describing the potential energy function, but it can be estimated that the bond length in a symmetrical single minimum O--O potential will decrease by a few thousands of an angstrom when deuterium is substituted for protium. Thus this effect would also give rise to negative isotope effects, although seemingly smaller than the values actually observed in the hydrogen maleate and hydrogen phthalate anions (Table I).

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Characterization and Molecular Structure of [(PPh₃)RhC₂B₉H₁₁]₂, a Phosphinorhodacarborane **Dimer Containing Rh-H-B Bridges**

Sir:

We have recently shown that a number of B-H-containing substrates undergo catalytic isotopic exchange of terminal hydrogen with deuterium gas¹ in the presence of the hydridorhodacarborane [3,3-(PPh₃)₂-3-H-3,1,2-RhC₂B₉H₁₁] (I) and a mechanism was postulated which involved the oxidative addition of boron-hydrogen bonds to the catalytic species. The complex I is also an efficient homogeneous catalyst for the hydrogenation of terminal olefins² and it was observed during hydrogenation studies³ that exposure of a yellow solution of 1 and substrate olefin to air produced a purple product.⁴ We report the complete characterization of the purple complex II,5 which can be viewed as a model intermediate in the oxidative addition of a terminal boron-hydrogen bond to rhodium.

The complex II was prepared by heating a solution of I in benzene with 2 equiv of benzoyl peroxide. The reaction mixture was purified by column chromatography (silica gel, 2:1 heptane-benzene) and the complex was obtained in 40% yield as dark purple microcrystals.⁶

The infrared spectrum of II (Nujol) showed a band characteristic of terminal B-H bonds at 2600 cm⁻¹ and peaks due to the coordinated dicarbollide and triphenylphosphine ligands. The visible spectrum in benzene exhibited peaks at 570 nm (log ϵ 3.76) and 390 (3.76) and the elemental analysis supported the formulation of II as $[(Ph_3P)RhC_2B_9H_{11}]_n$ which resembled a partially characterized compound previously reported in the literature.⁷ Calcd for $C_{20}H_{26}PRhB_9$: C, 48.28; H, 5.27; B, 19.55; P, 6.22; Rh, 20.68. (Anal. Found: C, 48.27; H, 5.21; B, 19.76; P, 5.72; Rh, 20.01.) Osmometric molecular weight studies in benzene gave mol wt 965 \pm 32 (three determinations). Calcd for [C₂₀H₂₆PRhB₉]₂: mol wt 995.22. The 200-MHz ¹H NMR spectrum in CD₂Cl₂ showed a complex multiplet centered at δ 7.33 due to the PPh₃ ligands, three carborane C-H resonances⁸ at 3.52 (area 2), 2.57 (1) and 1.62 (1) and a complex multiplet at 1.23 due to B-H resonances. A broad resonance at $\delta - 18.5$ due to the hydrogen atoms of the inequivalent Rh-H-B bridges sharpens to two resonances at 233 K (δ -18.0 and -19.0). The 80.5-MHz ¹¹B{¹H} NMR spectrum in $CD_2Cl_2^9$ exhibited peaks at -26.2, -16.3, -4.8,3.5, and 24.2 ppm in a ratio of 1:8:7:1:1. The 81.02-MHz ³¹P{¹H} NMR spectrum in $C_6 D_6^{10}$ gave two doublets of equal



Figure 1. Molecular structure of II (CH₂Cl₂ solvate molecules and phenyl rings on phosphorus atoms are omitted for clarity).

