sistent with present procedures for numbering coordination polyhedra and boron polyhedral frameworks. Comments on this proposal are encouraged.

Polyhedral structures belonging to D_n, T, and C_s symmetry point groups, capped polyhedral systems, encapsulating polyhedra, and extensions specific to metal clusters are not included in this paper, but proposals in this area are in preparation.

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A Designed Metallacarborane Catalyst. Synthesis, Structure, and Reactions of [*closo*-1,3-[μ-(η^2-3-$CH_2{=}CHCH_2CH_2$)]-3-H-3-PPh_3-3,1,2-$RhC_2B_9H_{10}$]

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Received September 26, 1980

The synthesis and reactions of a designed metallacarborane catalyst, [*closo*-1,3-[μ-(η^2-3-$CH_2{=}CHCH_2CH_2$)-3-H-3-PPh_3-3,1,2-$RhC_2B_9H_{10}$] (I), are reported. Complex I contains a chelating 4-butenyl side chain attached to the dicarbollide ligand, the alkenyl function of which formally replaces one of the triphenylphosphine ligands of the parent compound [*closo*-3-H-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{11}$] (II). When I was exposed to conditions employed for the hydrogenation of alkenes or alkynes, the alkenyl ligand was hydrogenated to a noncoordinating butyl group, leaving an open coordination site on rhodium which greatly enhanced the rate of hydrogenation of added alkene. Complex I was, indeed, found to be among the most active homogeneous hydrogenation catalysts reported. Complex I also catalyzed the isomerization of hex-1-ene. The crystal and molecular structure of I has been determined by three-dimensional X-ray diffraction techniques. The compound crystallizes in the monoclinic space group $P2_1/a$ with $a = 16.494$ (4) Å, $b = 11.193$ (2) Å, $c = 17.006$ (3) Å, $\beta = 122.49$ (1)°, and $Z = 4$. The observed and calculated densities are 1.229 and 1.386 g cm^{-3}, respectively. Diffraction data to 2θ maximum = 45° (Mo Kα radiation) were collected on a Syntex P$\bar{1}$ automated diffractometer, and the structure was solved by conventional Patterson, Fourier, and full-matrix least-squares techniques to a final discrepancy index of $R = 0.044$ for the 2253 independent observed reflections. All atoms, including hydrogen atoms, were located. The molecule has the closo 12-vertex icosahedral geometry, and the rhodium is bonded to one hydrogen atom and one triphenylphosphine ligand and π bonded to the alkene function as well as symmetrically bonded to the C_2B_3 face of the C_2B_9 dicarbollyl group. The molecule is monomeric, and there are no intermolecular distances shorter than van der Waals distances. The reactions of I with hydrogen in the presence and absence of triphenylphosphine are reported.

Introduction

During the course of our studies of alkene hydrogenations catalyzed by [*closo*-3-H-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{11}$] (II),[1] the first metallacarborane catalyst, we have noted that the rate of hydrogenation is inversely proportional to the concentration of added triphenylphosphine. This observation suggests that reversible dissociation of triphenylphosphine is an important equilibrium preceding the rate-determining step of the hydrogenation sequence. The ease with which the parent catalyst could be modified through synthesis led us to explore the possibility of obtaining enhanced hydrogenation rates by replacing one of the triphenylphosphine ligands with a chelated η^2-3-buten-1-yl side chain attached to one of the dicarbollide carbon atoms. The resulting rhodacarborane [*closo*-1,3-[μ-(η^2-3-$CH_2{=}CHCH_2CH_2$)]-3-H-3-PPh_3-3,1,2-$RhC_2B_9H_{10}$][2] (I) might well undergo irreversible hydrogenation of the alkenyl side chain to produce an open coordination site on rhodium and a noncoordinating butyl group attached to the dicarbollide ligand. The use of alkenyl ligands to produce an open coordination site in hydrogenation catalysts was first proposed by Schrock and Osborn in their studies of hydrogenations catalyzed by $[(COD)MCl]_2$ (COD = 1,5-cyclooctadiene, M = Rh, Ir)[3]. To our knowledge, I is the first rhodium member of the relatively rare hydrido alkene class of complexes[4-12] to be isolated and structurally characterized. Regardless of the detailed mechanism of rhodacarborane-catalyzed hydrogenation (a subject which will be reported elsewhere), the removal of one coordinated triphenylphosphine molecule from the manifold of available ligands should facilitate alkene or hydrogen coordination and lead to a marked rate acceleration. Preliminary catalytic screening of I conclusively demonstrated this effect; indeed I is among the most active homogeneous hydrogenation catalysts reported to date (vide infra).

Experimental Section

Solvents and Reagents. All solvents were reagent grade and distilled under argon prior to use. Tetrahydrofuran (THF) was dried over

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basic alumina and distilled from potassium metal. Benzene was distilled from potassium metal, heptane and toluene from sodium metal. Methanol was distilled from $Mg(OMe)_2$. Absolute ethanol was saturated with nitrogen prior to use. Dichloromethane was purified according to a literature procedure[13] and distilled from P_2O_5.

Triphenylphosphine (Aldrich), 4-bromobut-1-ene (Aldrich), and phenyl lithium (Alfa) were used as received. Rhodium trichloride trihydrate (Matthey Bishop) was converted to $[RhCl(PPh_3)_3]$ by a literature procedure.[14] Trimethylvinylsilane (Alfa), butyl acrylate, styrene (Eastman), 3,3-dimethylbut-1-ene, hex-1-ene (Aldrich), cyclohexene (J. T. Baker), phenylacetylene (MCB), and 3,3-dimethylbutyne (Pfaltz and Bauer) were purified by passage through an alumina column followed by vacuum distillation from calcium hydride prior to use. Ethylbenzene (MCB), *cis*-and *trans*-hex-2-ene, and *cis*- and *trans*-hex-3-ene (Chemical Samples Co.) were used as gas chromatographic standards without further purification. Hydrogen (Liquid Carbonics) was passed through warm BTS catalyst (BASF) and anhydrous $CaSO_4$ prior to use. All reactions were performed under an atmosphere of dry nitrogen or argon unless otherwise indicated.

Physical Measurements. ^1H NMR spectra were recorded at 200 MHz and ^{31}P NMR spectra at 81 MHz with a Bruker WP-200 Fourier Transform NMR spectrometer. The ^{11}B NMR spectra were recorded at 127 MHz with an instrument designed and constructed by Professor F. A. L. Anet of UCLA. The ^{31}P NMR spectra were referenced to external H_3PO_4 and the ^{11}B NMR spectra to external $BF_3{\cdot}OEt_2$. Infrared spectra were recorded with a Perkin-Elmer 137 infrared spectrometer. Microanalyses and molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

$1\text{-}(CH_2{=}CHCH_2CH_2)\text{-}1,2\text{-}C_2B_{10}H_{11}$.[15] A 500-mL three-neck round-bottom flask was equipped with a magnetic stirrer, an addition funnel, and a reflux condenser with a nitrogen inlet. The system was flushed with nitrogen, a solution of 32.0 g (222 mmol) of $1,2\text{-}C_2B_{10}H_{12}$ in 50 mL of benzene was placed in the flask, and 233 mmol of phenyllithium in benzene solution was placed in the addition funnel. The stirred carborane solution was brought to reflux and the phenyllithium slowly added. After 3 h, 34.4 g (255 mmol) of 4-bromobut-1-ene was slowly added via the addition funnel and heating continued for 10 h. The solution was then cooled and carefully hydrolyzed with water, and the benzene layer was separated and dried over anhydrous $MgSO_4$. The $MgSO_4$ was separated by filtration, the benzene removed in vacuo and unreacted $1,2\text{-}C_2B_{10}H_{12}$ removed from the resultant brown viscous oil by sublimation at 1 torr at 40 °C. The brown oil was then repeatedly distilled at 1 torr to yield 35.2 g of a low-melting, white solid, $1\text{-}(CH_2{=}CHCH_2CH_2)\text{-}1,2\text{-}C_2B_{10}H_{11}$ (mp 45–46 °C) (80%).

