ability. Since $Rh_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2$ is electron-rich and polarizable, it will form stronger axial bonds with ligands having a π-acceptor ability. The σ interactions with pyridine or PMe_2Ph, for example, are thus augmented by the synergistic π-acceptor abilities of these ligands. It is likely that this will destabilize both the unoccupied σ* levels and also the π* levels,[33] but it may be expected that the latter will be affected to a smaller extent than the former. Thus, there is a more cathodic oxidation potential as the donor ability of the axial ligands increase, in accord with the experimentally observed trend.

On the basis of data available the following description is proposed for oxidation–reduction of $Rh_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2$:

$$\begin{tikzcd}
{[Rh_2(O_2CCH_3)_2\{(C_6H_5)_2P(C_6H_4)\}_2} \arrow[r, "+e"] \arrow[d, shift left, "-e"] & {[Rh_2(O_2CCH_3)_2\{(C_6H_5)_2P(C_6H_4)\}_2]^-} \arrow[d] \\
{[Rh_2(O_2CCH_3)_2\{(C_6H_5)_2P(C_6H_4)\}_2]^+} \arrow[u, shift left, "+e"] & \text{decomposition products}
\end{tikzcd}$$

Finally, although the oxidation of the PMe_2Ph adduct is facile, occurring at potentials between +0.51 and +0.25 V vs. Ag–AgCl, no second oxidation wave was observed. This is perhaps surprising in view of Bear and Kadish's recent results,[15] which indicated that the complexes $Rh_2(O_2CCH_3)_n(HNOCCH_3)_{4-n}$ (n = 0, 1) underwent an initial oxidation at potentials comparable to those exhibited by our phosphine adduct and then a further reversible oxidation to the Rh(III) dicationic dimer at a potential about 1.3V more positive.

Clearly these ortho-metalated dimers are worthy of further study, and our investigations into their physical and chemical properties are continuing.

Acknowledgment. We are grateful to the National Science Foundation for financial support.

Registry No. 1, 91837-70-6; 2, 92669-58-4; $Rh_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2$, 92669-59-5; $Rh_2(O_2CCH_3)_4$, 30553-94-7.

Supplementary Material Available: Tables of structure factors and anisotropic thermal parameters and complete lists of bond distances and bond angles (45 pages). Ordering information is given on any current masthead page.

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[33] This assumes that the molecular orbital scheme calculated for $Rh_2(O_2CR)_4$ complexes is equally applicable to the ortho-metalated complex.

Model Intermediates for Rhodacarborane Catalysis: Isolation of a Disubstituted *closo*-Bis(triphenylphosphine)hydridorhodacarborane[1]

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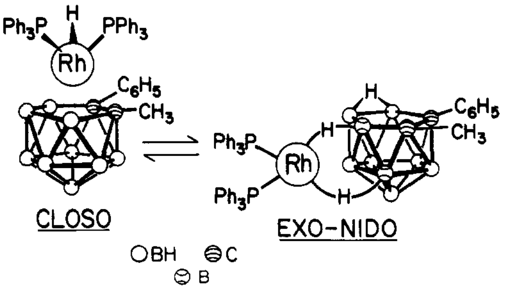
Reaction of a carbon-disubstituted [*nido*-7-(R)-9-(R′)-7,9-$C_2B_9H_{10}$]$^-$ (R = CH_3; R′ = C_6H_5) (V) ion with [$(PPh_3)_3RhCl$] in ethanol at the reflux temperature for 24 h yielded [*closo*-2,2-$(PPh_3)_2$-2-H-1-(CH_3)-7-(C_6H_5)-2,1,7-$RhC_2B_9H_9$] (VI) rather than the corresponding exo-nido tautomer expected. In addition to spectroscopic characterization (IR, NMR), the molecular structure of VI was determined crystallographically for [$C_{45}H_{49}B_9P_2Rh\cdot C_4H_8O\cdot C_2H_5OH$]: M_r = 970.215; monoclinic; space group $P2_1/n$; a = 24.694 (6) Å, b = 18.714 (6) Å, c = 12.117 (2) Å, β = 112.33 (2)°, V = 5180 (2) Å^3, and Z = 4. The structure was refined to R = 0.067 and R_w = 0.081 using 3421 reflections (of 6396 reflections measured) with 2θ < 43.0° (Mo Kα radiation).

Introduction

Mechanisms have recently been proposed[2] describing how *closo*-bis(triphenylphosphine)hydridorhodacarboranes[3,4] and *exo-nido*-bis(triphenylphosphine)rhodacarboranes[5,6] act as homogeneous catalyst precursors for the hydrogenation and isomerization of alkenes. Although the several closo- and exo-nido isomers are very efficient catalysts, major emphasis for the kinetic and mechanistic studies was placed on the more stable

Scheme I. Proposed Mechanistic Scheme for Closo-Exo-Nido Tautomerism[a]



[a] In this particular example, the equilibrium lies far to the right.

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[1] Dedicated to the memory of our friend and colleague, Earl L. Muetterties.

