

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  $[(CH_3)_4N][(CO)_4CrB_3H_8]$ .<sup>16</sup> A Rh-H distance of 2.1 Å has been reported for the Rh-H-B bridge in  $[(PPh_3)_2Rh(CB_{10}H_{10}C-C_6H_5)]$ .<sup>17</sup> The Rh-Rh distance of 2.763 (1) Å is well within the range reported for Rh-Rh single bonds (cf. Rh<sup>I</sup>-Rh<sup>I</sup> = 2.68 Å in  $[(\eta^5-C_5H_5)_2Rh_2(CO)_3]$ ,<sup>18</sup> Rh<sup>III</sup>-Rh<sup>III</sup> = 2.906 (1) Å in  $[(\mu-H)(\mu-Cl)\{\eta^5-C_5(CH_3)_5\}-RhCl_2]_2$ ).<sup>19</sup>

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  $[Rh(PPh_3)_3](ClO_4)$ ,<sup>20</sup> 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 observed<sup>21</sup> with both *d* and *l* enantiomers present in the unit cell.

Homogeneous olefin hydrogenation experiments were performed to determine the catalytic activity of II.<sup>22</sup> In typical experiments it was found that II is an active hydrogenation catalyst exhibiting rates comparable with those of I, per rhodium center.<sup>23</sup> Further studies concerning the mechanism<sup>3</sup> of homogeneous hydrogenation of olefins using I and II as catalysts are presently underway in these laboratories.

**Acknowledgments.** The authors thank Professor F. A. L. Anet for the use of the 80.5-MHz <sup>11</sup>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 thank the National Science Foundation 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.

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3. Mechanistic hydrogenation studies are presently underway using an automatic gas titration apparatus to be described later: B. A. Anfield, M. S. Delaney, and M. F. Hawthorne, unpublished work.
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. [*cis*-o-3,3'-(PPh<sub>3</sub>)<sub>2</sub>-3,8':3',7-μ-H,H'-3,8':3',7-Rh<sub>2</sub>-1,2:1',2'-(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>].
6. The compound is soluble in most organic solvents except alcohols and alkanes: *R<sub>f</sub>* 0.65 (benzene-silica gel), mp 187–189 °C in vacuo (uncorrected).
7. A. R. Siedle, *J. Organomet. Chem.*, **249** (1975). We have repeated this work and shown that the "[C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)Rh(PPh<sub>3</sub>)C<sub>6</sub>H<sub>6</sub>]<sub>2</sub>" compound is in fact the benzene solvate of II, [(PPh<sub>3</sub>)Rh(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>-2C<sub>6</sub>H<sub>6</sub>], and the reported visible spectrum is in error (~50 nm). Crystals of the solvate suitable for X-ray work could not be obtained owing 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 <sup>1</sup>H 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 Et<sub>2</sub>O·BF<sub>3</sub>.
10. Referenced to the external standard D<sub>3</sub>PO<sub>4</sub>.
11. A further splitting of 5 Hz is observed for this resonance due to <sup>31</sup>P coupling to the Rh-H-B hydrogen nucleus. This splitting is removed by suitably offsetting the broad-band <sup>1</sup>H decoupling frequency.
12. The crystals contain two molecules of CH<sub>2</sub>Cl<sub>2</sub> per molecule of II and were coated with epoxy resin for X-ray work.
13. X-ray intensity data were collected by the θ-2θ technique with Mo Kα radiation (graphite monochromator) on a Syntex P1 automated diffractometer equipped with a scintillation counter and a pulse height analyzer. The low-temperature attachment<sup>14</sup> maintained the crystal temperature at -160 ± 1 °C with a temperature stability of ±0.5 °C. Of a total of 6388 reflections examined, 5535 had *I* > 3σ(*I*) and were used in 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<sub>w</sub>* = 0.0072.

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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, H<sub>2</sub> inlet, mercury manometer, and bubbler. The olefin is injected through a septum on the side arm using a Gilmont ultraprecision syringe and H<sub>2</sub> (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  $9.84 \times 10^{-3}$  M and catalyst concentrations of  $2.72 \times 10^{-3}$  M, the initial hydrogenation rates (±10%) at 24.6 °C for I and II were  $5.36 \times 10^{-5}$  and  $1.27 \times 10^{-4}$  mol/s, respectively.

