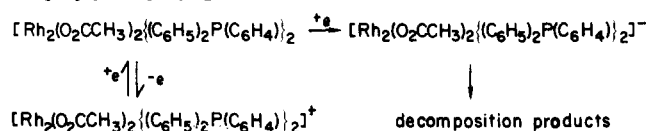


ability. Since $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2$ is electron-rich and polarizable, it will form stronger axial bonds with ligands having a π -acceptor ability. The σ interactions with pyridine or PMe_2Ph , for example, are thus augmented 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 $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2$:



(33) This assumes that the molecular orbital scheme calculated for $\text{Rh}_2(\text{O}_2\text{CR})_4$ complexes is equally applicable to the ortho-metalated complex.

Finally, although the oxidation of the PMe_2Ph adduct is facile, occurring at potentials between +0.51 and +0.25 V vs. $\text{Ag}-\text{AgCl}$, 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 $\text{Rh}_2(\text{O}_2\text{CCH}_3)_n(\text{HNOCCCH}_3)_{4-n}$ ($n = 0, 1$) underwent an initial oxidation at potentials comparable to those exhibited by our phosphine adduct and then a further reversible oxidation to the $\text{Rh}(\text{III})$ 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; $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)]_2$, 92669-59-5; $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$, 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.

Model Intermediates for Rhodacarborane Catalysis: Isolation of a Disubstituted *closo*-Bis(triphenylphosphine)hydridorhodacarborane¹

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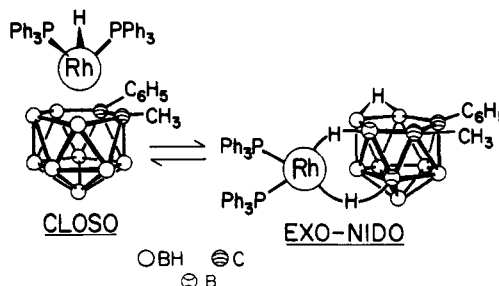
Received September 13, 1984

Reaction of a carbon-disubstituted $[\text{nido-7-(R)-9-(R')-7,9-\text{C}_2\text{B}_9\text{H}_{10}]^-$ ($\text{R} = \text{CH}_3$; $\text{R}' = \text{C}_6\text{H}_5$) (V) ion with $[(\text{PPh}_3)_3\text{RhCl}]$ in ethanol at the reflux temperature for 24 h yielded $[\text{closo-2,2-(PPh}_3)_2\text{-2-H-1-(CH}_3\text{)-7-(C}_6\text{H}_5\text{)-2,1,7-RhC}_2\text{B}_9\text{H}_9]$ (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 $[\text{C}_{45}\text{H}_{49}\text{B}_9\text{P}_2\text{Rh}\cdot\text{C}_4\text{H}_9\text{O}\cdot\text{C}_2\text{H}_5\text{OH}]$: $M_r = 970.215$; monoclinic; space group $P2_1/n$; $a = 24.694$ (6) Å, $b = 18.714$ (6) Å, $c = 12.117$ (2) Å, $\beta = 112.33$ (2)°, $V = 5180$ (2) Å³, and $Z = 4$. The structure was refined to $R = 0.067$ and $R_w = 0.081$ using 3421 reflections (of 6396 reflections measured) with $2\theta < 43.0^\circ$ (Mo K α radiation).

Introduction

Mechanisms have recently been proposed² describing how *closo*-bis(triphenylphosphine)hydridorhodacarboranes^{3,4} and *exo-nido*-bis(triphenylphosphine)rhodacarboranes^{5,6} act as homogeneous catalyst

Scheme I. Proposed Mechanistic Scheme for *Closo*-*Exo*-*Nido* Tautomerism^a



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

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

(1) Dedicated to the memory of our friend and colleague, Earl L. Muettterties.

(2) (a) Behnken, P. E.; Belmont, J. A.; Busby, D. C.; Delaney, M. S.; King, R. E. III; Kreimendahl, C. W.; Marder, T. B.; Wilczynski, J. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1984, 106, 3011. (b) Metallocarboranes in Catalysis. 7: Behnken, P. E.; Busby, D. C.; Delaney, M. S.; King, R. E. III; Kreimendahl, C. W.; Marder, T. B.; Wilczynski, J. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1984, 106, 0000-0000.

(3) Paxson, T. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1974, 96, 4674.

(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.* 1984, 106, 2965.

(5) Long, J. A.; Marder, T. B.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1984, 106, 2979.

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species [*closo*-3,3-(PPh₃)₂-3-H-3,1,2-RhC₂B₉H₁₁]^{3,4} (I) and [*exo-nido*-(PPh₃)₂Rh][7,8-μ-(CH₂)₃-7,8-C₂B₉H₁₀]^{5,6} (II); the isomeric catalyst [*closo*-2,2-(PPh₃)₂-2-H-2,1,7-RhC₂B₉H₁₁]^{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-C₂B₉H₁₁]²⁻ and [*nido*-7,9-C₂B₉H₁₁]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 metallocarboranes is currently being studied to allow the "fine tuning" of future catalysts and to further understand existing ones, as described here.