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species [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$][3,4] (I) and [*exo-nido*-{$(PPh_3)_2Rh$}{7,8-μ-$(CH_2)_3$-7,8-$C_2B_9H_{10}$}][5,6] (II); the isomeric catalyst [*closo*-2,2-$(PPh_3)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$][3,4] (III) was characterized by chemical instability that resulted in poor reproducibility during hydrogenation rate studies.

The significant chemical differences observed in the several bis(triphenylphosphine)rhodacarborane catalyst precursors are attributable to the electronic and charge distributions of the respective carborane ligands [*nido*-7,8-$C_2B_9H_{11}]^{2-}$ and [*nido*-7,9-$C_2B_9H_{11}]^{2-}$ as determined by the characteristic molecular orbitals of each isomeric carborane ligand. The bulk of carborane ligand substituents also imparts characteristic stereochemical properties. The role of such combined stereochemical directive effects in metallacarboranes is currently being studied to allow the "fine tuning" of future catalysts and to further understand existing ones, as described here.

The reversible formation of catalytically active exo-nido species in solution, and the associated existence of a closo-exo-nido tautomerism (Scheme I) was demonstrated to be essential in the alkene hydrogenation and isomerization mechanisms involving I and II. These exo-nido species have also been demonstrated[7] to be the reactive intermediates necessary for carborane ligand exchange reactions.

It was found that the stabilization and isolation of *exo-nido*-bis(triphenylphosphine)rhodacarborane catalyst precursors such as II could be accomplished by increasing the steric bulk either of the phosphine ligands attached to the rhodium atom or of the carborane cage substituents.[5,6] Thus, the reaction of doubly alkyl- and/or aryl-substituted [*nido*-7-R-8-R′-7,8-$C_2B_9H_{10}]^-$ ligands with [$(PPh_3)_3RhCl$] provided isolatable models of the catalytically active exo-nido species postulated to arise from I. One isomeric species, [*closo*-1,2-(1′,2′-μ-$CH_2C_6H_4CH_2$)-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_9$] (IVa), which exhibits an equilibrium concentration of both closo and exo-nido tautomers in solution,[4,5] reacted with tricyclohexylphosphine (PCy_3) to produce a mixed-phosphine complex, [*exo-nido*-{$(PPh_3)(PCy_3)Rh$}{7,8-μ-$(CH_2C_6H_4CH_2)$-7,8-$C_2B_9H_{10}$}] (IVb).

To further study the isomeric and catalytically active III and in an effort to isolate stable models for the exo-nido tautomers derived from III which are believed to exist in solution, we attempted the synthesis of a bis(triphenylphosphine)rhodacarborane having bulky substituents at carbon atoms C(7) and C(9) of the carborane ligand [*nido*-7-(R)-9-(R′)-7,9-$C_2B_9H_{10}]^-$ (R = CH_3; R′ = C_6H_5) (V). (Attempts to prepare the corresponding diphenyl derivative were not successful due to the poor yields associated with the synthesis of [*closo*-1,2-$(C_6H_5)_2$-1,2-$C_2B_{10}H_{10}$]).[8] It was assumed that such substitution at the carborane ligand would destabilize the closo tautomer relative to the exo-nido isomer through the enhancement of steric requirements and at least allow the spectroscopic detection of the latter tautomer.

The inertness of [*closo*-1-(CH_3)-7-(C_6H_5)-1,7-$C_2B_{10}H_{10}$] toward base degradation,[9] even under extreme conditions, necessitated a synthetic route to V via [*closo*-1-(CH_3)-8-(C_6H_5)-1,8-$C_2B_9H_9$].[10] Protonation of [*nido*-7-(CH_3)-8-(C_6H_5)-7,8-$C_2B_9H_{10}]^-$ with polyphosphoric acid, to produce the neutral species [*nido*-7-(CH_3)-8-(C_6H_5)-7,8-$C_2B_9H_{11}$], followed by thermal dehydrogenation at 110 °C, gave [*closo*-1-(CH_3)-8-(C_6H_5)-1,8-$C_2B_9H_9$]. Subsequent reduction of the latter species using $NaBH_4$ gave Na[*nido*-7-(CH_3)-9-(C_6H_5)-7,9-$C_2B_9H_{10}$] (V).[11] The desired anion V was converted to the trimethylammonium salt by the addition of a saturated solution of [$(CH_3)_3NH$]Cl to an aqueous solution of [Na][(V)]; extraction of the carborane salt using CH_2Cl_2 and recrystallzation from hydrocarbon solvents gave [$(CH_3)_3NH$][(V)]. Finally, reaction of [$(CH_3)_3NH$][(V)] with [$(PPh_3)_3RhCl$] in ethanol at the reflux temperature gave the yellow compound [*closo*-2,2-$(PPh_3)_2$-2-H-1-(CH_3)-7-(C_6H_5)-2,1,7-$RhC_2B_9H_9$] (VI). Equations 1–3 illustrate the synthesis route.