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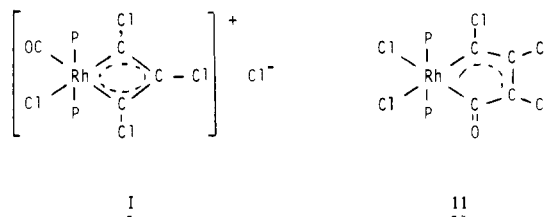
Received July 28, 1978

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

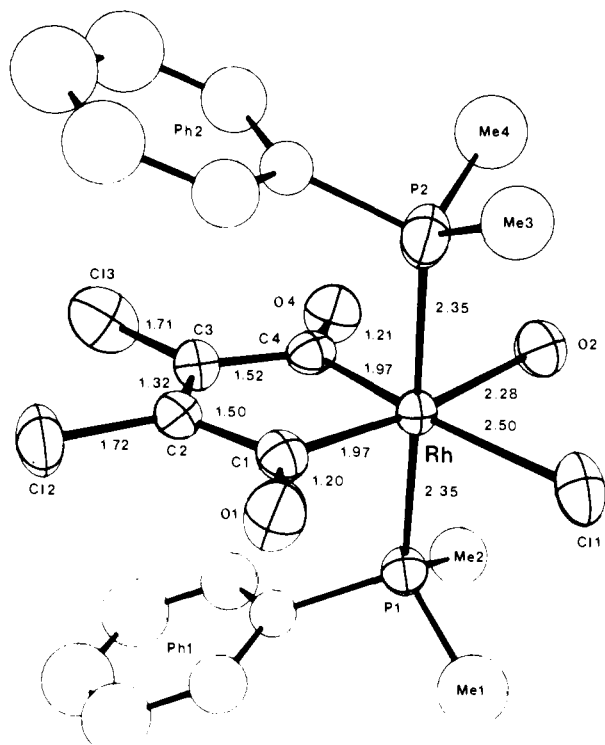
Sir:

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,<sup>1</sup> reactions of α,ω-dithio-substituted hydrocarbons,<sup>2</sup> and metal-promoted cleavage of the C—C bonds in strained cyclic hydrocarbons.<sup>3</sup> We have been investigating the latter method in our laboratory using square-planar d<sup>8</sup> complexes of Rh(I) and Ir(I) together with the unsaturated cyclic hydrocarbons C<sub>3</sub>Ph<sub>3</sub><sup>+</sup> and C<sub>3</sub>Cl<sub>4</sub>. Previous work on the C<sub>3</sub>Ph<sub>3</sub><sup>+</sup> aromatic cation has led to the facile preparation of 1,2,3-triphenylpropenyl-1,3-diyl complexes of Ir(III)<sup>3b</sup> and Rh(III).<sup>3c</sup> In this communication we report some preliminary synthetic and structural results on compounds formed from reactions of C<sub>3</sub>Cl<sub>4</sub>.<sup>4</sup>

Under anhydrous conditions in methylene chloride or benzene, Rh(CO)Cl(PMe<sub>2</sub>Ph)<sub>2</sub> and C<sub>3</sub>Cl<sub>4</sub> 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. C<sub>3</sub>Ph<sub>3</sub><sup>+</sup> chemistry). Complex I is a red powder with ν<sub>C≡O</sub>



at 2085 cm<sup>-1</sup>, while II is a yellow powder with ν<sub>C≡O</sub> at 1670 cm<sup>-1</sup>. 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-

