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CHARACTERIZATION AND MOLECULAR STRUCTURE OF ((PPH₃)RHC₂B₉H₁₁)₂, A

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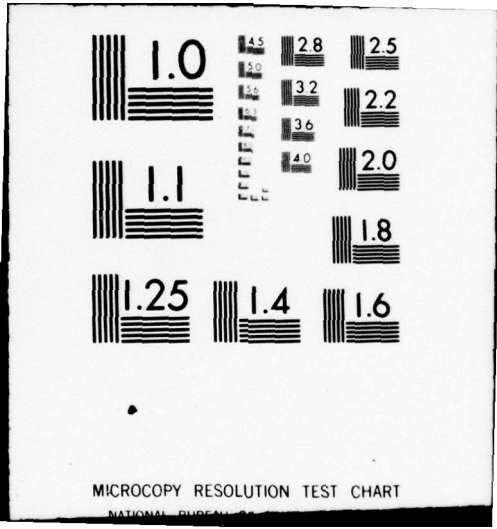
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Characterization and Molecular Structure of $[(PPh_3)_2RhC_2B_9H_{11}]_2$

a Phosphinorhodacarborane Dimer Containing Rh-H-B Bridges •

by

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R. T. Baker, R. E. King, C. Knobler, C. A. O'Conor and M. F. Hawthorne

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Characterization and Molecular Structure of $[(PPh_3)RhC_2B_9H_{11}]_2$,

a Phosphinorhodacarborane Dimer Containing Rh-H-B Bridges

by

R. T. Baker, R. E. King, C. Knobler, C. A. O'Con and M. F. Hawthorne*

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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 I and substrate olefin to air produced a purple product.⁴ We wish to 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 equivalents of benzoyl peroxide. The reaction mixture was purified by column chromatography (silica gel/2:1/heptane-benzene) and the complex 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 nm(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 [Anal. Found: C, 48.27; H, 5.21; B, 19.76; P, 5.72; Rh, 20.01; Calcd for C₂₀H₂₆PRhB₉: C, 48.28; H, 5.27; B, 19.55; P, 6.22; Rh, 20.68]. Osmometric molecular weight studies in benzene gave MW = 965 ± 32 (3 determinations). Calcd for [C₂₀H₂₆PRhB₉]₂: 995.22. The 200 MHz ¹H NMR spectrum in CD₂Cl₂ showed a complex multiplet centered at 7.33δ due to the PPh₃ ligands, three carborane C-H resonances⁸ at 3.52 (area 2), 2.57(1) and 1.62(1)δ and a complex multiplet at 1.23δ due to B-H resonances. A broad resonance at -18.5δ due to the hydrogen atoms of the inequivalent Rh-H-B bridges

sharpens to two resonances at 233^oK (-18.0 and -19.0 δ). 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 intensity centered at 36.7 ppm, 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 1.¹³ The molecular structure of

Table I

II is shown in Figure 1; significant bond distances and angles are presented in Table 2.

Figure 1

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) $\overset{\circ}{\text{A}}$ compare well with those in other M-H-B bridges such as the Co-H distance of 1.82(7) $\overset{\circ}{\text{A}}$ found in [(C₂H₅)₄N][Co[(C₂B₁₀H₁₀)₂]₂]¹⁵ and the Cr-H distance of 1.78(6) $\overset{\circ}{\text{A}}$ found in [(CH₃)₄N][(CO)₄CrB₃H₈].¹⁶ A Rh-H distance of 2.1 $\overset{\circ}{\text{A}}$ has been reported for the Rh-H-B bridge in [(PPh₃)₂Rh(CB₁₀H₁₀^{C-C}₆H₅)].¹⁷ The Rh-Rh distance of 2.763(1) is well within the range reported for Rh-Rh single bonds (cf. Rh^I-Rh^I = 2.68 $\overset{\circ}{\text{A}}$ in [(η^5 -C₅H₅)₂Rh₂(CO)₃],¹⁸ Rh^{III}-Rh^{III} = 2.906(1) in [(μ -H)(μ -Cl){(η^5 -C₅(CH₃)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 $[\text{Rh}(\text{PPh}_3)_3](\text{ClO}_4)$,²⁰ in which the metal atom appears to interact with the C-H bond of a phenyl ring ($\text{Rh-H} = 2.56 \overset{\text{O}}{\text{Å}}$). 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 to I, per rhodium center.²³ Further studies concerning the mechanism³ of homogeneous hydrogenation of olefin utilizing I and II as catalysts are presently underway in these laboratories.

Acknowledgements

The authors wish to thank Professor F. A. L. Anet for the use of the 80.5 MHz ^{11}B NMR spectrometer, Ms. Betsy Anfield for the preliminary kinetic data, Drs. J. J. Wilczynski and S. B. Miller for their preliminary work on II and Mr. B. A. Katz for assistance with the crystal structure. We also wish to thank the NSF for the purchase of the Bruker WP-200 NMR Spectrometer (Grant No. CHE76-05926) and the Syntex Diffractometer (Grant No. GP28248). This research was supported in part by the Office of Naval Research.

