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THE PRECURSOR OF AN EXTRAORDINARILY REACTIVE HOMOGENEOUS HYDRO6--ETC(U)

JUL 80 M S DELANEY, K B KNOBLER

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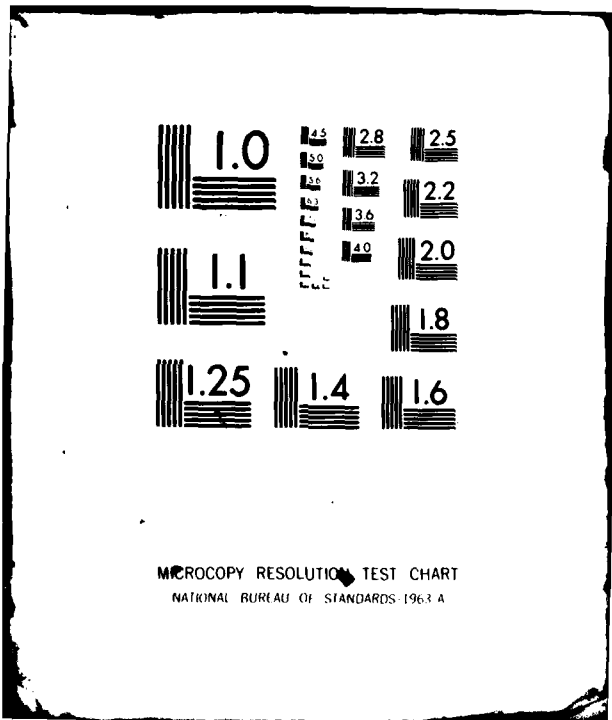
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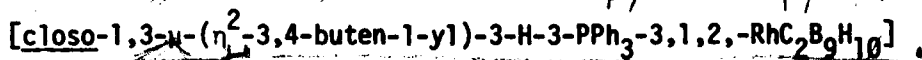
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THE PRECURSOR OF AN EXTRAORDINARILY REACTIVE HOMOGENEOUS HYDROGENATION CATALYST.

SYNTHESIS, STRUCTURE AND REACTIONS OF



By

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Department of Chemistry  
University of California  
Los Angeles, California 90024

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THE PRECURSOR OF AN EXTRAORDINARILY REACTIVE HOMOGENEOUS HYDROGENATION CATALYST.

SYNTHESIS, STRUCTURE AND REACTIONS OF

[ $\text{closo-1,3-}\mu\text{-(}\eta^2\text{-3,4-buten-1-yl)-3-H-3-PPh}_3\text{-3,1,2,-RhC}_2\text{B}_9\text{H}_{10}$ ]

By

M.S. Delaney, C.B. Knobler and M.F. Hawthorne

Department of Chemistry  
University of California  
Los Angeles, California 90024

SUMMARY

The synthesis, reactions and structure of the catalyst precursor [closo-1,3- $\mu$ -( $\eta^2$ -3,4-buten-1-yl)-3-H-3-PPh<sub>3</sub>-3,1,2,-RhC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (I) and the initial rates of some alkene hydrogenations catalyzed by (I) are reported.

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Sir:

In our studies of alkene reduction catalyzed by [closo-3-H-3,3-(PPh<sub>3</sub>)<sub>2</sub>-3,1,2-RhC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>1</sup>, we have noted that the rate of hydrogenation is inversely proportional to the concentration of added triphenylphosphine. This observation suggests that reversible triphenylphosphine dissociation is an important equilibrium which precedes the rate determining step of the hydrogenation sequence. The ease with which the parent catalyst could be modified through synthesis led us to explore the possibility of obtaining enhanced hydrogenation rates by replacing one of the triphenylphosphine ligands with a chelated  $\eta^2$ -3,4-buten-1-yl side chain attached to one of the dicarbollide ligand carbon atoms. The resulting rhodacarborane (I), [closo-1,3- $\mu$ -( $\eta^2$ -3,4-buten-1-yl)-3-H-3-PPh<sub>3</sub>-3,1,2-RhC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>], might well undergo irreversible hydrogenation of the alkenyl side chain under the conditions for alkene hydrogenation to produce an open coordination site on rhodium<sup>2</sup> resulting in a marked rate acceleration in the hydrogenation of alkenes. Complex (I) is among the most active homogeneous hydrogenation catalysts reported to date (vide infra), demonstrating this effect. In addition (I) is to our knowledge the first rhodium complex of the relatively rare hydrido alkene class of complexes<sup>3-11</sup> to be isolated and structurally characterized.

A methanol solution of [RhCl(PPh<sub>3</sub>)<sub>3</sub>] and a 20% molar excess of Cs<sup>+</sup>[7-butenyl-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>-12</sup> heated to reflux under nitrogen for three hours precipitated a yellow microcrystalline product in 90% yield<sup>13</sup> which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-ethanol under an inert atmosphere (m.p. 170-3°C dec). Elemental analysis, NMR and infrared spectra<sup>†</sup> supported the proposed formula for (I).

