

## Some Reactions of Organorhodium Compounds for the Utilization of Carbon Dioxide

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### Introduction

Carbon dioxide is contained much to about  $2.3 \times 10^{12}$  tons (330 ppm) in atmosphere, its concentration being increasing 1 ppm per year. And the sunlight is radiating the light of wavelength from  $0.17$  to  $4 \mu$  to the earth, then the radiation energy of wavelength from  $13$  to  $17 \mu$  only in the radiation light from the surface of the earth which shows the wavelength from  $3$  to  $120 \mu$  is absorbed with carbon dioxide and changed heat to the earth, though on the other hand steam from waters of rains, lakes and oceans is absorbed the light of  $5$  to  $8 \mu$  and upward of  $25 \mu$ . It is so called "the green house effect", and the temperature of climate is rising  $6^\circ\text{C}$  gradually within two hundred years<sup>2)</sup>.

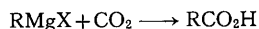
This phenomenon has made a terrible conclusion especially in the United States that, by a warmer atmosphere at the poles, some sea ice would melt, and the sea level could rise about  $5$  m in coming three hundred years. Then, many sea coasted cities would sink into the sea, and agroclimate zones would shift north into Canada where the soils are acid, badly leached, and far less productive<sup>2)</sup>, then the increase of human population would be much more a big problem.

On the other hand, it is known that plants and living things having chlorophyll could utilize carbon dioxide through photosynthesis. Many scientists have

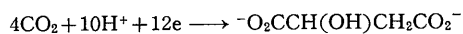
tried to utilize carbon dioxide which is not so reactive, but none reaches to the good goal on the industrial level after urea.

Outlines of these researches are shown as follows :

- (1) the reaction of a nucleophilic reagent with carbon dioxide<sup>3)</sup>

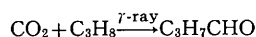
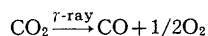


- (2) an electrochemical reduction of carbon dioxide<sup>4)</sup>

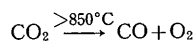


malic acid was made from  $\text{CO}_2^-$  which was produced by discharging electricity into diluted carbon dioxide.

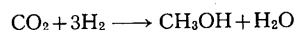
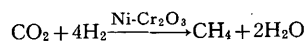
- (3) the irradiation of  $\gamma$ -ray<sup>5)</sup>



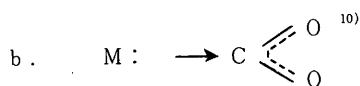
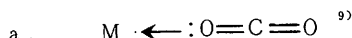
- (4) the heating<sup>6)</sup>

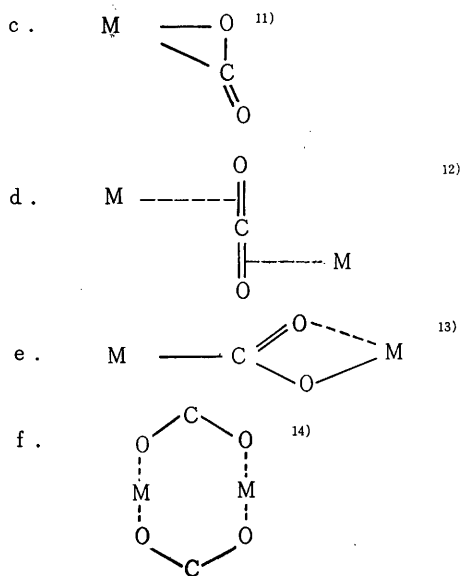


- (5) catalytic reductions<sup>7)</sup>

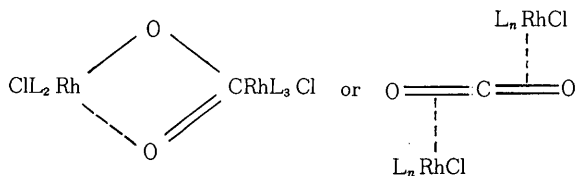


- (6) coordination compounds of transition metal complexes with carbon dioxide<sup>8)</sup>



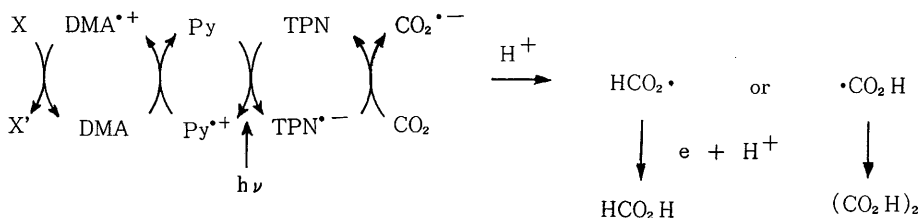


In this section, it is interested in Vol'pin's rhodium compound with carbon dioxide, and he proposed two types of chemical structures about it<sup>86)</sup> as follows :