$$[closo\text{-}1\text{-}(CH_3)\text{-}2\text{-}(C_6H_5)\text{-}1,2\text{-}C_2B_{10}H_{10}] + 2KOH \xrightarrow[\Delta]{EtOH} K[nido\text{-}7\text{-}(CH_3)\text{-}8\text{-}(C_6H_5)\text{-}7,8\text{-}C_2B_9H_{10}] \quad (1)$$

$$[nido\text{-}7\text{-}(CH_3)\text{-}8\text{-}(C_6H_5)\text{-}7,8\text{-}C_2B_9H_{10}]^- + H^+ \xrightarrow{110\ ^\circ C} H_2 + [closo\text{-}1\text{-}(CH_3)\text{-}8\text{-}(C_6H_5)\text{-}1,8\text{-}C_2B_9H_9] \quad (2)$$

$$[closo\text{-}1\text{-}(CH_3)\text{-}8\text{-}(C_6H_5)\text{-}1,8\text{-}C_2B_9H_9] + NaBH_4 \rightarrow Na[nido\text{-}7\text{-}(CH_3)\text{-}9\text{-}(C_6H_5)\text{-}7,9\text{-}C_2B_9H_{10}]\ (V) \quad (3)$$

Experimental Section

General Comments. All reactions were carried out in dried Schlenk equipment under an atmosphere of dry nitrogen or argon, using standard techniques.[12] Tetrahydrofuran, toluene, ethanol, 1,2-diethoxyethane, heptane, and pentane were purified according to literature methods,[13] distilled under argon, and argon-purged immediately prior to use. Cyclooctadiene (Aldrich), polyphosphoric acid (Aldrich), triphenylphosphine (Aldrich), tri-*o*-tolylphosphine (Alfa), tri-*m*-tolylphosphine (Alfa), and tricyclohexylphosphine (Alfa), and rhodim trichloride trihydrate (Matthey-Bishop) were used as received. The compounds [$(PPh_3)_3RhCl$],[14] [$(PR_3)_2Rh(COD)$]PF_6,[15] and [Rh(COD)Cl]$_2$[16] were prepared according to published methods. The compounds [*closo*-1-(CH_3)-2-(C_6H_5)-1,2-$C_2B_{10}H_{10}$] and Cs[*nido*-7-(CH_3)-8-(C_6H_5)-7,8-$C_2B_9H_{10}$] were prepared according to literature techniques.[19] The ^1H and $^{31}P\{^1H\}$ FT-NMR spectra were obtained by using a Bruker WP-200 spectrometer operating in the Fourier Transform mode at 200.133 and 81.02 MHz, respectively, and equipped with a B-VT-1000 temperature controller. The 126-MHz ^{11}B FT-NMR spectra were obtained by using a Fourier transform spectrometer designed and build by Professor F. A. L. Anet of this department; the 160-MHz ^{11}B FT-NMR spectra were obtained by using a Bruker WM-500 spectrometer.[17] Proton chemical shifts were referenced to residual protons in the solvent (CD_2Cl_2, 5.32 ppm; $(CD_3)_2CO$, 2.04 ppm vs. Me_4Si) unless noted otherwise. Phosphorus chemical shifts were referenced to external 85% H_3PO_4 with downfield shifts taken as positive. Boron chemical shifts were referenced to external $BF_3{\cdot}Et_2O$, with downfield shifts taken as positive. Mass spectral data were obtained by using an AEC MS-9 mass spectrometer. Infrared spectra were obtained as Nujol mulls by using a Perkin-Elmer 137 or a Beckman Model FT 1100 FTIR. Elemental analyses were obtained from Schwartzkopf Microanalytical Laboratories, Woodside, NY. Gas

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chromatographic analyses were performed on a Hewlett-Packard Model 5880 equipped with a 30-m fused silica OV-101 capillary column and a flame ionization detector.

Preparation of [*closo*-1-(CH$_3$)-8-(C$_6$H$_5$)-1,8-C$_2$B$_9$H$_9$]. A 500-mL, three-neck flask, equipped with a Dean-Stark Trap/reflux condenser assembly, a mercury thermometer, and mechanical stirrer was charged with Cs[7-(CH$_3$)-8-(C$_6$H$_5$)-7,8-C$_2$B$_9$H$_{10}$] (8.54 g, 24.3 mmol) and 200 mL of toluene. After heating to the reflux temperature and removal of wet toluene from the Dean-Stark trap, ca. 100 mL of polyphosphoric acid was added to the cooled reaction mixture. The suspension was refluxed for 3 h and cooled to ambient temperature, and the yellow organic layer was cannulated from the reaction flask. Repeated washings of the polyphosphoric acid using hot toluene were essential. The toluene from the collected organic fractions were distilled under N$_2$ until a head temperature of 114 °C was attained. The remaining yellow oil was purified by vacuum sublimation (75 °C) yielding white, crystalline [*closo*-1-(CH$_3$)-8-(C$_6$H$_5$)-1,8-C$_2$B$_9$H$_9$] (4.40 g, 20.2 mmol) (83%): IR 2780 (s), 2520 (s), 1580 (w), 1480 (m), 1080 (m), 1020 (w), 845 (m), 800 (m), 755 (s), 690 (s) cm^{-1}; mp 65–67 °C (sealed capillary, uncorrected); ^{1}H NMR (ppm, CD$_2$Cl$_2$) 7.60 (d, 2 H), 7.37, (d, 3 H), 2.59 (s, 3 H), 0.5–4.5 (m, 9 H); ^{11}B NMR (ppm, THF) –22.9 (1 B), –17.4 (1 B), –15.9 (1 B), –4.6 (2 B), –1.8 (1 B), –11.5 (3 B); mass spectrum, m/e 224 (M$^+$). Anal. Calcd for C$_9$H$_{17}$B$_9$: C, 48.58; H, 7.70. Found: C, 48.96; H, 7.63.