$Cs^+[7\text{-}(CH_2{=}CHCH_2CH_2)\text{-}7,8\text{-}C_2B_9H_{11}]^-$. A three-neck 100-mL round-bottom flask, equipped with a magnetic stirrer and reflux condenser with nitrogen inlet, was charged with 1.00 g (5.0 mmol) of $1\text{-}(CH_2{=}CHCH_2CH_2)\text{-}1,2\text{-}C_2B_{10}H_{11}$, 0.92 g (16.4 mmol) of KOH, and 45 mL of degassed ethanol. The solution was then refluxed for 12 h. After the solution was cooled, excess CO_2 was bubbled through the solution and the precipitated $KHCO_3$ removed by filtration and washed with ethanol and diethyl ether. The washings were combined with the filtrate, and the solvent was removed in vacuo. The resulting oil was dissolved in 200 mL of water and filtered through Celite. A 20-mL saturated aqueous solution of CsCl was slowly added to the filtrate, precipitating a white solid. The solution was heated until the white solid completely dissolved and was then allowed to cool slowly, giving white crystals which were collected and dried in vacuo to yield 1.13 g of $Cs^+[7\text{-}(CH_2{=}CHCH_2CH_2)\text{-}7,8\text{-}C_2B_9H_{11}]^-$ (mp 225–228 °C) (70%). Anal. Calcd for $CsC_6H_{18}B_9$: C, 22.48; H, 5.66; B, 30.38. Found: C, 21.99; H, 5.56; B, 30.67.

[*closo*-$1,3\text{-}\mu\text{-}(\eta^2\text{-}3\text{-}CH_2{=}CHCH_2CH_2)\text{-}3\text{-}H\text{-}3\text{-}PPh_3\text{-}3,1,2\text{-}RhC_2B_9H_{10}$] (I). A 500-mL Schlenk flask equipped with a reflux condenser with nitrogen inlet, a magnetic stirrer, and a septum on the side arm was charged with 0.652 g (2.03 mmol) of $Cs^+[7\text{-}(CH_2{=}CHCH_2CH_2)\text{-}7,8\text{-}C_2B_9H_{11}]^-$, 1.343 g (1.45 mmol) of $[RhCl(PPh_3)_3]$, and 250 mL of methanol. The solution was refluxed for 3 h, yielding a yellow precipitate which was collected, dried in vacuo, and recrystallized from CH_2Cl_2–ethanol to give 0.730 g of yellow crystals of I (90%) (mp 170–173 °C dec): IR ν(B–H) 2550, ν(Rh–H) 2060 cm^{-1}. Anal. Calcd for $C_{24}H_{33}B_9PRh$: C, 52.14; H, 6.02; B, 17.62; P, 5.60; Rh, 18.62. Found: C, 51.74; H, 5.82; B, 17.24; P, 5.56; Rh, 17.74. The 200-MHz ^1H NMR spectrum in CD_2Cl_2 at 25 °C displayed resonances at δ 7.58–7.47 (phenyl protons, integration 15), 4.25 (carboranyl C–H, integration 1), 4.78, 3.77, and 3.75 (vinyl protons, multiplet, and a pair of overlapping doublets, $|^3J_{H_5-H_6}| = 16$ Hz (cis), $|^3J_{H_5-H_6'}| = 24$ Hz (trans), integrations 1, 1, and 1), and 2.55–1.48 (alkyl protons, integration 4), –7.42 (rhodium hydride, doublet of doublets, $|J_{Rh-H}| = 20$ Hz, $|^2J_{P-H}| = 33$ Hz, integration 1). The 81-MHz $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ at 25 °C displayed a doublet centered at 54.5 ppm, $|J_{Rh-P}| = 125$ Hz. The 112-MHz $^{11}B\{^1H\}$ NMR spectrum in the THF at 25 °C displayed resonances at –17.8, –15.3, –11.4, –9.4, –7.7, –4.6, 0.0, 1.1, and 3.3 ppm.

$[1\text{-}(CH_3CH_2CH_2CH_2)\text{-}3\text{-}PPh_3\text{-}3,1,2\text{-}RhC_2B_9H_{10}]_2$ (III). A 100-mL Schlenk flask was charged with 0.553 g (1 mmol) of I and attached to a vacuum manifold equipped with an oil diffusion pump, mercury manometer, hydrogen inlet, Nujol bubbler, and another inlet. The solvent, THF (28 mL), was placed in a 100-mL round-bottom flask and attached to the vacuum manifold, freeze–pump–thaw degassed three times, and vacuum distilled into the reaction flask. The solution was allowed to thaw and was equilibrated to 25 °C. Hydrogen was introduced, and the hydrogen uptake of the solution was recorded as a function of time. The solution rapidly took up nearly 1 mmol of hydrogen and then slowly evolved hydrogen until the total hydrogen uptake was 0.5 mmol. After the reaction was complete, the solvent was removed in vacuo and the residue chromatographed on a 10 × 150 mm silica gel column with CH_2Cl_2–hexane eluant under nitrogen. The solvent was removed and the residue recrystallized from CH_2Cl_2–heptane to yield 0.111 g of purple-black crystals of III (20%) (mp 192–194 °C): IR ν(B–H) 2520 cm^{-1}. Anal. Calcd for $C_{48}H_{68}B_{18}P_2Rh_2$: C, 51.96; H, 6.36; B, 17.55; P, 5.58; Rh, 18.55. Found: C, 51.72; H, 6.78; B, 16.95; P, 5.71; Rh, 18.73. The 200-MHz ^1H NMR spectrum in $CDCl_3$ at 25 °C displayed resonances at δ 7.51–7.31 (phenyl protons, integration 15), 2.51–0.75 (butyl protons, integration 9), and –8.73 (broad multiplet, Rh–H–B bridges, integration 1). The 81-MHz $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ displayed a doublet centered at 43.4 ppm, $|J_{Rh-P}| = 190$ Hz, and a doublet centered at 43.2 ppm, $|J_{Rh-P}| = 188$ Hz. The two doublets are possibly due to the presence of two closely related isomers in III. The 112-MHz $^{11}B\{^1H\}$ NMR spectrum in $CDCl_3$ displayed resonances at –13.7, –9.4, –6.4, –0.8, and 21.1 ppm at 25 °C. The molecular weight determinations supported the proposed formula.[16]

[*closo*-$1\text{-}(CH_3CH_2CH_2CH_2)\text{-}3\text{-}H\text{-}3,3\text{-}(PPh_3)_2\text{-}RhC_2B_9H_{10}$] (IV). A 100-mL Schlenk flask was charged with 0.553 g (1 mmol) of I and 0.630 g (2.4 mmol) of triphenylphosphine and attached to a vacuum manifold equipped with an oil diffusion pump, mercury manometer, hydrogen inlet, Nujol bubbler, and magnetic stirrer. The solvent, THF (28 mL), was placed in a 100-mL round-bottom flask and attached to the vacuum manifold, freeze–pump–thaw degassed three times, and vacuum distilled into the reaction flask. The solution was allowed to thaw and was equilibrated to 25 °C. Hydrogen was introduced and the uptake of hydrogen measured (total uptake = 1 mmol). The solvent was removed in vacuo and the residue chromatographed on a 10 × 150 mm silica gel column with use of CH_2Cl_2–hexane eluant under nitrogen. The solvent was removed in vacuo and the residue recrystallized from CH_2Cl_2–heptane to give 0.735 g of orange crystals of IV (90%) (mp 184–185 °C dec). Complex IV was also prepared in a 74% yield by stirring $[RhCl(PPh_3)_3]$ with a 20% molar excess of $Cs^+[7\text{-}(CH_3CH_2CH_2CH_2)\text{-}7,8\text{-}C_2B_9H_{11}]^-$ in methanol.[17] The