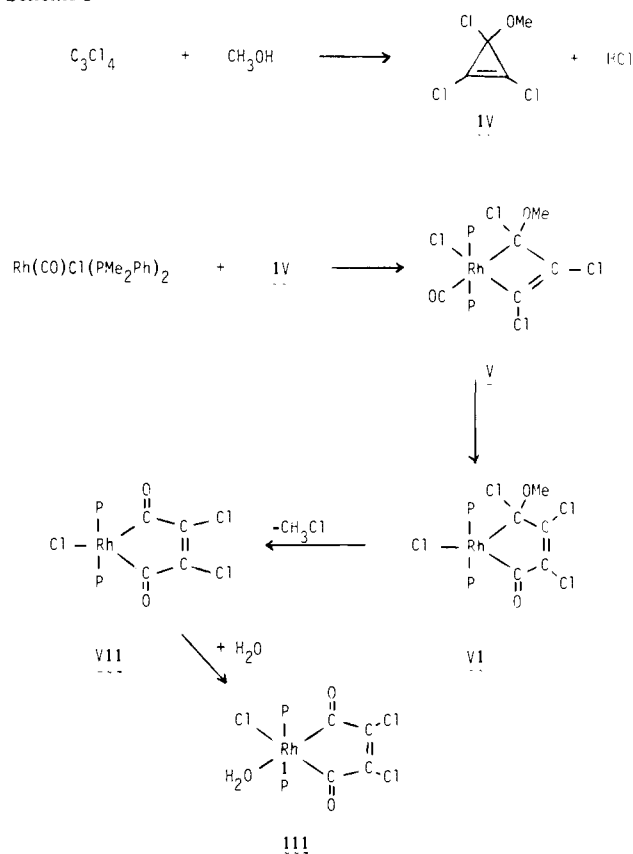


**Figure 1.** Perspective view of the  $\text{RhCl}(\text{H}_2\text{O})(\text{PMe}_2\text{Ph})_2(\text{C}_4\text{O}_2\text{Cl}_2)$  molecule showing the molecular geometry and some important bond distances. Standard deviations in the bond distances are 0.002 Å for Rh-P and Rh-Cl, 0.006 Å for Rh-C and Rh-O, and 0.01 Å for C-C and C-O.

talline products directly or to obtain one adduct preferentially over the other, but attempts thus far have failed. It was discovered during the course of these experiments that, when methanol was used as the solvent, a yellow crystalline product III could be isolated upon workup. This compound differed spectroscopically from II in two ways: viz., the carbonyl stretching frequency (KBr) broadened and shifted from 1670  $\text{cm}^{-1}$  in II to 1635  $\text{cm}^{-1}$  in III and bands at 3550 and 3350  $\text{cm}^{-1}$  attributable to a coordinated aquo or hydroxo ligand were found. Spectroscopic and analytical data<sup>5</sup> were insufficient to assign the structure conclusively; so a full single-crystal X-ray diffraction study was performed.

The results of the X-ray study,<sup>6</sup> shown in Figure 1, demonstrate that III is an octahedral Rh(III) complex of formulation  $\text{RhCl}(\text{H}_2\text{O})(\text{PMe}_2\text{Ph})_2(\text{C}_4\text{O}_2\text{Cl}_2)$  which possesses a metallocyclic 3,4-dichlororhodiacyclopent-3-ene-2,5-dione ring<sup>7</sup> and a coordinated aquo ligand. A mixed isotropic-anisotropic refinement model was used applying rigid body constraints to the phenyl groups and idealized coordinates for the methyl hydrogens. The two hydrogen atoms of the coordinated water molecules were located and included in the final stages of the least-squares refinement. Some selected bond distances are shown in Figure 1. All of these are in close agreement with values reported for related complexes except the Rh-Cl (2.50 Å) and the Rh-OH<sub>2</sub> (2.28 Å) bonds which are both noted to be especially long as a consequence of the strong trans influence exerted by the organic group.<sup>3c,8-10</sup> The  $\text{Rh}(\text{C}_4\text{O}_2\text{Cl}_2)$  fragment is planar to within 0.10 Å and the C-C, C=C, and C=O bond distances<sup>11</sup> indicate a localized bonding network. The Rh-C bonds which both measure 1.97 (1) Å are in the range of 1.96-2.00 Å<sup>3c,8-10,13</sup> normally observed for Rh(III)-C(sp<sup>2</sup>) bonds. On the basis of these crystallographically observed Rh-C distances, the extent to which electrons are delocalized onto the metal center is questionable; however, it is necessary to postulate some degree of electron delocalization in order to account for the abnormally

**Scheme I**



low value of 1635  $\text{cm}^{-1}$  for the acyl carbonyl stretching mode<sup>7b</sup> in the electronically more sensitive infrared data.

