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REACTIONS AT THE RHODIUM VERTEX OF A RHODACARBORANE CLUSTER. PR--ETC(U)
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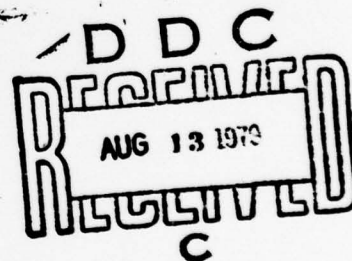
REACTIONS AT THE RHODIUM VERTEX OF A RHODACARBORANE CLUSTER. PREPARATION, CRYSTAL AND SOLUTION STRUCTURE, AND REACTIONS OF $3,3-(\text{Ph}_3\text{P})_2-3-(\text{HSO})_4-3,1,2-\text{RhC}_2\text{B}_9\text{H}_{11}\cdot\text{O}(\text{C}_2\text{H}_5)_2$.

By

W. C. Kalb, R. G. Teller, and M. F. Hawthorne

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Reactions at the Rhodium Vertex of a Rhodacarborane Cluster. Preparation, Crystal and Solution Structure, and Reactions of 3,3-(Ph₃P)₂-3-(HSO₄)-3,1,2-RhC₂B₉H₁₁·O(C₂H₅)₂

By

W. C. Kalb, R. G. Teller, and M. F. Hawthorne*

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Sir:

Since our discovery¹ that the hydridorhodacarborane 3,3-(Ph₃P)₂-3-H-3,1,2-RhC₂B₉H₁₁(I) is an active catalyst for the isomerization and hydrogenation of olefins, we have explored the extensive chemistry of this cluster in depth, particularly with regard to the Rh vertex. As an example, the reaction of I with sulfuric acid generates H₂² and a novel metallocarborane species (Ph₃P)₂(HSO₄)-RhC₂B₉H₁₁(II). The addition of hydrogen gas or primary alcohols to solutions of II regenerates I, with accompanying elimination of sulfuric acid from the cluster. We report here the synthesis, crystal and solution structure, and reactivity of 3,3-(Ph₃P)₂-3(HSO₄)-3,1,2-RhC₂B₉H₁₁·O(C₂H₅)₂(II). It is of note that II represents the first reported metallocarborane containing a metal-oxygen bond.

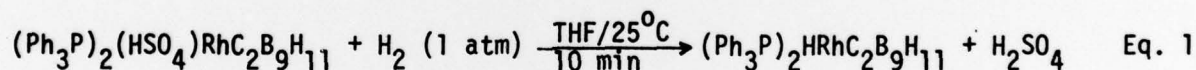
To a solution of 2.0 g (2.62 mmol) of I in 100 ml of dichloromethane, 3 ml of H₂SO₄ (50 mmol) was added with rapid stirring. Evolution of H₂ was evident within 30 seconds and an orange precipitate formed. After 15 minutes the precipitate was separated by filtration, washed with CH₂Cl₂ and triturated with diethyl ether to produce bright orange crystals of II in 56% yield. Recrystallization from tetrahydrofuran (THF)/heptane affords (Ph₃P)₂(HSO₄)RhC₂B₉H₁₁·OC₄H₈. Anal. calcd for C₄₂H₅₀B₉RhP₂SO₅ C, 54.30, H, 5.42, B, 10.47, Rh, 11.08, P, 6.67, S, 3.45. Found: C, 54.51, H, 5.71, B, 10.66, Rh, 11.29, P, 6.47, S, 3.42.

The 200 MHz ¹H NMR of II in d₆-DMSO shows a complex multiplet centered at δ7.6 (area 30) due to the Ph₃P ligands and a singlet at 5.45(2) assigned to carborane C-H. Multiplets present at 3.55(4) and at 1.75(4) are due to the two sets of methylene protons present in OC₄H₈.

The 80.5 MHz ¹¹B {¹H} NMR is uninformative, consisting of two broad resonances centered at -9 ppm and +5 ppm relative to BF₃O(C₂H₅)₂. The 81.02 MHz ³¹P {¹H} NMR in THF/DMSO (Fig. 1) is temperature dependent and is discussed below. The infrared spectrum of II (Nujol) exhibits a band characteristic of

terminal B-H bonds at 2550 cm^{-1} in addition to absorptions due to the coordinated dicarbollide and triphenylphosphine ligands. Three bands at 1150, 1050, and 800 cm^{-1} are assigned to the bisulfate ligand.

