

hydrogen atoms, and a listing of the observed and calculated structure amplitudes (56 pages). Ordering information is given on any current masthead page.

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## Studies on the Reactions of Carbon Dioxide with Transition Metal Complexes.

### Preparation and Structure of

### $\mu$ -Carbonato-pentakis(triphenylphosphine)dirhodium-Benzene

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The rhodium-hydrido complex  $\text{RhH}(\text{PPh}_3)_4$  ( $\text{Ph} = \text{C}_6\text{H}_5$ ) in toluene reacts with carbon dioxide at room temperature to give, on crystallization from benzene, red crystals of  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5\text{C}_6\text{H}_6$ , as characterized by diffraction methods. One mole of  $\text{CO}_2$  per mole of the complex is evolved on thermolysis and acidolysis of the complex and by treatment with methyl iodide and triphenyl phosphite. The compound crystallizes in space group  $C_2^1-P1$  with four formula units in the cell. The unit cell has dimensions of  $a = 22.518$  (9) Å,  $b = 28.051$  (12) Å,  $c = 12.841$  (7) Å,  $\alpha = 96.12$  (3)°,  $\beta = 97.91$  (3)°,  $\gamma = 92.66$  (3)°, and  $V = 7972$  Å<sup>3</sup>. The observed density of 1.39 (1) g cm<sup>-3</sup> is in good agreement with that of 1.38 g cm<sup>-3</sup> calculated for four  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5\text{C}_6\text{H}_6$  formula units per cell. There are thus two independent dimeric molecules in the cell. Refinement by full-matrix least-squares methods using 12330 observations for which  $F_o^2 \geq 3\sigma(F_o^2)$  yielded a conventional agreement index of 0.079. Each independent molecule of the compound was found to consist of two Rh atoms, both having square-planar coordination and linked by a planar carbonato ligand. Two oxygen atoms of the carbonate group are coordinated to one Rh atom while the remaining carbonato oxygen atom is bound to the second Rh atom. Triphenylphosphine ligands fill out the four-coordinate geometry of each Rh atom. The bidentate coordination of the carbonato group to the metal atom creates a four-membered ring. The average O-C-O angle involved in this ring is 115.9°, a slight decrease from the 120° value found in the free carbonate ion. The O-Rh-O angle of the four-membered ring averages 62.6°. No trend in the carbonato group C-O bond lengths is evident, the average value being 1.29 Å. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the complex in benzene is compatible with the unsymmetrical binuclear structure consisting of two rhodium(I) nuclei coordinated respectively with two and three triphenylphosphine ligands, as found in the solid state.

### Introduction

Recently much attention has been focused on the interaction of carbon dioxide with transition metal compounds as a step toward an efficient catalytic system of carbon dioxide fixation. For example, insertions of  $\text{CO}_2$  into metal-hydrogen,<sup>2-7</sup> -carbon,<sup>8-13</sup> -nitrogen,<sup>14</sup> and -oxygen<sup>15-17</sup> bonds are known as well as the formation of  $\text{CO}_2$ -coordinated complexes.<sup>10-12,18-23</sup> Reactions of carbon dioxide with some rhodium complexes have been reported to produce  $\text{CO}_2$ -coordinated complexes, e.g.,  $\text{Rh}_2\text{Cl}_2(\text{CO}_2)(\text{PPh}_3)_5$ <sup>18</sup> ( $\text{Ph} = \text{C}_6\text{H}_5$ ),  $\text{Rh}_2(\text{CO}_2)(\text{CO})_2(\text{PPh}_3)_3$ ,<sup>19</sup> and  $\text{Rh}(\text{OH})(\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ .<sup>20</sup> Previously, we reported that the reaction of  $\text{RhH}(\text{PPh}_3)_4$  with carbon dioxide afforded a red crystalline compound, to which,

on the basis of its ir and Raman spectra and chemical behavior, a formula of  $\text{Rh}_2\text{H}_2(\text{CO}_2)(\text{PPh}_3)_6$  was assigned.<sup>5</sup> By x-ray analysis, however, we now show that the compound in question contains not carbon dioxide but the carbonate moiety, as in the earlier case of two other suspected carbon dioxide complexes.<sup>23-25</sup> The crystallographic evidence indicates that the compound is in fact  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5\text{C}_6\text{H}_6$ . The present paper reports the preparation, characterization, and structure of this carbonato complex.

### Experimental Section

All manipulations were carried out under deoxygenated dinitrogen or under a vacuum. Solvents were dried in the usual manner, distilled, and stored under a dinitrogen atmosphere.

Infrared spectra were recorded on Hitachi EPI-G3 and 295 spectrometers using KBr pellets prepared under an inert atmosphere.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were measured by Mr. Y. Nakamura<sup>1b</sup> on a JEOL PS-100 spectrometer operating in a Fourier-transform mode and its signals are referred to triphenylphosphine (downfield positive) as an external standard. Microanalyses for carbon and hydrogen were carried out by Mr. T. Saito<sup>1b</sup> using a Yanagimoto CHN Type MT-2 Autocorder and for phosphorus and rhodium by Mr. K. Mizubayashi.<sup>1b</sup> Analysis of the gases evolved in various chemical treatments was carried out by gas chromatography after collecting gases fractionally using a Toeppler pump, by which the volumes of gases were also measured.

Hydrotetrakis(triphenylphosphine)rhodium(I) was prepared either from  $\text{RhCl}(\text{PPh}_3)_3$ <sup>26</sup> or directly from  $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ <sup>27</sup> by the methods previously reported. Hydrottris(triphenylphosphine)rhodium(I) was prepared according to the literature method.<sup>26</sup>

**Preparation of  $\mu$ -Carbonato-pentakis(triphenylphosphine)di-rhodium-Benzene.** Carbon dioxide was bubbled into a suspension of  $\text{RhH}(\text{PPh}_3)_4$  (1.00 g, 0.87 mmol) in toluene (20 ml) for 10–15 days. It was necessary to keep the temperature of the system below 20 °C throughout the reaction. The initial yellow suspension changed gradually to a brownish orange suspension, and the reaction was continued until the yellow precipitate of  $\text{RhH}(\text{PPh}_3)_4$  disappeared completely. After the reaction, 20 ml of hexane was added to complete the precipitation of a pale orange powder, which was washed several times with hexane and dried in vacuo. The orange powdery crude product thus obtained weighed 0.60 g (83%). Crystallization of the crude product from a mixture of benzene and diethyl ether gave red crystals of  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5\text{-C}_6\text{H}_6$ . Anal. Calcd for  $\text{C}_{97}\text{H}_{81}\text{O}_3\text{P}_5\text{Rh}_2$ : C, 70.4; H, 4.9; P, 9.4; Rh, 12.4. Found: C, 71.2; H, 5.3; P, 9.4; Rh, 11.9. Benzene of crystallization was detected in a yield of 0.0652 mmol on treatment of the crystals (103.2 mg, 0.0623 mmol) with triphenyl phosphite (ca. 1 ml) at room temperature for 1 day.

**Reactions of  $\mu$ -Carbonato-pentakis(triphenylphosphine)di-rhodium-Solvent.** (i) **Acidolysis.** Treatment of  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5\text{-C}_6\text{H}_6$  (120 mg, 0.0726 mmol) with ca. 1.5 ml of concentrated sulfuric acid in vacuo at room temperature released 0.063 mmol of carbon dioxide.

(ii) **Thermolysis.** Thermolysis of  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5\text{-C}_6\text{H}_6$  (124 mg, 0.0749 mmol) at 220 °C in vacuo released 0.069 mmol of carbon dioxide.

(iii) **Reaction with Methyl Iodide.** The reaction of  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5\text{-C}_6\text{H}_6$  (114 mg, 0.0678 mmol) with ca. 2 ml of methyl iodide in vacuo at room temperature liberated methane (0.076 mmol) and carbon dioxide (0.067 mmol) as analyzed by gas chromatography and mass spectrometry.

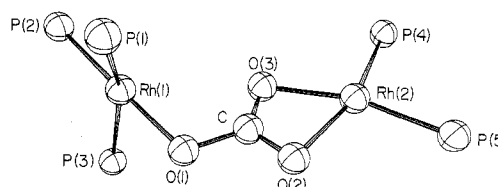
(iv) **Reaction with Triphenyl Phosphite.** An unpurified sample of  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5\text{-C}_6\text{H}_5\text{CH}_3$  (122 mg, 0.0730 mmol) reacting with ca. 2 ml of  $\text{P}(\text{OPh})_3$  afforded carbon dioxide (0.063 mmol) and toluene (0.065 mmol) which were identified by gas chromatography and mass spectrometry.