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(16) On a sample correctly analyzed for $[C_4H_9PPh_3RhC_2B_9H_{10}]_2{\cdot}CH_2Cl_2$, the molecular weight by osmometry in benzene of III was found to be 617 ± 13 (theoretical $M_r = 596$). Anal. Calcd for $C_{49}H_{70}B_{18}Cl_2P_2Rh_2$: C, 49.36; H, 5.92; B, 16.32; Cl, 5.95; P, 5.20; Rh, 17.26. Found: C, 48.88; H, 6.15; B, 16.53; Cl, 5.88; P, 5.01; Rh, 16.54.

(17) $Cs^+[7\text{-}(CH_3CH_2CH_2CH_2)\text{-}7,8\text{-}C_2B_9H_{11}]^-$ may be prepared from $1\text{-}(CH_3CH_2CH_2CH_2)\text{-}1,2\text{-}C_2B_{10}H_{11}$ in a manner analogous to the preparation of $Cs^+[7\text{-}(CH_2{=}CHCH_2CH_2)\text{-}7,8\text{-}C_2B_9H_{11}]^-$ from $1\text{-}(CH_2{=}CHCH_2CH_2)\text{-}1,2\text{-}C_2B_{10}H_{11}$. $1\text{-}(CH_3CH_2CH_2CH_2)\text{-}1,2\text{-}C_2B_{10}H_{11}$ may be prepared by the method of T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *Inorg. Chem.*, **2** 1097 (1963).

precipitate obtained was recrystallized by the method above. IR: ν(B–H) 2460 and ν(Rh–H) = 2080 cm^{-1}. Anal. Calcd for $C_{42}H_{50}B_9P_2Rh$: C, 61.74; H, 6.17; B, 11.92; P, 7.58; Rh, 12.60. Found: C, 61.70; H, 6.48; B, 11.60; P, 7.55; Rh, 12.06. The 200-MHz ^1H NMR spectrum in $CDCl_3$ at 25 °C displayed resonances at δ 7.47–7.12 (phenyl protons, integration 30), 2.20–0.86 (butyl protons, integration 9), and −8.83 (rhodium hydride, integration 1). The 81-MHz $^{31}P\{^1H\}$ NMR spectrum in CH_2Cl_2–C_6D_6 at 25 °C displayed a doublet of doublets centered at 39.9 ppm, $|J_{Rh-P}|$ = 128 Hz and $|^2J_{P-P}|$ = 16 Hz. The 112-MHz $^{11}B\{^1H\}$ NMR spectrum in CD_2Cl_2 at 25 °C displayed resonances at −17.0, −11.8, −9.9, −7.5, −2.1, and 1.2 ppm.

X-ray Crystal Structure Determination of I. Collection and Reduction of X-ray Data. A single crystal bounded by {001} and {110} and {323} with dimensions normal to these of 0.0145, 0.0195, and 0.0065 cm, respectively, was mounted on a glass fiber. Preliminary oscillation and Weissenberg photographs indicated the compound crystallized in the space group $P2_1/a$. The automatic centering, autoindexing, and least-squares routines of a Syntex $P\bar{1}$ diffractometer were used to determine the unit cell parameters of a = 16.494 (4) Å, b = 11.193 (2) Å, c = 17.006 (3) Å, β = 122.49 (1)°, and V = 2648.22 (95) Å on the basis of 15 reflections in the region 15° < 2θ < 25°. A graphite crystal was used to provide monochromatic Mo Kα radiation (0.71073 Å). The crystal density was found to be 1.229 g cm^{-3} by flotation in aqueous KI, while the calculated density was 1.386 g cm^{-3} based on Z = 4.

Intensity data were collected with a θ–2θ scan technique to a limit of 2θ = 45°, with a takeoff angle of 4°. Reflections were scanned at a constant rate of 2.0°/min from 1.25° below the Kα_1 to 1.25° above the Kα_2 reflection. The total background counting time, measured at each end of the scan, was equal to the scan time for each reflection. The intensities of three standard reflections were measured every 97 reflections. No significant deviations were observed.

The data were corrected for Lorentz and polarization effects and for absorption (μ = 7.02 cm^{-1}; maximum, minimum, and average transmission factors are 0.9677, 0.9025, and 0.9344, respectively).[18] The intensity of a reflection, $I(hkl)$, and its estimated standard deviation, $\sigma I(hkl)$, were calculated according to the equations $I = CT - (t_c/t_b)(B_1 + B_2)/2$ and $\sigma(I) = [\sigma_s^2 + 0.04I^2]^{1/2}$, where I is the net integrated intensity, CT is the total integrated count, t_c and t_b are the count times for the scan and background, respectively, B_1 and B_2 are the background counts on the low and high sides of the reflection, and σ_s is the standard deviation in intensity due to counting statistics. Of 3840 unique reflections, 1504 with intensities less than 3 times their standard deviations were considered to be unobserved and were omitted from subsequent calculations.

Solution and Refinement of the Structure. The coordinates of the rhodium atom were determined by solution of a three-dimensional Patterson map, and a subsequent Fourier summation resulted in the location of all 35 nonhydrogen atoms. The three phenyl groups were described as rigid C_6 hexagons with C–C = 1.39 Å and C–H = 1.0 Å. After several cycles of full-matrix least-squares refinement, with anisotropic thermal parameters for Rh and P and isotropic thermal parameters for C and B, convergance was reached with R = 0.057 and R_w = 0.072.[19] Hydrogen atom positions were then obtained from a difference map. In the final least-squares cycle, 245 parameters were refined. The refinement included positional and anisotropic thermal parameters for Rh, P, the C_2B_9 cage and the C_4 butene atoms, positional and isotropic thermal parameters for the metal hydride, positional and carbon isotropic thermal parameters for the C_6H_5 groups, and positional parameters for the remaining nongroup hydrogen atoms. For all the hydrogen atoms except the metal hydride, B was fixed at 0.5 + B of the carbon or boron atoms to which the hydrogen is attached. The final least-squares cycle converged at R = 0.044 and R_w = 0.048; the "goodness of fit" was 1.245 as defined by $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, with N_o (number of observations) = 2253 and N_v (number of variables) = 245. On a final difference map, the highest peak was 0.5 e/Å^3 and there were 15 peaks ≥ 0.3 e/Å^3. All but one of these was within 0.9 Å of a phenyl group carbon atom.