Preparation of [(CH$_3$)$_3$NH][*nido*-7-(CH$_3$)-9-(C$_6$H$_5$)-7,9-C$_2$B$_9$H$_{10}$] (V). A 250-mL three-neck flask, equipped with a magnetic stir bar, reflux condenser, and a 125-mL pressure equalizing funnel, was charged with NaBH$_4$ (1.6 g, 40 mmol) and 30 mL of 1,2-diethoxyethane. A solution of [*closo*-1-(CH$_3$)-8-(C$_6$H$_5$)-1,8-C$_2$B$_9$H$_9$] (4.40 g, 20.2 mmol) in 50 mL of 1,2-diethoxyethane was added dropwise to the rapidly stirred borohydride suspension. The B$_2$H$_6$ was vented from the top of the reflux condenser under a flow of N$_2$ into a gas scrubber containing triethylamine in heptane. When the addition was complete, the reaction mixture was heated to the reflux temperature for 2 h. Concentration of the filtered solution in vacuo and addition of a saturated aqueous solution of [(CH$_3$)$_3$NH]Cl (5 g) yielded an oily white precipitate. Extraction of this oil from the aqueous layer using CH$_2$Cl$_2$, followed by recrystallization from CH$_2$Cl$_2$/heptane and acetonitrile/heptane, gave [(CH$_3$)$_3$NH] [*nido*-7-[(CH$_3$)-9-(C$_6$H$_5$)-7,9-C$_2$B$_9$H$_{10}$] (5.35 g, 18.9 mmol) in 86% yield. This material is slightly air- and temperature-sensitive: IR 3000 (s), 2800 (s), 2400 (s), 1800 (w), 1595 (s), 1450 (s), 1400 (m), 1325 (s), 1250 (s), 810 (m), 710 (m) cm^{-1}; ^{1}H NMR (ppm, (CD$_3$)$_2$CO) 7.14 (d, 2 H), 6.72 (m, 3 H), 2.90 (s, 9 H), 1.77 (s, 3 H); ^{11}B NMR (ppm, THF) –35.1 (1 B), –31.9 (1 B), –21.8 (1 B), –20.2 (1 B), –17.3 (2 B), –3.9 (1 B), –1.3 (2 B). Anal. Calcd for C$_{12}$H$_{28}$B$_9$N: C, 50.81, H, 9.95, B, 34.30, N, 4.94. Found: C, 51.02, H, 9.65, B, 34.68, N, 5.02.

Preparation of [*closo*-2,2-(PPh$_3$)$_2$-2-H-1-(CH$_3$)-7-(C$_6$H$_5$)-2,1,7-RhC$_2$B$_9$H$_9$] (VI). A 50-mL flask equipped with a magnetic stir bar was charged with [(CH$_3$)$_3$NH][*nido*-7-(CH$_3$)-9-(C$_6$H$_5$)-7,9-C$_2$B$_9$H$_9$] (0.266 g, 0.94 mmol), [(PPh$_3$)$_3$RhCl] (0.500 g, 0.54 mmol), and 20 mL of absolute ethanol. A reflux condenser was fitted, and the mixture was heated to the reflux temperature for 24 h. After being cooled, the yellow precipitate was filtered and recrystallized from THF/ethanol and THF/heptane to give VI (0.26 g, 0.3 mmol) in 57% yield based on rhodium: IR 2936 (s), 2490 (s), 2132 (s), 1580 (m), 1290 (w), 1080 (m), 690 (s) cm^{-1}; ^{1}H NMR (ppm, CD$_2$Cl$_2$, 273 K) 6.61–7.26 (35 H), 1.76 (3 H), –14.7 (1 H, qd, $J_{\mathrm{Rh-H}}$ = 10 Hz, $J_{\mathrm{P-H}}$ = 7 Hz); ^{31}P NMR (ppm, 15% C$_6$D$_6$/THF) 273 K, 39.4 (dd, $J_{\mathrm{Rh-P}}$ = 144 Hz, $J_{\mathrm{P-P}}$ = 6 Hz), 34.0 (d, $J_{\mathrm{Rh-P}}$ = 144 Hz), 26.2 (dd, $J_{\mathrm{Rh-P}}$ = 124 Hz, $J_{\mathrm{P-P}}$ = 3 Hz), 25.1 (d, $J_{\mathrm{Rh-P}}$ = 125 Hz), 183 K, 40.1 (dd, $J_{\mathrm{Rh-P}}$ = 144 Hz, $J_{\mathrm{P-P}}$ = 6 Hz), 34.5 (d, $J_{\mathrm{P-P}}$ = 6 Hz), 25.9 (t, $J_{\mathrm{Rh-P}}$ = 125 Hz) (an apparent triplet caused by the coincidental overlap of the upfield doublets); ^{11}B{^{1}H} NMR (ppm, THF) spectra consisted of broad peaks characteristic of bis(triphenylphosphine)rhodacarboranes; in situ addition of excess PEt$_3$ sharpened the resonances,[4] which were centered at –16.3 (2 B), –9.9 (3 B), –5.6 (2 B), –1.2 (2 B). Anal. Calcd for C$_{45}$H$_{48}$B$_9$P$_2$Rh: C, 63.51; H, 5.69; B, 11.43; P, 7.28; Rh, 12.09. Found: C, 63.28; H, 5.85; B, 11.24; P, 7.01; Rh, 12.12.