### X-Ray Data Collection

Weissenberg and precession photographs of a crystal of what proved to be  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5\text{-C}_6\text{H}_6$  yielded approximate cell dimensions and indicated that the crystal belonged to the triclinic system. Subsequent calculations have shown the space group to be  $C_1^1\text{-P}\bar{1}$ .

The crystal chosen for data collection was sealed in a glass capillary. This crystal exhibited eight faces of the forms  $\{010\}$ ,  $\{110\}$ ,  $\{1\bar{1}0\}$ , and  $\{10\bar{1}\}$ . Its dimensions along the principal crystallographic axes are 0.18, 0.098, and 0.55 mm. With the use of a Picker four-circle diffractometer and  $\text{Cu K}\alpha_1$  radiation ( $\lambda$  1.54056 Å) 15 high-order reflections were hand centered. The usual<sup>28</sup> least-squares refinement of the setting angles led to lattice constants at 22 °C of  $a = 22.518$  (9) Å,  $b = 28.051$  (12) Å,  $c = 12.841$  (7) Å,  $\alpha = 96.12$  (3)°,  $\beta = 97.91$  (3)°,  $\gamma = 92.66$  (3)°, and  $V = 7972$  Å<sup>3</sup>. Ultimately, four molecules of the title compound and four benzene molecules were found to be contained in the unit cell ( $\rho_{\text{calcd}} = 1.38$  g/cm<sup>3</sup>,  $\rho_{\text{obsd}} = 1.39$  (1) g/cm<sup>3</sup>).

Data were collected by the  $\theta$ - $2\theta$  scan technique using nickel-filtered  $\text{Cu K}\alpha$  radiation. Scans of 0.9° were made above and below the  $\text{K}\alpha_1$  and  $\text{K}\alpha_2$  peaks, respectively, at a rate of 2°/min. Ten-second stationary-crystal, stationary-counter background measurements were obtained at each end of the  $2\theta$  scan range. Copper foil attenuators were automatically placed in the path of the diffracted beam when its intensity exceeded about 7000 counts/s. In the range  $3.5^\circ < 2\theta$



**Figure 1.** View of the coordination about the rhodium atoms. The thermal ellipsoids are drawn at the 50% probability level.

$< 98.0^\circ$ , 16 576 reflections ( $\pm h, \pm k, -l$ ) were recorded. Six standard reflections were measured after every 100 reflections. The standard reflections uniformly decreased in intensity by approximately 11% during the course of data collection. A correction for this decomposition was made.

The data were processed as previously described.<sup>28,29</sup> Those 12 330 unique reflections which obeyed the condition  $F_o^2 \geq 3\sigma(F_o^2)$  were used in subsequent calculations.

### Solution and Refinement of the Structure

A three-dimensional Patterson synthesis<sup>30</sup> revealed the coordinates of the eight Rh atoms in the unit cell. Because of the unusually large number of potential independent variables, the structure was initially refined by successive Fourier syntheses. During this process, temperature factors were assigned arbitrarily constant values. Standard atomic scattering factors were used with the inclusion of anomalous terms for the Rh atoms.<sup>31</sup> Several successive Fourier syntheses resulted in the location of all nonhydrogen atoms and an unweighted agreement index of 0.20.<sup>32</sup>

Prior to starting least-squares refinement of the model, the intensity data were corrected for absorption ( $\mu = 47.8$  cm<sup>-1</sup>,  $\text{Cu K}\alpha$ ). Transmission factors varied between 0.43 and 0.67. The function minimized during full-matrix least-squares refinement was  $\sum w(|F_o| - |F_c|)^2$ . The phenyl rings and solvate benzene molecules were treated as rigid groups with  $D_{6h}$  symmetry and C–C bond lengths of 1.392 Å. An overall temperature factor was used for each group. Nongroup atoms were assigned individual isotropic temperature factors, with the exception of the Rh atoms, whose thermal vibration was treated anisotropically. Hydrogen atoms were not included in the final refinement. The final values for the weighted and unweighted agreement indices are 0.102 and 0.079, respectively,<sup>32</sup> for the 333 variables and 12 330 data. Certainly, relaxation of the rigid-group approximation or assignment of individual temperature factors to the group atoms would have improved the agreement indices. The resulting slight increase in precision, however, would not have been justified by the greatly increased computing expense.

The presence of two independent  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5\text{-C}_6\text{H}_6$  units in the cell raises the question of undetected symmetry in the cell. Certainly the cell reduction did not suggest any hidden symmetry. Also, analysis of the absorption-corrected data sorted on the scattering angle failed to reveal reflections of similar intensity and  $2\theta$  values. Examination of the refined atom positions indicates that the two independent molecules are related roughly by a  $2_1$  axis.

The maximum electron density of the final difference Fourier map of 0.80 e/Å<sup>3</sup> was located in the vicinity of phenyl ring R152. This peak height is about 20% of a typical carbon atom peak. Examination of  $\sum w(|F_o| - |F_c|)^2$  for various classes of reflections based on Miller indices,  $|F_o|$ , and setting angles shows no unusual trends.

Atomic positional and thermal parameters along with their standard deviations are given in Table I. Tables II and III list derived positions for the phenyl ring carbon atoms and parameters for the rigid groups. Selected bond distances and angles are tabulated in Table IV. A table giving the final values for the observed and calculated structure amplitudes is available.<sup>33</sup>

In these tables and elsewhere each atom is uniquely named according to the following systematic numbering scheme. Nongroup atoms are designated by the chemical symbol for the atom plus one or two numbers: the first indicates of which independent molecule the atom is a part; the second number (if present) refers to the numbering scheme in Figure 1. Names for phosphine phenyl groups consist of the letter "R" followed by three numbers. The first number refers to either molecule one or two, the second refers to the phosphorus atom to which the ring is attached, and the third refers to the number of the ring on the phosphine. Names for the carbon atoms are composed of the identifier for the ring of which they are a part, plus

Table I. Positional and Thermal Parameters for the Nongroup Atoms of  $\text{Rh}_2(\text{CO}_3)(\text{P}(\text{C}_6\text{H}_5)_3)_5 \cdot \text{C}_6\text{H}_6$ 

ATOM	X <sup>A</sup>	Y	Z	B <sub>11</sub> <sup>a</sup> OR B <sub>22</sub> <sup>a</sup>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
Rh(11)	-0.11695(4)	0.17725(3)	-0.28280(7)	12.70(23)	8.10(15)	47.7(7)	-1.02(14)	7.7(3)
Rh(12)	-0.24997(4)	0.03523(3)	-0.18656(7)	12.72(22)	10.01(14)	44.8(7)	-1.99(14)	5.2(3)
Rh(21)	0.38326(4)	0.30678(3)	-0.30496(7)	14.51(24)	9.14(15)	48.0(8)	0.12(14)	6.6(3)
Rh(22)	0.24617(4)	0.44750(3)	-0.37681(8)	14.34(24)	9.98(16)	63.3(8)	0.03(15)	4.4(3)
P(11)	-0.10250(14)	0.14177(12)	-0.44963(26)	2.71(7)				
P(12)	-0.02101(14)	0.19656(12)	-0.22477(26)	2.62(7)				
P(13)	-0.15980(14)	0.23352(11)	-0.17653(25)	3.16(7)				
P(14)	-0.20613(14)	-0.00488(11)	-0.06239(25)	2.79(7)				
P(15)	-0.33735(15)	-0.00642(12)	-0.21200(27)	2.95(7)				
P(21)	0.38620(14)	0.30997(12)	-0.12226(26)	2.96(7)				
P(22)	0.48002(14)	0.29827(12)	-0.30734(26)	2.97(7)				
P(23)	0.35188(15)	0.27449(12)	-0.48043(27)	3.17(7)				
P(24)	0.29849(15)	0.51400(12)	-0.38626(27)	3.26(7)				
P(25)	0.15535(15)	0.47142(12)	-0.42440(27)	3.33(7)				
O(11)	-0.2040(3)	0.14349(27)	-0.3154(6)	2.95(17)				
O(12)	-0.2725(3)	0.08781(26)	-0.2884(6)	3.21(16)				
O(13)	-0.1813(3)	0.08806(27)	-0.2029(6)	2.90(16)				
O(21)	0.2937(3)	0.32653(23)	-0.3066(6)	3.06(17)				
O(22)	0.2213(4)	0.37659(29)	-0.3478(6)	3.81(18)				
O(23)	0.3163(3)	0.40304(28)	-0.3350(6)	3.23(17)				
C(1)	-0.2185(5)	0.1070(4)	-0.2681(9)	2.63(24)				
C(2)	0.2788(6)	0.3872(5)	-0.3289(10)	3.47(27)				

<sup>a</sup> Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. <sup>b</sup> The form of the anisotropic thermal ellipsoid is  $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$ . The quantities given in the table are the thermal coefficients  $\times 10^4$ . The minimum, intermediate, and maximum values (A) of rms displacement for the anisotropically refined atoms are as follows: Rh(11), 0.155 (2), 0.186 (2), 0.206 (1); Rh(12), 0.152 (2), 0.192 (1), 0.215 (1); Rh(21), 0.174 (2), 0.195 (2), 0.203 (1); Rh(22), 0.181 (2), 0.195 (2), 0.232 (1).

the suffix C(*I*) where *I* varies from 1 to 6.