Table I. Atomic Positions and Temperature Factors

atom	x	y	z	B, Å^2
HRh	−0.1390 (53)	0.0575 (71)	0.6339 (50)	6 (2)
HC2	0.0248 (52)	−0.2821 (62)	0.7354 (47)	3.80^a
HC31	−0.0513 (62)	−0.2895 (80)	0.5614 (60)	5.50
HC32	−0.1581 (58)	−0.3091 (74)	0.4849 (54)	5.50
HC41	−0.1951 (60)	−0.1186 (68)	0.4422 (55)	5.20
HC42	−0.1017 (60)	−0.1452 (75)	0.4460 (57)	5.20
HC5	−0.0783 (56)	0.0276 (67)	0.5312 (51)	3.90
HC61	0.0798 (51)	−0.0016 (66)	0.6646 (49)	3.80
HC62	0.0635 (52)	−0.1395 (67)	0.6475 (48)	3.80
H4	−0.2733 (50)	−0.1048 (59)	0.5316 (47)	4.10
H5	−0.2736 (55)	−0.3424 (67)	0.5364 (51)	4.80
H6	−0.0987 (47)	−0.4489 (65)	0.6420 (45)	4.10
H7	−0.0029 (50)	−0.1452 (62)	0.8530 (46)	3.80
H8	−0.2025 (48)	−0.0282 (63)	0.7356 (47)	4.10
H9	−0.3264 (53)	−0.2056 (65)	0.6516 (48)	4.50
H10	−0.2335 (49)	−0.4383 (66)	0.7132 (46)	4.50
H11	−0.0237 (49)	−0.3899 (61)	0.8423 (47)	4.00
H12	−0.1704 (51)	−0.2299 (63)	0.8376 (47)	4.40

^{a} These thermal parameters were not included in the least-squares refinement.

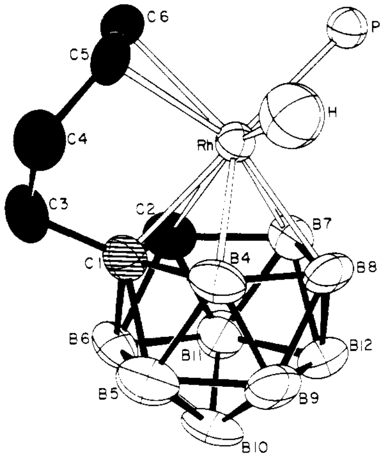

Figure 1. Molecular structure of I. (All hydrogen atoms except the rhodium hydride and the phenyl rings on phosphorus have been omitted for clarity.)

Scattering factors for Rh, P, C, and B were taken from the International Tables for X-ray Crystallography[20] and for H from Stewart, Davidson, and Simpson.[21] Real and imaginary terms for anomalous scattering were taken from the International Tables for X-ray Crystallography.[20] The function $\sum w||F_o| - |F_c||^2$ was minimized in the refinement.

Atomic and positional coordinates are presented in Table I, thermal parameters are listed in Table II, and group parameters are listed in Table III.

Isomerization Reactions. The alkene isomerization reaction was studied by stirring a THF solution 4.5 × 10^{-3} M in I and 4 M in hex-1-ene under nitrogen for 120 h. The solution was then analyzed by gas chromatography with a 30-ft 10% $AgNO_3$–propylene glycol on Chromosorb P column at a flow rate of 40 mL/min.

Alkene and Alkyne Hydrogenation Reactions. Complex I was screened for hydrogenation of alkenes and alkynes on a glass vacuum line equipped with an oil diffusion pump, hydrogen inlet, Nujol bubbler, a reaction flask with magnetic stirrer, and a mercury manometer. The reaction flask was charged with an accurately weighed amount of I and evacuated. The solvent was placed in a 100-mL round-bottom flask which was then attached to the vacuum manifold. The solvent was freeze–pump–thaw degassed three times and vacuum distilled into the reaction flask. The substrate (alkene or alkyne) was introduced similarly. The contents of the reaction flask were equilibrated to the desired temperature and hydrogen introduced. The initial pressure

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(18) Programs used in this work have been previously described by K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1397 (1974).

(19) The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = [\sigma|F_o|]^{-2}$. The discrepancy indices are defined as $R = [\sum||F_o| - |F_c||/\sum|F_o|]$ and $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$.

(20) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1975.

(21) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

Table II. Atomic Positions and Temperature Factors[a] ($\times 10^5$)

atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	−0.0732 (4)	−0.0641 (5)	0.6772 (4)	304 (3)	451 (5)	310 (3)	3 (5)	162 (3)	10 (4)
P	0.0147 (14)	0.0864 (17)	0.7793 (13)	338 (12)	493 (20)	341 (11)	−7 (12)	186 (10)	7 (12)
C1	−0.1297 (56)	−0.2404 (69)	0.6116 (53)	416 (52)	671 (80)	340 (48)	−103 (52)	167 (43)	−99 (49)
C2	−0.0414 (61)	−0.2580 (67)	0.7218 (58)	425 (54)	512 (76)	419 (49)	106 (52)	188 (45)	144 (50)
C3	−0.1085 (81)	−0.2546 (94)	0.5352 (71)	875 (88)	948 (115)	493 (66)	−123 (76)	420 (68)	−229 (67)
C4	−0.1191 (80)	−0.1381 (95)	0.4867 (62)	784 (76)	1115 (112)	328 (56)	−135 (77)	308 (54)	−104 (65)
C5	−0.0570 (65)	−0.0401 (76)	0.5534 (60)	605 (65)	734 (93)	419 (53)	53 (62)	393 (53)	36 (56)
C6	0.0117 (58)	−0.0590 (86)	0.6319 (58)	404 (53)	719 (84)	459 (52)	−39 (62)	290 (47)	−21 (62)
B4	−0.2183 (69)	−0.1460 (88)	0.6008 (69)	340 (59)	738 (99)	370 (57)	−92 (61)	92 (49)	9 (61)
B5	−0.2322 (79)	−0.3060 (95)	0.5968 (78)	479 (70)	694 (103)	550 (71)	−190 (69)	173 (59)	−19 (70)
B6	−0.1158 (77)	−0.3736 (84)	0.6703 (71)	629 (73)	320 (79)	547 (67)	13 (68)	301 (60)	31 (59)
B7	−0.0603 (72)	−0.1730 (86)	0.7925 (66)	477 (68)	602 (92)	313 (56)	−45 (62)	182 (52)	23 (57)
B8	−0.1771 (70)	−0.1030 (87)	0.7185 (76)	406 (62)	628 (98)	711 (73)	46 (60)	412 (58)	47 (65)
B9	−0.2592 (73)	−0.2204 (97)	0.6644 (80)	303 (59)	883 (109)	751 (80)	−89 (67)	322 (60)	33 (75)
B10	−0.2014 (78)	−0.3597 (88)	0.7073 (75)	596 (76)	488 (95)	589 (70)	−166 (66)	283 (61)	40 (64)
B11	−0.0789 (77)	−0.3317 (88)	0.7828 (73)	549 (70)	585 (93)	504 (65)	29 (66)	314 (58)	49 (63)
B12	−0.1630 (79)	−0.2338 (94)	0.7826 (76)	668 (78)	782 (105)	581 (71)	−235 (72)	476 (67)	−106 (69)

[a] Estimated standard deviations, shown in parentheses, refer to the last digit or digits of the preceding number. For x, y, and z they have been multiplied by a factor of 10. [b] The anisotropic temperature factor T is defined as $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III

Group Parameters[a]

group	x	y	z	ϕ	θ	ρ
phenyl 1	0.1316 (3)	0.0425 (4)	0.8829 (3)	−2.548 (4)	2.557 (3)	1.887 (4)
phenyl 2	0.0451 (4)	0.2060 (4)	0.7252 (3)	−1.650 (4)	−2.294 (3)	−2.479 (4)
phenyl 3	−0.0415 (3)	0.1677 (4)	0.8324 (3)	−0.324 (3)	2.723 (3)	2.565 (3)