Since methanolysis of I and II did not yield a rhodiacyclopentenedione complex of type III, neither I nor II can be an intermediate in the methanol reaction and a different pathway is suggested. We believe that III is formed via a metal-promoted cleavage of the C-C bond of an in situ generated methoxycyclopropane, IV. The mechanism of this reaction can be accommodated by Scheme I.

Fortuitously we were able to isolate the intermediate VI in a pure crystalline form<sup>5</sup> by treating  $\text{Rh}(\text{CO})\text{Cl}(\text{PMe}_2\text{Ph})_2$  with  $\text{C}_3\text{Cl}_4$  in a small amount of  $\text{CH}_3\text{OH}$  (2 mL) at lower temperatures (0 °C). This reaction goes instantaneously and VI precipitates out as a microcrystalline yellow-orange solid in ~50% yield. Attempts to increase this yield are hampered by its subsequent decomposition into VII. The infrared spectrum of VI shows, in addition to the C=O stretching mode at 1660  $\text{cm}^{-1}$ , a sharp band at 1350  $\text{cm}^{-1}$ , assignable to the C-O-CH<sub>3</sub> stretching mode.<sup>14</sup> Intermediate VI is unstable in solution ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ), the band at 1350  $\text{cm}^{-1}$  disappears, and VII can be isolated from the decomposed solution. Conversion of VI to VII with concurrent loss of  $\text{CH}_3\text{Cl}$  can be demonstrated by NMR. In addition to the resonances accounting for the presence of the trans phosphines, the NMR spectrum of VI in  $\text{CDCl}_3$  shows a single sharp resonance at  $\delta$  5.3 assignable to the -OCH<sub>3</sub> group of the metallocycle and a weak resonance at  $\delta$  3.0 ( $\text{CH}_3\text{Cl}$ ). During a period of approximately 30 min, the peak at  $\delta$  5.3 disappears while the one at  $\delta$  3.0 increases in intensity.

Complex VII can be directly obtained by carrying out the reaction in rigorously dried methanol. It is a yellow solid whose infrared is identical with that of III except that the water modes are absent. The coordinated water ligand is picked up during the course of the recrystallization.<sup>8</sup> It was initially thought that dichlorocyclopropenone, which is known to be formed by hydrolysis of tetrachlorocyclopropene,<sup>15</sup> was the

species which reacts with Rh(I). The preceding mechanistic discussion clearly eliminates this possibility. Furthermore Tobey and West<sup>16</sup> have shown that alcoholysis of C<sub>3</sub>Cl<sub>4</sub> does not lead to dichlorocyclopropanone but rather to a mixture of acrylic acid esters via ring opening of an unstable cyclopropane intermediate which could not lead to a product of the type isolated.

On the basis of this proposed mechanism, synthetic studies are currently in progress to prepare metallocyclobutenes similar to intermediate V and to demonstrate the subsequent insertion step. It is interesting to note that, since IV can add to the Rh(I) complex in two ways to produce V as well as its geometric isomer, one may a priori expect a mixture of two products resulting from CO cis migration<sup>3a</sup> into two different Rh—C bonds. In our studies no evidence for the isomeric 2,3-dione has been found, although platinum complexes of this type have been prepared by a different route.<sup>17</sup>

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- Rh(H<sub>2</sub>O)Cl(PMe<sub>2</sub>Ph)<sub>2</sub>(C<sub>4</sub>O<sub>2</sub>Cl<sub>2</sub>): monoclinic; *P*<sub>2</sub>/*c*; unit cell parameters are *a* = 8.924 (8) Å, *b* = 18.965 (10) Å, *c* = 14.775 (12) Å, β = 102.90 (8)°, *V* = 2445.2 Å<sup>3</sup>. The structure was solved by the heavy-atom method and refined by iterative Fourier and least-squares analyses to a final residual of  $R_1(F) = \sum |F_o| - |F_c| / \sum |F_o| = 0.046$  for the 2878 independent reflections with *I* > 2σ(*I*).
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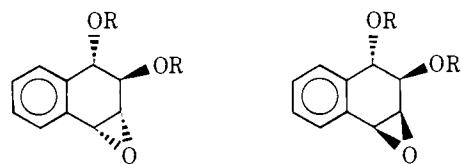
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Received June 26, 1978