Solution and Refinement of the Structure. A single crystal of [*closo*-2,2-(PPh$_3$)$_2$-2-H-1-(CH$_3$)-7-(C$_6$H$_5$)-2,1,7-RhC$_2$B$_9$H$_9$] (VI), a parallelepiped with dimensions 0.23 × 0.20 × 0.15 mm, suitable for X-ray study was obtained from THF/pentane by vapor diffusion. Pertinent crystal and intensity data are collected in Table I. All calculations were performed on a DEC VAX-11/780 computer using the SHELX76 structure determination system and locally written programs.

Table I. Experimental Details of the X-ray Diffraction Study of [*closo*-2,2-(PPh$_3$)-2-H-1-(CH$_3$)-7-(C$_6$H$_5$)-2,1,7-RhC$_2$B$_9$H$_9$] (VI)

(A) Crystal Parameters

cryst system	monoclinic
space group	$P2_1/n$
a, Å	24.694 (6)
b, Å	18.714 (6)
c, Å	12.117 (2)
β, deg	112.33 (2)
V, Å^3	5180 (2)
Z	4
d_{calcd}, g cm^{-3}	1.238
T, °C	20
abs coeff, cm^{-1}	3.8

(B) Measurement of Intensity Data

diffractometer	Syntex P$\bar{1}$
radiatn	Mo Kα, 0.7107 Å
monochromator	graphite
scan method	θ–2θ
scan rate	3.0° min^{-1}
scan range	±1.25° above and below Kα_1 and Kα_2
reflns measd	6396
data limits	$2\theta < 43°$
obsd data	3421 [$I > 3\sigma(I)$]
std reflns	6 measured every 300
R[a]	0.067
R_{w}[a]	0.081
GOF[a]	2.0

[a] See text for definition of R, R_{w}, and "goodness of fit".

Structure factor calculations employed the atomic form factors for N from Stewart et al.[18] and for other atoms as well as for anomalous dispersion correction to the scattering factors of the rhodium and phosphorus atoms from ref 19. The positional coordinates were deduced from the Patterson synthesis. Difference Fourier maps revealed the location of the remaining non-hydrogen atoms, all terminal hydrogen atoms on boron, the metal hydride, and many of the other hydrogen atoms. All phenyl groups were constrained to be rigid C$_6$H$_5$ hexagons, C–C = 1.395 Å and C–H = 1.0 Å. The methyl group was constrained to be tetrahedral, C–H = 1.0 Å. The tetrahydrofuran molecule was constrained to have C–C = ~1.5 Å and C–C = 1.5 Å. Ethanol was constrained to have C–C = 1.54 Å and C–O = 1.45 Å. No hydrogen atoms were included for either solvate molecule. All non-hydrogen atoms, with the exception of phenyl groups on phosphine and of the ethanol solvate, were allowed to vibrate anisotropically. With the exception of positional parameters for the terminal hydride atom on rhodium, parameters for hydrogen atoms were not allowed to vary.

Positional coordinates for the highly vibrational tetrahydrofuran and ethanol solvate molecules were deduced from several difference Fourier maps calculated at various stages of isotropic refinement. Full-matrix least-squares refinement converged at $R = 0.067$ and $R_{\mathrm{w}} = 0.081$. R and R_{w} are defined as $R = [\sum(|F_{\mathrm{o}}| - |F_{\mathrm{c}}|)/\sum|F_{\mathrm{o}}|]$, $R_{\mathrm{w}} = [\sum w(|F_{\mathrm{o}}| - |F_{\mathrm{c}}|)^2/\sum w|F_{\mathrm{o}}|^2]^{1/2}$, and "goodness of fit" was 2.90 as defined by $[\sum w|F_{\mathrm{o}}| - |F_{\mathrm{c}}|)^2/N_{\mathrm{obsd}} - N_{\mathrm{variables}}]^{1/2}$, where $N_{\mathrm{variables}}$ was 313.

One molecule of ethanol and one molecule of THF per molecule of VI were observed to be present in the crystal structure. However, disorder in the solvate molecules prevented an accurate estimation of their parameters.

