh₃) complexes in a series of relatively rapid equilibria which precede the catalytic reaction. The identity of the rate laws for A isomerization and A hydrogenation (excluding hydrogen dependence) combined with the fact that the rates of both reactions have an inverse first-order dependence on $[PPh_3]$ suggests that the closo and exo-nido precursors I–III and IV, respectively, undergo rapid and reversible replacement of one PPh_3 ligand by alkene. Quite probably, Rh(3+) *closo-* and Rh-(1+) *exo-nido*-(alkene)(PPh₃) complexes may be directly interconverted by closo–exo-nido tautomerization as in the case of the bis(triphenylphosphine) precursors, themselves.[4,5,7] The intermediates in these closo–exo-nido interconversions of (alkene)-(PPh₃) complexes should closely resemble the intermediates proposed[7] in the closo–exo-nido tautomerization of the bis(triphenylphosphine) complexes, a single BH_u-Rh(1+) connection (see Figure 1) emanating from the periphery of the open face of the carborane ligand. Consequently, two kinetically indistinguishable pathways may exist for the rapid and reversible formation of *exo-nido*-(alkene)(PPh₃) complexes, **1**, as shown in Scheme II. If these prior equilibria lie largely to the left in (6)

$$\underset{\text{Exo-Nido}}{\overset{\text{Closo}}{\text{or}}} \quad \text{Precursor } (PPh_3)_2 + \text{Alkene} \underset{}{\overset{K}{\rightleftharpoons}} \underset{\underline{\mathbf{1}}}{\underline{\text{Exo-Nido}} \text{(Alkene)}(PPh_3)} + PPh_3 \qquad (6)$$

and are sufficiently rapid when compared to the slower steps of the catalytic alkene isomerization and hydrogenation cycles, the concentration of the *exo-nido*-(alkene)(PPh₃) complex at any time may be expressed in terms of composite equilibrium constants and the concentrations of alkene, PPh_3, and the total rhodium $[Rh]_t$ added as either the closo or exo-nido catalyst precursor, as the case may be. Since the equilibrium concentration of **1** is undoubtedly low, the instantaneous concentration of this species may be adequately expressed as $[1] = K[\text{alkene}][Rh]_t/[PPh_3]$.

The hydrogen dependence observed for the rate of A hydrogenation with catalyst precursors I, III, and IV (eq 3) proved that H_2 and PPh_3 do not compete for a common intermediate. This is a necessary conclusion derived from the fact that at infinite hydrogen pressure the rate of reaction is still dependent upon $[PPh_3]^{-1}$, as seen in eq 3. If PPh_3 and H_2 were in competition for reaction with a common intermediate, the limiting rate expression at infinite H_2 pressure would not retain the $[PPh_3]^{-1}$ rate dependency. Consequently, at least one reaction step must intervene between the Rh(1+) *exo-nido*-(alkene)(PPh₃) complex and the activation of hydrogen.

Scheme III

$$k_h = \frac{k_4 k_5 [H_2]}{k_{-4} + k_5} \qquad k_i = \frac{k_2 k_3}{k_{-2} + k_3}$$
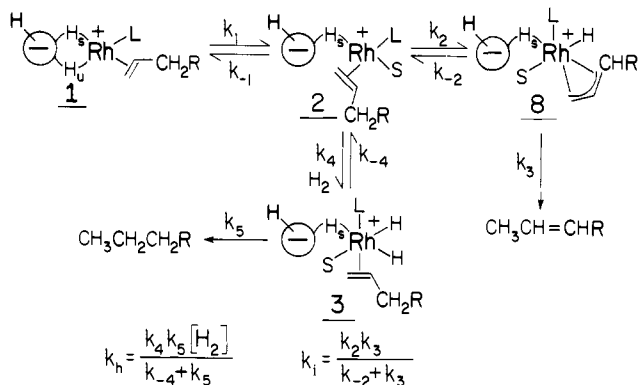
An Intermediate Common to Alkene Isomerization and Hydrogenation. The competitive hydrogenation and isomerization of B with catalyst precursor I proved that B isomerization was the dominant reaction in this case and that the small amount of hexane produced was proportional to the H_2 pressure. These results suggest, but do not prove, that hydrogenation and isomerization could proceed through a common intermediate which is partitioned between the two pathways. The hydrogenation of B using the catalyst precursor IV similarly gave evidence in agreement with the competitive hydrogenation and isomerization of B through a common intermediate. This conclusion is supported by the fact that the ratio of the rates of hydrogenation and isomerization, when measured separately, is 2.7:1, respectively, while the amount of B isomerized to the relatively inert 2-hexenes which are observed as coproducts in hydrogenation experiments provided a ratio of 11.5:1. These data, taken together in the context of Scheme III and an effective first-order rate constant, k_h, measured at 0.58 atm of H_2, give the relationships $k_i = 0.38$ k_{-1} and $k_h = 4.25\ k_{-1}$. In similar reactions which employed D_2 rather than H_2 (Table VII) and therefore subject to kinetic isotope effects, this reduction to isomerization ratio becomes approximately 5–6:1 as determined by product analysis. Thus, hydrogen may effectively capture an intermediate common to both hydrogenation and alkene isomerization and the rate of formation of 2-hexenes produced is proportionately decreased.

In Scheme III it is postulated that the very reactive three- or four-coordinate Rh(1+) species (**2**) having mutually *trans*-PPh₃ and alkene ligands, an optional coordinated solvent molecule, and a monodentate carborane ligand linked by a single $B-H_s-Rh$ bond arises via a BH–Rh dissociation reaction from the *cis-exo-nido*-(PPh₃)(alkene) complex (**1**). The BH–Rh bond dissociation postulated in the formation of **2** from **1** differs from the BH–Rh bond dissociation process suggested[7] as a key step in closo–exo-nido equilibria in that **2** is proposed to arise through the rupture of a BH_u–Rh(1+) interaction which is in the periphery of the open face of the carborane ligand. Consequently, **2** would not be capable of internal oxidative addition to directly regenerate the corresponding closo species, but oxidative addition of H_2 or alkene could proceed as indicated and initiate a catalytic cycle.

The cis addition of H_2 to **1** would appear to be unsatisfactory since the cis stereochemistry of this complex would lead to either a dihydride with one hydrido ligand trans to PPh₃ or trans to coordinated alkene. On the other hand, loosening these stereochemical constraints in forming **2** from **1** should augment both H_2 addition and the formation of a η^3-allylic complex such as **8**. The conversion of **1** to **2** provides the step which separates the PPh₃ dissociation and the H_2 activation steps as required by the hydrogenation rate law. Thus, if this mechanism is correct, the limiting hydrogenation rate which would be observed at infinite H_2 pressure is the rate of formation of **2**; rate = $k_1[1] = k_1 K$-$[Rh]_t[A]/[PPh_3]$ where k_1 and K are characteristic of the catalyst precursor (Rh) and the alkene (A).