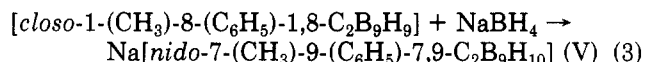
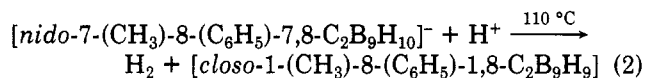
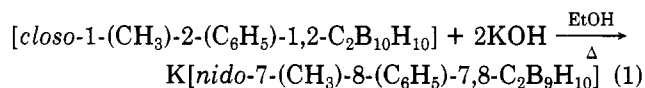
The reversible formation of catalytically active *exo-nido* species in solution, and the associated existence of a *closo*-*exo-nido* tautomerism (Scheme I) was demonstrated to be essential in the alkene hydrogenation and isomerization mechanisms involving I and II. These *exo-nido* species have also been demonstrated⁷ 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-C₂B₉H₁₀]⁻ ligands with [(PPh₃)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-CH₂C₆H₄CH₂)-3,3-(PPh₃)₂-3-H-3,1,2-RhC₂B₉H₉] (IVa), which exhibits an equilibrium concentration of both *closo* and *exo-nido* tautomers in solution,^{4,5} reacted with tricyclohexylphosphine (PCy₃) to produce a mixed-phosphine complex, [*exo-nido*-(PPh₃)(PCy₃)Rh][7,8-μ-(CH₂C₆H₄CH₂)-7,8-C₂B₉H₁₀] (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-C₂B₉H₁₀]⁻ (R = CH₃; R' = C₆H₅) (V). (Attempts to prepare the corresponding diphenyl derivative were not successful due to the poor yields associated with the synthesis of [*closo*-1,2-(C₆H₅)₂-1,2-C₂B₁₀H₁₀].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-(CH₃)-7-(C₆H₅)-1,7-C₂B₁₀H₁₀] toward base degradation,⁹ even under extreme conditions, necessitated a synthetic route to V via [*closo*-1-(CH₃)-8-(C₆H₅)-1,8-C₂B₉H₉].¹⁰ Protonation of [*nido*-7-(CH₃)-8-

(C₆H₅)-7,8-C₂B₉H₁₀]⁻ with polyphosphoric acid, to produce the neutral species [*nido*-7-(CH₃)-8-(C₆H₅)-7,8-C₂B₉H₁₁], followed by thermal dehydrogenation at 110 °C, gave [*closo*-1-(CH₃)-8-(C₆H₅)-1,8-C₂B₉H₉]. Subsequent reduction of the latter species using NaBH₄ gave Na[*nido*-7-(CH₃)-9-(C₆H₅)-7,9-C₂B₉H₁₀] (V).¹¹ The desired anion V was converted to the trimethylammonium salt by the addition of a saturated solution of [(CH₃)₃NH]Cl to an aqueous solution of [Na][V]; extraction of the carborane salt using CH₂Cl₂ and recrystallization from hydrocarbon solvents gave [(CH₃)₃NH][V]. Finally, reaction of [(C₆H₅)₃NH][V] with [(PPh₃)₃RhCl] in ethanol at the reflux temperature gave the yellow compound [*closo*-2,2-(PPh₃)₂-2-H-1-(CH₃)-7-(C₆H₅)-2,1,7-RhC₂B₉H₉] (VI). Equations 1-3 illustrate the synthesis route.



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 rhodium trichloride trihydrate (Matthey-Bishop) were used as received. The compounds [(PPh₃)₃RhCl],¹⁴ [(PR₃)₂Rh(COD)]PF₆,¹⁵ and [Rh(COD)Cl]₂¹⁶ were prepared according to published methods. The compounds [*closo*-1-(CH₃)-2-(C₆H₅)-1,2-C₂B₁₀H₁₀] and Cs[*nido*-7-(CH₃)-8-(C₆H₅)-7,8-C₂B₉H₁₀] were prepared according to literature techniques.¹⁹ The ¹H and ³¹P{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 ¹¹B FT-NMR spectra were obtained by using a Fourier transform spectrometer designed and built by Professor F. A. L. Anet of this department; the 160-MHz ¹¹B FT-NMR spectra were obtained by using a Bruker WM-500 spectrometer.¹⁷ Proton chemical shifts were referenced to residual protons in the solvent (CD₂Cl₂, 5.32 ppm; (CD₃)₂CO, 2.04 ppm vs. Me₄Si) unless noted otherwise. Phosphorus chemical shifts were referenced to external 85% H₃PO₄ with downfield shifts taken as positive. Boron chemical shifts were referenced to external BF₃·Et₂O, 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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(17) NSF Southern California Regional NMR Facility, California Institute of Technology, Pasadena, California. NSF Grant No. CHE-79-16324.