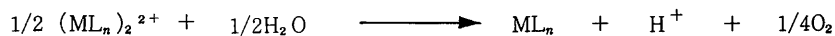
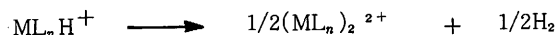
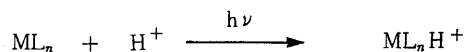
It could react with methyl iodide to produce methyl acetate. It was very much noticeable to make active carbon dioxide with the transition metal and react with another reagent to produce the compound including carbon dioxide. In addition, it could react with carbon monoxide to produce bis (triphenylphosphine)-carbonylchlororhodium, carbon dioxide and triphenylphosphine.

(7) the reduction of carbon dioxide by light<sup>15)</sup>



In this section, the researches on the photolysis of water are included. So then Gray's rhodium wind-mill compound<sup>17)</sup>, which was closely connected with the

meaning of reduction of carbon dioxide, was only picked up in this paper. The quantum yield of this reaction was still low to about 0.4%.



Author expected at first in the researches of utilization of carbon dioxide to obtain carbon dioxide derivatives such as pyruvic acid and so on, through the

reaction of carbon dioxide on transition metals such as rhodium and rhenium, and some results obtained were reported in this paper.

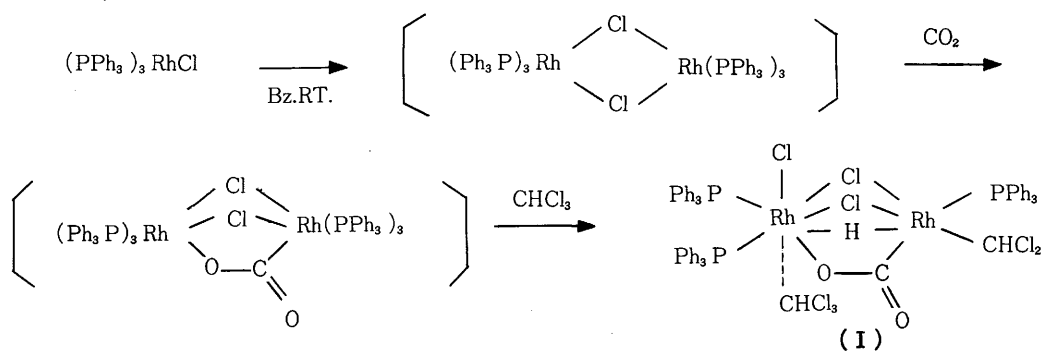
### Results and Discussion

About the transition metal compounds, Wilkinson et al<sup>18)</sup> have expanded their researches to the large field, especially about the reaction of carbon dioxide with transition metals, which Vol'pin et al<sup>18a)</sup> had proceeded their researches.

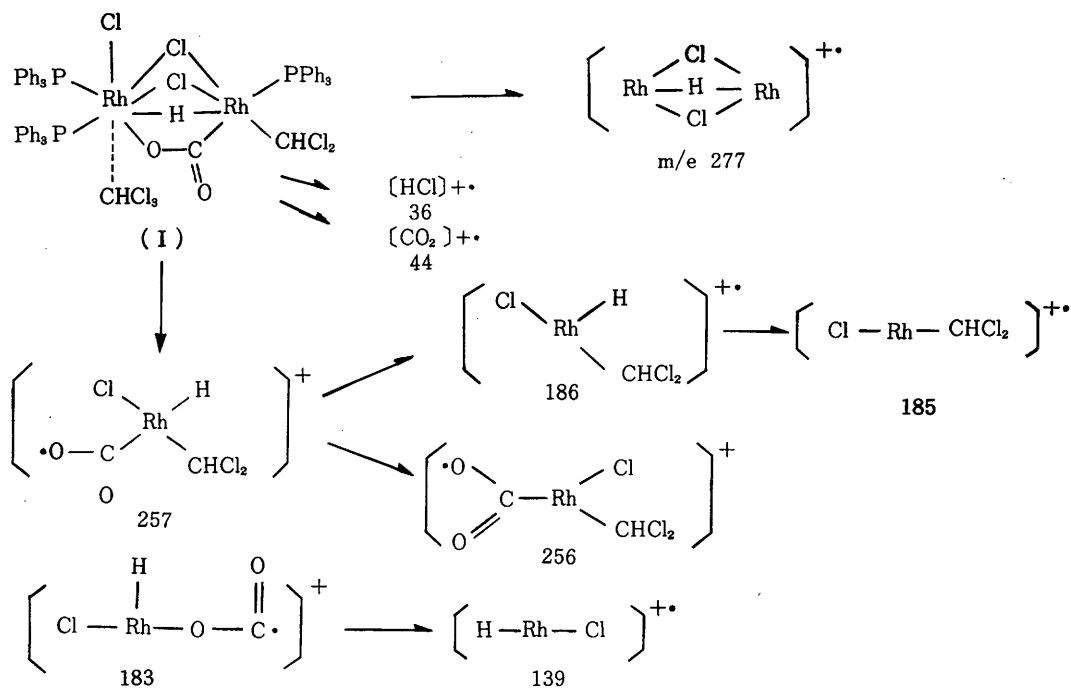
So then at first, author traced Vol'pin's reaction of carbon dioxide with tris (triphenylphosphine) chlororhodium. About the behavior of tris (triphenylphosphine) chlororhodium in benzene, it was concerned