## Results and Discussion

**Preparation of  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5$  and Its Chemical Properties.** Passing gaseous carbon dioxide through a yellow suspension of the hydridorhodium complex  $\text{RhH}(\text{PPh}_3)_4$  in toluene at about 20 °C for 10–15 days yielded an orange diamagnetic compound, which was recrystallized from benzene–diethyl ether to give red crystals. These crystals have been unambiguously characterized as the carbonato complex  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5 \cdot \text{C}_6\text{H}_6$  (Figure 1) on the basis of the x-ray structure determination (see below). Although the reaction temperature can be raised to ca. 50 °C at an initial stage of the reaction, it is important to keep it below 20 °C subsequently or an uncharacterized compound, whose infrared spectrum possesses strong bands characteristic of triphenylphosphine oxide, is produced predominantly. The reaction rate did not increase on raising the  $\text{CO}_2$  pressure up to 50 atm. Existence of a small amount of free triphenylphosphine in the reaction mixture hindered the formation of the carbonato complex. The reaction was completed in a much shorter period (several days) when  $\text{RhH}(\text{PPh}_3)_3$  was employed in place of  $\text{RhH}(\text{PPh}_3)_4$ . These results suggest that pre-dissociation of triphenylphosphine ligand from  $\text{RhH}(\text{PPh}_3)_4$  is necessary to initiate the reaction. Addition of a small amount of water affected neither the reaction rate nor the yield of the carbonato complex.

The infrared spectrum of the carbonato complex exhibits no band from  $\nu(\text{Rh}-\text{H})$  but does possess several new bands, probably from the bridging carbonato group, as follows: 1485 (s), 1460 (vs), 1360 (m), 1350 (m), 820 (w), and 500 (m)  $\text{cm}^{-1}$ . Bands at 1300 (s) and 1660 (m)  $\text{cm}^{-1}$  were observed in the Raman spectrum of the carbonato complex. These vibrational spectral data differ significantly not only from those reported for a di- $\mu$ -carbonato complex of molybdenum,  $\text{Mo}_2(\text{CO}_3)_2(\text{CO})_2(\text{PMe}_2\text{Ph})_6$ , in which the carbonato absorption is observed at 1835  $\text{cm}^{-1}$ ,<sup>23</sup> but also from a mononuclear chelate carbonato complex,  $\text{Pt}(\text{CO}_3)(\text{PPh}_3)_2$ .<sup>25</sup> Furthermore, marked differences are observed between

characteristic ir bands in the present complex and in the reported  $\text{CO}_2$ -coordinated Rh complexes, e.g., 1498 (s), 1368 (s), and 813 (s)  $\text{cm}^{-1}$  for  $\text{Rh}_2(\text{CO}_2)(\text{CO})_2(\text{PPh}_3)_3$ ,<sup>34</sup> 1600 (s), 1355 (s), and 825 (m)  $\text{cm}^{-1}$  for  $\text{Rh}_2(\text{CO}_2)_2(\text{CO})_2(\text{PPh}_3)_3 \cdot \text{C}_6\text{H}_6$ ,<sup>19</sup> 1602 (s), 1351 (s), and 821 (m)  $\text{cm}^{-1}$  for  $\text{Rh}(\text{OH})(\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ <sup>20</sup> and 1630  $\text{cm}^{-1}$  for  $\text{Rh}_2\text{Cl}_2(\text{CO}_2)(\text{PPh}_3)_5$ .<sup>10</sup>

The following chemical behavior of the carbonato complex is compatible with the observed binuclear  $\mu$ -carbonato structure. Acidolysis of the complex by concentrated sulfuric acid releases only carbon dioxide mole for mole of the starting complex. Half a mole of carbon dioxide per rhodium atom is liberated either on thermolysis or on the reaction of the complex with triphenyl phosphite. Treatment of the complex with methyl iodide releases the calculated amount of carbon dioxide per mole of the complex together with methane, evolution of which may arise from a hydride intermediate produced by ortho metalation of the triphenylphosphine ligand. The complex dissolves in pyridine to give a deep brown solution. Heating this solution at 70 °C liberates carbon dioxide and gives an unidentified complex containing pyridine and triphenylphosphine ligands. Heating the toluene solution of the complex at ca. 80 °C also causes decomposition to yield carbon dioxide and some species containing triphenylphosphine oxide. In some cases, red crystals having an approximate composition of  $\text{RhH}(\text{PPh}_3)_2(\text{OPPh}_3)_2$  were isolated from this system. Anal. Calcd for  $\text{C}_{64}\text{H}_{61}\text{O}_2\text{P}_4\text{Rh}$ : C, 70.6; H, 5.7. Found: C, 70.1; H, 5.2. Ir:  $\nu(\text{P}=\text{O})$  1180, 1120, 720  $\text{cm}^{-1}$ ;  $\nu(\text{Rh}-\text{H})$  was not observable.

<sup>31</sup>P NMR Study of  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5$ . The <sup>1</sup>H NMR spectrum of the complex shows only phenyl proton signals. A thorough examination of the high-field region using a FT mode spectrometer<sup>35</sup> did not show any indication of a signal from a possible hydride ligand.

The <sup>31</sup>P{<sup>1</sup>H}NMR spectrum of the complex in benzene, as shown in Figure 2, is compatible with the unsymmetrical dimeric structure found in the solid state. A doublet of doublets with a chemical shift of 36.3 ppm (downfield from the external free  $\text{PPh}_3$  reference) may be assigned to the

Table II. Derived Parameters for the Rigid-Group Atoms of  $\text{Rh}_2(\text{CO}_3)(\text{P}(\text{C}_6\text{H}_5)_3)_5$  Molecule 1