Thermal Parameters for Members of Groups

atom	B	atom	B	atom	B	atom	B	atom	B	atom	B
C11	2.7 (2)	C21	2.9 (2)	C31	2.8 (2)	C14	4.2 (2)	C24	4.1 (2)	C34	4.1 (2)
C12	3.8 (2)	C22	4.2 (2)	C32	3.7 (2)	C15	4.5 (2)	C25	3.5 (2)	C35	3.7 (2)
C13	4.3 (2)	C23	5.0 (2)	C33	4.3 (2)	C16	3.9 (2)	C26	3.1 (2)	C36	3.3 (2)

Group Atom Derived Positional Parameters

	atom	x	y	z	atom	x	y	z
phenyl 1	C1-1	0.1316	0.0425	0.8829	H1-2	0.1586	−0.0899	0.8141
	C1-2	0.1845	−0.0481	0.8750	H1-3	0.3116	−0.1456	0.9462
	C1-3	0.2735	−0.0804	0.9519	H1-4	0.3736	−0.0456	1.0918
	C1-4	0.3096	−0.0223	1.0366	H1-5	0.2826	0.1101	1.1054
	C1-5	0.2566	0.0682	1.0445	H1-6	0.1296	0.1657	0.9733
	C1-6	0.1677	0.1006	0.9676				
phenyl 2	C2-1	0.0451	0.2060	0.7252	H2-2	0.1909	0.2094	0.8278
	C2-2	0.1391	0.2469	0.7683	H2-3	0.2289	0.3694	0.7599
	C2-3	0.1613	0.3400	0.7288	H2-4	0.1053	0.4591	0.6178
	C2-4	0.0893	0.3921	0.6462	H2-5	−0.0565	0.3887	0.5436
	C2-5	−0.0047	0.3512	0.6030	H2-6	−0.0945	0.2288	0.6115
	C2-6	−0.0269	0.2582	0.6425				
phenyl 3	C3-1	−0.0415	0.1677	0.8324	H3-2	−0.0423	0.3362	0.7805
	C3-2	−0.0563	0.2905	0.8224	H3-3	−0.1013	0.4380	0.8635
	C3-3	−0.0906	0.3497	0.8707	H3-4	−0.1348	0.3287	0.9636
	C3-4	−0.1101	0.2861	0.9289	H3-5	−0.1093	0.1176	0.9807
	C3-5	−0.0953	0.1633	0.9388	H3-6	−0.0503	0.0158	0.8977
	C3-6	−0.0610	0.1041	0.8906				

[a] ϕ, θ, and ρ are given in radians. For the definition of these terms see ref 29.

was measured, and the uptake of hydrogen as a function of time was recorded. The products were analyzed by gas chromatography. A few of the hydrogenation reactions were performed with an automatic gas titration apparatus.[22]

Results and Discussion

Molecular Structure of I. Intramolecular distances and their estimated standard deviations are listed in Table IV. Bond angles are presented in Table V. The structure is shown in Figure 1, which also illustrates the numbering system employed.[23]

In this complex Rh(III) exhibits pseudooctahedral coordination with the carborane cage occupying three coordination sites. The triphenylphosphine ligand, the hydride ligand, and the alkene occupy the remaining sites. The bonding of the metal atom to the carborane cage is highly symmetric and ranges from Rh–C1 = 2.211 (8) to Rh–C2 = 2.266 (8) Å, which is almost identical to the range of 2.22 (1)–2.28 (1) Å found in II.[7]

Within the carborane polyhedron, the C–C distance is 1.65 Å, the C–B distances in the coordinated face are 1.69 (1) and 1.73 (1) Å, and the B–B distances in this face are 1.82 (1)

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(22) R. E. King, III, M. S. Delaney, and M. F. Hawthorne, to be submitted for publication.

(23) R. M. Adams, *Pure Appl. Chem.*, **30**, 683 (1972).

Table IV

Interatomic Distances (Å)

Rh-H	1.65 (3)	C3-C4	1.50 (1)	B7-H7	1.00 (7)
Rh-C1	2.211 (8)	C4-HC42	0.88 (8)	B7-B12	1.75 (1)
Rh-B8	2.217 (9)	C4-HC41	1.08 (8)	B7-B11	1.80 (1)
Rh-B4	2.217 (9)	C4-C5	1.51 (1)	B7-B8	1.82 (1)
Rh-B7	2.220 (9)	C5-HC5	0.84 (7)	B8-H8	1.05 (7)
Rh-C6	2.242 (8)	C5-C6	1.37 (1)	B8-B9	1.75 (1)
Rh-C2	2.266 (8)	C6-HC61	0.94 (7)	B8-B12	1.76 (1)
Rh-C5	2.276 (8)	C6-HC62	1.00 (7)	B9-H9	1.02 (7)
Rh-P	2.291 (2)	B4-H4	1.13 (7)	B9-B10	1.77 (1)
C1-C3	1.53 (1)	B4-B9	1.76 (1)	B9-B12	1.78 (2)
C1-C2	1.65 (1)	B4-B8	1.80 (1)	B10-H10	1.06 (7)
C1-B4	1.73 (1)	B4-B5	1.80 (1)	B10-B11	1.74 (1)
C1-B5	1.73 (1)	B5-H5	0.97 (7)	B10-B12	1.78 (1)
C1-B6	1.75 (1)	B5-B9	1.73 (2)	B11-H11	1.13 (7)
C2-HC2	1.02 (7)	B5-B6	1.76 (1)	B11-B12	1.77 (1)
C2-B11	1.68 (1)	B5-B10	1.77 (1)	B12-H12	1.01 (7)
C2-B7	1.69 (1)	B6-H6	1.11 (7)	P-C11	1.848[a]
C2-B6	1.70 (1)	B6-B11	1.72 (1)	P-C21	1.840
C3-HC31	0.89 (8)	B6-B10	1.77 (1)	P-C31	1.843
C3-HC32	1.01 (8)				

Average Bond Lengths (Å)

atoms	no.	range	av[b]
Rh-B	3	2.217 (9)-2.220 (9)	2.218 (2)
C-B	6	1.68 (1)-1.75 (1)	1.71 (3)
B-B	18	1.72 (1)-1.82 (1)	1.77 (3)
B-H(terminal)	9	0.97 (7)-1.13 (7)	1.05 (6)

[a] Standard deviations are not reported for distances involving atoms that are members of rigid groups. [b] Esd's for average bond lengths were calculated with use of the equation $\sigma^2 = [\Sigma_{i=1}{}^{i=N}(x_i - \bar{x})^2]/(N-1)$, where x_i is the ith bond length and $\bar{x}$ is the mean of the N equivalent bond lengths.

and 1.80 (1) Å. The average distances from C and B in this face to adjacent boron atoms in the lower ring are 1.72 (3) and 1.77 (2) Å, respectively.

The Rh–P distance in this compound, 2.291 (2) Å, is nearly identical with the shorter of the two Rh–P distances, 2.301 (1) Å, found in II and quite similar to that observed in other triphenylphosphine complexes of rhodium.[24]

The hydride ligand occupies a pseudooctahedral coordination site on the rhodium very nearly cis to B4 and B8 and trans to C2 (the angles are 80 (3), 82 (2), and 156 (3)°, respectively). There is no evidence of interaction with the carborane ligand. The Rh–H distance of 1.65 (8) Å, obtained by least-squares refinement, is not significantly different from the distance of 1.72 (15) Å found in $[RhH(CO)(PPh_3)_3]$[25] or that of 1.54 (9) Å found in II.[1]

The alkene is π bonded to the metal atom with Rh–C distances of 2.242 (8) and 2.276 (8) Å. The C=C distance is 1.37 (1) Å. These distances are quite similar to those found in $[(COD)\text{-}(2S,3S)\text{-}(CH_3CH(PPh_2)CH(PPh_2)CH_3)Rh^I]^+\text{-}ClO_4$,[26] 2.24 (average) and 1.36 Å, respectively. The complex is monomeric; there are no intermolecular distances within 3.0 Å other than H···H. The closest H···H approach, 2.38 Å, is between H4 and H2-5.