that the active dimer<sup>19)</sup> of it was made and carbon dioxide was reacted with the dimer to make a coordinated compound including it. From the data of elementary analyses, IR spectra and mass spectra, the chemical structure of it was proposed as follows :

IR spectra of the above compound (I) showed 1480 (sh.) 1380 (s. piling up shoulderly with nujol signal) and 854 (m), suggesting the bent structure of carbon dioxide molecule.



And mass spectra were given  $M^+$  277 peak and fragment peaks which meant the existence of the chemical structure of compound (I).

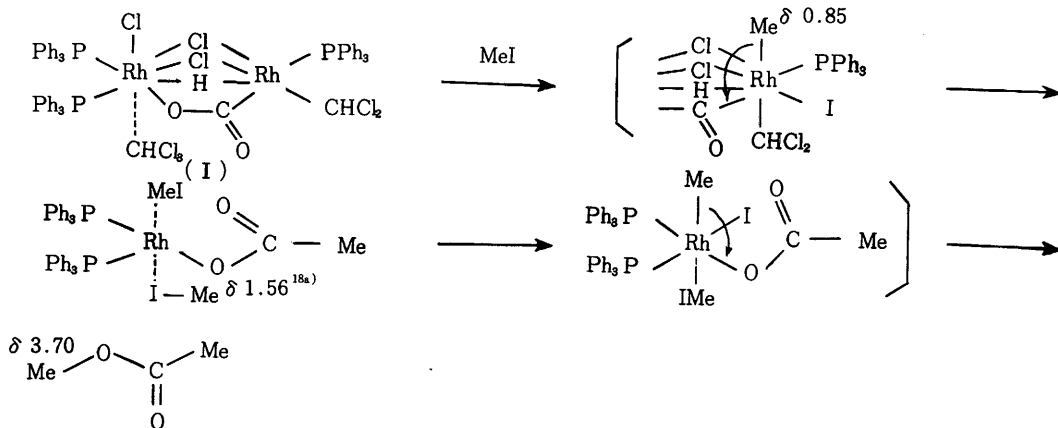


To compound (I), methyl iodide was added in the NMR tube, and the NMR spectra were measured in the room temperature from every time to time.

It was concerned that the signal of  $\delta$  0.85 meant that methyl iodide was soon reacted to the rhodium atom and made carbonyliodomethylrhodium, though it was not distinguished whether acetyl group was made at once or not, because the signal of  $\delta$  2.1 was piled

up with methyl group of methyl iodide. But it was clarified in this experiment that the signals of  $\delta$  1.56 based on methyl group of methyl iodide coordinated to the rhodium atom with iodide and  $\delta$  2.8 based on methyl group of chloriodomethylrhodium were occurring.

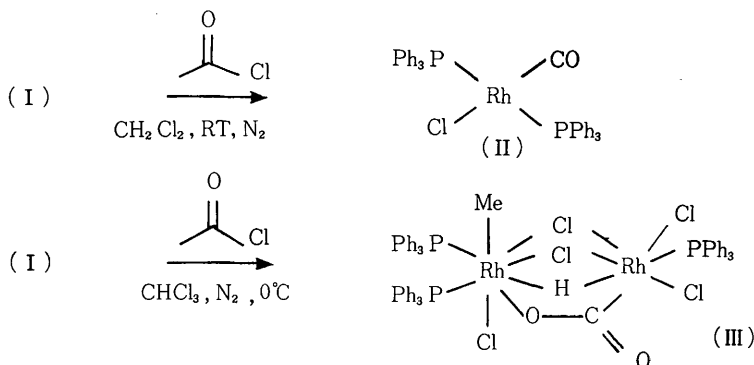
Their spectra showed the reaction mechanism of compound (I) with methyl iodide as follows :