ATOM	X	Y	Z	$B_i^2$	ATOM	X	Y	Z	$B_i^2$
R111C1	-0.147(4)	0.0846(24)	-0.492(7)	4.64(13)	R132C4	-0.294(4)	0.309(3)	-0.404(7)	5.47(15)
R111C2	-0.177(4)	0.0721(29)	-0.594(6)	4.64(13)	R132C5	-0.299(4)	0.260(3)	-0.403(7)	5.47(15)
R111C3	-0.204(4)	0.026(3)	-0.624(5)	4.64(13)	R132C6	-0.258(4)	0.2381(24)	-0.334(8)	5.47(15)
R111C4	-0.202(4)	-0.0074(24)	-0.551(7)	4.64(13)	R133C1	-0.210(4)	0.212(4)	-0.087(8)	6.37(17)
R111C5	-0.172(4)	0.0051(29)	-0.449(6)	4.64(13)	R133C2	-0.196(4)	0.172(4)	-0.037(9)	6.37(17)
R111C6	-0.145(4)	0.051(3)	-0.419(5)	4.64(13)	R133C3	-0.232(5)	0.155(3)	0.032(8)	6.37(17)
R112C1	-0.130(4)	0.1820(29)	-0.549(6)	4.59(13)	R133C4	-0.243(4)	0.179(4)	0.051(8)	6.37(17)
R112C2	-0.162(4)	0.221(3)	-0.514(5)	4.59(13)	R133C5	-0.297(4)	0.219(4)	0.000(9)	6.37(17)
R112C3	-0.184(4)	0.2524(27)	-0.584(7)	4.59(13)	R133C6	-0.261(5)	0.236(3)	-0.069(8)	6.37(17)
R112C4	-0.175(4)	0.246(3)	-0.689(6)	4.59(13)	R141C1	-0.1375(28)	0.026(3)	0.014(6)	3.98(12)
R112C5	-0.143(4)	0.207(3)	-0.724(5)	4.59(13)	R141C2	-0.089(4)	0.034(3)	-0.040(5)	3.98(12)
R112C6	-0.121(4)	0.1752(27)	-0.655(7)	4.59(13)	R141C3	-0.034(3)	0.054(3)	0.014(6)	3.98(12)
R113C1	-0.032(3)	0.125(3)	-0.500(7)	4.19(12)	R141C4	-0.0277(28)	0.067(3)	0.123(6)	3.98(12)
R113C2	-0.017(3)	0.0776(26)	-0.514(7)	4.19(12)	R141C5	-0.076(4)	0.061(3)	0.177(5)	3.98(12)
R113C3	0.033(4)	0.0654(22)	-0.561(7)	4.19(12)	R141C6	-0.131(3)	0.041(3)	0.123(6)	3.98(12)
R113C4	0.068(3)	0.101(3)	-0.595(7)	4.19(12)	R142C1	-0.175(4)	-0.0625(23)	-0.099(7)	4.39(13)
R113C5	0.054(3)	0.1488(26)	-0.580(7)	4.19(12)	R142C2	-0.193(4)	-0.085(3)	-0.201(6)	4.39(13)
R113C6	0.004(4)	0.1610(22)	-0.533(7)	4.19(12)	R142C3	-0.174(4)	-0.130(3)	-0.232(5)	4.39(13)
R121C1	-0.006(4)	0.211(3)	-0.078(5)	4.58(13)	R142C4	-0.136(4)	-0.1527(23)	-0.160(7)	4.39(13)
R121C2	0.020(4)	0.2511(29)	-0.025(7)	4.58(13)	R142C5	-0.117(4)	-0.130(3)	-0.058(6)	4.39(13)
R121C3	0.034(4)	0.2598(26)	0.084(7)	4.58(13)	R142C6	-0.137(4)	-0.085(3)	-0.028(5)	4.39(13)
R121C4	0.007(4)	0.228(3)	0.142(5)	4.58(13)	R143C1	-0.250(4)	-0.017(3)	0.044(6)	4.66(13)
R121C5	-0.027(4)	0.1875(29)	0.090(7)	4.58(13)	R143C2	-0.251(4)	-0.0591(29)	0.091(7)	4.66(13)
R121C6	-0.034(4)	0.1788(26)	-0.020(7)	4.58(13)	R143C3	-0.288(4)	-0.0656(26)	0.167(7)	4.66(13)
R122C1	0.021(4)	0.1414(23)	-0.243(7)	4.06(12)	R143C4	-0.325(4)	-0.030(3)	0.196(6)	4.66(13)
R122C2	-0.0090(28)	0.099(3)	-0.227(7)	4.06(12)	R143C5	-0.325(4)	0.0129(28)	0.149(7)	4.66(13)
R122C3	0.018(4)	0.0555(23)	-0.261(7)	4.06(12)	R143C6	-0.287(4)	0.0194(25)	0.073(7)	4.66(13)
R122C4	0.075(4)	0.0548(23)	-0.271(7)	4.06(12)	R151C1	-0.397(4)	0.026(3)	-0.155(8)	5.55(15)
R122C5	0.1052(28)	0.097(3)	-0.287(7)	4.06(12)	R151C2	-0.454(5)	0.0059(26)	-0.157(8)	5.55(15)
R122C6	0.078(4)	0.1487(23)	-0.273(7)	4.06(12)	R151C3	-0.496(3)	0.032(4)	-0.108(8)	5.55(15)
R123C1	0.023(4)	0.244(3)	-0.276(7)	4.89(13)	R151C4	-0.480(4)	0.078(3)	-0.058(8)	5.55(15)
R123C2	0.084(4)	0.255(3)	-0.240(6)	4.89(13)	R151C5	-0.423(5)	0.0983(26)	-0.056(8)	5.55(15)
R123C3	0.1145(29)	0.290(3)	-0.286(7)	4.89(13)	R151C6	-0.381(3)	0.072(4)	-0.105(8)	5.55(15)
R123C4	0.085(4)	0.313(3)	-0.367(7)	4.89(13)	R152C1	-0.368(5)	-0.020(4)	-0.355(7)	7.44(19)
R123C5	0.024(4)	0.301(3)	-0.403(6)	4.89(13)	R152C2	-0.337(4)	-0.002(4)	-0.430(10)	7.44(19)
R123C6	-0.0067(29)	0.266(3)	-0.357(7)	4.89(13)	R152C3	-0.360(5)	-0.012(4)	-0.537(9)	7.44(19)
R131C1	-0.116(5)	0.285(3)	-0.093(8)	6.44(17)	R152C4	-0.414(5)	-0.039(4)	-0.569(7)	7.44(19)
R131C2	-0.122(4)	0.296(4)	0.012(9)	6.44(17)	R152C5	-0.445(4)	-0.057(4)	-0.494(10)	7.44(19)
R131C3	-0.091(5)	0.337(4)	0.070(6)	6.44(17)	R152C6	-0.422(5)	-0.048(4)	-0.387(9)	7.44(19)
R131C4	-0.053(4)	0.366(3)	0.022(8)	6.44(17)	R153C1	-0.350(4)	-0.0673(26)	-0.174(8)	5.29(14)
R131C5	-0.047(4)	0.354(4)	-0.084(9)	6.44(17)	R153C2	-0.332(4)	-0.106(4)	-0.237(6)	5.29(14)
R131C6	-0.078(5)	0.313(4)	-0.142(6)	6.44(17)	R153C3	-0.336(4)	-0.152(3)	-0.205(7)	5.29(14)
R132C1	-0.214(4)	0.266(3)	-0.265(7)	5.47(15)	R153C4	-0.357(4)	-0.1591(26)	-0.111(8)	5.29(14)
R132C2	-0.209(4)	0.316(3)	-0.266(7)	5.47(15)	R153C5	-0.374(4)	-0.120(4)	-0.048(6)	5.29(14)
R132C3	-0.250(4)	0.3373(24)	-0.335(8)	5.47(15)	R153C6	-0.371(4)	-0.074(3)	-0.079(7)	5.29(14)

## RIGID GROUP PARAMETERS

GROUP	$X_C^A$	$Y_C^A$	$Z_C^A$	$\Delta^B$	EPSILON	ETA
R11	-0.17450(24)	0.03860(22)	-0.5214(5)	-2.45338(19)	-2.05403(9)	-0.47154(19)
R12	-0.15240(24)	0.21380(21)	-0.6191(5)	-2.46344(16)	2.21384(9)	-1.75181(16)
R13	0.01830(24)	0.11320(21)	-0.5471(4)	-0.20106(8)	3.01277(9)	-0.59059(9)
R121	0.00040(24)	0.21930(21)	0.0323(5)	2.53787(9)	-3.02974(9)	1.62603(9)
R122	0.04810(24)	0.09810(20)	-0.2568(4)	-1.03551(8)	2.77484(9)	-0.20427(10)
R123	0.05390(27)	0.27810(21)	-0.3216(5)	1.30009(11)	2.61912(10)	-0.60196(11)
R131	-0.08470(29)	0.32520(25)	-0.0357(6)	-0.98615(22)	2.07720(11)	1.91623(22)
R132	-0.25400(28)	0.28770(24)	-0.3345(5)	2.65251(10)	2.83921(10)	-0.60322(11)
R133	-0.2465(3)	0.19550(25)	-0.0184(5)	0.64805(11)	3.06289(11)	2.33767(11)
R141	-0.08260(25)	0.04760(18)	0.0684(4)	1.55865(23)	-1.97130(8)	1.24917(23)
R142	-0.15540(24)	-0.10760(20)	-0.1298(5)	-1.80132(16)	-2.13799(9)	-0.64574(17)
R143	-0.28770(25)	-0.02310(21)	0.1199(4)	0.34622(9)	3.09416(9)	2.24261(10)
R151	-0.43840(29)	0.05210(24)	-0.1065(5)	-0.76159(10)	-2.96724(10)	2.55370(11)
R152	-0.3910(3)	-0.02970(26)	-0.4620(6)	2.15858(13)	-2.78964(13)	-1.43119(13)
R153	-0.35320(25)	-0.11320(23)	-0.1421(5)	0.87894(21)	-2.05337(10)	2.44777(21)

$X_C^A$ ,  $Y_C^A$ , AND  $Z_C^A$  ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP.  $\Delta^B$  THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA (RADIAN) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

mutually trans  $P_a$  phosphorus nuclei which are cis from the oxygen atom of the bridging carbonato group and the  $P_b$  ligand. The  $P_b$  resonance is partly obscured in the slope of the  $P_c$  signal but a triplet and a part of another triplet, which constitute together a doublet of triplets, are discernible. These signals are best accounted for by assuming the  $\text{AMX}_2$  spin system in which  $P_b$ , Rh ( $I = 1/2$ ), and  $P_a$  nuclei constitute the A, M, and  $X_2$  portions, respectively.