Reactions of I with Hydrogen. The fate of I following the hydrogenation of its chelated alkenyl side chain was explored in two sets of experiments: hydrogenation in the presence of added triphenylphosphine and, more importantly, hydrogenation in the total absence of added ligands.

In the presence of added triphenylphosphine, I smoothly reacted with low-pressure hydrogen at 25 °C in THF to produce $[closo\text{-}1\text{-}(CH_3CH_2CH_2CH_2\text{-})\text{-}3\text{-}H\text{-}3,3\text{-}(PPh_3)_2\text{-}3,1,2\text{-}RhC_2B_9H_{10}]$ (IV). Authentic IV was synthesized from $[RhCl(PPh_3)_3]$ and the correspondingly substituted $[C_2B_9H_{12}]^-$ ion and shown to be an effective catalyst for the isomerization and hydrogenation of alkenes and the hydrogenation of alkynes.[28]

Hydrogenation of I in THF at 25 °C with low-pressure hydrogen and in the absence of added ligands resulted in the rapid uptake of 1 mol of hydrogen followed by the *slow evolution* of $^1/_2$ mol of hydrogen/mol of I. The course of this reaction sequence was also monitored by ^{31}P NMR spectroscopy at 25 °C in THF solution. As the doublet at 54.7 ppm ($|J_{Rh-P}| = 127$ Hz) assigned to I decreased in intensity, a new pair of doublets appeared at 40.1 ppm ($|J_{Rh-P}| = 122$ Hz) and 39.9 ppm ($|J_{Rh-P}| = 127$ Hz), assigned to the species resulting from the uptake of 1 mol of hydrogen. This latter set of doublets was replaced by doublets at 43.4 ppm ($|J_{Rh-P}| = 190$ Hz) and 43.2 ppm ($|J_{Rh-P}| = 188$ Hz) associated with the final products of the reaction (III) which were formed with concommitant evolution of $^1/_2$ mol of hydrogen. That the dark purple III is a mixture of two closely related species is indicated by the observation of the two $^{31}P\{^1H\}$ doublets separated by only 0.2 ppm present in an approximately 2:1 ratio at 43.4 and 43.2 ppm, respectively. Similar experiments monitored by ^1H NMR spectroscopy did not reveal the presence of an intermediate. No new hydride resonances were observed, and the disappearance of the metal hydride and vinylic hydrogen resonances was the only change observed. The final product mixture III contained a resonance at δ −8.73 characteristic of Rh–H–B bridge protons. The ^{11}B NMR spectrum of III was generally uninformative except for the presence of a low-field resonance at 21.1 ppm which may be associated with the boron atom of the Rh–H–B bridge array.

Elemental analyses, molecular weight determinations,[16] and the NMR evidence presented above suggest the mixture (III), whose components we have been unable to separate, is composed of two species, each of which may be formulated as $[1\text{-}(CH_3CH_2CH_2CH_2)\text{-}3\text{-}PPh_3\text{-}3,1,2\text{-}RhC_2B_9H_{10}]_2$ and thus closely related to the fully characterized purple dimer[27] $[3\text{-}PPh_3\text{-}3,1,2\text{-}RhC_2B_9H_{11}]_2$. The latter species is novel in that the two Rh–H–B bridges linking the Rh atoms with neighboring C_2B_9 fragments are not equivalent. This is reflected by $^{31}P\{^1H\}$ doublets at 36.7 ($|J_{Rh-P}| = 172$ Hz) and 29.7 ppm ($|J_{Rh-P}| = 135$ Hz). In addition, the ^{11}B NMR spectrum of this dimer contained a lowest field resonance at 24.2 ppm which is similar to that seen in the mixture III at 21.1 ppm. We therefore suggest that III is composed of two isomers which differ only with respect to the relative positions of their *n*-butyl substitutents in the dimer structure. We further suggest that, unlike the $[3\text{-}PPh_3\text{-}3,1,2\text{-}RhC_2B_9H_{11}]_2$ dimer,[27] the Rh–H–B bridge linkages in both isomers of III are formed with the positionally equivalent B atoms of the two cages present in each isomer, the B atom symmetrically disposed with respect to the two C atoms in the face of the dicarbollide ligands. Figure 2 suggests a possible pathway for the formation of the two isomers suggested to be present in III.

Isomerization and Hydrogenation of Alkenes and Alkynes Catalyzed by I. Complex I was found to catalyze the isomerization of hex-1-ene in THF. After stirring a THF solution of I (4.5×10^{-3} M) and hex-1-ene (4.0 M) for 120 h, the observed products were 0.25% hex-1-ene, 67% *trans*-hex-2-ene, 24% *cis*-hex-2-ene, 2.5% trans-hex-3-ene, and 6.4% *cis*-hex-3-ene.

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(24) K. S. Y. Lau, Y. Becker, F. Juang, N. Baenziger, and J. K. Stille, *J. Am. Chem. Soc.*, **99**, 5664 (1977); R. W. Baker and P. Pauling, *J. Chem. Soc., Dalton Trans.*, 1495 (1969).

(25) S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.*, **85**, 3501 (1963).

(26) R. G. Ball and N. C. Payne, *Inorg. Chem.*, **16**, 1187 (1977).

(27) R. T. Baker, R. E. King, III, C. Knobler, C. A. O'Con, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **100**, 8266 (1978).

(28) A. THF solution of IV (2.72×10^{-3} M) catalyzed (at 25 °C, $p(H_2) =$ 585 mm) the hydrogenations of 3,3-dimethylbut-1-ene (0.0984 M) and phenylacetylene (0.0492 M) with initial rates of 5.2×10^{-2} and 2.7×10^{-2} mol s^{-1}/mol of Rh, respectively.

(29) C. Scheringer, *Acta Crystallogr.*, **16**, 546 (1963).

Table V. Bond Angles (Deg)