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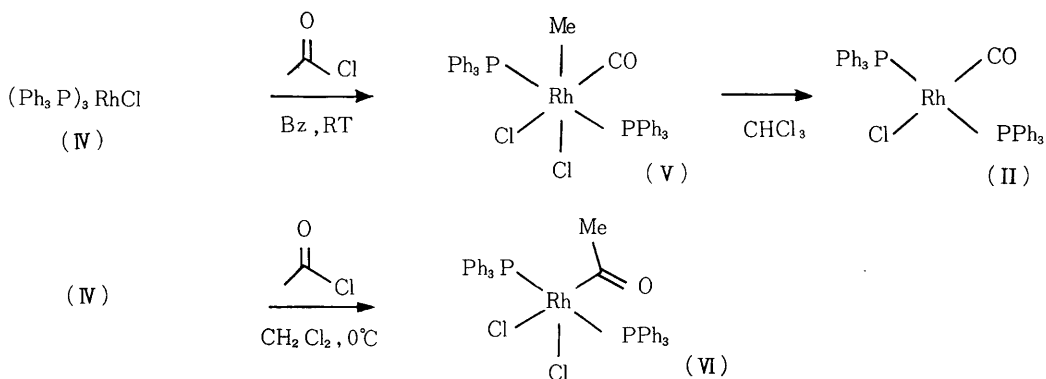
To the next, acetyl chloride was reacted with compound (I). It was expected that pyruvic acid would

be obtained, but only bis (triphenylphosphine) carbonylchlororhodium was obtained.

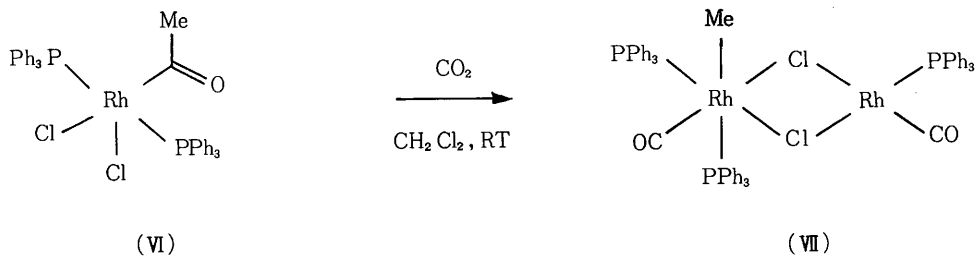


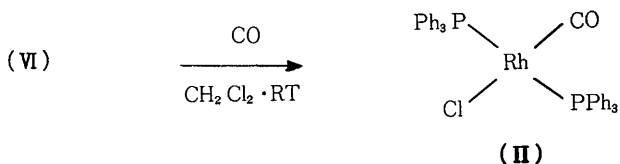
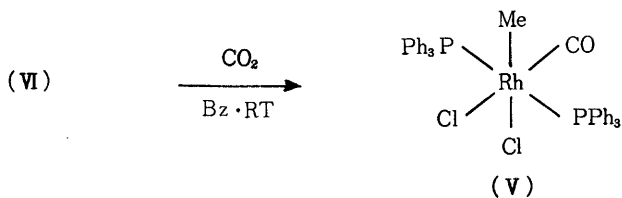
In this time, the starting material to obtain pyruvic acid was changed to tris (triphenylphosphine) chloro-

rhodium, so a few reactions of it with acetyl chloride were tried as follows :

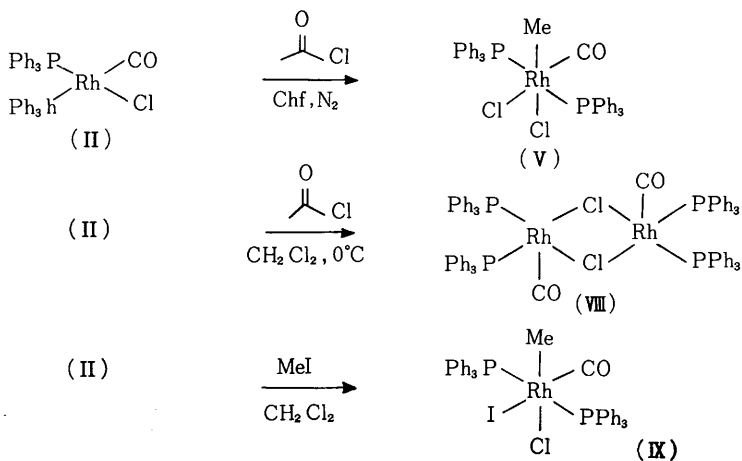


The further reactions with carbon dioxide were proceeded on compound (VI) as follows :