TABLE I

| Cell Data | | 298 ^o K | 113 ^o K |
|--------------------------------------|------------|--------------------------------|--------------------|
| Cell Dimensions | <u>a</u> = | 11.202(2) Å ^o | 11.118(2) |
| | <u>b</u> = | 13.660(3) | 13.456(3) |
| | <u>c</u> = | 18.565(3) | 18.390(3) |
| | <u>α</u> = | 93.48(2) ^o | 93.09(2) |
| | <u>β</u> = | 76.44(1) | 76.22(1) |
| | <u>γ</u> = | 76.80(2) | 76.90(2) |
| Cell Volume | V= | 2669.1(1.0) Å ³ | 2585.7(9) |
| X-ray density | ρ= | 1.350 gmcm ⁻³ ; Z=2 | 1.362 |
| Flotation density KI _(aq) | | 1.32(5)gmcm ⁻³ | |

TABLE II

| Selected Bond Distances and Angles | | | | | |
|------------------------------------|------------------------------------|------------------------------------|------------------------|----------|---------|
| Distances (Å) | Rh(3) | Rh(3') | Angles (°) | 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* | 75.7(2) | 77.2(2) |
| Rh-C | { 2.251(6) 2.280(7) | { 2.214(7) 2.269(7) | B _σ -Rh-P | 101.1(2) | 96.2(2) |
| Rh-B | { 2.190(8) 2.211(8) 2.220(8) | { 2.173(8) 2.190(8) 2.221(8) | Rh-Rh*-B _σ | 50.6(2) | 49.7(2) |
| Rh-P | 2.338 | 2.360(2) | P-Rh-H | 85(2) | 89(2) |
| Rh-Rh | 2.7628(9) | | | | |

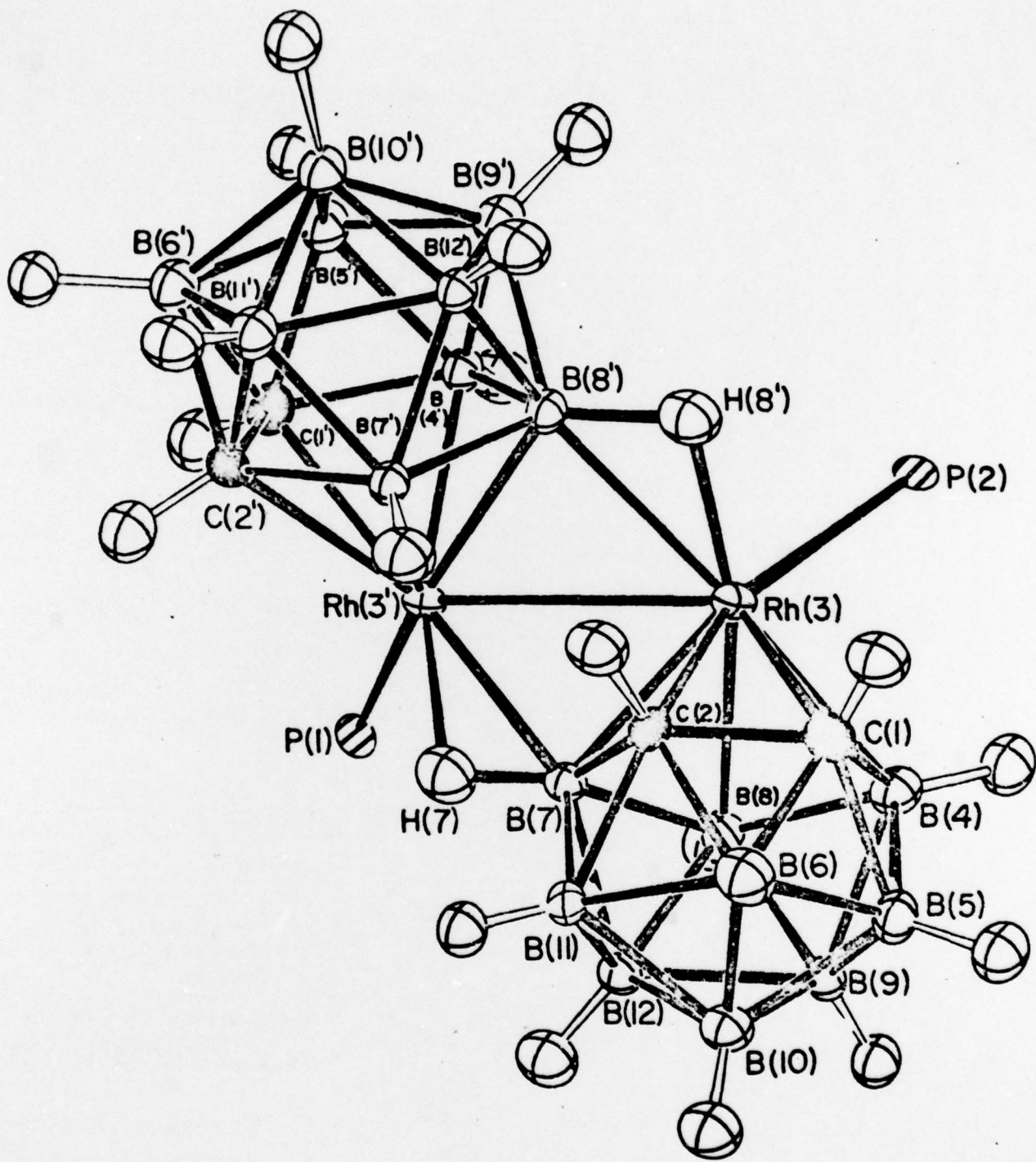
*Refers to Rh atom not indicated by column heading.