Table I

298 K	113 K
11.202 (2)	11.118 (2)
13.660 (3)	13.456 (3)
18.565 (3)	18.390 (3)
93.48 (2)	93.09 (2)
76.44 (1)	76.22(1)
76.80 (2)	76.90(2)
2669.1 (1.0)	2585.7 (9)
1.350 (Z = 2)	1.362
1.32 (5)	
	298 K 11.202 (2) 13.660 (3) 18.565 (3) 93.48 (2) 76.44 (1) 76.80 (2) 2669.1 (1.0) 1.350 ($Z = 2$) 1.32 (5)

fable II. Selected Bond	Distances :	and /	Angles
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dis- tances, Å	Rh(3)	Rh(3')	angles, deg	Rh(3)	Rh(3')
Rh-H	1.78 (6)	1.77 (6)	Rh-H-B _a	97 (4)	102 (5)
Rh-B _a	2.327 (8)	2.238 (8)	$Rh-B_{a}-Rh^{a}$	75.7 (2)	77.2 (2)
Rh-C	2.251 (6)	2.214 (7)	B _a -Rh-P	101.1(2)	96.2 (2)
	2.280(7)	2.269 (7)	- 0	()	. ,
Rh-B	2.190 (8)	2.173 (8)	$Rh-Rh^{a}-B_{a}$	50.6 (2)	49.7 (2)
	2.211 (8)	2.190 (8)	0	. ,	. ,
	2.220 (8)	2.221 (8)	PRhH	85(2)	89 (2)
Rh-P	2.338	2.360 (2)			
RhRh	2,762	8 (9)			

^a Refers to Rh atom not indicated by column heading.

intensity centered at 36.7 $(J_{P-Rh} = 172 \text{ Hz})^{11}$ and 29.7 ppm $(J_{\rm P-Rh} = 135 {\rm ~Hz}).$

Suitable crystals for X-ray diffraction studies were obtained by layering a CH_2Cl_2 solution of II with heptane.¹² The dark purple crystals of II are triclinic, $P\overline{1}$. Cell data are presented in Table I.13 The molecular structure of II is shown in Figure 1; significant bond distances and angles are presented in Table II.

As can be seen from Figure 1, each rhodium atom is symmetrically bound to the pentagonal face of the dicarbollide ligand and interacts with the other dicarbollide ligand via a three-center Rh-H-B bridge. The Rh-H distances of 1.77 (6) and 1.78 (6) Å compare well with those in other M-H-B bridges such as the Co-H distance of 1.82 (7) Å found in $[(C_2H_5)_4N]$ {Co[$(C_2B_{10}H_{10})_2$]₂}¹⁵ and the Cr-H distance of 1.78 (6) Å found in [(CH₃)₄N][(CO)₄CrB₃H₈].¹⁶ A Rh-H distance of 2.1 Å has been reported for the Rh-H-B bridge in $[(PPh_3)_2Rh(CB_{10}H_{10}C-C_6H_5)]$.¹⁷ The Rh-Rh distance of 2.763 (1) Å is well within the range reported for Rh-Rh single bonds (cf. Rh¹-Rh¹ = 2.68 Å in $[(\eta^5 - C_5H_5)_2Rh_2(CO)_3]$,¹⁸ $Rh^{111}-Rh^{111} = 2.906 (1) \text{ Å in } [(\mu-H)(\mu-Cl)\{\eta^5-C_5(CH_3)_5]$ -RhCl]2]).19

The transformation of a terminal B-H bond in I into a Rh-H-B bridge in II may represent an intermediate step in the oxidative addition of terminal B-H bonds to Rh. A similar situation is seen in the molecular structure of $[Rh(PPh_3)_3]$ - (ClO_4) ,²⁰ in which the metal atom appears to interact with the C-H bond of a phenyl ring (Rh-H = 2.56 Å). The two terminal B-H bonds involved in the Rh-H-B interactions determine a specific stereoisomer and of the four possibilities only II is observed²¹ with both d and l enantiomers present in the unit cell.

Homogeneous olefin hydrogenation experiments were performed to determine the catalytic activity of II.²² In typical experiments it was found that II is an active hydrogenation catalyst exhibiting rates comparable with those of I, per rhodium center.²³ Further studies concerning the mechanism³ of homogeneous hydrogenation of olefins using I and II as catalysts are presently underway in these laboratories.