The other part of the spectrum which shows an apparent doublet of doublets in Figure 2 is from the  $\text{Rh}(\text{PPh}_3)_2$  portion

of the dinuclear complex. A close examination of the spectrum reveals that this portion is not a doublet of doublets but rather two pairs of doublets. The doublet which appears at the higher field with the greater intensity may be assigned to the  $P_c$  ligands, which are mutually cis and coupled with the Rh(2) atom. The other doublet labeled  $P_d$  in Figure 2 with a  $|^2J(\text{Rh}-P_d)|$  value of 189 Hz varied in its intensity from one sample to the other and is considered to be associated with a yet unidentified species formed by dissociation or partial decomposition of the carbonato complex. Heating the benzene

Table III. Derived Parameters for the Rigid-Group Atoms of  $\text{Rh}_2(\text{CO}_3)(\text{P}(\text{C}_6\text{H}_5)_3)_2$  Molecule 2 plus Solvate Benzene Molecules

ATOM	X	Y	Z	$B_1 A^2$	ATOM	X	Y	Z	$B_1 A^2$
R211C1	0.378(4)	0.3677(25)	-0.044(7)	4.74(13)	R233C4	0.479(4)	0.208(3)	-0.703(6)	4.25(12)
R211C2	0.370(4)	0.408(3)	-0.099(5)	4.74(13)	R233C5	0.446(4)	0.247(3)	-0.731(5)	4.25(12)
R211C3	0.364(4)	0.4524(27)	-0.045(7)	4.74(13)	R233C6	0.408(4)	0.2668(26)	-0.664(7)	4.25(12)
R211C4	0.365(4)	0.4573(25)	0.064(7)	4.74(13)	R241C1	0.292(5)	0.568(3)	-0.305(7)	5.93(16)
R211C5	0.373(4)	0.417(3)	0.120(5)	4.74(13)	R241C2	0.257(5)	0.5610(29)	-0.214(8)	5.93(16)
R211C6	0.379(4)	0.3726(27)	0.066(7)	4.74(13)	R241C3	0.245(4)	0.600(4)	-0.146(7)	5.93(16)
R212C1	0.449(4)	0.286(3)	-0.037(7)	5.21(14)	R241C4	0.257(5)	0.647(3)	-0.169(7)	5.93(16)
R212C2	0.494(4)	0.3173(24)	0.022(8)	5.21(14)	R241C5	0.282(5)	0.6540(28)	-0.260(8)	5.93(16)
R212C3	0.543(4)	0.299(3)	0.079(7)	5.21(14)	R241C6	0.294(4)	0.615(4)	-0.328(6)	5.93(16)
R212C4	0.546(4)	0.249(3)	0.078(7)	5.21(14)	R242C1	0.3793(28)	0.512(3)	-0.334(7)	4.85(13)
R212C5	0.501(4)	0.2183(24)	0.019(8)	5.21(14)	R242C2	0.413(4)	0.487(3)	-0.395(6)	4.85(13)
R212C6	0.452(4)	0.237(3)	-0.038(7)	5.21(14)	R242C3	0.475(4)	0.482(3)	-0.364(7)	4.85(13)
R213C1	0.322(4)	0.270(3)	-0.101(8)	5.87(15)	R242C4	0.5025(28)	0.509(3)	-0.272(7)	4.85(13)
R213C2	0.296(4)	0.273(3)	-0.008(7)	5.87(15)	R242C5	0.468(4)	0.538(3)	-0.210(6)	4.85(13)
R213C3	0.249(4)	0.242(4)	0.004(6)	5.87(15)	R242C6	0.407(4)	0.539(3)	-0.241(7)	4.85(13)
R213C4	0.227(4)	0.206(3)	-0.078(8)	5.87(15)	R243C1	0.337(4)	0.533(3)	-0.518(5)	4.86(13)
R213C5	0.252(5)	0.202(3)	-0.171(7)	5.87(15)	R243C2	0.267(3)	0.511(3)	-0.605(7)	4.86(13)
R213C6	0.300(4)	0.234(4)	-0.183(6)	5.87(15)	R243C3	0.274(4)	0.521(3)	-0.706(6)	4.86(13)
R221C1	0.530(4)	0.340(3)	-0.208(6)	4.90(13)	R243C4	0.321(4)	0.553(3)	-0.721(5)	4.86(13)
R221C2	0.510(3)	0.386(3)	-0.184(7)	4.90(13)	R243C5	0.361(3)	0.574(3)	-0.635(7)	4.86(13)
R221C3	0.545(4)	0.4189(25)	-0.109(7)	4.90(13)	R243C6	0.354(4)	0.564(3)	-0.533(6)	4.86(13)
R221C4	0.599(4)	0.406(3)	-0.057(6)	4.90(13)	R251C1	0.137(5)	0.526(3)	-0.490(9)	6.64(17)
R221C5	0.619(3)	0.361(3)	-0.081(7)	4.90(13)	R251C2	0.148(5)	0.571(4)	-0.431(6)	6.64(17)
R221C6	0.585(4)	0.3277(25)	-0.156(7)	4.90(13)	R251C3	0.137(5)	0.512(3)	-0.441(9)	6.64(17)
R222C1	0.505(4)	0.319(3)	-0.429(6)	4.76(13)	R251C4	0.117(5)	0.608(3)	-0.549(9)	6.64(17)
R222C2	0.480(4)	0.361(3)	-0.459(7)	4.76(13)	R251C5	0.107(5)	0.563(4)	-0.647(6)	6.64(17)
R222C3	0.493(4)	0.3786(26)	-0.551(7)	4.76(13)	R251C6	0.117(5)	0.522(3)	-0.598(9)	6.64(17)
R222C4	0.532(4)	0.355(3)	-0.512(6)	4.76(13)	R252C1	0.108(4)	0.476(4)	-0.319(7)	5.69(15)
R222C5	0.556(4)	0.313(3)	-0.582(7)	4.76(13)	R252C2	0.114(4)	0.441(3)	-0.250(8)	5.69(15)
R222C6	0.543(4)	0.2950(26)	-0.490(7)	4.76(13)	R252C3	0.078(5)	0.441(3)	-0.169(7)	5.69(15)
R223C1	0.509(4)	0.2384(25)	-0.295(8)	5.27(14)	R252C4	0.036(4)	0.475(4)	-0.159(7)	5.69(15)
R223C2	0.568(4)	0.227(3)	-0.304(8)	5.27(14)	R252C5	0.030(4)	0.510(3)	-0.227(8)	5.69(15)
R223C3	0.584(3)	0.180(4)	-0.299(8)	5.27(14)	R252C6	0.056(5)	0.511(3)	-0.307(7)	5.69(15)
R223C4	0.542(4)	0.1442(25)	-0.285(8)	5.27(14)	R253C1	0.111(4)	0.424(4)	-0.517(7)	4.97(14)
R223C5	0.483(4)	0.156(3)	-0.276(8)	5.27(14)	R253C2	0.048(4)	0.423(3)	-0.533(7)	4.97(14)
R223C6	0.467(3)	0.203(4)	-0.280(8)	5.27(14)	R253C3	0.0155(28)	0.387(3)	-0.505(8)	4.97(14)
R231C1	0.310(4)	0.312(3)	-0.571(7)	5.19(14)	R253C4	0.045(4)	0.353(3)	-0.622(7)	4.97(14)
R231C2	0.270(4)	0.2914(24)	-0.658(8)	5.19(14)	R253C5	0.108(4)	0.355(3)	-0.646(7)	4.97(14)
R231C3	0.247(4)	0.320(3)	-0.735(6)	5.19(14)	R253C6	0.1405(28)	0.390(3)	-0.574(8)	4.97(14)
R231C4	0.264(4)	0.369(3)	-0.724(7)	5.19(14)	BNZ1C1	-0.374(7)	0.140(5)	0.246(8)	9.78(25)
R231C5	0.303(4)	0.3890(24)	-0.636(8)	5.19(14)	BNZ1C2	-0.416(5)	0.110(5)	0.300(11)	9.78(25)
R231C6	0.327(4)	0.361(3)	-0.560(6)	5.19(14)	BNZ1C3	-0.406(6)	0.096(4)	0.401(13)	9.78(25)
R232C1	0.296(4)	0.225(3)	-0.474(8)	5.73(15)	BNZ1C4	-0.353(7)	0.111(5)	0.467(8)	9.78(25)
R232C2	0.308(3)	0.177(4)	-0.488(8)	5.73(15)	BNZ1C5	-0.310(5)	0.141(5)	0.433(11)	9.78(25)
R232C3	0.264(5)	0.1411(26)	-0.481(8)	5.73(15)	BNZ1C6	-0.321(6)	0.156(4)	0.33(4)	9.78(25)
R232C4	0.207(4)	0.154(3)	-0.460(8)	5.73(15)	BNZ2C1	0.134(8)	0.372(6)	0.060(16)	13.5(3)
R232C5	0.195(3)	0.202(4)	-0.446(8)	5.73(15)	BNZ2C2	0.177(7)	0.367(9)	-0.008(12)	13.5(3)
R232C6	0.239(5)	0.2375(26)	-0.453(8)	5.73(15)	BNZ2C3	0.210(9)	0.407(5)	-0.370(14)	13.5(3)
R233C1	0.402(4)	0.248(3)	-0.570(6)	4.25(12)	BNZ2C4	0.200(8)	0.453(6)	0.018(16)	13.5(3)
R233C2	0.435(4)	0.209(3)	-0.542(5)	4.25(12)	BNZ2C5	0.157(7)	0.458(9)	0.046(12)	13.5(3)
R233C3	0.474(4)	0.1894(26)	-0.609(7)	4.25(12)	BNZ2C6	0.124(9)	0.418(5)	0.107(14)	13.5(3)