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for [*closo*-2,2-$(PPh_2)_3$-2-H-1-(CH_3)-7-(C_6H_5)-2,1,7-$RhC_2B_9H_9$] (VI)

atom	*x*	*y*	*z*	*B*
Rh(2)	0.32232 (4)	0.13196 (5)	0.02901 (8)	*a*
P(1)	0.2299 (1)	0.1207 (2)	0.0510 (3)	*a*
P(2)	0.3642 (1)	0.0231 (2)	0.1096 (3)	*a*
B(3)	0.2910 (6)	0.2268 (8)	−0.0961 (12)	*a*
B(4)	0.3403 (7)	0.2992 (9)	−0.1029 (15)	*a*
B(5)	0.4112 (8)	0.2731 (9)	−0.0104 (17)	*a*
B(6)	0.4055 (7)	0.1867 (8)	0.0476 (14)	*a*
B(8)	0.3127 (7)	0.2428 (8)	−0.2245 (14)	*a*
B(9)	0.3881 (8)	0.2666 (10)	−0.1667 (17)	*a*
B(10)	0.4272 (8)	0.1956 (10)	−0.0725 (17)	*a*
B(11)	0.3743 (6)	0.1242 (9)	−0.0838 (14)	*a*
B(12)	0.3674 (8)	0.1775 (9)	−0.2127 (15)	*a*
C(1)	0.3535 (5)	0.2508 (7)	0.0250 (11)	*a*
C(7)	0.3079 (5)	0.1580 (6)	−0.1759 (10)	*a*
C(Me)	0.3461 (7)	0.2942 (7)	0.1261 (11)	*a*
C(71)	0.2627 (4)	0.1133 (6)	−0.2643 (9)	*a, b*
C(72)	0.2786 (4)	0.0538 (6)	−0.3144 (9)	*a*
C(73)	0.2357 (4)	0.0131 (6)	−0.4002 (9)	*a*
C(74)	0.1769 (4)	0.0320 (6)	−0.4358 (9)	*a*
C(75)	0.1610 (4)	0.0915 (6)	−0.3856 (9)	*a*
C(76)	0.2039 (4)	0.1322 (6)	−0.2999 (9)	*a*
H(2)	0.338 (4)	0.126 (5)	0.152 (8)	7.44

[a] Anisotropic thermal parameters are tabulated separately. [b] Carbon atoms 71 through 76 have been defined as a rigid hexagon with C–C = 1.395 Å and C–H = 1.0 Å. The thermal parameter for H(2) was assigned.

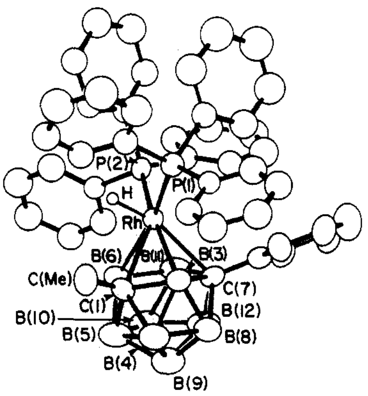

Figure 1. An ORTEP diagram of [*closo*-2,2-$(PPh_3)_2$-2-H-1-(CH_3)-7-(C_6H_5)-2,1,7-$RhC_2B_9H_9$] (VI), showing 50% probabiltiy thermal ellipsoids.

The atomic coordinates and selected bond lengths and bond angles are presented in Tables II, III, and IV, respectively.

Results and Discussion

The molecular structure of VI (Figure 1) is closo, demonstrating the propensity of bis(triphenylphosphine)rhodacarboranes to adopt a closo structure despite substantial steric crowding. This result also shows unambiguously that VI prefers a solid-state conformation having the phenyl groups attached to P(1) lying between the carborane methyl and phenyl groups, the terminal metal hydride trans to C(7), and P(2) trans to C(1). As in I, but not in some other closo isomers,[3,4] VI has an asymmetry in the rhodium–phosphorus bonding distances, with Rh–P(1) and Rh–P(2) distances of 2.405 (3) and 2.325 (3) Å, respectively. The conformation shown for VI contrasts with the preferred conformation of IVa in which the two triphenylphosphine groups are as far away from the xylenyl group as possible and the terminal metal hydride projects over the xylenyl group.

Table III. Selected Interatomic Distances (Å) with Esd's for [*closo*-2,2-$(PPh_2)_3$-2-H-1-(CH_3)-7-(C_6H_5)-2,1,7-$RhC_2B_9H_9$] (VI)