The Relationship of Reversible Rhodium Alkyl Formation and the Rate-Determining Step in Hydrogenation to the Nature of *exo-nido*-$C_2B_9H_{12}^-$ Ligands. One of the striking general char-

Scheme IV

Scheme V

L = PPh₃
S = Solvent
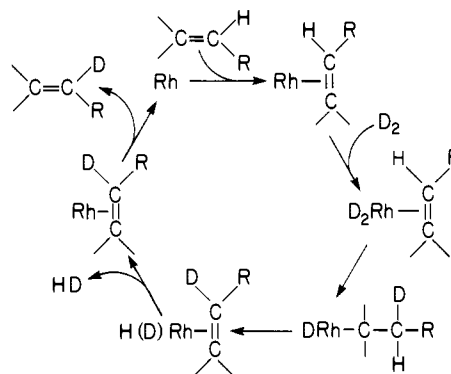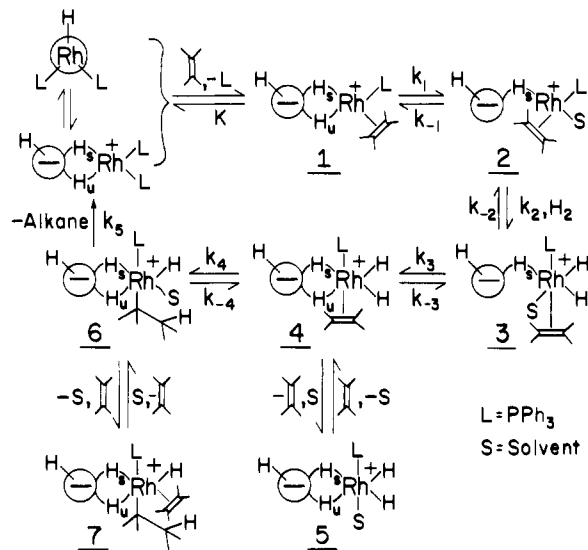
acteristics of alkene hydrogenation catalyzed by rhodacarborane precursors I and IV is the D scrambling observed when A or B was reduced with D_2. In every case examined, deuterium was observed both in recovered alkene and in alkane product. In addition, alkane-d_0 was observed in those cases which employed IV as the catalyst precursor and Δ, the deuterium balance parameter, was about 1.6 in the reaction of B and IV. The latter fact is a manifestation of some exchange of D_2 with CH of the alkene.

Results of this sort must be attributed to the reversible formation of Rh(alkyl) species from RhH and alkene in a step which is not necessarily related to hydrogenation. The RhH species necessary for this reaction could conceivably be a monohydride, of uncertain origin, which is capable of exchange with D_2. On the other hand,

$$RhH + D_2 \rightleftharpoons RhD + HD$$
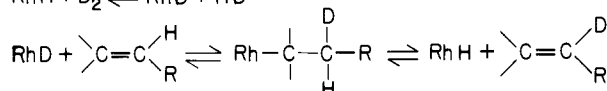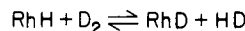
the RhH species could be a dihydride, RhH_2, which forms a HRh(alkyl) intermediate in a reversible reaction with alkene (Scheme IV). In this case the dihydride intermediate would arise through the H_2 activation step in hydrogenation and the decomposition of the HRh(alkyl) intermediate to form alkane would be rate determining. As a consequence of these possibilities, considerable effort was expended in the present case to identify an HRh(alkene) species that could communicate with both $H_2(D_2)$ and a Rh(alkyl) complex by direct or indirect means. As indicated above, no species of this sort could be identified. Aside from H_2 and the C–H bonds present in the carborane ligand, PPh₃, and solvent, the only potential sources of hydride ligand available to Rh were those formed by oxidative addition of Rh(1+) with the

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B–H–B bridge array of the *nido*-$C_2B_9H_{12}^-$ ions to form *closo* precursors (rapid) as well as certain of the B–H terminal bonds (very slow) present in this same ion. In both cases, the resulting Rh(3+) hydride proved to be ineffective in alkene hydrogenation (or isomerization). The conclusion was therefore inescapable that the bidentate B–H–Rh bridge-bonded *nido*-$C_2B_9H_{12}^-$ ligands proposed (Scheme V) as a component of hydrogenation intermediates were in some way responsible for the rate-determining elimination of alkane from Rh(3+) *exo-nido*-hydrido (alkyl) intermediates, 6, and at the same time allowed the facile and reversible formation of these same intermediates. Scheme V presents a more detailed view of the proposed hydrogenation mechanism than that of Scheme III. Equation 7 reconciles the mechanism

$$-\frac{d[H_2]}{dt} = \frac{K k_1 k_2 k_3 k_4 k_5 [Rh]_t [A] [H_2]}{[L](k_{-1} k_{-2} k_{-3} k_{-4} + k_{-1} k_{-2} k_3 k_5 + k_{-1} k_2 k_4 k_5 + k_{-1} k_3 k_4 k_5 + k_2 k_3 k_4 k_5 [H_2])}$$

$$-\frac{d[H_2]}{dt} = \frac{[Rh]_t [A][H_2]}{[L](m + C[H_2])} \text{ where } m = \frac{k_{-1} k_{-2} k_{-3} k_{-4} + k_{-1} k_{-2} k_{-3} k_5 + k_{-1} k_{-2} k_4 k_5 + k_{-1} k_3 k_4 k_5}{K k_1 k_2 k_3 k_4 k_5}$$

$$C = k_2 k_3 k_4 k_5 / K k_1 k_2 k_3 k_4 k_5 = 1/K k_1$$

(7)

of Scheme V with the experimentally observed rate law and defines the nature of the experimental parameters C and m.