## RIGID GROUP PARAMETERS

GROUP	$X_C^A$	$Y_C^A$	$Z_C^A$	$\Delta^B$	$\epsilon^B$	$\eta^B$
R211	0.37150(23)	0.41250(22)	0.0133(5)	-2.97736(18)	-2.10694(3)	1.61337(18)
R212	0.49750(28)	0.26780(23)	0.0237(5)	2.72358(10)	2.87814(10)	2.70152(10)
R213	0.27430(28)	0.23780(23)	-0.0896(5)	3.23028(28)	1.94310(11)	0.62793(28)
R221	0.56460(27)	0.37330(22)	-0.1325(5)	-2.39128(9)	-3.09042(9)	2.48681(10)
R222	0.51810(25)	0.33680(21)	-0.5206(5)	-2.49837(10)	-2.89017(9)	-2.02331(10)
R223	0.52580(28)	0.19130(23)	-0.2898(4)	1.83326(10)	-2.87914(10)	-3.14762(11)
R231	0.28660(25)	0.34020(23)	-0.6472(5)	-0.62704(11)	-2.67978(10)	-2.33191(11)
R232	0.2515(3)	0.18930(25)	-0.4672(5)	0.72554(10)	-2.86053(10)	2.96716(11)
R233	0.44080(24)	0.22810(20)	-0.6367(4)	0.32428(11)	2.48512(9)	-1.08725(12)
R241	0.26920(26)	0.60750(25)	-0.2367(5)	-0.46834(14)	2.42960(11)	2.10200(14)
R242	0.44090(27)	0.51050(21)	-0.3027(5)	0.11000(16)	-2.17171(10)	0.25626(16)
R243	0.31380(26)	0.54260(20)	-0.6197(5)	-0.97890(10)	-2.87522(9)	-1.75434(10)
R251	0.12710(27)	0.56720(27)	-0.5391(6)	2.58566(21)	2.14301(12)	-0.91755(12)
R252	0.07200(28)	0.47570(23)	-0.2384(5)	0.46687(11)	2.89687(10)	2.13784(11)
R253	0.07800(26)	0.38870(22)	-0.5896(5)	-2.00522(10)	2.79492(10)	-0.67347(11)
BNZ1	-0.3634(4)	0.1258(3)	0.3665(8)	-1.08199(15)	3.18596(17)	1.12421(14)
BNZ2	0.1671(5)	0.4126(4)	0.0389(8)	0.7280(4)	-2.38908(19)	-0.3820(3)

<sup>A</sup>  $X_C$ ,  $Y_C$ , AND  $Z_C$  ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP, <sup>B</sup> THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA (RADIAN) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, *ACTA CRYSTALLOGR.*, 18, 511(1965).

solution at 80 °C caused the complete broadening of the  $P_A$ ,  $P_B$ , and  $P_C$  signals, whereas the peaks  $P_D$  and that of free triphenylphosphine oxide (observed at 30.7 ppm), which may

be present in the system as impurity, remained unchanged. Cooling the system caused the reappearance of the  $P_A$ ,  $P_B$ , and  $P_C$  signals indicating the exchange of the coordinated tri-

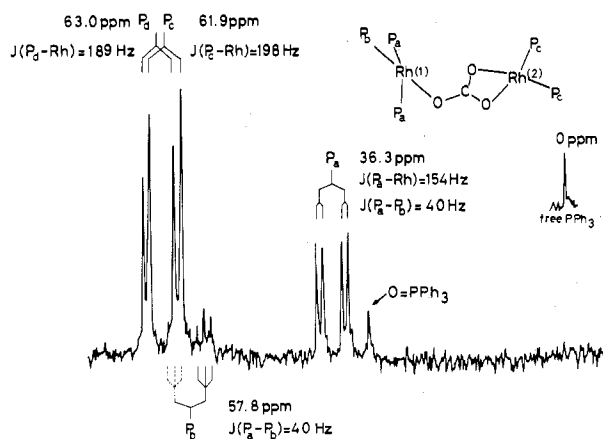


Figure 2.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5\cdot\text{C}_6\text{H}_6$  in  $\text{C}_6\text{H}_6$  at 25 °C.

phenylphosphine ligands with each other at the higher temperature. Prolonged heating of the solution at 80 °C, however, caused a considerable irreversible increase in the intensity of the  $\text{P}_d$  signals at the expense of the signals  $\text{P}_a$ ,  $\text{P}_b$ , and  $\text{P}_c$ . The intensity of the signal of free triphenylphosphine oxide did not change significantly throughout this process. Evolution of  $\text{CO}_2$  by heating the benzene solution at 80 °C for several hours was confirmed by gas chromatography. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the carbonato complex in pyridine at room temperature showed only signals of  $\text{P}_d$  and triphenylphosphine oxide. This may result from the exchange of the triphenylphosphine ligands in pyridine. Heating the pyridine solution to 70 °C caused the evolution of carbon dioxide from the complex.

The main features of the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the benzene solution of the rhodium complex are in agreement with the unsymmetrical binuclear structure of the rhodium(I)-carbonato complex in the following aspects. The chemical shifts of  $\text{P}_a$ ,  $\text{P}_b$ , and  $\text{P}_c$  are normal for  $\text{Rh}(\text{I})$  complexes as compared with reported values for  $\text{RhX}(\text{PPh}_3)_3$ , where X stands for halogen.<sup>36</sup> The  $|J(\text{Rh}-\text{P})|$  coupling constant is known to be sensitive to the nature of the ligand trans to the phosphorus nucleus but insensitive to the cis ligand.<sup>36-38</sup>  $|J(\text{Rh}-\text{P})|$  values of 139–142 Hz for mutually trans P ligands in  $\text{RhX}(\text{PPh}_3)_3$  and of 189–194 Hz for the P ligand trans to X have been reported.<sup>36</sup> The observed value of  $|J(\text{Rh}-\text{P}_a)|$  of 154 Hz is therefore reasonable for the trans P ligands here.