HRh-Rh-C1	121 (3)
HRh-Rh-B8	82 (2)
HRh-Rh-B4	81 (3)
HRh-Rh-B7	125 (2)
HRh-Rh-C5	105 (2)
HRh-Rh-C2	157 (3)
HRh-Rh-C5	82 (2)
HRh-Rh-P	74 (3)
C1-Rh-B8	78.3 (3)
C1-Rh-B4	46.0 (3)
C1-Rh-B7	76.7 (3)
C1-Rh-C6	92.5 (3)
C1-Rh-C2	43.4 (3)
C1-Rh-C5	82.3 (3)
C1-Rh-P	164.2 (2)
B8-Rh-B4	47.9 (4)
B8-Rh-B7	48.4 (4)
B8-Rh-C6	170.1 (4)
B8-Rh-C2	77.6 (3)
B8-Rh-C5	144.2 (4)
B8-Rh-P	100.7 (3)
B4-Rh-B7	81.5 (4)
B4-Rh-C6	126.8 (3)
B4-Rh-C2	77.5 (3)
B4-Rh-C5	97.6 (4)
B4-Rh-P	142.4 (3)
B7-Rh-C6	126.4 (3)
B7-Rh-C2	44.2 (3)
B7-Rh-C5	151.5 (3)
B7-Rh-P	90.8 (3)
C6-Rh-C2	93.3 (3)
C6-Rh-C5	35.2 (3)
C6-Rh-P	87.2 (2)
C2-Rh-C5	107.6 (3)
C2-Rh-P	120.8 (2)
C5-Rh-P	105.8 (2)
C3-C1-C2	119.2 (7)
C3-C1-B4	122.6 (7)
C3-C1-B5	119.0 (7)
C3-C1-B6	113.8 (7)
C3-C1-Rh	107.2 (6)
C2-C1-B4	111.8 (6)
C2-C1-B5	108.1 (6)
C2-C1-B6	59.8 (5)
C2-C1-Rh	70.1 (4)
B4-C1-B5	62.7 (5)
B4-C1-B6	113.3 (6)
B4-C1-Rh	67.2 (4)
B5-C1-B6	60.5 (5)
B5-C1-Rh	124.4 (6)
B6-C1-Rh	125.9 (5)
HC2-C2-C1	118 (4)
HC2-C2-B11	115 (4)
HC2-C2-B7	124 (4)
HC2-C2-B6	110 (4)
HC2-C2-Rh	111 (4)
C1-C2-B11	111.5 (7)
C1-C2-B7	110.6 (6)
C1-C2-B6	62.9 (5)
C1-C2-Rh	66.6 (4)
B11-C2-B7	64.4 (6)
B11-C2-B6	61.0 (6)
B11-C2-Rh	125.5 (6)
B7-C2-B6	114.5 (7)
B7-C2-Rh	66.5 (4)
B6-C2-Rh	125.5 (6)
HC31-C3-HC32	108 (8)
HC31-C3-C4	116 (6)
HC31-C3-C1	107 (6)
HC32-C3-C4	105 (5)
HC32-C3-C1	109 (5)
C4-C3-C1	111.5 (8)
HC42-C4-HC41	102 (7)
HC42-C4-C3	111 (6)
HC42-C4-C5	106 (6)
HC41-C4-C3	108 (4)
HC41-C4-C5	116 (4)
C3-C4-C5	112.7 (8)
HC5-C5-C6	123 (6)
HC5-C5-C4	112 (6)
HC5-C5-Rh	107 (5)
C6-C5-C4	123.9 (8)
C6-C5-Rh	71.0 (5)
C4-C5-Rh	103.9 (6)
HC61-C6-HC62	108 (6)
HC61-C6-C5	126 (5)
HC61-C6-Rh	112 (5)
HC62-C6-C5	122 (4)
HC62-C6-Rh	106 (4)
C5-C6-Rh	73.8 (5)
H4-B4-C1	121 (3)
H4-B4-B9	118 (3)
H4-B4-B8	131 (4)
H4-B4-B5	111 (3)
H4-B4-Rh	117 (3)
C1-B4-B9	103.1 (7)
C1-B4-B8	104.6 (6)
C1-B4-B5	58.7 (5)
C1-B4-Rh	66.8 (4)
B9-B4-B8	58.9 (6)
B9-B4-B5	58.0 (6)
B9-B4-Rh	119.0 (6)
B8-B4-B5	105.8 (7)
B8-B4-Rh	66.0 (4)
B5-B4-Rh	120.5 (6)
H5-B5-B9	131 (5)
H5-B5-C1	114 (5)
H5-B5-B6	117 (5)
H5-B5-B10	128 (5)
H5-B5-B4	118 (5)
B9-B5-C1	104.4 (7)
B9-B5-B6	108.4 (8)
B9-B5-B10	60.7 (6)
B9-B5-B4	59.8 (6)
C1-B5-B6	60.2 (5)
C1-B5-B10	106.8 (7)
C1-B5-B4	58.6 (5)
B6-B5-B10	60.4 (6)
B6-B5-B4	109.7 (7)
B10-B5-B4	109.9 (8)
H6-B6-C2	118 (4)
H6-B6-B11	131 (4)
H6-B6-C1	111 (4)
H6-B6-B5	118 (4)
H6-B6-B10	134 (4)
C2-B6-B11	58.9 (5)
C2-B6-C1	57.3 (5)
C2-B6-B5	105.0 (7)
C2-B6-B10	105.2 (7)
B11-B6-C1	105.3 (7)
B11-B6-B5	107.9 (8)
B11-B6-B10	59.9 (6)
C1-B6-B5	59.2 (5)
C1-B6-B10	105.7 (7)
B5-B6-B10	60.1 (6)
H7-B7-C2	118 (4)
H7-B7-B12	124 (4)
H7-B7-B11	115 (4)
H7-B7-B8	130 (4)
H7-B7-Rh	109 (4)
C2-B7-B12	104.6 (7)
C2-B7-B11	57.6 (5)
C2-B7-B8	106.4 (7)
C2-B7-Rh	69.3 (4)
B12-B7-B11	59.8 (6)
B12-B7-B8	59.3 (6)
B12-B7-Rh	120.1 (6)
B11-B7-B8	107.3 (7)
B11-B7-Rh	122.1 (6)
B8-B7-Rh	65.7 (4)
H8-B8-B9	116 (4)
H8-B8-B12	116 (4)
H8-B8-B4	124 (4)
H8-B8-B7	126 (4)
H8-B8-Rh	115 (4)
B9-B8-B12	60.7 (6)
B9-B8-B4	59.5 (6)
B4-B8-B7	106.3 (7)
B4-B8-Rh	66.1 (4)
B7-B8-Rh	65.9 (4)
H9-B9-B5	126 (4)
H9-B9-B8	116 (4)
H9-B9-B4	121 (4)
H9-B9-B10	121 (4)
H9-B9-B12	118 (4)
B5-B9-B8	111.2 (7)
B5-B9-B4	62.1 (6)
B5-B9-B10	60.7 (6)
B5-B9-B12	108.3 (8)
B8-B9-B4	61.6 (6)
B8-B9-B10	110.6 (7)
B8-B9-B12	60.0 (6)
B4-B9-B10	111.8 (8)
B4-B9-B12	109.3 (7)
B10-B9-B12	60.2 (6)
H10-B10-B11	121 (4)
H10-B10-B9	126 (4)
H10-B10-B5	121 (4)
H10-B10-B6	118 (4)
H10-B10-B12	126 (4)
B11-B10-B9	107.5 (7)
B11-B10-B5	106.2 (7)
B11-B10-B6	58.4 (6)
B11-B10-B12	60.2 (6)
B9-B10-B5	58.6 (6)
B9-B10-B6	106.0 (7)
B9-B10-B12	60.2 (6)
B5-B10-B6	59.5 (6)
B5-B10-B12	106.5 (7)
B6-B10-B12	106.3 (7)
H11-B11-C2	117 (4)
H11-B11-B6	119 (3)
H11-B11-B10	128 (4)
H11-B11-B12	128 (3)
H11-B11-B7	118 (4)
C2-B11-B6	60.0 (5)
C2-B11-B10	107.3 (7)
C2-B11-B12	104.1 (7)
C2-B11-B7	58.9 (5)
B6-B11-B10	61.6 (6)
B6-B11-B12	109.2 (8)
B6-B11-B7	108.5 (7)
B10-B11-B12	60.8 (6)
B10-B11-B7	108.5 (7)
B12-B11-B7	58.7 (5)
H12-B12-B7	119 (4)
H12-B12-B8	120 (4)
H12-B12-B11	121 (4)
H12-B12-B9	125 (4)
H12-B12-B10	122 (4)
B7-B12-B8	62.3 (5)
B9-B8-B7	105.8 (7)
B9-B8-Rh	119.5 (6)
B12-B8-B4	108.1 (7)
B12-B8-B7	58.4 (6)
B12-B8-Rh	119.4 (6)
B7-B12-B11	61.4 (6)
B7-B12-B9	107.8 (7)
B7-B12-B10	109.3 (7)
B8-B12-B11	111.0 (7)
B8-B12-B9	59.3 (6)
B8-B12-B10	109.5 (7)
B11-B12-B9	106.1 (7)
B11-B12-B10	59.0 (6)
B9-B12-B10	59.7 (6)
Rh-P-C1-1	116.0[a]
Rh-P-C2-1	112.8
Rh-P-C3-1	117.0
C1-1-P-C2-1	104.2
C1-1-P-C3-1	101.9
C2-1-P-C3-1	103.2

[a] No standard deviations are reported for angles including atoms described as members of groups.