The B–H–M (M = transition metal) three-center, two-electron bridge bond is ubiquitous in metallaborane chemistry,[23,24] and the terminal B–H bond plays an important role as a two-electron donor in coordination chemistry.[25] However, aside from the chemistry described in a previous paper of this series[5] and a brief communication,[20] no information is available which pertains to the stereoelectronic characteristics of the *exo-nido*-$C_2B_9H_{12}^-$ family of ligands. However, $^{31}P\{^1H\}$ FTNMR studies[5] suggest that the BH–Rh bonds are labile with respect to rapid migration of the Rh center about the polyhedral surfaces of the *exo-nido*-$C_2B_9H_{12}^-$ ligands. These fluxional processes do not require direct η^2-$(BH)_2$–Rh to η^1-BH–Rh bond breaking, but could proceed via an associative process characterized by 5-coordinate η^3-$(BH)_3$–Rh intermediates or transition states. In addition, it was proposed above that intermediates such as 2 are readily available through rupture of a single peripheral (vide ultra) BH_u–Rh interaction in 1 and perhaps followed by the capture of solvent. Structural studies[5,6] have proven, as well, that at least two isomeric variations of the η^2-*exo-nido*-7,8-$C_2B_9H_{12}^-$ complexes formed with Rh(1+) can be isolated, depending upon the nature of the substitution on the cage carbon atoms. Thus, the exo-nido ligands derived from each of the catalyst precursors I–IV undoubtedly provide an equilibrium mixture of fluxional η^2-complexes which differ from one another only with respect to the positions of the B–H near-neighbor pairs used in η^2 bridge bonding to Rh(1+) or Rh(3+). The relative stabilities and reactivities of the individual members of these fluxional equilibria are impossible to delineate at this time although it is assumed that these η^2-$(BH)_2$–Rh species have both BH_u–Rh and BH_s–Rh bonds.

The arrangement of the polyhedral carbon atoms in the isomeric carborane cages found in I–III also produces characteristic effects upon rates and equilibria which are not clearly understood. However, the presence of the 7,8-μ-$(CH_2)_3$-substituents on precursor IV markedly enhances the extent of B hydrogenation as opposed to isomerization when compared to the similar reaction catalyzed by I. In the latter case nearly exclusive isomerization of B to 2-hexenes is observed. This result is most likely due to the steric inhibition of B isomerization afforded by IV.

The presence of any sort of η^2-*exo-nido*-$C_2B_9H_{12}^-$ ligand in a Rh(1+) or Rh(3+) complex must imbue the metal center with certain gross characteristics common to this class of ligand. Although the BH two-center, two-electron terminal bond which comprises the ligand in B–H–Rh bridge bonds is formally counted

as a two-electron donor, it is clear that the extensive delocalization of the bonding electron pair in these bridged bonds does little to enhance the electron density about the Rh center. Consequently, electron-deficient ligands of this sort should provide a very small trans influence (or effect) while fully saturating a coordination site in a stereochemical sense. The stability of the η^2-exo-nido interactions proposed for Rh(1+) and Rh(3+) complexes in the mechanisms advanced here are augmented by chelation and by the Coulombic interaction of the formal charges associated with the cationic Rh center and the anionic ligand. Thus, the expected weak electron-donor properties of η^2-*exo-nido*-BH ligands is reflected in the generally reduced ability of the Rh(3+) alkyl hydride 6 to dissociate solvent and reductively eliminate alkane product, thus rendering this step rate determining. Rate-determining reductive elimination of alkane from 6 provides a qualitative explanation for the small inverse deuterium kinetic isotope effects of about 0.85 observed using A with I or IV and 0.58 atm of H_2 or D_2. The formation of a relatively strong C–H bond and the concerted loss of a weaker Rh–H bond[26] by the motion of the hydrido ligand of 6 from Rh to alkyl carbon in the product forming transition state would provide a net gain in zero point energy for the bonding of the H-atom and produce an inverse isotope effect, as observed.

Equilibria Preceding Alkane Formation along the Hydrogenation Pathway. In Scheme V the intermediate 2 oxidatively adds H_2 to produce *cis*-dihydride 3 which, in turn, collapses to *cis*-dihydride 4. The species 4 is stereochemically identical with the structurally characterized[20] *cis*-dihydride formed from H_2 and [*exo-nido*-$(PPh_3)_2IrC_2B_9H_{12}$]. As pointed out above, reaction of 1 with H_2 would not lead to a stereochemically satisfactory *cis*-dihydride nor would such a pathway be in agreement with the observed rate law due to the competition of PPh_3 and H_2 for 1. The stereochemistry proposed in 4 is favorable for the formation of alkyl hydride 6 and the decomposition of 6 to alkane since the coordinated alkene molecule in 4 is cis to both hydrido ligands. The reversible formation and decomposition of 6 from 4 attended by the proposed reversible alkene exchange via 5 nicely accounts for the appearance of D scrambling in those reductions of A and B with D_2 using catalyst precursors I and IV. The observation of a deuterium balance parameter, Δ, of 1.6 in the case of B reduction with the cage-substituted IV could be explained by steric inhibition of the collapse of 6 to products. Under these conditions the rate of scrambling of deuterium and alkene between 4, 5, and 6 could be increased relative to that of product formation, and the reversion of 4 to 1, with loss of HD or H_2, could also become an important process. The parameter, Δ, would then be larger than unity (CH exchange with D_2), as observed. The fact that the use of precursor IV in the hydrogenation of B leads to dominant alkene reduction over isomerization suggests that the cage substituents present on IV inhibit the η^3-allylic isomerization pathway relative to H_2 capture and the latter is the dominant reaction of 2. The accumulation of very high concentrations of deuterated B during D_2 product runs (Table VII) proves that the hydrido alkyl 6 produced in this case is predominantly 1-hexyl, a result of steric encumbrance in 6. Thus, hydrogenation proceeds since B isomerization is not accomplished by the hydrido alkyl pathway or by η^3-allylic intermediates. As shown above, the isomeric 2-hexenes are essentially inert toward reaction with IV and a very high *cis* to *trans* ratio persists.

The proposed species 7 is possibly present in solutions containing alkene and 6. However, since no second-order alkene term is apparent in the rate law the direct decomposition of 7 to alkane cannot be an important step. However, the reversible formation of a dialkyl species from 7 might contribute to D scrambling or to the isomerization of B during hydrogenation with precursor I, etc.