The P atoms trans to the carbonato group would be expected to have coupling constants with the Rh atom similar to the

Table IV. Selected Bond Distances and Angles in  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5$

Atoms	Distances, Å		
	Molecule 1	Molecule 2	Average
Rh(1)–P(1)	2.335 (4)	2.330 (4)	2.328 (13) <sup>a</sup>
Rh(1)–P(3)	2.309 (4)	2.337 (4)	
Rh(1)–P(2)	2.209 (3)	2.207 (3)	2.208 (3)
Rh(1)–O(1)	2.105 (7)	2.113 (7)	2.109 (7)
C–O(1)	1.295 (12)	1.255 (13)	
C–O(2)	1.290 (12)	1.328 (13)	1.290 (24)
C–O(3)	1.275 (12)	1.299 (13)	
Rh(2)–P(4)	2.199 (3)	2.183 (5)	2.199 (9)
Rh(2)–P(5)	2.207 (3)	2.208 (5)	
Rh(2)–O(2)	2.107 (8)	2.126 (8)	
Rh(2)–O(3)	2.138 (7)	2.104 (7)	2.119 (16)

Atoms	Angles, deg		
	Molecule 1	Molecule 2	Average
P(1)–Rh(1)–P(2)	95.9 (1)	96.7 (1)	96.3 (5)
P(1)–Rh(1)–P(3)	151.0 (1)	154.4 (1)	152.7 (24)
P(1)–Rh(1)–O(1)	86.4 (2)	85.5 (2)	86.0 (6)
P(2)–Rh(1)–P(3)	99.7 (1)	96.2 (1)	97.9 (25)
P(2)–Rh(1)–O(1)	165.0 (2)	170.8 (2)	167.9 (41)
P(3)–Rh(1)–O(1)	84.7 (2)	85.3 (2)	85.0 (4)
Rh(1)–O(1)–C	121.0 (7)	121.2 (8)	121.1 (8)
O(1)–C–O(2)	119.4 (10)	120.9 (11)	120.1 (11)
O(1)–C–O(3)	123.3 (10)	124.6 (11)	123.9 (9)
O(2)–C–O(3)	117.3 (10)	114.5 (11)	115.9 (20)
C–O(2)–Rh(2)	90.8 (7)	90.4 (7)	90.6 (7)
C–O(3)–Rh(2)	89.8 (7)	92.1 (7)	90.9 (16)
P(4)–Rh(2)–P(5)	96.7 (1)	98.9 (1)	97.8 (15)
P(4)–Rh(2)–O(2)	164.2 (2)	162.5 (2)	163.3 (12)
P(4)–Rh(2)–O(3)	102.9 (2)	99.8 (2)	101.3 (22)
P(5)–Rh(2)–O(2)	98.4 (2)	98.4 (2)	98.4 (2)
P(5)–Rh(2)–O(3)	160.4 (2)	161.1 (2)	160.8 (5)
O(2)–Rh(2)–O(3)	62.1 (3)	63.0 (3)	62.6 (6)

<sup>a</sup> The number in parentheses is the standard deviation of a single observation. It is the larger of (1) the quantity estimated from the values averaged on the assumption that they are from the same population or (2) the average standard deviation as estimated from the inverse matrix.

values found for the P atom trans to the X atom in the above examples. In fact, the nitrate ligand, which is obviously similar to the carbonate species, has been shown to cause an even larger increase in the Rh–P coupling constant of the P atom trans to it than do halide ligands.<sup>39</sup> It is not surprising then to find  $|J(\text{Rh}-\text{P}_c)|$  equal to 198 Hz, slightly larger than the corresponding values in the  $\text{RhX}(\text{PPh}_3)_3$  compounds. Although the  $|J(\text{Rh}-\text{P}_b)|$  value was not measured precisely owing to partial overlap with the intense  $\text{P}_c$  signals, it appears to have a value larger than  $|J(\text{Rh}-\text{P}_a)|$  and close to  $|J(\text{Rh}-\text{P}_c)|$ .

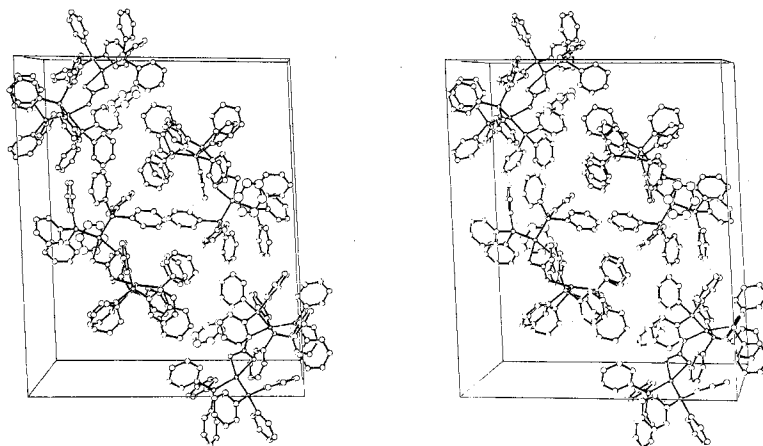


Figure 3. Stereoscopic packing diagram of  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5\cdot\text{C}_6\text{H}_6$ . The atom shapes represent 20% probability contours of thermal motion. Hydrogen atoms have been omitted for the sake of clarity. The x axis is horizontal and to the right, the y axis is vertical, and the z axis is out of the page.

**Table V.** Closest Contacts between the Phosphine Hydrogen Atoms and the Conjectured Hydride Positions<sup>a</sup>

Hydride	Phosphine hydrogen <sup>b</sup>	Distance, <sup>c</sup> Å
Rh(11)H1	R122H2	1.6
Rh(11)H2	R112H2	1.3
Rh(12)H1	R151H6	1.6
Rh(12)H2	R142H2	2.0
Rh(21)H1	R222H2	1.9
Rh(21)H2	R213H6	1.4
Rh(22)H1	R241H2	1.8
Rh(22)H2	R253H6	1.9

<sup>a</sup> See text for description of idealized geometry. <sup>b</sup> Hydrogen atom  $RwxyHz$  is bound to carbon atom  $RwxyzCz$ . <sup>c</sup> These distances may be compared with a value of 2.4 Å for the sum of two hydrogen van der Waals radii.<sup>58</sup>

Finally,  $|J(\text{Rh-P})|$  values of Rh(I) complexes are known to be larger than those of Rh(III) by a factor of ca. 1.5, owing to the larger fraction of both  $\sigma$  and  $\pi$  character of the rhodium bonding orbitals in four-coordinate Rh(I) complexes than in six-coordinate Rh(III) complexes.<sup>36-38</sup> A similar decrease in coupling constants is also seen when going from four-coordinate Pt(II) complexes to six-coordinate Pt(IV) complexes.<sup>37</sup> In the present case both  $|J(\text{Rh-P}_a)|$  and  $|J(\text{Rh-P}_c)|$  are in the Rh(I) range, excluding a possible rhodium(III) dihydride structure (also, see below).

**Description and Discussion of Structure.** Discrete molecules of  $\text{Rh}_2(\text{CO})_3(\text{PPh}_3)_5$  occupy general positions in the unit cell, as do the solvate benzene molecules. Figure 3 shows a stereoview of the molecular packing in the unit cell. The only unusual nonbonded contacts occur between oxygen atoms and hydrogen atoms on the phenyl rings. Two of the O---H atom distances are about 2.3 Å and therefore fall in the range expected for weak hydrogen bonds.<sup>40</sup> The minimization of nonbonded contacts between the phenyl rings is, however, the most important factor influencing their orientation.

The coordination about both rhodium atoms is best described as square planar, although the Rh(1)<sup>41</sup> coordination is slightly distorted toward tetrahedral geometry. A square-planar ligand arrangement is, of course, the normal geometry for four-coordinate  $d^8$  Rh(I) (see Figure 1). Consideration of steric factors shows that the fifth and sixth coordination positions of the rhodium atoms are not occupied by hydride ligands as might be implied from the original formulation of the compound.<sup>5</sup> Assuming normal phenyl ring geometry with a C-H bond length of 0.95 Å and a Rh-H bond length of 1.65 Å, unreasonably short hydrogen-hydrogen contacts are calculated. These contacts are given in Table V.

If the orientations of the phenyl rings are ignored, the molecule is seen to contain a mirror plane. This plane contains atoms Rh(1), Rh(2), P(2), P(4), P(5), and the carbonate group atoms (Table VI). The least-squares plane of the Rh(1) coordination sphere makes an angle of 87° with this pseudo mirror plane (Table VI).