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-(CH₃)-8-(C₆H₅)-1,8-C₂B₉H₁₀]. 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-(CH₃)-8-(C₆H₅)-7,8-C₂B₉H₁₀] (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 canulated 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 N₂ 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-(CH₃)-8-(C₆H₅)-1,8-C₂B₉H₁₀] (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); ¹H NMR (ppm, CD₂Cl₂) 7.60 (d, 2 H), 7.37, (d, 3 H), 2.59 (s, 3 H), 0.5–4.5 (m, 9 H); ¹³C 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 C₉H₁₁B₉: C, 48.58; H, 7.70. Found: C, 48.96; H, 7.63.

Preparation of [(CH₃)₃NH][nido-7-(CH₃)-9-(C₆H₅)-7,9-C₂B₉H₁₀] (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 NaBH₄ (1.6 g, 40 mmol) and 30 mL of 1,2-diethoxyethane. A solution of [closo-1-(CH₃)-8-(C₆H₅)-1,8-C₂B₉H₁₀] (4.40 g, 20.2 mmol) in 50 mL of 1,2-diethoxyethane was added dropwise to the rapidly stirred borohydride suspension. The B₂H₆ was vented from the top of the reflux condenser under a flow of N₂ 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 [(CH₃)₃NH]Cl (5 g) yielded an oily white precipitate. Extraction of this oil from the aqueous layer using CH₂Cl₂, followed by recrystallization from CH₂Cl₂/heptane and acetonitrile/heptane, gave [(CH₃)₃NH][nido-7-(CH₃)-9-(C₆H₅)-7,9-C₂B₉H₁₀] (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; ¹H NMR (ppm, (CD₃)₂CO) 7.14 (d, 2 H), 6.72 (m, 3 H), 2.90 (s, 9 H), 1.77 (s, 3 H); ¹³C 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 C₁₂H₂₈B₉N: 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-(PPh₃)₂-2-H-1-(CH₃)-7-(C₆H₅)-2,1,7-RhC₂B₉H₉] (VI). A 50-mL flask equipped with a magnetic stir bar was charged with [(CH₃)₃NH][nido-7-(CH₃)-9-(C₆H₅)-7,9-C₂B₉H₁₀] (0.266 g, 0.94 mmol), [(PPh₃)₃RhCl] (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; ¹H NMR (ppm, CD₂Cl₂, 273 K) 6.61–7.26 (35 H), 1.76 (3 H), –14.7 (1 H, qd, *J*_{Rh-H} = 10 Hz, *J*_{P-H} = 7 Hz); ³¹P NMR (ppm, 15% C₆D₆/THF) 273 K, 39.4 (dd, *J*_{Rh-P} = 144 Hz, *J*_{P-P} = 6 Hz), 34.0 (d, *J*_{Rh-P} = 144 Hz), 26.2 (dd, *J*_{Rh-P} = 124 Hz, *J*_{P-P} = 3 Hz), 25.1 (d, *J*_{Rh-P} = 125 Hz), 183 K, 40.1 (dd, *J*_{Rh-P} = 144 Hz, *J*_{P-P} = 6 Hz), 34.5 (d, *J*_{P-P} = 6 Hz), 25.9 (t, *J*_{Rh-P} = 125 Hz) (an apparent triplet caused by the coincidental overlap of the upfield doublets); ¹³B{¹H} NMR (ppm, THF) spectra consisted of broad peaks characteristic of bis(triphenylphosphine)rhodacarboranes; in situ addition of excess PEt₃ 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 C₄₆H₄₈B₉P₂Rh: 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-(PPh₃)₂-2-H-1-(CH₃)-7-(C₆H₅)-2,1,7-RhC₂B₉H₉] (VI), a parallelepiped with dimensions 0.23 × 0.20 × 0.15 mm, suitable

Table I. Experimental Details of the X-ray Diffraction Study of [closo-2,2-(PPh₃)₂-2-H-1-(CH₃)-7-(C₆H₅)-2,1,7-RhC₂B₉H₉] (VI)

(A) Crystal Parameters	
cryst system	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	24.694 (6)
<i>b</i> , Å	18.714 (6)
<i>c</i> , Å	12.117 (2)
<i>β</i> , deg	112.33 (2)
<i>V</i> , Å ³	5180 (2)
<i>Z</i>	4
<i>d</i> _{calcd} , g cm ⁻³	1.238
<i>T</i> , °C	20
abs coeff, cm ⁻¹	3.8
(B) Measurement of Intensity Data	
diffractometer	Syntex P1
radiation	Mo Kα, 0.7107 Å
monochromator	graphite
scan method	<i>θ</i> -2 <i>θ</i>
scan rate	3.0° min ⁻¹
scan range	±1.25° above and below Kα ₁ and Kα ₂
reflms measd	6396
data limits	2 <i>θ</i> < 43°
obsd data	3421 [<i>I</i> > 3 <i>σ</i> (<i>I</i>)]
std reflns	6 measured every 300
<i>R</i> ^a	0.067
<i>R</i> _w ^a	0.081
GOF ^a	2.0

^a See text for definition of *R*, *R*_w, and "goodness of fit".