Reactions of η^3-Allylic Intermediates. Scheme VI illustrates the proposed sequence of reactions and intermediates which may
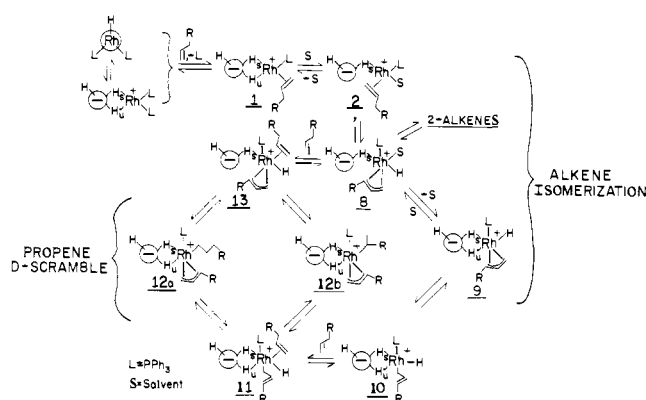
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Scheme VI

Scheme VII

$L = PPh_3$ $R = CH_3-, (CH_3)_3C-$ and $Ph(CH_3)_2C-$

arise from the assumed BH_s–Rh intermediate **2** by the initial formation of the η^3-allylic species **8**. The rate law for B isomerization using rhodacarboranes I–IV is strictly first order in B, which effectively eliminates from consideration the isomerization of the reversibly coordinated **B** molecule in species such as **12b**. The operation of such a process would produce a term in the rate law which is second order in B. The facile isomerization of 1-alkenes is therefore attributed to the reversible formation and decomposition of **8** to produce **2** or the analogue of **2** containing 2-alkene which subsequently releases *cis*- and *trans*-2-alkenes.

The intermolecular D scrambling observed with regiospecifically labeled propenes is thought to be a special case due to the low steric requirements of propene and the structural degeneracy of the required rearrangements. Species such as **12a** and **12b** are therefore suggested as feasible intermediates for these reactions.

Species **8** is depicted as either directly undergoing displacement of a solvent molecule, S, by propene to form **13** or collapsing with loss of S to form the η^3-allylic hydride **9**. The isomeric η^3-allylic alkyls **12a** and **12b** both follow directly from **13** as indicated. Another possible pathway to **12a** and **12b** is through the conversion of η^3-allyl hydride **9** to η^1-allyl hydride **10** and further reaction of **10** with propene as indicated.

The *cis*- and *trans*-2-hexenes are apparently not capable of easy coordination and rapid reaction with the sterically encumbered exo-nido precursor (IV). Consequently, the products of B isomerization with IV should reflect kinetic control. The observed cis:trans ratio of ca. 5:1 apparently represents this situation and describes the preferred stereochemistry of the conversion of species which correspond to **8** to the related **2** analogue. In contrast, isomerization of B with precursor I produces an essentially equilibrium mixture of isomeric 2-hexenes. This result may be due to the near coincidence of the kinetically controlled product mixture composition with the equilibrium composition, or *cis*-2-hexene may be the predominant kinetically controlled initial product, as in the case of isomerization with IV, which rapidly equilibrates with its trans isomer by further reaction with I. The experimental fact that under the same conditions using I *cis*-2-hexene is converted to the trans isomer at a greater rate than B is converted to mixed 2-hexenes does not distinguish between these two possibilities.

The apparent ability of the rhodacarborane catalyst systems described here to rapidly form η^3-allylic hydrides such as **8** and **9** is uncommon.[10b,11] If correct, this propensity for oxidative addition of allylic CH bonds must arise from the stereoelectronic properties of the η^2-*exo-nido*-carborane cage ligands and the reduced electron density which they impart to species such as **2** and **8**. The suggested formation of propene derivatives **12a** and **12b** is reasonable, based upon the experimental evidence at hand, and may find application in the interpretation of observations made elsewhere.

Slow Exchange of BH with CD. One of the more interesting reactions discovered in this study was the very slow regiospecific exchange of deuterium between isotopically normal I and an approximately equivalent quantity of A-*1,1,2-d₃* at 40 °C in THF solution. Deuterium was smoothly transferred to the 9, 10, and
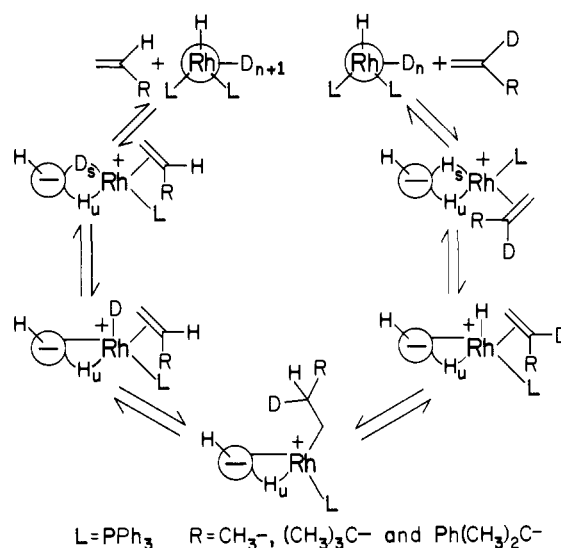
12 vertices of I which are also the three most reactive BH vertices involved in BH/D_2 autocatalyzed exchange of I described earlier. These three vertices are the positions furthest removed from the CH vertices in I and presumably support the highest electron density of all BH vertices present. Consequently, the BH/CD exchange appears to be associated with an electrophilic driving force directed toward BH, and key steps may be common to both BH/D_2 and BH/CD exchange. This reaction is most easily formulated as proceeding through the sequence shown in Scheme VII wherein the BH_s vertex which exchanges undergoes oxidative addition with Rh(1+).

We have previously described[27] the facile oxidative addition of Ir(1+) to specific terminal BH bonds present in 1,2-, 1,7-, and $1,12$-$C_2B_{10}H_{12}$ carboranes and related species to produce stable Ir(3+) products which contained the B–Ir–H σ-bonded array. Other workers have also observed similar chemistry[28] with other low-valent metal species. As a consequence, we view the B–H–Rh(1+) linkages present in the Rh(1+) *exo-nido*-(alkene)(PPh₃) intermediate **1** as a logical source of an analogous, though less stable, B–Rh–H σ-bonded arrangement which provides the rhodium monohydride function required for D exchange in Scheme VII. Since the *exo-nido*-alkene complexes are undoubtedly fluxional with respect to Rh walking about the surface of the carborane ligand, several terminal BH vertices may be available for reversible attack by Rh(1+) as observed.

The very slow exchange of A-*2-d* with propene or 3,3-dimethyl-1-butene ($t_{1/2}$ = ca. 60 h at 40 °C using I in THF solution) may proceed through an indirect exchange process in which, for example, A-*2-d* first transfers D to I followed by the transfer of D from I to propene or 3,3-dimethyl-1-butene. In both steps, reactions such as those shown in Scheme VII would be employed.