The small yellow prisms of (I) crystallized in the space group  $P2_1/c$ . The cell data are:<sup>14</sup>  $a = 16.494(4) \text{ \AA}$ ,  $b = 11.193(2) \text{ \AA}$ ,  $c = 17.006(3) \text{ \AA}$ ,  $\beta = 122.49(1)^\circ$ ,  $V = 2648.22(95) \text{ \AA}^3$ ,  $\rho = 1.386 \text{ g} \cdot \text{cm}^{-3}$  (x-ray density),  $\rho = 1.229 \text{ g} \cdot \text{cm}^{-3}$  (flotation density, aqueous KI)<sup>15</sup>. The molecular structure of I is shown in Figure I with significant bond distances and angles. The rhodium atom is symmetrically bound to the pentagonal face of the dicarbollide ligand. The vinyl moiety of the butenyl group is bound to the rhodium in such a fashion that the C=C bond is nearly parallel to the pentagonal face of the dicarbollide ligand.

A THF solution,  $1.8 \times 10^{-4} \text{ M}$  in (I) and  $0.13 \text{ M}$  in trimethylvinylsilane displayed an initial rate of  $2.4 \times 10^{-1} \text{ mol} \cdot \text{sec}^{-1} / \text{mol Rh}$  for the reduction of the alkene when exposed to hydrogen ( $P_{\text{H}_2} = 705 \text{ mm Hg}$ ) at  $0^\circ\text{C}$ . A THF solution of  $[\text{RhCl}(\text{PPh}_3)_3]$  under the same conditions exhibited an initial rate of  $7.8 \times 10^{-3} \text{ mol} \cdot \text{sec}^{-1} / \text{mol Rh}$ , thirty times slower than the rate exhibited by (I). A THF solution of (I) under the same conditions as described above displayed an initial rate of  $8.9 \text{ mol} \cdot \text{sec}^{-1} / \text{mol Rh}$  in the reduction of 3,3-dimethylbut-1-ene. A  $\text{CH}_2\text{Cl}_2$  solution  $5.0 \times 10^{-4} \text{ M}$  in  $[\text{Ir}(\text{cod})\text{P}(\text{i-Pr})_3(\text{py})]^+\text{PF}_6^-$  and  $0.5 \text{ M}$  in 3,3-dimethylbut-1-ene displayed an initial rate of  $2.3 \text{ mol} \cdot \text{sec}^{-1} / \text{mol Ir}$  when exposed to hydrogen ( $P_{\text{H}_2} = 600 \text{ mm Hg}$ ) at  $0^\circ\text{C}$ <sup>5c,d</sup>. The compound  $[\text{Ir}(\text{cod})\text{P}(\text{i-Pr})_3(\text{py})]^+\text{PF}_6^-$ , apparently the most active previously reported homogeneous hydrogenation catalyst, must be used in  $\text{CH}_2\text{Cl}_2$  due to the need for a non-coordinating polar solvent. Complex (I), on the other hand, has been found to be effective as a homogeneous hydrogenation catalyst in THF, o-dichlorobenzene, benzene and toluene.

When  $1 \text{ mmol}$  of (I) in the THF was exposed to hydrogen while in the presence  $2.4 \text{ mmol}$  of triphenylphosphine, the solution took up  $1 \text{ mmol}$  of hydrogen. Solvent removal in vacuo followed by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ -hexane

eluent under nitrogen) gave an orange compound which was recrystallized from  $\text{CH}_2\text{Cl}_2$ -heptane in 90% yield. This compound was shown to be [closo-1-butyl-3-H-3,3-( $\text{PPh}_3$ )<sub>2</sub>-3,1,2- $\text{RhC}_2\text{B}_9\text{H}_{10}$ ], (II), on the basis of elemental analysis, infrared and NMR spectra<sup>†</sup>, thus demonstrating the facile hydrogenation of the alkenyl side chain. Complex II was identical to the product obtained from [ $\text{RhCl}(\text{PPh}_3)_3$ ] and  $\text{Cs}^+[\text{7-butyl-7,8-}\text{C}_2\text{B}_9\text{H}_{11}]^{-16}$  in methanol and was also found to be an effective hydrogenation catalyst.

When 1 mmol of (I) in the THF was exposed to hydrogen in the absence of triphenylphosphine the solution rapidly took up 1 mmol of hydrogen with the hydrogenation of the butenyl side chain and then slowly evolved 0.5 mmol of hydrogen. Use of a procedure similar to that described above for (II) gave an air sensitive dark purple compound (III) which will be reported elsewhere. At this time we suggest that (III) is a dimer similar to [ $\text{PPh}_3\text{RhC}_2\text{B}_9\text{H}_{11}$ ]<sub>2</sub>.<sup>17</sup>

The results reported above support the view that the great diversity of structural parameters available in metallocarborane chemistry may be usefully exploited for the development of novel catalytic systems.