II was found to react readily with H_2 gas to regenerate I and H_2SO_4 . A solution of II, 200 mg (0.215 mmol) in 100 ml of THF was treated with hydrogen gas (1 atm) for 10 minutes. An equal volume of water was added and the acid liberated was titrated potentiometrically with NaOH, giving an equivalent weight of 963 for II, calcd 931. Evaporation of the THF provided crystals of I in 82% of isolated yield. When deuterium gas was used³ I could be isolated in high yield and contained only a trace of Rh-H by IR ($\nu_{\text{Rh-D}}$, 1520 cm^{-1}). Similarly, II reacted rapidly with ethanol or propanol at 50°C to produce I in quantitative yield and acetaldehyde or propionaldehyde,⁴ respectively.



Metathesis of II with NaCl or NaBr afforded the corresponding halogen complexes 3,3-(Ph_3P)₂-3-Cl-3,1,2-RhC₂B₉H₁₁⁵ and 3,3-(Ph_3P)₂-3-Br-3,1,2-RhC₂B₉H₁₁ in greater than 80% yield. Anal. calcd for C₃₈H₄₁B₉RhP₂Br C, 54.35, H, 4.92, B, 11.58, Rh, 12.25, P, 7.38, Br, 9.52. Found: C, 54.60, H, 5.21, B, 11.60, Rh, 12.02, P, 7.34, Br, 8.94.

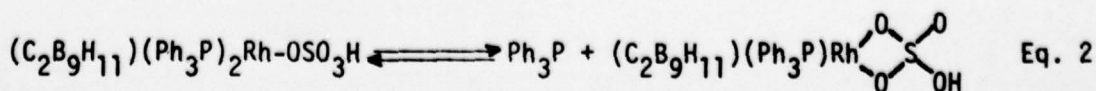
Crystal data: [$\text{P}(\text{C}_6\text{H}_5)_3$]₂HSO₄RhC₂B₉H₁₁·OC₄H₁₀(II) M = 931.08, triclinic, space group P $\bar{1}$, a = 13.049(5), b = 15.179(8), c = 11.378(5) Å, $\alpha = 79.10(3)^\circ$, $\beta = 92.30(3)^\circ$, $\gamma = 94.51(3)^\circ$, Z = 2, $\mu(\text{MO}_{\text{K}\alpha}) = 5.53\text{ cm}^{-1}$. Data were collected on a Picker FACS-I four circle diffractometer at -154°C and were corrected for Lorentz, polarization, absorption, and decay effects. The structure was solved by standard Patterson and Fourier techniques. At the present stage of refinement (all non-hydrogen atomic and thermal parameters varied in full matrix least

squares) the agreement factor stands at 0.086.

The molecule is illustrated in Fig. 2 along with some pertinent interatomic distances. The structure consists of two triphenylphosphine ligands and a bisulfate moiety bound to the Rh vertex of a $\text{RhC}_2\text{B}_9\text{H}_{11}$ icosahedral cluster. The bisulfate fragment is bonded to the metal atom via an oxygen atom (Rh-O 2.245(8) Å), the only example of such a bond in the literature. This bond distance is significantly larger than Rh-O distances in various Rh(III) complexes⁶ (Rh-O distances range from 2.049 to 2.151 Å in several complexes), but compares favorably with "long" Rh-O bonds in two Rh(III) aquo species (2.28(1) and 2.24(1) Å).⁷ The length of this bond is not dictated by steric interactions between the bisulfate and triphenylphosphine ligands. The P-Rh-P angle of 98.7(1)^o is smaller than other reported P-Rh-P angles in d⁶ metallocarboranes.⁸ Whether this feature is indicative of a weak bond or merely a reflection of the effect of a carborane cage is unknown.

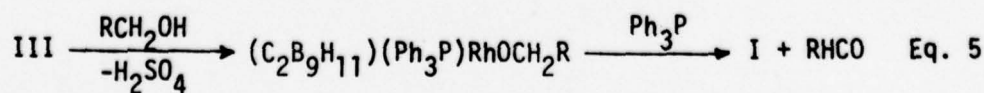
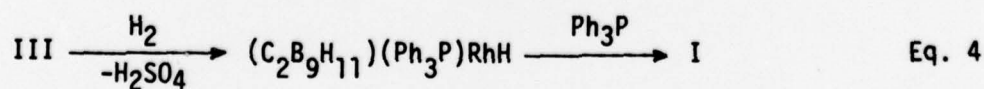
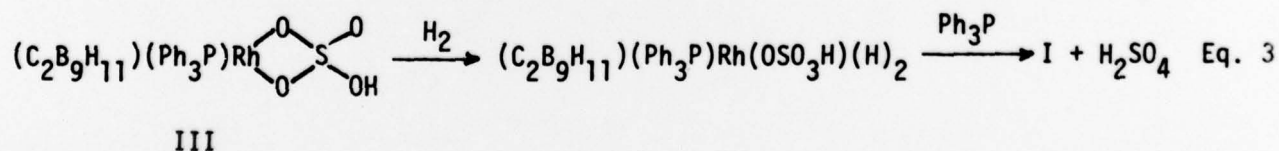
Although the hydrogen atoms have not been located in the structure the length of the S-O(3) bond, as compared to the other S-O bonds, indicates that this oxygen is protonated. Also the proximity of this oxygen to O(2) of another molecule (O(3)-O(2)' 2.534(12) Å) indicates its involvement in intermolecular hydrogen bonding.