Applications of Bis(phosphine)rhodacarborane Catalysts. While we have not undertaken an extensive survey of unsaturates amenable to isomerization and hydrogenation catalyzed by rhodacarboranes, we have investigated the reactivities of I and IV with a limited cross section of alkenes, dienes, and alkynes. The experimental conditions were essentially those employed in the mechanism study: THF solvent, 40.8 °C, and 0.58 atm partial pressure of H_2. It was generally observed that IV could not be used with activated alkenes such as acrylate esters, acrylonitrile, and dimethyl fumarate due to catalyst decomposition. On the other hand, I was successfully employed in the hydrogenation of these activated alkenes in the absence of added PPh₃. Styrene was hydrogenated by I in the presence of added PPh₃ while 1,1-diphenylethylene and 2,3-dimethyl-1-butene were unreactive

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with I even in the absence of added PPh_3. Allylbenzene was isomerized and hydrogenated by both I and IV in the presence of PPh_3. Phenylacetylene was reduced by I and IV in the presence of PPh_3 in two distinct steps which correspond to rapid styrene formation and slower reduction to ethylbenzene. In the presence of PPh_3, precursor IV slowly reduced 2,3-dimethylbutadiene to the alkane while I was inactive. Nonterminal alkenes and cycloalkenes are slowly hydrogenated by I or IV in the absence of added PPh_3. However, detailed studies of this sort have not been carried out.

The ability of sterically encumbered exo-nido precursor IV to smoothly isomerize 1-hexene to a 2-hexene isomer mixture which is very rich in *cis*-2-hexene (ca. 85%) is notable and suggests this procedure as a route to other thermodynamically labile alkenes available through a similar kinetically controlled isomerization reaction.

The study of the mechanism of acrylate ester hydrogenation using catalyst precursors I and III will be the subject of the following contribution of this series while a further contribution will describe the novel catalytic hydrogenolysis of alkenyl acetates to produce alkenes and acetic acid. The latter reactions employed catalyst precursors I–IV and mild conditions.

$$CH_2{=}CHOCOCH_3 + H_2 \longrightarrow CH_2{=}CH_2 + CH_3COOH$$

Conclusions

This study has attempted to describe the mechanisms of the catalytic alkene isomerization and hydrogenation reactions brought about by bis(phosphine)rhodacarborane catalyst precursors. The results of this study prove that the characteristic icosahedral cluster structure does not support catalysis and that the operational catalytic species contains a Rh(1+) center which must be developed from the closo structure by a tautomeric process. Thus I functions as a catalyst precursor by supplying a spectroscopically invisible "retractable" catalytic site. Other examples of apparent cluster catalysis, when examined in detail, may prove to be the result of similar tautomeric equilibria.

Catalysis using metallacarborane systems promises to be of more than passing interest since the cluster structures provided by these systems can simultaneously accommodate more than one reactive metal center and the stereoelectronic environment of the metal centers can be varied nearly at will and made chiral,[29] as well, by placing substituents upon the carborane ligands. In addition, earlier work proved that bis(triphenylphosphine)rhodacarboranes such as I could be immobilized by attachment of their dicarbollide ligands to polymeric supports.[30a–c] Work in this area continues.

Experimental Section

General Methods. All reactions involving air-sensitive materials were performed[31] under deoxygenated argon in a standard vacuum line or in an efficient glovebox. NMR solvents were dried, degassed, and vacuum transferred into NMR tubes containing the solid samples at −196 °C and sealed in vacuo. ^1H and ^{31}P NMR spectra were recorded on a Bruker WP-200 spectrometer at 200.133 and 81.02 MHz, respectively. Proton chemical shifts are referenced to residual protons in the solvent. Phosphorus chemical shifts were determined as described elsewhere[32] with respect to 85% H_3PO_4. The ^{11}B NMR spectra were recorded at either 126.7 or 160.4 MHz. The lower frequency spectrometer was designed and built by Prof. Anet of this department and the higher frequency sepctrometer was a Bruker WM-500.[33] Infrared spectra were obtained by using Perkin-Elmer 137 or 521 instruments. Mass spectra were obtained at 70 eV by using a Perkin-Elmer Sigma 3/Kratos MS 25 system equipped with a J and W Scientific, Inc., SE 52 glass capillary column.

Routine GLC analyses were performed with a Varian 1700 or Hewlett-Packard 5880 instrument using either 10% Carbowax 20M on acid-washed Chromosorb P column, a 27% $AgNO_3$/37% Carbowax 600 on Chromosorb P column, or a J and W DB-1 capillary column.

Benzene and tetrahydrofuran were distilled from potassium metal, and ether was distilled from sodium–potassium alloy.

Materials. The following were commercially available: benzene, tetrahydrofuran, diethyl ether (Mallinckrodt); triphenylphosphine, 1-hexene, 1-heptene, *trans*-2-hexene, *cis*- and *trans*-2-hexene, 2,3-dimethylbutadiene, 1,1-diphenylethene, allylbenzene, styrene, diisopropylethylamine, methyl iodide, methyltriphenylphosphonium bromide (Aldrich); calcium hydride, *n*-butyllithium (2 M in hexane), $BF_3 \cdot OEt_2$, *p*-methoxyphenol, sodium hydride (60% dispersion in mineral oil) (Alfa Products); argon, hydrogen (special purity 99.999%), deuterium (Liquid Carbonic); activity I alumina (Merck); hydratropaldehyde (Fluka); hydroquinone, ethynylbenzene, 3-methylpentane (Matheson, Coleman, and Bell); and cyclohexene (J. T. Baker). *closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ (I) and I-3-*d*,[4] *closo*-2,2-$(PPh_3)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$[4] (II), *closo*-2,2-$(PPh_3)_2$-2-H-2,1,12-$RhC_2B_9H_{11}$[34] (III), *exo-nido*-$(PPh_3)_2Rh$-7,8-$(CH_2)_3$-$C_2B_9H_{10}$[5] (IV), *nido*-7,8-$C_2B_9H_{12}^-$,[35] *nido*-7,9-$C_2B_9H_{12}^-$,[35] *nido*-2,9-$C_2B_9H_{12}^-$,[34] and *nido*-7,8-$(CH_2)_3$-$C_2B_9H_{10}^{36}$ were prepared by literature methods. (Methyl-d_3)triphenylphosphonium iodide was prepared by reaction of triphenylphosphine with methyl-d_3-iodide (Aldrich) in ether. Alkenes used in catalytic experiments were generally passed through activity I alumina, freeze–pump–thawed over CaH_2 three times, and distilled in high vacuum just prior to use.