## The Importance of Intramolecular Hydrogen Bonding on the Reactivity of Tetrahydro Diol Epoxides

Sir:

The chemistry of the tetrahydro diol epoxides (TDE) of polycyclic aromatic hydrocarbons is presently of much concern. This is due to the fact that these compounds have been proposed to be the ultimate carcinogenic and mutagenic derivatives of the ubiquitous benzo[*a*]pyrene<sup>1</sup> as well as benz[*a*]anthracene.<sup>2</sup> Both syn- and anti-TDE isomers are produced in the metabolism of benzo[*a*]pyrene through the combined action of cytochrome P-450 and epoxide hydrase.<sup>3</sup> Many workers<sup>4</sup> have suggested that intramolecular hydrogen bonding between epoxide oxygen and hydroxyl group in the syn isomers provides assistance to ring opening. The anti isomer, in its most stable conformation, possesses no such structural feature. The



R = -H (DE-1)  
R = -CH<sub>3</sub> (DME-1)

R = -H (DE-2)  
R = -CH<sub>3</sub> (DME-2)

relevant syn and anti structures for the compounds of this study are abbreviated as DE-1 and DE-2, respectively. Herein the chemistry<sup>5</sup> of DE-1 and DE-2 is compared with that of their dimethyl ethers (i.e., DEM-1 and DEM-2) to delineate the relative importance of conformation as opposed to internal hydrogen bonding in determining the rates for epoxide ring opening. The NMR coupling constant of H<sub>1</sub> and H<sub>2</sub> of both DE-1 and DME-1 is at ~3 Hz, in accord with their diequatorial conformation, so that the *trans*-hydroxyl and *trans*-methoxyl groups must be diaxial. The *J* value for both DE-2 and DME-2 is ~9, implying a conformation in which the *trans*-hydroxyl and *trans*-methoxyl groups are diequatorial. These results dictate that the conformation of DE-1 is that of DME-1 and that of DE-2 is the same as DME-2 under the solvent conditions used in these NMR studies.<sup>5</sup>

In the present study we have determined the acid (*k<sub>H</sub>*) and spontaneous or water-catalyzed (*k<sub>0</sub>*) rate constants for solvolysis of DE-1, DE-2, DME-1, and DME-2 and the second-order rate constants for nucleophilic attack of β-mercaptoethanol anion (*k<sub>s</sub>*) upon the various substrates as a function of the composition of dioxane-water mixed solvent. We would expect the effect of any intramolecular hydrogen bonding to be accelerated upon decrease in the protic nature of the solvent. Values of *k<sub>H</sub>* and *k<sub>0</sub>* (Table I) were obtained from plots of the logarithm of the first-order rate constants (*k<sub>obsd</sub>*) of solvolysis vs. the pH values at which the *k<sub>obsd</sub>* values were determined. Examination of Table I reveals that in water the *k<sub>H</sub>* values for both DE-1 and DME-1 are less than those for both DE-2 and DME-2, while exactly the reverse is true for the *k<sub>0</sub>* constants. Conformation, therefore, rather than internal hydrogen bonding, appears to be the feature of importance in determining both the spontaneous and acid-catalyzed solvolysis rate constants in water. (The observation that *k<sub>0</sub>* for DE-1 is twice that for DME-1 might be interpreted as a small contribution of 0.4 kcal M<sup>-1</sup> to Δ*G*<sup>‡</sup> due to hydrogen bonding.) Transfer from water to 75% dioxane-water (v/v) has little effect on the ratio of *k<sub>H</sub>* values for *syn*- and *anti*-hydroxyl compounds, while the value of *k<sub>H</sub>* for the *syn*-methoxyl compound is actually enhanced over that for its anti isomer (Tables I and II).<sup>6,7</sup> Again, however, there is no apparent influence of the *syn*-hydroxyl group of DE-1 upon rate. Jerina and co-workers,<sup>8</sup> working with the bay region syn and anti diol epoxides of benzo[*a*]pyrene (BP-1 and BP-2, respectively), have suggested