The room temperature 81.02 MHz ³¹P {¹H} NMR in THF/DMSO revealed a doublet centered at 33.4 ppm rel. to D₃PO₄, J_{P-Rh} = 152 Hz and a singlet due to free Ph₃P.⁹ Cooling to -32°C provided a spectrum with 3 doublets centered at 36.2 ppm (J_{P-Rh} 166 Hz), 33.0 ppm (J_{P-Rh} 157 Hz) and 26.8 ppm (J_{P-Rh} 132 Hz) in addition to the resonance for free Ph₃P. (The doublet at 26.8 ppm is equal in intensity to the free triphenylphosphine resonance.) We believe the low temperature spectrum indicates the equilibrium shown in Equation 2.



Ligand dissociation is well established for transition metal phosphine complexes and in this instance is favored by the chelate effect of the formed bidentate bisulfate ligand. The doublet at 33.0 ppm was therefore assigned to the monodentate complex (II) while that at 26.8 ppm was attributed to the bidentate species. The remaining doublet at 36.2 ppm may be due to either bisulfate dissociation from II or an acid-base equilibrium involving the proton of the coordinated bisulfate ligand.

The reaction of II with H_2 could proceed by oxidative addition of H_2 to III followed by reductive elimination of H_2SO_4 (Eq. 3). Alternatively, a 4-centered intermediate¹⁰ in which dihydrogen interacts simultaneously with both the Rh center and an oxygen atom of the bisulfate ligand could collapse to produce I and H_2SO_4 (Eq. 4). We favor the latter mechanism insofar as oxidative addition of H_2 to III (formally Rh(III)) would yield a formal Rh(V) dihydride. The reaction of II with alcohols is most reasonably envisioned as proceeding through coordination of alcohol to III followed by loss of H_2SO_4 . The resulting alkoxy-rhodium species could then react via α -hydride abstraction and addition of Ph_3P to produce I and the corresponding aldehyde (Eq. 5).



Further studies aimed at utilizing the complex (II) for catalytic dehydrogenation of alcohols are currently underway in these laboratories. The reactions of II with cyanide ion¹¹ and with phenylacetylene¹¹ produce species quite unlike those discussed above and they will be reported at a later date.

Acknowledgements

We wish to thank the Office of Naval Research and the National Science Foundation (Grant No. CHE78-05679) for their generous support of this work. The authors thank Professor F. A. L. Anet for the use of the 80.5 MHz ¹¹B NMR spectrometer, Mr. Conrad A. O'Con for providing the ¹¹B and ³¹P NMR, Mr. R. T. Baker for the ¹H NMR, and Dr. C. B. Knobler for help with the crystal structure.

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1. T. E. Paxson and M. F. Hawthorne, J. Am. Chem. Soc., **96**, 4674 (1974).
2. HO_3SCF_3 , HO_3SF , and H_2SO_4 all react with I to produce H_2 gas. The most thoroughly characterized product is that reported here, from the reaction with H_2SO_4 .
3. One equivalent of triphenylphosphine was added to this reaction to suppress exchange of Rh-D for terminal B-H.
4. Acetaldehyde was verified by its isolation as the 2,4-dinitrophenylhydrazone derivative. Propionaldehyde was verified by VPC. These reactions appear to be stoichiometric in alcohol and complex II.
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11. W. C. Kalb and M. F. Hawthorne, unpublished results.