3-Methyl-3-phenyl-1-butene (A). (a) **2-Methyl-2-phenylpropanal.** Ninety grams (2.25 mol) of sodium hydride (60% in mineral oil) was added to a 5-L flask, washed with diethyl ether, and suspended in 2 L of THF. Hydratropaldehyde (200 g, 1.50 mol) was diluted with 300 mL of THF and added slowly (3 h) to the stirred suspension. The reaction was stirred for 1 h and cannula filtered into a dry, Ar-flushed 5-L flask, yielding a clear, light orange solution. Ninety-five milliliters (1.50 mol) of methyl iodide was diluted with 300 mL of THF and added (0.5 h) to the stirred reaction mixture followed by reflux (2 h). The sodium iodide produced was removed via filtration and washed with three 300-mL portions of diethyl ether. The filtrates were combined, washed twice with 500-mL portions of water, and dried ($MgSO_4$). The solvents were removed via rotary evaporation, and the product was purified by vacuum distillation (58–60 °C (2.5 mm)), yielding 204 g (52%) of 2-methyl-2-phenylpropanal as a colorless liquid which was identified by ^1H NMR and GLC.

(b) 3-Methyl-3-phenyl-1-butene (A). Methyltriphenylphosphonium bromide (152 g, 0.43 mol) was added to a 5-L flask along with 2.5 L of diethyl ether. A solution of 225 mL of *n*-butyllithium (2.24 M in hexane, 0.50 mol) diluted with 200 mL of diethyl ether was added (15 min) to the stirred reaction suspension, yielding an orange slurry. The reaction was stirred at room temperature for 4 h. A solution containing 59 g (0.40 mol) of 2-methyl-2-phenylpropanal dissolved in 200 mL of diethyl ether was added slowly (2 h) followed by 12 h at reflux with stirring. The reaction was vacuum filtered and the collected solid washed with four 500-mL portions of diethyl ether. The filtrates were combined and solvent was removed by rotary evaporation. The crude orange product was purified via vacuum distillation from sodium hydride (42–44 °C, (2.5 mm)) and 42 g (72%) of A was isolated. A chemical purity of >99% was estimated by GLC and ^1H NMR.

2-(1-Methyl-1-phenylethyl)-1,3-dithiane. Employing a procedure described by Corey and co-workers,[37] 17 mL of $BF_3 \cdot Et_2O$, 34 mL of acetic acid, and 50 mL of $CHCl_3$ were stirred at reflux while a solution of 20.5 g (0.14 mol) of 2-methyl-2-phenylpropanal and 14 mL (0.14 mol) of 1,3-propanedithiol in 200 mL of $CHCl_3$ was added over a period of 1 h. When the addition was complete, the reaction was cooled, quenched with H_2O, and washed three times with H_2O, twice with 10% KOH, and twice with H_2O. After drying (K_2CO_3) and removal of solvent, the dithiane was distilled under high vacuum; yield 27.5 g (83%) (viscous oil); NMR ($CHCl_3$) 1.60 ppm (s, 6 H, CH_3), 1.98 (m, 2 H, CH_2) 2.84 (m, 4 H, CH_2S), 4.42 (s, 1 H, S_2CH), 7.4 (m, 5 H, aromatic).

2-(1-Methyl-1-phenylethyl)-1,3-dithiane-2-*d*. A 1.5 M solution (120 mL) of *n*-butyllithium in hexane was added over 1 h to a solution of 27.5 g of the undeuterated dithiane in 150 mL of dry diethyl ether at −30 °C. After stirring for 2–3 h, 10 mL of D_2O was added and the mixture allowed to warm to room temperature. The diethyl ether solution was

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decanted under Ar and treated with *n*-butyllithium and D_2O two more times. The resulting solution was dried over $MgSO_4$, and the product was then distilled; yield 19.7 g (72%). NMR demonstrated deuterium incorporation to be >97%.

2-Methyl-2-phenylpropanal-*1-d*. A solution of 147 g (268 mmol) of $Ce(NH_4)_2(NO_3)_6$ in 200 mL of acetonitrile and 65 mL of H_2O at 0 °C was added to a 0 °C suspension of 19.5 g (82 mmol) of the deuterated dithiane, 7.5 mL of H_2O, and 25 mL of acetonitrile. The color of the $Ce^{(IV)}$ was immediately discharged. After the solution was stirred for 5 min, 150 mL of H_2O was added and the product was extracted with diethyl ether. The ether extracts were washed with H_2O, dried over $MgSO_4$, and concentrated in vacuo. Vacuum distillation gave 7.8 g (65%) of aldehyde.

3-Methyl-3-phenyl-1-butene-*2-d* (A-*2-d*). The olefin was prepared from the aldehyde and $CH_2{=}PPh_3$ as described above.

3-Methyl-3-phenyl-1-butene-*1,1,2-d_3* (A-*1,1,2-d_3*). The olefin was prepared from the aldehyde and the Wittig reagent derived from CD_3PPh_3I as described above.

Preparation of 3,1,2-Rh(H)(PPh₃)₂C₂B₉D₉H₂ (I-*d_9*). A solution of I (1.50 g, 1.97 mmol) in THF (50 mL) at 50 °C was treated with D_2 (1 bubble/5 s) for 5 days. The solvent was removed under vacuum and residue placed on a silica gel column. Elution with CH_2Cl_2 gave product which was crystallized by addition of heptane and vacuum dried; yield of I-*d_9* 1.32 g, 88%. Infrared analysis (vide infra) of (I-*d_9*) showed 89% B–D and 11% B–H labels. No RhD was detected by the ^1H NMR method described below.

Analyses for B–D and Rh–D Content in I. Percent B–H (and percent B–D by difference) was determined by measuring the absorbance at 2580 cm⁻¹ (B–H stretch) of solutions of I in CH_2Cl_2 of known concentrations. The absorbance of isotopically normal I was shown to be linear with concentration over a range of concentration from 5 to 25 mg mL⁻¹ with a molar extinction coefficient of 704 cm⁻¹ M⁻¹. Percent Rh–H (and percent Rh–D by difference) was determined by integrating the hydride resonance (8.4 ppm) vs. the phenyl resonances (7.27 ppm) in the 200-MHz ^1H FTNMR spectrum of I in CD_2Cl_2. An isotopically normal sample of I integrated to 100 (±5%) Rh–H.

Exchange of RhD in I-*3-d* with Alkenes. The alkenes 3-methyl-3-phenyl-1-butene (A), 1-hexene (B), and a 68:32 cis/trans mixture of 2-hexenes were employed as follows: THF solutions containing 5.24×10^{-3} M (I-*3-d*, 95% isotopic purity), 2.3×10^{-4} M PPh₃, and 0.20 M alkene were equilibrated at 40.8 °C under argon. Samples were periodically withdrawn and the catalyst precursor isolated by precipitation with degassed heptane, separated by filtration, washed with diethyl ether, and dried. The recovered I was analyzed for RhH content as described above.