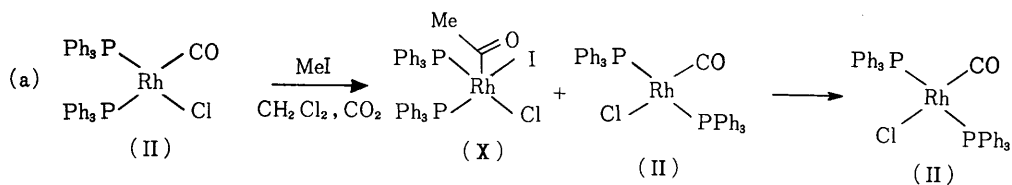


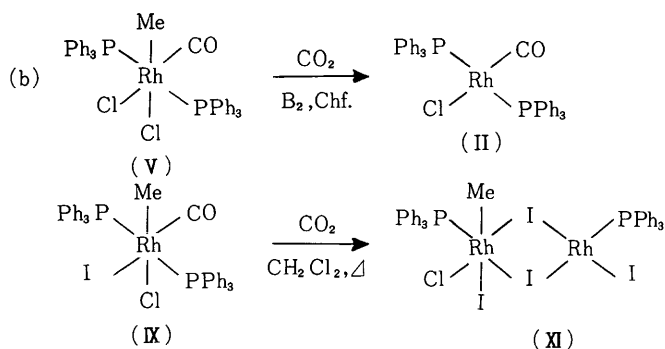


Using bis (triphenylphosphine) carbonylchlororhodium as the starting material, a few reactions were tried as follows :



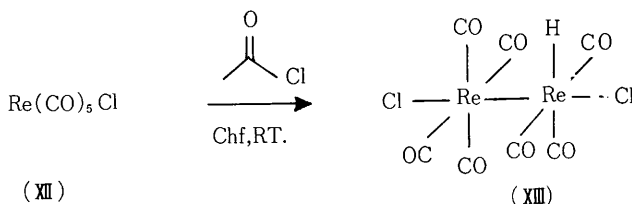
The reaction products of the starting material, rhodium chloride were shown as follows :  
 compound (V) and compound (IX) with carbon diox-





In addition, pentacarbonyl chloro rhenium (XII) was tried to react with acetyl chloride, and the rhenium

chloride dimer was obtained as follows :



### Experimental

Infrared spectra were taken by a Grubb-Parsons spectrometer and a Perkin-Elmer 21B spectrometer. Nuclear magnetic resonance spectra were recorded using a Perkin-Elmer-Hitachi EM-360 60 MHz and a Varian EM-340 60 MHz spectrometer using tetramethylsilane as an internal reference. Low resolution mass spectra were taken on an MS-9 instrument attached an autoreader controlled with a computer.

The data of elementary analyses and measurements of mass spectroscopy were taken by staffs of the analyses center at University of California, Berkeley.

**Materials :** All chemicals used were of the highest and reagent-grade quality of Vertron Corp. and Allied Chemical Corp. commercially.

**Preparations : A rhodium-carbon dioxide complex (I) chloroform solvate.**\*—Two grams of tris(triphenylphosphine)chlororhodium was emulsified to 25 ml of freshly distilled benzene in 100 ml one-necked flask jointed to 1.8 l glass-cylinder filled with carbon dioxide pressurized with the head of liquid paraffin which could measure

the volume of carbon dioxide spent for the reaction.

The content in the flask was stirred with a magnetic stirrer for 24 hrs. The color of emulsion was turned white-red from dark red after 3 hrs, and finally about 40 ml of carbon dioxide was spent. Then the precipitate was filtered, washed with benzene, recrystallized with chloroform, diethyl ether and *n*-hexane, washed again with chloroform, and finally dried in vacuo.

M. P. : 120.0°C (0.6 g, 40.5%). IR spectrum in nujol :  $\nu_{\text{max}}$ . 1480, 1430, 1380 (piled up with nujol signal), 1270, 1175, 1090, 1000, 975, 857, 765, 745, 725, 705, 695  $\text{cm}^{-1}$ . NMR :  $\delta$   $^{\text{CH}_2\text{Cl}_2}$  6.85 (m), 7.25 (m), 8.42 (m) p. p. m., using tetramethylsilane as the internal reference. Mass spectrum : base m/e : 277, scan 20, retention time : 11 : 20, total ionization : 382640. Elementary analyses : Found : C : 52.19, H : 3.80, Cl : 18.48, P : 6.75%.  $\text{C}_{57}\text{H}_{48}\text{Cl}_7\text{P}_3\text{Rh}_2\text{O}_2$  requires C : 52.18, H : 3.70, Cl : 18.91, P : 7.08%.

**Methyl acetate from rhodium-carbon dioxide complex (I) with methyl iodide.**—To 10 mg of compound (I) in the NMR tube, 0.5 ml of purified methyl iodide was added at room temperature, then NMR spectra

were taken every 3 min. In this case, the methyl signal of methyl iodide was used as an internal NMR reference. Then the signal of  $\delta$  3.6 based on the methyl ester was occurred finally after 30 min. The mixture in the NMR tube was filtered, and the NMR spectrum of the filtrate was taken. It also showed the signals of  $\delta$  3.6 based on the methyl group of the methylester and  $\delta$  2.1 based on one of the acetyl group piled up with the signal of methyl iodide.