Figure 1. The 81.02 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR of II in THF/DMSO at -32°C . (Refer to text for explanation)

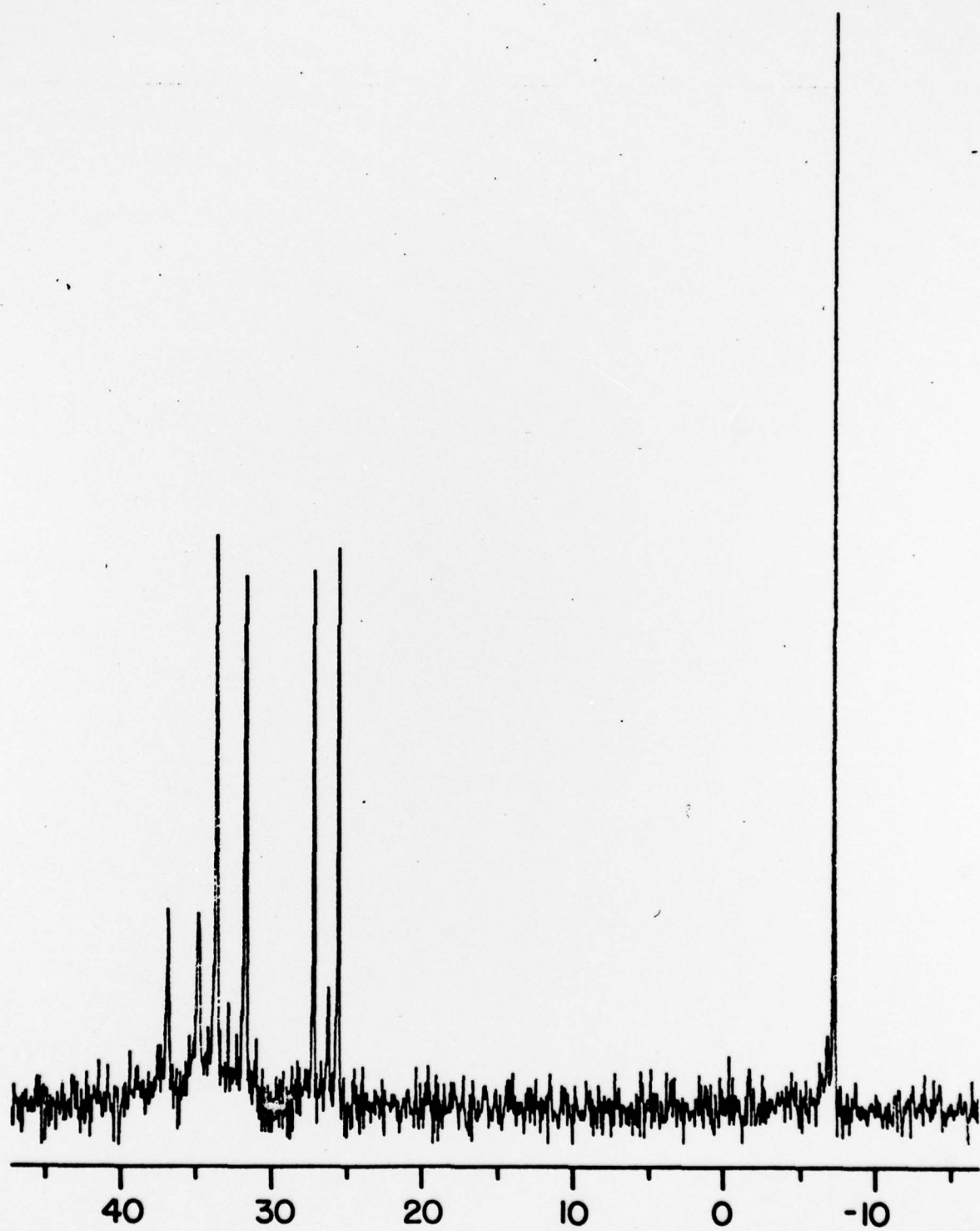
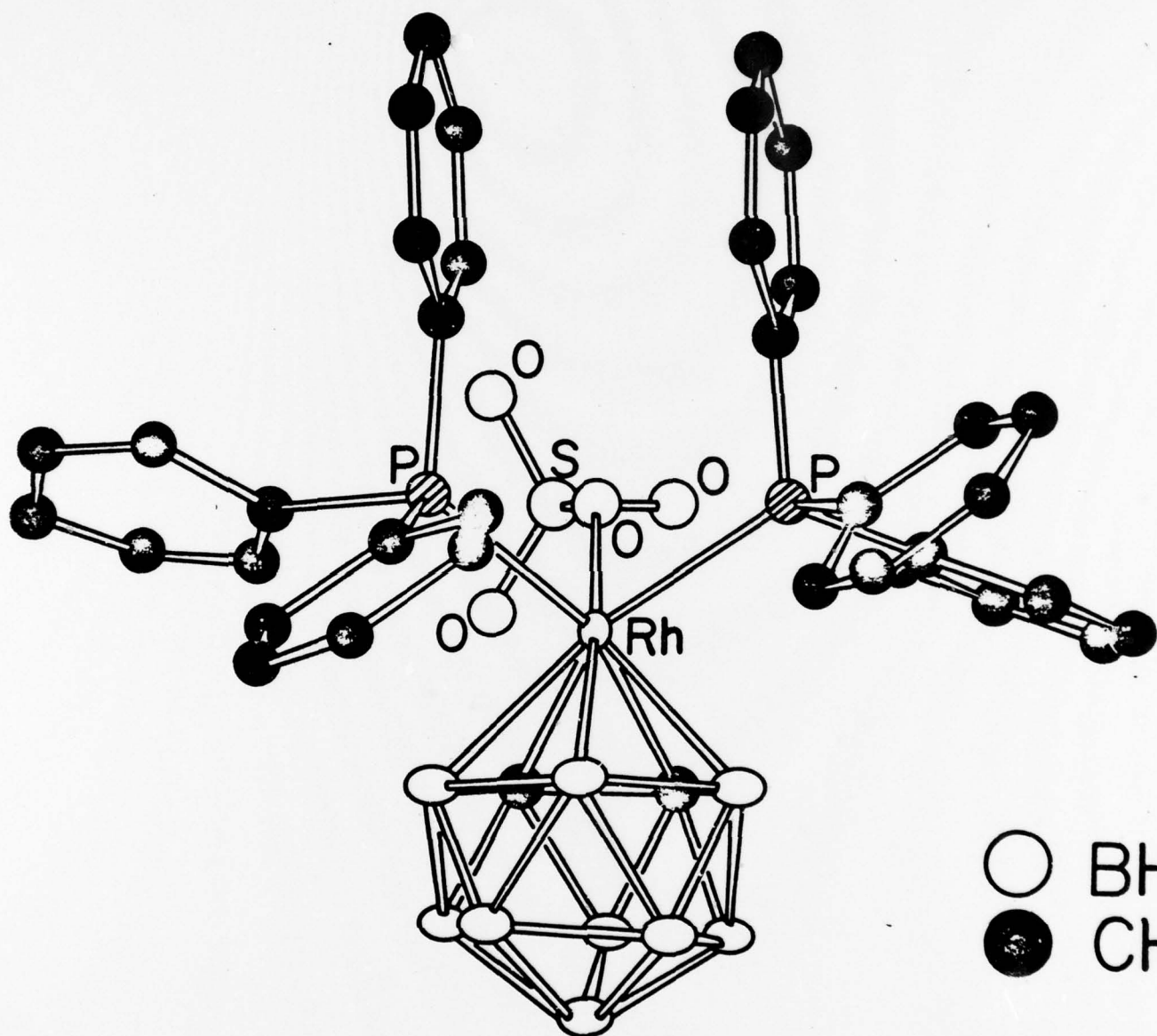