General Procedure for Hydrogenation Reactions. All experiments were conducted in a constant-pressure hydrogen titrator described previously.[38] When used, PPh₃ was delivered into the reaction flask under argon as a benzene stock solution and the solvent was removed in vacuo. THF was distilled from K under Ar into a Schlenk flask. The solvent was then cannulated into an Ar flushed solvent reservoir, a 25-mL volumetric flask equipped with a rotaflow stopcock, and 12/30 standard taper through joint.

The catalyst precursor was transferred under Ar into the jacketed reaction flask containing the PPh₃ which was then fitted with the solvent reservoir and the ice water reflux condenser of the hydrogen titrator. The reaction flask was evacuated and refilled with argon, and the rotaflow stopcock of the reservoir was opened to allow the solvent to enter the flask. The solution was stirred until the catalyst was dissolved. The system was then sealed and the solution frozen by passing a stream of liquid nitrogen between the reaction flask and the outer jacket. The gas remaining above the solution was removed by high-vacuum pumping, the system sealed, and the solution allowed to thaw. After three freeze–pump–thaw cycles, the system was refilled with hydrogen and the solid solution allowed to thaw. The reaction flask was fitted with hoses supplying water maintained at 40.8 °C from the constant temperature bath and allowed to equilibrate under a hydrogen atmosphere along with vigorous stirring of the solution.

After the system reached thermal equilibrium, the stirring was stopped, the olefin was injected with an ultraprecision syringe, and the solution was pressurized to the desired hydrogen pressure. The similarly pressurized mercury switch was opened to the reaction, the stirring resumed, and the timing counter reset.

General Procedure for Isomerization Reactions. Isomerization reactions were conducted by using the same method as that employed in the hydrogenation reactions except that argon was used in lieu of hydrogen

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(38) A complete description of the hydrogen titrator is beyond the scope of this article. References 1 and 15 provide a detailed description of components, design and operation of this useful device.

and the products were periodically analyzed by GLC.

General Procedure for Alkene Exchange and Reduction with Deuterium. The apparatus used in these studies consisted of a 100-mL Schlenk flask attached via Viton o-ring joints and a reflux condenser to a high-vacuum line. The system was equipped with a gas inlet valve and an oil bubbler which permitted the reaction atmosphere to be constantly purged with fresh deuterium at a rate of ca. 2 mL min⁻¹. A typical experiment is described below. The catalyst precursor and purified PPh₃ were placed in the reaction flask with an efficient magnetic stirring bar. The system was evacuated and refilled with argon. Alkene and THF were added by syringe through the flask sidearm and the reaction mixture was subjected to three freeze–pump–thaw cycles. Dry, purified (BTS catalyst) deuterium was added to the flask. The flask was immersed in a 40.8 °C oil bath and the gas flow rate was adjusted at atmospheric pressure as described above. At suitable time intervals small samples of reaction mixture were removed by syringe. The volatile components were separated from the residual catalyst precursor by vaporization and analyzed by GC/MS. When convenient, the catalyst precursor residue was examined for RhD and BD using the methods described above.

As a control, alkene (A) was reduced with D_2 by this procedure using $(PPh_3)_3RhCl$ as catalyst. Analysis proved the product to be pure alkane-*d_2*, as expected.

Hydrogenation of A in the Presence of D_2O Using Catalyst Precursor I. Hydrogenation of 5.4×10^{-1} M solution of A in THF containing 2.2 M D_2O, 3.9×10^{-3} M I, and 1.5×10^{-4} M PPh₃ was conducted in the apparatus described above for D_2/alkene exchange. Isolation and GC/MS analysis of the 3-methyl-3-phenylbutane resulting from complete reduction of A proved the sample to be devoid of deuterium.

General Procedure for Propene D Scrambling Experiments. (a) Reactions Monitored by NMR. A THF solution containing 1.53 mg (2.0×10^{-6} mol) of I and 0.022 mg (8.5×10^{-8} mol) of PPh₃ was transferred into a NMR tube in a drybox. The THF was removed in vacuo, 0.42 mL of dry THF-*d_8* vacuum transferred into the tube followed by 5.7 mL (2.4×10^{-4} mol) of propene-*d_1* or -*d_3* gas, and the NMR tube sealed under vacuum. The reaction was monitored by ^1H NMR at 41 °C.

(b) Crossover Experiment. A solution of 6.1 mg (8.1×10^{-6} mol) of I and 0.089 mg (3.4×10^{-7} mol) of PPh₃ in 1.68 mL of THF was prepared. After freezing and concentrating, 11.4 mL (4.7×10^{-4} mol) of propene and 11.4 mL (4.7×10^{-4} mol) of propene-*3,3,3-d_3* were condensed into the solution. The reaction was kept at 40.8 °C and periodically sampled by using vacuum line techniques. The propenes present were analyzed by GC/MS and the extent of scrambling determined from the relationship

$$\% \text{ scrambling} = 100 \times \frac{1}{7} \sum_{n=42}^{48} (I_n{}^0 - I_n{}^t)/(I_n{}^0 - I_n{}^e)$$

where $I_n{}^0$, $I_n{}^t$ and $I_n{}^e$ are the intensities of signals of mass n of samples taken at times 0, t, and 18 h, respectively.

General Procedure for Detecting BD/CH Exchange between I-*d_9* and Alkenes during Alkene Isomerization and Hydrogenation Reactions. General Procedure for B–D/B–H Analysis by ^{11}B NMR. Recovered samples of $Rh(H)(PPh_3)_2C_2B_9D_9H_2$ (I-*d_9*) were subjected to in situ triethylphosphine exchange employing a published procedure,[19] and ^{11}B FTNMR spectra were obtained at 160.44 MHz with a Bruker WM-500 spectrometer. Loss of deuterium label on any boron was observed by the appearance of proton coupling.

1-Hexene. A solution of I-*d_9* (0.100 g, 0.130 mmol) and PPh₃ (3.4 mg, 0.013 mmol) in THF (25 mL) under argon was maintained at 40.8 °C, and 1-hexene (1.000 mL, 8.00 mmol) was added via syringe. The reaction was then stirred 35 min. The volatiles were removed under reduced pressure and analyzed by VPC which indicated that 15 equiv of 1-hexene (per mol of Rh) had been isomerized. The ^{11}B FTNMR analysis of recovered I showed no loss of deuterium label.

3-Methyl-3-phenyl-1-butene. (a) A solution of I-*d_9* (0.100 g, 0.130 mmol) and PPh₃ (3.4 g, 0.013 mmol) in THF (25 mL) under H_2 (446 mm) was maintained at 40.8 °C in the hydrogen titrator, and the alkene (A) (2.100 mL, 13.0 mmol) was added via syringe. The reaction was stirred for 100 min when uptake of 10 equiv H_2 (per mol of Rh) had taken place. ^{11}B FTNMR analysis of recovered I showed no loss of deuterium label.

