

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 ångström 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 hydrido-rhodacarborane [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 I 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 [(Ph₃P)RhC₂B₉H₁₁]_n which resembled a partially characterized compound previously reported in the literature.⁷ Calcd for C₂₀H₂₆PRhB₉: 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 ± 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 carborene 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 δ -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 CD₂Cl₂⁹ 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 C₆D₆¹⁰ gave two doublets of equal

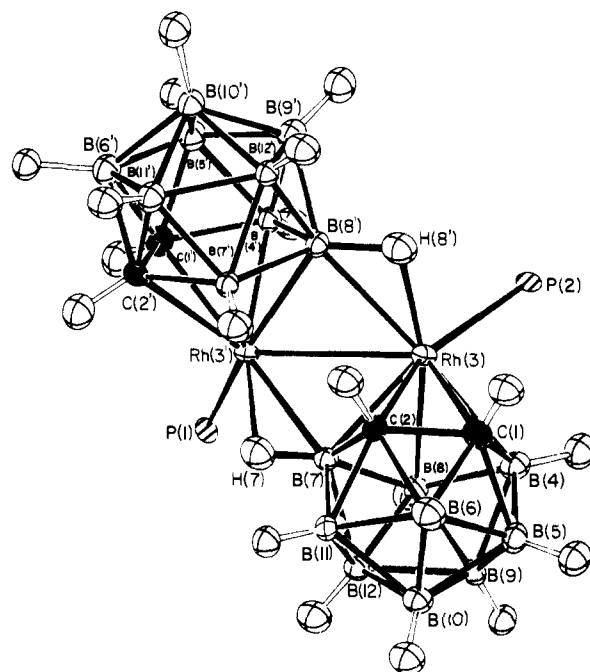


Figure 1. Molecular structure of II (CH₂Cl₂ solvate molecules and phenyl rings on phosphorus atoms are omitted for clarity).

Table I

cell data	298 K	113 K
cell dimensions		
a, Å	11.202 (2)	11.118 (2)
b, Å	13.660 (3)	13.456 (3)
c, Å	18.565 (3)	18.390 (3)
α, deg	93.48 (2)	93.09 (2)
β, deg	76.44 (1)	76.22 (1)
γ, deg	76.80 (2)	76.90 (2)
cell volume, V, Å ³	2669.1 (1.0)	2585.7 (9)
X-ray density, ρ, g cm ⁻³	1.350 (Z = 2)	1.362
floatation density, KI _(aq) , g cm ⁻³	1.32 (5)	

Table II. Selected Bond Distances and Angles

dis- tances, Å	Rh(3)		angles, deg	Rh(3')	
	Rh(3)	Rh(3')		Rh(3)	Rh(3')
Rh-H	1.78 (6)	1.77 (6)	Rh-H-B _σ	97 (4)	102 (5)
Rh-B _σ	2.327 (8)	2.238 (8)	Rh-B _σ -Rh ^a	75.7 (2)	77.2 (2)
Rh-C	2.251 (6)	2.214 (7)	B _σ -Rh-P	101.1 (2)	96.2 (2)
	2.280 (7)	2.269 (7)			
Rh-B	2.190 (8)	2.173 (8)	Rh-Rh ^a -B _σ	50.6 (2)	49.7 (2)
	2.211 (8)	2.190 (8)			
	2.220 (8)	2.221 (8)	P-Rh-H	85 (2)	89 (2)
Rh-P	2.338	2.360 (2)			
Rh-Rh	2.7628 (9)				

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

intensity centered at 36.7 (*J*_{P-Rh} = 172 Hz)¹¹ and 29.7 ppm (*J*_{P-Rh} = 135 Hz).

Suitable crystals for X-ray diffraction studies were obtained by layering a CH₂Cl₂ solution of II with heptane.¹² The dark purple crystals of II are triclinic, *P* $\bar{1}$. 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