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- (4) This color change is also effected by dissolution of I in wet reagent grade acetonitrile or tetrahydrofuran and is accelerated in benzene by heating with benzoyi peroxide. [*c*/oso-3,3'-(PPh₃)₂-3,8':3',7-µ-H,H'-3,8':3',**7**-Rh₂-1,2:1',2'-(C₂B₉H₁₁)₂].
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- (8) Examination of Figure 1 indicates that, while C(2) and C(1) are α and β (respectively) to the boron atom (B(7)) Involved In the Rh-H-B bridge, C(2') and C(1') are both β to B(8'), and thus the ¹H NMR chemical shifts of H(2') and H(1') are indistinguishable at 200 MHz and a resonance of area 2 is observed.
- Referenced to the external standard Et₂O·BF₃.
- (10) Referenced to the external standard D₃PO₄,
- A further splitting of 5 Hz is observed for this resonance due to ³¹P coupling to the Rh-H-B hydrogen nucleus. This splitting is removed by suitably offsetting the broad-band ¹H decoupling frequency. (11)
- The crystals contain two molecules of CH2Cl2 per molecule of II and were (12)coated with epoxy resin for X-ray work
- (13) X-ray intensity data were collected by the θ -2 θ -technique with Mo K α radiation (graphite monochromator) on a Syntex P1 automated diffractometer equipped with a scintillation counter and a pulse height analyzer. The low-temperature attachment¹⁴ maintained the crystal temperature at -160 ± 1 °C with a temperature stability of ± 0.5 °C. Of a total of 6388 reflection tions examined, 5535 had $l > 3\sigma(l)$ and were used in structure determination. The data were corrected for absorption, Lorentz, and polarization

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- (22) Potential catalysts are screened in purified tetrahydrofuran solvent using a gas-tight glass apparatus equipped with an oil diffusion pump, 100-mL Schlenk flask, H2 inlet, mercury manometer, and bubbler. The olefin is injected through a septum on the side arm using a Gilmont ultraprecision syringe and H₂ (1-atm initial pressure) uptake is recorded as a function of time. The reaction solution must be rapidly stirred to avoid diffusion control of the hydrogenation rates.
- (23) Using an initial hydrogen pressure of 1 atm, an initial vinyltrimethylsilane concentration of 9.84 × 10⁻³ M and catalyst concentrations of 2.72 × 10⁻³ M, the initial hydrogenation rates (±10%) at 24.6 °C for I and II were 5.36 × 10⁻⁵ and 1.27 × 10⁻⁴ mol/s, respectively.

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Synthesis and Crystal Structure Analysis of a Rhodiacyclopentenedione Complex Containing a Coordinated Water Ligand

Sir:

Recently there has been considerable synthetic and structural interest in metallocyclic complexes. Several synthetic routes have been used to obtain these complexes, the existence and characterization of which is key to many proposed mechanisms in catalysis-related reactions. These routes include coupling of acetylenes,¹ reactions of α, ω -dilithio-substituted hydrocarbons,² and metal-promoted cleavage of the C--C bonds in strained cyclic hydrocarbons.³ We have been investigating the latter method in our laboratory using squareplanar d^8 complexes of Rh(I) and Ir(I) together with the unsaturated cyclic hydrocarbons C₃Ph₃⁺ and C₃Cl₄. Previous work on the C₃Ph₃⁺ aromatic cation has led to the facile preparation of 1,2,3-triphenylpropenylium-1,3-diyl complexes of Ir(III)^{3b} and Rh(III).^{3c} In this communication we report some preliminary synthetic and structural results on compounds formed from reactions of C₃Cl₄.⁴

Under anhydrous conditions in methylene chloride or benzene, Rh(CO)Cl(PMe₂Ph)₂ and C₃Cl₄ react to give a mixture of two noncrystalline Rh(III) products which are believed to be the simple cationic oxidative addition adduct I and the corresponding neutral carbon monoxide insertion product II (cf. C₃Ph₃⁺ chemistry). Complex I is a red powder with $\nu_{C==0}$



at 2085 cm⁻¹, while II is a yellow powder with $\nu_{C=0}$ at 1670 cm^{-1} . This reaction proceeds instantaneously and in high yield, but the two compounds are hygroscopic and difficult to separate and obtain analytically pure. Various solvents and reaction conditions were employed in an effort either to obtain crys-

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