(b) Same as (a) with Ar replacing H_2. No scrambling of deuterium with A was observed.

(c) Alkene (A) (3.0 mL, 18.6 mmol) and THF (14 mL) were distilled under high vacuum into a tube containing I-*d_9* (0.125 g, 0.163 mmol). The tube was sealed and maintained at 40.8 °C for 24 h. Analysis of recovered I by ^{11}B TFNMR showed loss of deuterium label at B(9), B(10), and B(12).

Registry No. I, 53687-46-0; I-*3-d*, 82808-04-6; I-*d₉*, 89462-06-6; II, 53754-45-3; III, 76287-18-8; IV, 89437-71-8; A, 18321-36-3; A-*2-d*,

89278-57-9; A-*1,1,2-d₃*, 89437-72-9; B, 592-41-6; hydratropaldehyde, 93-53-8; 2-methyl-2-phenylpropanal, 3805-10-5; methyltriphenyl-phosphonium bromide, 1779-49-3; 1,3-propanedithiol, 109-80-8; 2-(1-methyl-1-phenylethyl)-1,3-dithiane, 89278-54-6; 2-(1-methyl-1-phenyl-ethyl)-1,3-dithiane-*2-d*, 89278-55-7; 1-methyl-2-phenylpropanal-*1-d*, 89278-56-8; *cis*-2-hexene, 7688-21-3; *trans*-2-hexene, 4050-45-7.

Communications to the Editor

Influence of Heme Orientation on Oxygen Affinity in Native Sperm Whale Myoglobin

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Myoglobin (Mb) has long been considered one of the best understood proteins on the basis of numerous high-resolution X-ray studies,[2] a simple physiological function of muscle oxygen transport,[3] and measurements of various binding processes involved in its function.[4] It is often the 'simple' model to which more complex O_2-binding hemeproeins are compared. It was then unexpected when ^1H NMR studies clearly demonstrated[5] that the native protein exists not only with the structure in the heme cavity as characterized by X-ray with the heme rotated by 180° about the α-γ-meso axis[6] (A and B in Figure 1). The two components exhibit indistinguishable optical spectra. However, recent NMR studies on the mechanisms of the reaction between heme- and apoMb demonstrated[7] that the resulting initial product is an equimolar mixture of the species with the heme orientations depicted in A and B of the figure. Characterization of the pH influence on the heme orientational equilibration rate has afforded the unusual ability to prepare Mb in states varying by simple relative ratios of the two heme orientations.[7,8] A wide range of O_2 affinities has been reported for Mb reconstituted with modified hemes.[9] There are few opportunities, however, when one can measure the influence on O_2 affinity of simple permutations of the same heme peripheral contacts with the protein side chains.

We report here on the O_2 affinity of sperm whale Mb as a function of the controlled and measured ratio of heme orientation, which demonstrates that the permutation of the heme methyl and vinyl peripheral contacts exerts a significant effect on the O_2-binding properties of the protein.

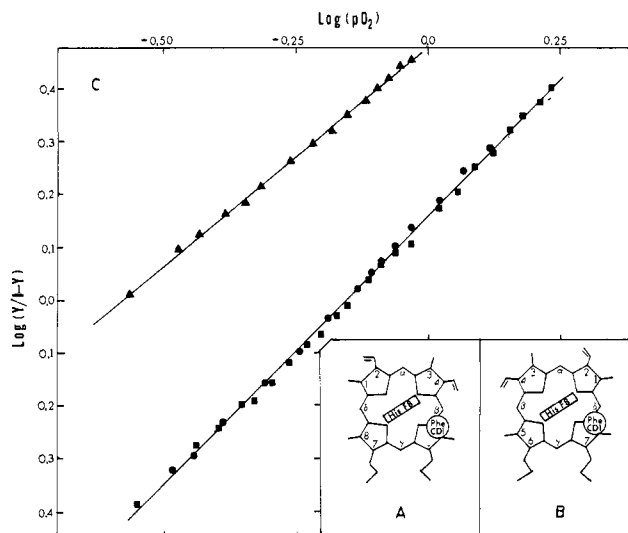Oxygen affinity measurements were performed[10] at 25 °C with

Figure 1. (A) Heme orientation as found[2] in the crystal structure. (B) Heme rotated by 180° about the α-γ-meso axis; the proximal histidyl π plane is indicated by the rectangle. (C) Hill plots (Y = fraction MbO₂) of oxygenation curves for sperm whale Mb at 25 °C. Shown are representative plots determined for a native sample (■), a 55:45 mixture of major/minor components (▲), and the previous disordered sample after reequilibrating to the native (10:1) ratio (●). For clarity, fewer points per curve are presented than were analyzed by linear regression.

an original spectrophotometric–polarographic device that has been routinely used in other experiments[11] to measure O_2 affinities of several Mbs with $P_{1/2}$s ranging from 0.07 to 2.5 mmHg. Similar devices have been previously described[12] and give consistent, reproducible binding curves in good agreement with those obtained by tonometric measurements. Oxygen off rates (k_{off}) were determined at 25 °C using a Gibson–Durrum stopped-flow spectrophotometer. The procedures used for preparation of apoMb, reconstitution with hemin, and equilibration to different mixtures of major and minor component have been reported.[5,7,8] The ratio of heme orientations was monitored by the ^1H NMR spectrum of the metMbCN form, for which the heme orientation disorder was first observed. The ^1H NMR spectra for the 55:45, 65:35, and reequilibrated (10:1) ratio of native/reversed heme orientation on which O_2 binding studies were performed have been reported

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(10) Disordered metMbCN was prepared as described in ref 6 and 7, the disorder ratio was determined by ^1H NMR,[5] and the solutions were diluted to 70 μM protein with 50 mM sodium phosphate buffer, pH 7.4. The solution (1.9 mL) was placed in the measuring cuvette of the apparatus, and a 20-fold excess of Na₂S₂O₄ (in 0.1 mL) was added. The deoxy Mb sample was then swept with H₂O-saturated air and the oxygenation curve recorded at 25 °C. The presence of the cyanide had a neglible influence on O_2 binding, as determined for the native protein. Redetermination of the ^1H NMR spectrum of a disordered sample treated in the identical fashion as for O_2 affinity measurements indicated less than 5% change in the ratio of heme disorder components during the elapsed time (the sample was run as metMbCN by adding ferricyanide and concentrating by ultrafiltration).

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