Rh(2)–P(1)	2.405 (3)	B(5)–B(6)	1.79 (2)
Rh(2)–P(2)	2.325 (3)	B(5)–B(9)	1.76 (2)
Rh(2)–B(3)	2.27 (1)	B(5)–B(10)	1.75 (3)
Rh(2)–B(6)	2.23 (1)	B(5)–C(1)	1.69 (2)
Rh(2)–B(11)	2.21 (1)	B(6)–B(10)	1.74 (2)
Rh(2)–C(1)	2.36 (1)	B(6)–B(11)	1.89 (2)
Rh(2)–C(7)	2.42 (1)	B(6)–C(1)	1.70 (2)
Rh(2)–H(2)	1.4 (1)	B(8)–B(9)	1.78 (2)
P(1)–C(111)	1.836 (9)	B(8)–B(12)	1.79 (2)
P(1)–C(121)	1.838 (8)	B(8)–C(7)	1.71 (2)
P(1)–C(131)	1.822 (10)	B(9)–B(10)	1.78 (2)
P(2)–C(211)	1.834 (8)	B(9)–B(12)	1.77 (2)
P(2)–C(221)	1.842 (8)	B(10)–B(11)	1.84 (2)
P(2)–C(231)	1.799 (9)	B(10)–B(12)	1.81 (2)
B(3)–B(4)	1.84 (2)	B(11)–B(12)	1.81 (2)
B(3)–B(8)	1.85 (2)	B(11)–C(7)	1.72 (2)
B(3)–C(1)	1.74 (2)	B(12)–C(7)	1.73 (2)
B(3)–C(7)	1.75 (2)		
B(4)–B(5)	1.75 (2)		
B(4)–B(8)	1.73 (2)		
B(4)–B(9)	1.75 (2)		
B(4)–C(1)	1.72 (2)		

The nonplanar geometry of the carborane bonding face, atoms C(1), C(7), B(3), B(6), and B(11), is indicated in the deviations of 0.12 and 0.17 Å for atoms C(1) and C(7), respectively, below the plane described by atoms B(3), B(6), and B(11); the angle between the planes described by C(1)–B(6)–B(11)–C(7) and C(1)–B(3)–B(7) is 14.4°. This nonplanarity is observed in the unsubstituted isomer III,[4] in its anion,[20] in [*closo*-2,2-$(PEt_3)_2$-2-H-1-(CH_3)-8-(C_6H_5)-2,1,8-$RhC_2B_9H_9$],[4] and in [*closo*-2-(PPh_3)-2-Cl-2,1,7-$RhC_2B_9H_{11}$][4] but not in the closo isomers having adjacent carbon atoms in the carborane ligand, such as I. The atoms lying in the lower belt of the carborane ligand are unaffected by this geometry and are within 0.06 Å from the least-squares plane defined by these atoms (B(4)–B(5)–B(10)–B(12)–B(8)).

The solution state chemistry of previously reported[21] *closo*-(phosphine)metallacarboranes is characterized by the hindered rotation of the metal center about the pentagonal bonding face of the carborane ligand. Steric effects derived from both the phosphine ligands and from the substituents on the carborane ligand and metal center–carborane ligand molecular orbital interactions are contributing factors that determine the activation energy of this rotation.

Variable-temperature FT-NMR analysis of VI in the range 183–333 K (15% C_6D_6/THF) indicated nonequivalent sets of phosphorus atoms for the two possible diastereomers that were present in approximately equal concentrations at all temperatures investigated. This demonstrates that a formidable energy barrier exists for the rotation of the L_2RhH moiety and only a slight twist about the metal–carborane axis is allowed within the steric constraints imposed by the phosphine and carborane ligand groups. The solid-state molecular structure of VI indicates that the closest approach distances between the carborane phenyl and methyl substituents and the phenyl group attached to P(1) are 3.364 Å (C(76)–C(122)) and 4.216 Å (C(Me)–C(126)), respectively. Therefore, the solid-state conformation shown in Figure 1, and probably one of those observed in solution, must represent the combined effects of the steric as well as molecular orbital interactions that determine the relative positions of the

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[20] Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1983**, *105*, 3368.

[21] Marder, T. B.; Baker, R. T.; Long, J. A.; Doi, J. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1981**, *103*, 2988.

Table IV. Selected Interatomic Angles (deg) with Esd's for [*closo*-2,2-$(PPh_3)_2$-2-H-1-(CH_3)-7-(C_6H_5)-2,1,7-$RhC_2B_9H_9$] (VI)

P(2)-Rh(2)-P(1)	99.5 (1)	B(6)-Rh(2)-B(3)	77.0 (0.5)	C(1)-Rh(2)-P(2)	137.6 (0.3)
B(3)-Rh(2)-P(1)	92.6 (0.4)	B(11)-Rh(2)-P(1)	149.6 (0.4)	C(7)-Rh(2)-P(1)	110.8 (0.3)
B(3)-Rh(2)-P(2)	161.8 (0.4)	B(11)-Rh(2)-P(2)	86.1 (0.4)	H(2)-Rh(2)-P(1)	76.8 (3.8)
B(6)-Rh(2)-P(1)	154.9 (0.4)	C(1)-Rh(2)-P(1)	114.6 (0.4)	H(2)-Rh(2)-P(2)	65.2 (3.9)
B(6)-Rh(2)-P(2)	96.6 (0.4)				

phosphine ligands relative to the carborane bonding face.