The Rh-P bond lengths for the phosphine ligands trans to each other are normal.<sup>42,43</sup> They range from 2.309 (4) to 2.337 (4) Å. For the phosphine groups trans to the oxygen atoms of the carbonate groups, the average Rh-P distance is 2.202 Å. This shortening of the Rh-P bond length from the value for the mutually trans phosphine groups to the value for the phosphorus atom trans to an oxygen atom is also observed in the structure of benzoatotris(triphenylphosphine)rhodium.<sup>13</sup> Platinum(II) compounds also exhibit a similar trend. For example, the Pt-P bond distance in *trans*-PtCl(CO)(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub><sup>+</sup> is 2.34 Å.<sup>44</sup> This distance however decreases to 2.24 Å in *cis*-Pt(CO<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>.<sup>45</sup> Rather short Rh-P bond distances of 2.218 (8) and 2.211 (2) Å are also found for the

**Table VI.** Least-Squares Planes with Dihedral Angles

Atom <sup>a</sup>	Dev, Å	Atom <sup>a</sup>	Dev, Å
Plane 11: <sup>b</sup> $8.851x - 15.434y - 9.393z + 1.059 = 0$			
C(1)	-0.008 (10)	O(12)	0.001 (7)
O(11)	0.001 (8)	O(13)	0.001 (7)
Plane 21: $-3.177x + 5.480y + 12.254z + 2.901 = 0$			
C(2)	-0.002 (12)	O(22)	0.000 (8)
O(21)	0.000 (8)	O(23)	0.000 (8)
Plane 12: $-0.730x - 23.801y + 7.918z + 6.429 = 0$			
Rh(11)	0.057 (1)	P(13)	-0.410 (3)
P(11)	-0.430 (3)	O(11)	0.666 (8)
P(12)	-0.013 (3)		
Plane 22: $1.983x + 27.648y - 2.893z - 10.075 = 0$			
Rh(21)	0.049 (1)	P(23)	-0.398 (3)
P(21)	-0.385 (3)	O(21)	0.423 (6)
P(22)	0.013 (3)		
Plane 13: $10.227x - 15.795y - 8.943z + 1.449 = 0$			
Rh(12)	0.004 (1)	O(12)	-0.146 (8)
P(14)	-0.025 (3)	O(13)	0.018 (8)
P(15)	-0.004 (3)		
Plane 23: $4.790x - 5.623y - 12.207z - 3.263 = 0$			
Rh(22)	0.000 (1)	O(22)	-0.075 (8)
P(24)	-0.008 (3)	O(23)	0.075 (8)
P(25)	0.011 (3)		
Plane 14: $9.760x - 15.481y - 9.181z + 1.280 = 0$			
Rh(11)	-0.009 (1)	O(11)	-0.037 (8)
Rh(12)	0.008 (1)	O(12)	-0.091 (8)
P(12)	0.096 (3)	O(13)	0.010 (8)
P(14)	-0.083 (3)	P(11)*	2.213
P(15)	0.033 (3)	P(13)*	-2.274
C(1)	-0.048 (10)		
Plane 24: $-1.931x + 4.430y + 12.365z + 3.165 = 0$			
Rh(21)	0.013 (1)	O(21)	0.252 (8)
Rh(22)	0.013 (1)	O(22)	0.105 (8)
P(22)	-0.241 (3)	O(23)	0.197 (8)
P(24)	0.089 (3)	P(21)*	2.280
P(25)	-0.295 (3)	P(23)*	-2.239
C(2)	0.187 (12)		

Plane <sup>c</sup>	Dihedral angles, deg		
	2	3	4
11	87.3	4.3	2.7
21	85.7	4.2	3.8
12		85.6	86.7
22		85.9	87.5
13			1.8
23			7.7

<sup>a</sup> The atoms marked with an asterisk were not included in the calculations of the least-squares plane. <sup>b</sup> In the nomenclature for the planes, the first number refers to either molecule 1 or 2 and the second number serves to identify the plane within the molecule. <sup>c</sup> Only dihedral angles between planes within the same molecule are tabulated.

phosphine group trans to the chlorine atom in  $\text{RhCl}(\text{PPh}_3)_3$ <sup>42</sup> and  $\text{RhCl}((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2$ ,<sup>46</sup> respectively. These results are consistent with the relatively small trans influence and negligible  $\pi$ -bonding capabilities of the carbonate group in accordance with <sup>31</sup>P NMR spectral results (see above). The phosphorus ligand, however, does have an effect on the Rh-O bond trans to it. The compounds tetrakis( $\mu$ -acetato)-diaquodirrhodium and potassium tris(oxalato)-rhodite(III) can be taken as examples where the Rh-O bond experiences little trans influence. The average Rh-O bond length is 2.04 Å in the former<sup>47</sup> and 2.016 Å in the latter.<sup>48</sup> In contrast is acetatobis(phenylazophenyl-2C,N')rhodium(II), where the oxygen atoms of the acetate group are trans to the stabilizing ortho-metalated phenyl rings. There, the Rh-O bond distance lengthens to an average value of 2.230 Å.<sup>49</sup> The average Rh-O bond length in the compound reported here of

2.12 Å is intermediate in value.

Three other compounds, each with a tridentate bridging carbonate group similar to that found here, have previously been structurally characterized.<sup>23,51,52</sup> Here, as in the other structures, the carbonate moiety is essentially planar. Generally, four-membered ring formation causes the carbonate O–C–O bond angle to decrease from 120° to an average of 113°. The O(2)–C–O(3) angle reported here of 116° may represent a decrease from 120°. The average O(2)–Rh(2)–O(3) bond angle here of 62.6° is similar to the 64.0° angle found in the four-membered ring of the square-planar complex  $\text{Pt}(\text{CO}_3)(\text{PPh}_3)_2$ .<sup>45</sup> In other structures containing a metal-bonded carbonate group, the C–O bond length in the carbonate moiety has ranged from 1.36 (2)<sup>57</sup> to 1.245 (3) Å<sup>51</sup> depending on the strength of the various oxygen–metal interactions. Unfortunately, little can be said concerning the carbonate C–O bond distances here because of deviations in lengths between equivalent atoms in the two independent molecules. However, the average C–O bond length found here of 1.29 Å is virtually identical with that in the free carbonate ion of calcite, 1.294 (4) Å.<sup>50</sup>

### Conclusion

The red compound produced by the reaction of  $\text{RhH}(\text{PPh}_3)_4$  with  $\text{CO}_2$  thus has been characterized as a bridging carbonate complex,  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5\text{C}_6\text{H}_6$ , on the basis of vibrational and <sup>31</sup>P NMR spectra, chemical evidence, and x-ray crystallographic analysis.

The problem remains, however, as to how a carbonate complex is formed by the reaction of  $\text{RhH}(\text{PPh}_3)_4$  with  $\text{CO}_2$  in a nonaqueous system. There are several conceivable routes to the Rh–CO<sub>3</sub> complex: (1) disproportionation of CO<sub>2</sub> molecules to CO and CO<sub>3</sub><sup>2-</sup>; (2) reaction of CO<sub>2</sub> with oxygen introduced into the system as impurity to form CO<sub>3</sub><sup>2-</sup>; (3) reaction of H<sub>2</sub>O impurity in the CO<sub>2</sub> gas. The disproportionation of CO<sub>2</sub> was postulated by Chatt et al.<sup>23</sup> in the formation of a bis(μ-carbonato)–molybdenum complex. Yet in the present system the other two possibilities cannot be eliminated: the duration of CO<sub>2</sub> bubbling into the system is so long that introduction of oxygen and/or water as impurities is unavoidable despite vigorous attempts to remove them from the CO<sub>2</sub> gas. Attempts to detect the possible products, H<sub>2</sub> and/or CO, from the reaction system using a closed system under a normal pressure of CO<sub>2</sub> failed because of the lack of reactivity of  $\text{RhH}(\text{PPh}_3)_4$  toward carbon dioxide.

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**Registry No.**  $\text{Rh}_2(\text{CO}_3)(\text{PPh}_3)_5\text{C}_6\text{H}_6$ , 60364-00-3;  $\text{RhH}(\text{PPh}_3)_4$ , 18284-36-1; <sup>31</sup>P, 7723-14-0; sulfuric acid, 7664-93-9; methyl iodide, 74-88-4; P(OPh)<sub>3</sub>, 101-02-0.

**Supplementary Material Available:** Listing of structure amplitudes (84 pages). Ordering information is given on any current masthead page.

### References and Notes

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