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2. T. E. Paxson and M. F. Hawthorne, J. Am. Chem. Soc., **96**, 4674 (1974).
3. Mechanistic hydrogenation studies are presently underway utilizing an automatic gas titration apparatus to be described later. B. A. Anfield, M. S. Delaney, and M. F. Hawthorne (to be published).
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 benzoyl peroxide.
5. [closo-3,3'-(PPh₃)₂-3,8';3',7- μ -H,H'-3,8';3',7-Rh₂-1,2;1',2'-(C₂B₉H₁₁)₂].
6. The compound is soluble in most organic solvents except alcohols and alkanes; R_f=0.65 (benzene/silica gel). [Melting point: 187-189°C, in vacuo (uncorrected)].
7. A. R. Siedle, J. Organomet. Chem., 249 (1975). We have repeated this work and shown that the "[C₂B₉H₁₁)Rh(PPh₃)C₆H₆]₂" compound is in fact the benzene solvate of II, [(PPh₃)Rh(C₂B₉H₁₁)]₂·2C₆H₆, and the reported visible spectrum is in error (ca. 50 nm). Crystals of the solvate suitable for x-ray work could not be obtained due to loss of benzene which rapidly destroys the crystal.
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.
9. Referenced to the external standard Et₂O·BF₃.
10. Referenced to the external standard D₃PO₄.
11. A further splitting of 5Hz 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.
12. The crystals contain two molecules of CH₂Cl₂ per molecule of II and were coated with epoxy resin for x-ray work.

13. X-ray intensity data were collected by the θ -2 θ technique with MoK_α radiation [graphite monochromator] on a Syntex P1 automated diffractometer equipped with a scintillation counter and a pulse height analyzer. The low temperature attachment (ref. 14) maintained the crystal temperature at $-160 \pm 1^\circ\text{C}$ with a temperature stability of $\pm 0.5^\circ\text{C}$. Of a total of 6388 reflections examined, 5535 had $I > 3\sigma(I)$ and were used in the structure determination. The data were corrected for absorption, Lorentz and polarization effects. The structure was solved by heavy atom methods and refined by anisotropic least-squares refinement, converging at $R = 0.047$ and $R_w = 0.072$.
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21. Current investigation of mixed aryl-alkyl phosphine derivatives of I indicates that an identical stereoselective decomposition occurs to give analogs of II. R. T. Baker and M. F. Hawthorne (to be published).
22. Potential catalysts are screened in purified tetrahydrofuran solvent utilizing a gas-tight glass apparatus equipped with an oil diffusion pump, 100 ml Schlenk flask, H_2 inlet, mercury manometer and bubbler. The olefin is injected through a septum on the side-arm using a Gilmont ultra precision syringe and H_2 (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 $9.84 \times 10^{-3}\text{M}$ and catalyst concentrations of $2.72 \times 10^{-3}\text{M}$, the initial hydrogenation rates ($\pm 10\%$) at 24.6°C for I and II were 5.36×10^{-5} and 1.27×10^{-4} mol/sec, respectively.

Figure 1 Molecular Structure of II. (CH_2Cl_2 solvate molecules and phenyl rings on phosphorus atoms are omitted for clarity)



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| <p>The decomposition of Rh(H)(PPh₃)₂C₂B₉H₁₁ (I) yields [Rh(PPh₃)C₂B₉H₁₁]₂ (II) as the only tractable product. The spectral characterization and x-ray molecular structure determination indicate that a terminal B-H bond in (I) has become a Rh-H-B bridge in (II) and (II) is thus a model intermediate in the oxidative addition of a terminal B-H bond to rhodium, the catalytic activity of (II) for the homogeneous hydrogenation of olefins is comparable to that of (I) per rhodium center. ←</p> | | |

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