In an effort to synthesize an exo-nido tautomer derived from VI, we have conducted ligand substitution reactions using phosphine groups having large cone angles, such as those utilized[5] in the synthesis of IVb. The reaction of VI with a twofold molar excess of PCy_3 (Cy = cyclohexyl) (10% $C_6D_5CD_3/C_6H_5CH_3$, sealed 10-mm NMR tube) gave a red solution after 0.5 h at 70 °C. Analysis of the solution using $^{31}P\{^1H\}$ FT-NMR showed the formation of one resonance that was attributed to an exo-nido tautomer.[22] However, an attempt to isolate this red complex yielded only VI, suggesting that the exo-nido tautomers are transient in solution where formation is dependent upon a large excess of phosphine. Similar substitution reactions using P(*o*-tolyl)$_3$ and P(*m*-tolyl)$_3$ did not result in the observation of exo-nido species, probably due to the low basicity of these ligands compared to triphenylphosphine.[23]

The use of other rhodium-containing reagents, such as $[(PR_3)_2Rh(COD)]PF_6$ (COD = 1,5-cyclooctadiene; R = *o*-tolyl, *m*-tolyl) which readily results in the synthesis of the unsubsituted 12-vertex *closo*-bis(triphenylphosphine)hydridorhodacarboranes,[24] were not reactive toward the ion V. Furthermore, the reaction of [(P(*o*-tolyl)$_3$)$_2$Rh(COD)]PF_6 with the thallium salt of V yielded a rhodacarborane that retained the cyclooctadiene ligand with loss of the bulky phosphine ligands.[25] The ^1H FT-NMR spectrum of this product showed resonances characteristic of (η^3-octenyl)rhodacarboranes[26] and no resonances caused by phosphine group protons. Further study of this complex is anticipated.

The rate of the hydrogenationof the representative blocked alkene 3-methyl-3-phenyl-1-butene with the catalyst precursor VI was studied at 40.8 °C in THF solution.[27] With use of previously published[2] techniques, the observed rate (1.51×10^{-4} mol s^{-1}) was comparable with other rhodacarboranes, e.g., I. As mentioned previously, the unsubstituted catalyst precursor III was characterized by chemical instability and inconsistent hydrogen uptake in previous kinetics experiments.[2,4] The hydrogenation experiment using VI did not indicate these problems; in fact the catalyst solution containing alkene and hydrogen showed rather high chemical stability even when exposed to air. This behavior suggests that significant benefits to rhodacarborane catalysis may be realized through further study of substituent effects and use of the isomeric substituted carborane ligands.

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Registry No. [$(CH_3)_3NH$][V], 93349-03-2; VI, 93382-98-0; VI·C_4H_8O·C_2H_5OH, 93382-99-1; [*closo*-1-(CH_3)-8-(C_6H_5)-1,8-$C_2B_9H_9$], 93348-98-2; Cs[7-(CH_3)-8-(C_6H_5)-7,8-$C_2B_9H_{10}$], 89486-20-4; [$(PPh_3)_3RhCl$], 14694-95-2; 3-methyl-3-phenyl-1-butene, 18321-36-3; 2-methyl-2-phenylbutane, 2049-95-8.

Supplementary Material Available: Listings of the observed and calculated structure factor amplitudes, final atomic coordinates for hydrogen atoms and atoms refined as groups with isotropic thermal parameters, complete interatomic distances and angles, and final anisotropic thermal parameters (27 pages). Ordering information is given on any current masthead page.

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(22) The $^{31}P\{^1H\}$ FT-NMR consisted of resonances centered at 56.1 ppm (dd, J_{Rh-P} = 173 Hz, $^2J_{P-P}$ = 39 Hz), 48.4 ppm (d, J_{Rh-P} = 188 Hz), and those of the starting material.

(23) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(24) Unpublished results.

(25) The reaction of [(P(*o*-tolyl)$_3$)$_2$Rh(COD)]PF_6 (0.100 g, 0.10 mmol) with Tl[*nido*-7-(CH_3)-9-(C_6H_5)-7,9-$C_2B_9H_{10}$] (0.100 g, 0.23 mmol) was carried out in toluene at 25 °C for 48 h. The resulting red solution was filtered and concentrated, and heptane was added as a layer to yield orange crystals; ^1H FT-NMR (CD_2Cl_2, ppm) 7.5–7.2 (m, 5 H), 5.16 (q, 2 H), 2.35 (m, 3 H), 2.20 (s, 3 H), 1.63 (s, 3 H), 1.40 ns, 1 H), 1.27 (s, 1 H), 0.40 (sext, 1 H); IR 3064 (m), 1596 (w), 1236 (m), 1157 (m), 1081 (m), 894 (m), 749 (m) cm^{-1}.

(26) Speckman, D. M.; Knobler, C. B.; Hawthorne, M. F. submitted for publication in *Organometallics*.

(27) A solution of VI (0.150 g, 0.176 mmol) and PPh_3 (0.005 g, 0.0176 mmol) in THF (25 mL) under hydrogen gas (430 mmHg effective pressure) was maintained at 40.8 °C, and 3-methyl-3-phenyl-1-butene (0.764 mL, 3.52 mmol) was injected via syringe. The timer was started, and hydrogen uptake was measured. Analysis of the recovered catalyst (IR) confirmed no change in VI had occurrred. Analysis of the recovered solution (GC) showed 97% conversion of 2-methyl-2-phenylbutane after 20 h.