*Bis(triphenylphosphine)carbonylchlororhodium* (II) from rhodium-carbon dioxide complex (I) with acetyl chloride.—To 1.0 g of compound (I) dissolved in to 10 ml of dichloromethane, 0.5 ml of acetyl chloride was added and stirred for 24 hrs in the nitrogen atmosphere at room temperature. Ten millilitres of diethyl ether was then added and the color of the solution turned yellowish orange from brownish red. The precipitate was obtained through filtration. The filtrate was concentrated with a rotary evaporator and chloroform-diethyl ether was added to obtain yellow precipitate. The initial precipitate was large in amount and used as the starting material for the synthesis. And the second precipitate was given trans-RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub> by its infrared spectrum, but the reaction mechanism was not clarified.

*Dichlororhodium dimer deriv.* (III) from rhodium-carbon dioxide complex (I) with acetyl chloride.—To 0.38 g of compound (I) dissolved into 20 ml of dichloromethane, 0.02 ml of acetyl chloride was added and stirred in the nitrogen atmosphere at 0°C. After 2.5 hrs, 5 ml of water was added and the mixture was

\*The second attempt to synthesize the rhodium-carbon dioxide complex compound.—The synthesis of the rhodium carbon dioxide complex compound was tried again on the same condition of compound (I). The reaction was continued for 23 hrs at room temperature, and 80 ml of carbon dioxide was spent. The mixture was dried up with a rotary evaporator, and the residue was dissolved in dichloromethane. When a small amount of diethyl ether was added, the brownish red precipitate was obtained. It was recrystallized with dichloromethane-diethyl ether (yield : 65%, M.P. 119°C).

kept standing overnight. Two hundreds milligrams of the precipitate obtained was purified with a silica-gel (60-200 mesh) column-chromatography (1.5 cm × 23 cm), using the eluting solvent consisted of benzene, chloroform and acetone (2 : 1 : 1, by vol.) One hundred milligrams of the precipitate was obtained purely in the fraction 1 (28.6%). M. P. : >250°C. IR spectrum in nujol :  $\nu_{\max}$ . 1480 (sh), 1430 (sh), 1380 (piled up with nujol signal), 850, 760, 740, 690 cm<sup>-1</sup>. Elementary analyses : Found : C : 54.60, H : 4.04, Cl : 14.12 %, C<sub>58</sub>H<sub>49</sub>Cl<sub>5</sub>P<sub>3</sub>Rh<sub>2</sub>O<sub>2</sub> requires C : 54.68, H : 4.02, Cl : 14.41%.

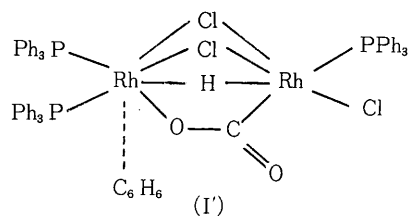
*Bis(triphenylphosphine)carbonyldichloromethylrhodium* (V)—To 2 g of tris(triphenylphosphine)chlororhodium emulsified in 20 ml of freshly distilled benzene, 2 ml of acetyl chloride was added and stirred for 2 hrs over the nitrogen atmosphere at room temperature. Then the mixture was concentrated with a rotary evaporator and yellowish red precipitate was filtered, washed with diethyl ether and dried in vacuo.

M. P. : 170.5°C (1.5 g. 88%). IR spectrum in nujol :  $\nu_{\max}$ . 2070, 1430 (sh), 1075, 750 (sh), 747, 690 cm<sup>-1</sup>. NMR. :  $\delta$  <sup>CDCl<sub>3</sub></sup> 0.83 (td), 1.58 (m), 7.40 (m), 7.65 (m), 7.90 (m) p. p. m., using tetramethylsilane as the internal reference.

When compound (V) was tried to recrystallize with chloroform, bis(triphenylphosphine)carbonylchlororhodium was formed with releasing methyl chloride.

*Bis(triphenylphosphine) acetyldichlororhodium* (VI)—To 2 g of tris(triphenylphosphine)chlororhodium dissolved in 20 ml of dichloromethane, 2 ml of acetyl

Elementary analyses showed C : 60.25, H : 4.58, Cl : 8.08, P : 7.25%, and then C<sub>55</sub>H<sub>46</sub>Cl<sub>3</sub>P<sub>3</sub>Rh<sub>2</sub>O<sub>2</sub>—C<sub>6</sub>H<sub>6</sub> (Cald : C : 59.95, H : 4.29, Cl : 8.70, P : 7.60%) was combined from these values. Thus, the structure of it could be proposed as the benzene solvate as follows :





chloride and 5 ml of diethyl ether were added and stirred for 2.5 hrs in the nitrogen atmosphere at 0°C. Then the mixture was dried up with a rotary evaporator, and 30 ml of acetone was added and stirred again for 5 min. The pale yellow precipitate formed was filtered, washed with acetone, and dried up in vacuo.