<sup>†</sup> Satisfactory elemental analyses, infrared and NMR spectra were obtained for all reported compounds.

#### ACKNOWLEDGEMENTS

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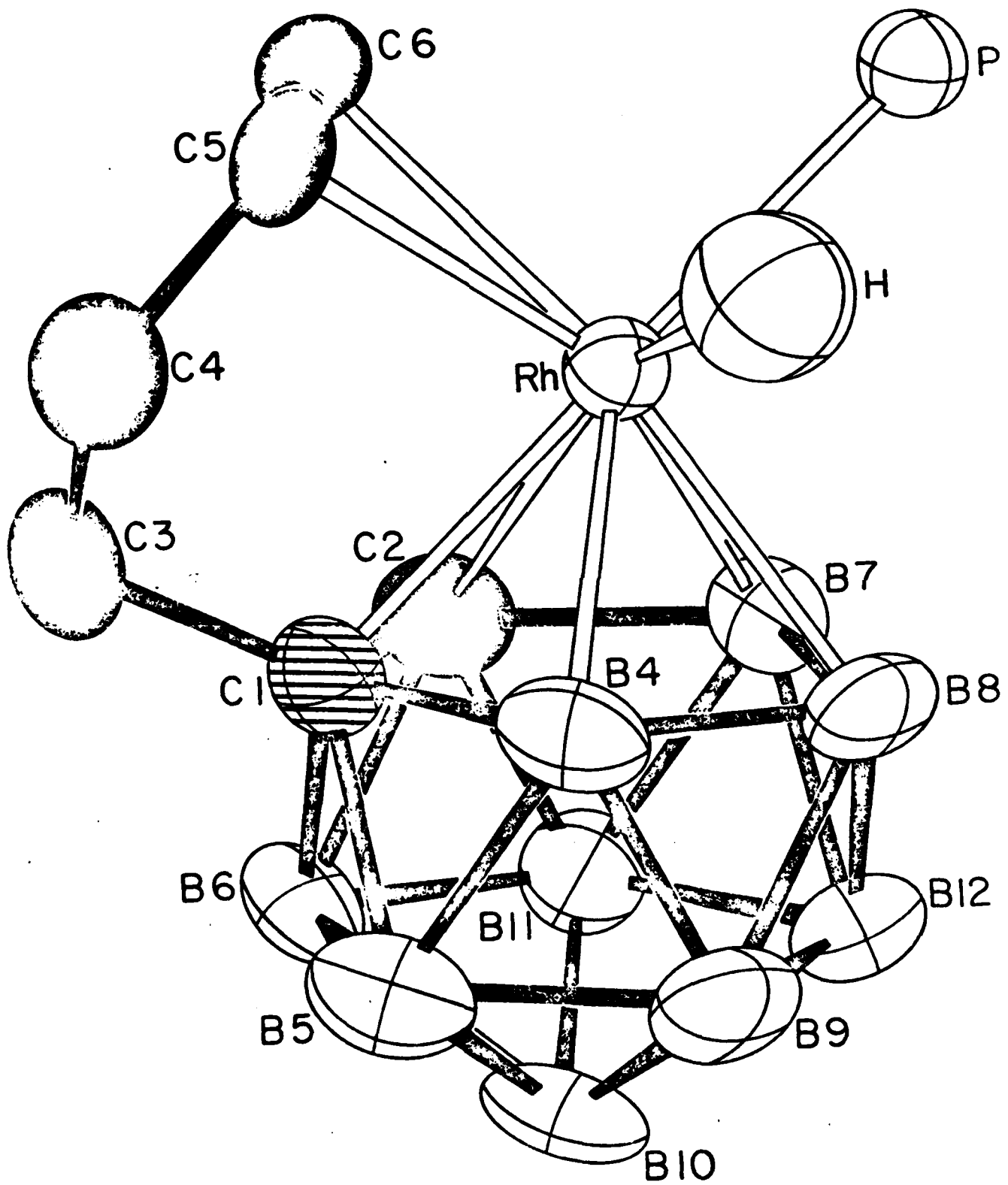
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FIGURE 1

Molecular Structure of (I) (the phenyl rings on phosphorus and all hydrogens except the rhodium hydride have been omitted for clarity). Distances from Rh to the attached atoms are H 1.65(3), C<sub>1</sub> 2.211(8), C<sub>2</sub> 2.266(8), B<sub>4</sub> 2.217(9) B<sub>7</sub> 2.220(9), B<sub>8</sub> 2.217(9), C<sub>5</sub> 2.276(8), C<sub>6</sub> 2.242(8), P 2.291(2). Some significant angles are C<sub>5</sub>-Rh-C<sub>6</sub> 35.2(3), C<sub>5</sub>-Rh-H 82 (2), H-Rh-P 74(3), C<sub>6</sub>-Rh-P 87.2 (2).<sup>15</sup>



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