Table VI

[I], M	solvent	temp, °C	substrate	[substrate], M	initial rate,[a] mol s^{-1}/mol of Rh	% completion after 5 h
1.8×10^{-3}	benzene	25	3,3-dimethylbut-1-ene	0.155	4.3×10^{-1}	100
7.2×10^{-4}	benzene	12	3,3-dimethylbut-1-ene	0.062	3.9×10^{-1}	100
7.2×10^{-4}	toluene	0	3,3-dimethylbut-1-ene	0.039	1.6×10^{-1}	100
7.2×10^{-4}	toluene	0	pent-1-ene	0.039	9.2×10^{-2}	100
1.8×10^{-4}	THF	0	3,3-dimethylbut-1-ene	0.130	8.9	100
1.8×10^{-4}	THF	0	trimethylvinylsilane	0.130	2.3×10^{-1}	100
1.8×10^{-4}	THF	0	cyclohexene	0.130	2.8×10^{-3}	*b*
1.5×10^{-3}	THF	25	styrene	0.098	6.6×10^{-2}	100
6.0×10^{-3}	THF	25	*n*-butyl acrylate	0.098	9.7×10^{-4} [c]	100
2.7×10^{-3}	THF	25	3,3-dimethylbut-1-ene	0.049	7.4×10^{-3}	*d*
2.7×10^{-3}	THF	25	phenylacetylene	0.049	1.5×10^{-1}	*e*

[a] Based on hydrogen consumed. [b] Complete after 120 h. [c] After a short induction period. [d] Products after 18 h were 78% neohexane and 17% 3,3-dimethylbut-1-ene. [e] The product after 18 h was 100% ethylbenzene.

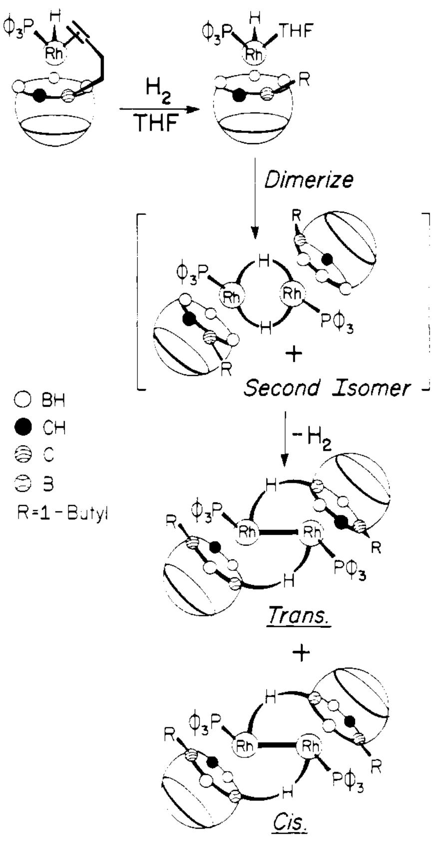

Figure 2. Possible pathway for the formation of the two isomers of binuclear rhodacarborane species which may comprise mixture III.

Complex I was found to be among the most active homogeneous hydrogenation catalysts reported to date. A THF solution of I (1.8×10^{-4} M) catalyzed the hydrogenation of 3,3-dimethylbut-1-ene (0.13 M) at 0 °C (pH_2 = 705 mm) with an initial rate of 8.9 mol s^{-1}/mol of Rh. In comparison, the compound $[(COD)Ir(P\text{-}i\text{-}Pr_3)py]^+PF_6^-$ (py = pyridine,-*i*-Pr = isopropyl), apparently the most active, homogeneous hydrogenation catalyst[6c,d] previously reported, gave an initial rate of 2.3 mol s^{-1}/mol of Ir for the hydrogenation of 3,3-dimethylbut-1-ene (0.5 M) by a CH_2Cl_2 solution of the catalyst (5.0×10^{-4} M) at 0 °C (pH_2 = 600 mm). The iridium catalyst also required a polar and noncoordinating solvent to function properly while I was effective in THF, benzene, and toluene. Complex I did, however, exhibit higher activity in THF than in benzene or toluene. Complex I was also found to be an effective catalyst for the hydrogenation of alkynes while II was not. The results of hydrogenations of alkenes and alkynes catalyzed by I under various conditions are presented in Table VI. The results of a detailed mechanism study pertaining to the isomerization and hydrogenation of alkenes with rhodacarborane catalysts will be reported elsewhere.

Conclusion

The use of an alkenyl-substituted carborane ligand has made possible the synthesis of a relatively rare hydrido alkene transition-metal complex. The chelating nature of the alkenyl carborane promotes stability of the metal complex in the absence of hydrogen while providing for the facile creation of an open coordination site via hydrogenation of the coordinated alkene leading to an extremely active homogeneous hydrogenation catalyst. This work effectively demonstrates the potential for the development of novel catalytic systems using the great diversity of structural parameters available in metallacarborane chemistry.

Acknowledgment. The authors wish to thank Dr. B. A. Katz for his help with the crystal structure, Dr. R. T. Baker and T. B. Marder for their help with the ^1H and ^{31}P NMR spectra, and Dr. D. C. Busby and Professor F. A. L. Anet for their assistance in obtaining ^{11}B NMR spectra. We also wish to thank the National Science Foundation for the purchase of the Syntex P$\bar{1}$ diffractometer and the Bruker WP-200 NMR spectrometer. Computing time was furnished by the Campus Computing Network of UCLA. This research was supported in part by the National Science Foundation and the Office of Naval Research.

Registry No. I, 76166-14-8; III, cis isomer, 76792-46-6; III, trans isomer, 76705-00-5; IV, 76146-56-0; 1-(CH_2=$CHCH_2CH_2$)-1,2-$C_2B_{10}H_{11}$, 17522-80-4; $Cs^+[7\text{-}(CH_2{=}CHCH_2CH_2)\text{-}7,8\text{-}C_2B_9H_{11}]^-$, 76723-25-6; 1,2-$C_2B_{10}H_{12}$, 16872-09-6; 4-bromobut-1-ene, 5162-44-7; $RhCl(PPh_3)_3$, 14694-95-2; hex-1-ene, 592-41-6; *trans*-hex-2-ene, 4050-45-7; *cis*-hex-2-ene, 7688-21-3; *trans*-hex-3-ene, 13269-52-8; *cis*-hex-3-ene, 7642-09-3; 3,3-dimethylbut-1-ene, 558-37-2; pentylene, 25377-72-4; trimethylvinylsilane, 754-05-2; cyclohexene, 110-83-8; styrene, 100-42-5; *n*-butyl acrylate, 141-32-2; phenylacetylene, 536-74-3.

Supplementary Material Available: A listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.