M. P. : 170.5°C. On heating, the color turned pale orange at 113°C, orange at 158°C, sinter at 162.5°C (1.60 g., 93.8%). IR spectrum in nujol :  $\nu_{\max}$ . 1710, 1470, 1430, 1225, 1180, 1085, 995, 895, 746, 735, 700 (sh), 690  $\text{cm}^{-1}$ . NMR. :  $\delta^{\text{CDCl}_3}$  2.16 (s), 2.50 (s), 7.40 (m), 7.65 (m), 7.90 (m) p. p. m., using tetramethylsilane as the internal reference.

*Triphenylphosphinechlorocarbonylrhodium dimer derivative* (VII)—To 0.18 g of compound (VI) was added 25 ml of dichloromethane, and stirred for 22 hrs in the atmosphere of carbon dioxide which was stored in the glass cylinder at room temperature. The color of the solution turned yellowish orange from orange. The solution was then concentrated with a rotary evaporator, and chloroform and diethyl ether were added to yield yellow precipitate. M. P. : 160.5°C (30 mg, 10.9%). IR spectrum in nujol :  $\nu_{\max}$ . 2070, 1980, 1940 (sh), 1445 (sh), 1275, 1100, 1035, 795, 750 (sh), 736, 697 (sh), 685  $\text{cm}^{-1}$ . NMR. :  $\delta^{\text{CDCl}_3}$  1.6 (m), 7.6 (m), 7.9 (m) p. p. m., using tetramethylsilane as the internal reference. Elementary analyses : Found : C : 60.58, H : 4.66, Cl : 6.87, P : 8.05%.  $\text{C}_5\text{H}_{48}\text{Cl}_2\text{P}_3\text{Rh}_2\text{O}_2$  requires C : 60.34, H : 4.26, Cl : 6.25, P : 8.19%.

*Bis(triphenylphosphine)carbonyldichloromethylrhodium* (V)—To 0.5 g of compound (VI) 25 ml of freshly distilled benzene was added and emulsified by stirring in the atmosphere of carbon dioxide which was stored in the glass cylinder at room temperature. Within 30 min of stirring, the yellow emulsion turned the orange-red solution the stirring being continued for further 3.5 hrs. This solution was concentrated with a rotary evaporator and a small amount of diethyl ether was added. The orange precipitate obtained was identified by the melting point and the IR spectrum.

*Bis(triphenylphosphine)carbonylchlororhodium* (II)—

To 0.5 g of compound (VI) 25 ml of dichloromethane was added and stirred for 18 hrs at room temperature in the atmosphere of carbon monoxide which was stored in the glass cylinder. After stirring for 1 hr, yellow precipitate was occurred in the clear orange-yellow solution. The stirring was continued for 18 hrs and the precipitate was filtered, washed with diethyl ether, and dried in vacuo. It was identified by the melting point and the IR spectrum.

*Bis(triphenylphosphine)carbonyldichloromethylrhodium* (V)—To 2.0 g of compound (II) dissolved in 20 ml of chloroform, 0.5 ml of acetyl chloride was added and stirred in the nitrogen atmosphere at room temperature for 24 hrs. The mixture was concentrated and, by adding acetone, the pale yellow precipitate was obtained. The precipitate was washed with chloroform and acetone, and dried in vacuo. It was identified by the melting point and the IR spectrum.

*Bis(triphenylphosphine)carbonylchlororhodium dimer* (VIII)—To 0.5 g of compound (II) emulsified in 10 ml of dichloromethane, 0.5 ml of acetyl chloride was added and stirred in the nitrogen atmosphere at 0°C. Within 5 min from the start of stirring, the color of crystals turned pale yellow from yellow. After 3 hrs, 20 ml of acetone was added and the yellow precipitate was filtered, washed with diethyl ether, and dried in vacuo. M. P. : 224.0—225.0°C (0.2 g., 80%). IR spectrum in nujol :  $\nu_{\max}$ . 2000, 1950, 1450, 1180, 1150, 1100, 1025, 985, 910, 738, 730 (sh), 680  $\text{cm}^{-1}$ . Elementary analyses : Found : C : 64.26, H : 4.45, Cl : 5.21, P : 8.95%.  $(\text{C}_{37}\text{H}_{30}\text{ClP}_2\text{RhO})_2$  requires C : 64.32, H : 4.38, Cl : 5.13, P : 8.97%.