Figure 2. The molecular geometry of $3,3-(\text{Ph}_3\text{P})_2-3-(\text{HSO}_4)-3,1,2-\text{RhC}_2\text{B}_9\text{H}_{11}\cdot\text{O}(\text{C}_2\text{H}_5)_2$ with the ether molecule and hydrogen atoms omitted for clarity. Some pertinent bond distances and angles are $\text{Rh-B(ave)} = 2.243(18) \text{ \AA}$, $\text{Rh-C(ave)} = 2.182(14) \text{ \AA}$, $\text{Rh-P(ave)} = 2.387(4) \text{ \AA}$, $\text{Rh-O} = 2.243(8)$, $\text{B-B(ave)} = 1.806(8) \text{ \AA}$, $\text{C-B(ave)} = 1.723(18) \text{ \AA}$, $\text{C-C(carborane)} = 1.682(17) \text{ \AA}$, $\text{P-Rh-P} = 98.7(1)^\circ$.



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The homogeneous hydrogenation catalyst 3,3-(Ph ₃ P) ₂ -3-H-3,1,2-RhC ₂ B ₉ H ₁₁ (I) was found to react with H ₂ SO ₄ to produce 3,3-(Ph ₃ P) ₂ -3-(HSO ₄)-3,1,2-RhC ₂ B ₉ H ₁₁ (II). Solutions of II activate H ₂ (1 atm) to regenerate I and H ₂ SO ₄ . II reacts with ethanol or propanol to produce the corresponding aldehyde and I. Reactions of II with NaX (X=Cl, Br) provide the halogen complexes 3,3-(Ph ₃ P) ₂ -3-X-3,1,2-RhC ₂ B ₉ H ₁₁ . II has been characterized by a single-crystal X-ray diffraction study. ←		

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