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.

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 C₆H₅ 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*_w = 0.081. *R* and *R*_w are defined as *R* = [Σ(|*F*_o| – |*F*_c|)/Σ|*F*_o|], *R*_w = [Σ*w*(|*F*_o| – |*F*_c|)²/Σ*w*|*F*_o|²]^{1/2}, and "goodness of fit" was 2.90 as defined by [Σ*w*|*F*_o| – |*F*_c|]²/*N*_{obsd} – *N*_{variables}]^{1/2}, where *N*_{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-(PPh₃)₂-2-H-1-(CH₃)-7-(C₆H₅)-2,1,7-RhC₂B₉H₉] (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.

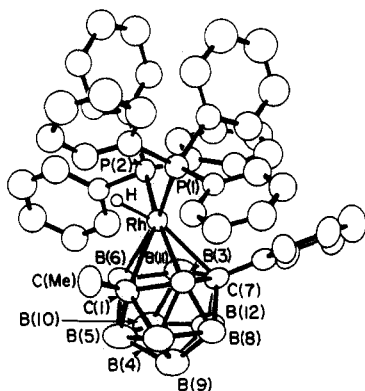


Figure 1. An ORTEP diagram of [closo-2,2-(PPh₃)₂-2-H-1-(CH₃)-7-(C₆H₅)-2,1,7-RhC₂B₉H₉] (VI), showing 50% probability thermal ellipsoids.

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.

The nonplanar geometry of the carborane bonding face, atoms C(1), C(7), B(3), B(6), and B(11), is indicated in the

Table III. Selected Interatomic Distances (Å) with Esd's for [closo-2,2-(PPh₃)₂-2-H-1-(CH₃)-7-(C₆H₅)-2,1,7-RhC₂B₉H₉] (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)		

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-(PEt₃)₂-2-H-1-(CH₃)-8-(C₆H₅)-2,1,8-RhC₂B₉H₉],⁴ and in [closo-2-(PPh₃)₂-2-Cl-2,1,7-RhC₂B₉H₁₁]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 reported²¹ 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% C₆D₆/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 L₂RhH 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

(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-(PPh₃)₂-2-H-1-(CH₃)-7-(C₆H₅)-2,1,7-RhC₂B₉H₉] (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 utilized⁵ in the synthesis of IVb. The reaction of VI with a twofold molar excess of PCy₃ (Cy = cyclohexyl) (10% C₆D₅CD₃/C₆H₅CH₃, sealed 10-mm NMR tube) gave a red solution after 0.5 h at 70 °C. Analysis of the solution using ³¹P{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 [(PR₃)₂Rh(COD)]PF₆ (COD = 1,5-cyclooctadiene; R = *o*-tolyl, *m*-tolyl) which readily results in the synthesis of the unsubstituted 12-vertex *closo*-bis(triphenylphosphine)hydridorhodacarboranes,²⁴ were not reactive toward the ion V. Furthermore, the reaction of [(P(*o*-tolyl)₃)₂Rh(COD)]PF₆ 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 (η³-octenyl)rhodacarboranes²⁶ and no reso-

nances caused by phosphine group protons. Further study of this complex is anticipated.

The rate of the hydrogenation of 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 published² 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.²⁴ 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. [(CH₃)₃NH][V], 93349-03-2; VI, 93382-98-0; VI·C₄H₈O·C₂H₅OH, 93382-99-1; [*closo*-1-(CH₃)-8-(C₆H₅)-1,8-C₂B₉H₉], 93348-98-2; Cs[7-(CH₃)-8-(C₆H₅)-7,8-C₂B₉H₁₀], 89486-20-4; [(PPh₃)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.

(22) The ³¹P{¹H} FT-NMR consisted of resonances centered at 56.1 ppm (dd, *J*_{Rh-P} = 173 Hz, *J*_{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)₂Rh(COD)]PF₆ (0.100 g, 0.10 mmol) with Tl[*nido*-7-(CH₃)-9-(C₆H₅)-7,9-C₂B₉H₁₀] (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 (CD₂Cl₂, 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 PPh₃ (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 occurred. Analysis of the recovered solution (GC) showed 97% conversion of 2-methyl-2-phenylbutane after 20 h.