*Bis(triphenylphosphine)carbonylchloriodomethylrhodium* (IX)—To 2.0 g of compound (II) 9.0 ml of freshly distilled methyl iodide was added and stirred in the nitrogen atmosphere at room temperature for 29 hrs. Then, 40 ml of *n*-hexane was added and the pale yellow precipitate was obtained. It was filtered, washed with chloroform-*n*-hexane, and dried in vacuo. M. P. : 170.5°C (1.6 g, 66.4%). IR spectrum in nujol :  $\nu_{\max}$ . 2025, 1440 (sh), 1150, 1100, 995, 890, 740, 720, 685  $\text{cm}^{-1}$ .

*Bis(triphenylphosphine)carbonylchlororhodium* (II)

—*a*—To 1.0 g of compound (II) dissolved in 13 ml of dichloromethane, 10 ml of methyl iodide was added and stirred for 24 hrs at room temperature in the atmosphere of carbon dioxide which was stored in the glass cylinder. The color of the solution turned yellowish orange from yellow within 1 hr from the start of stirring. By adding *n*-hexane-diethyl ether to the solution, the precipitate was occurred. It was collected by filtration and washed with dichloromethane and diethyl ether. IR spectrum of it in nujol showed two carbonyl absorptions, which were 1980 and 1700  $\text{cm}^{-1}$ . It could be concerned that the former meant the carbonyl of  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ , and the latter of  $\text{RhCl}(\text{COMe})(\text{PPh}_3)_2$ , because all precipitate turned  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$  through the recrystallization with dichloromethane and diethyl ether.

*Bis(triphenylphosphine)carbonylchlororhodium* (II)

—*b*—One gram of compound (V) was dissolved in the mixture of 0.5 ml of chloroform and 20 ml of benzene, and stirred for 24 hrs at room temperature in the atmosphere of carbon dioxide which was stored in the glass cylinder. Then the mixture was concentrated with a rotary evaporator, and the yellow precipitate was filtered, washed with diethyl ether and chloroform, and dried in vacuo. It was identified by the melting point and the IR spectrum.

*Triphenylphosphinediiodorhodium dimer deriv.* (XI)

—One gram of compound (IX) was dissolved in 35 ml of dichloromethane and heated at 40°C for 30 min with stirring in the atmosphere of carbon dioxide which was stored in the glass cylinder. After heating, it was stirred at room temperature for 24 hrs. Then the mixture was dried up with a rotary evaporator and the precipitate occurred by the addition of 20 ml of chloroform was filtered off. The filtrate was concentrated and *n*-hexane-chloroform was added. Then yellow precipitate was obtained through the filtration. It was next purified through the silica-gel (60—200 mesh) column-chromatography (1.5 cm × 20 cm), using the mixture of benzene, chloroform and acetone (1 : 1 : 4, by vol.) as the eluting solvent. Twenty milligrams

of the precipitate was obtained in the fraction 2 (2.4 %). M. P. : 190.0—192.0°C. IR spectrum in nujol :  $\nu_{\text{max}}$ . 1480 (sh), 1430 (sh), 1180, 1110, 1090, 895, 740, 722, 690  $\text{cm}^{-1}$ . Elementary analyses : Found : C : 34.16, H : 2.68, Cl : 2.09, I : 38.92, P : 4.78%.  $\text{C}_{37}\text{H}_{33}\text{I}_4\text{P}_2\text{ClRh}_2$  requires C : 34.46, H : 2.58, Cl : 2.75, I : 39.40, P : 4.80%.

*Tricarbonylchlororhenium dimer deriv.* (XIII)—To 2 g of pentacarbonylchlororhenium (XII) emulsified in 20 ml of chloroform, 0.5 g of acetyl chloride was added, and stirred in the argon atmosphere at room temperature for 28 hrs and refluxed for 3 hrs. White precipitate was filtered, washed with acetone and dried in vacuo. M. P. : 265.0—267.0°C (1.5 g, 84.7%). IR spectrum in nujol :  $\nu_{\text{max}}$ . 2170, 2080, 2050, 1980, 1010, 943, 910, 725  $\text{cm}^{-1}$ . Elementary analyses : Found : C : 13.26, H : 0.15, Cl : 9.52%.  $\text{C}_7\text{HCl}_2\text{O}_7\text{Re}_2$  requires C : 13.13, H : 0.16, Cl : 11.07%.

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## Literatures

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炭酸ガス利用についての有機ロジウム化合物の反応

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(昭和54年9月29日受理)

有機ロジウム化合物と炭酸ガスとの反応は、すでにソ連のヴォレピンらによって実験されていたが、筆者の追試により、少し異なる結果を得、それを基にして炭酸ガスと有機ロジウム化合物との反応の展開を試みた。すなわち、ロジウム化合物に炭酸ガスを付加させ活性化させて他の簡単なアセチルクロリドのような化合物を反応させて、生体内での有用な化合物であるビルビン酸の合成を目的として数種の反応を試みたが、結果は化学反応式に示す通り、炭酸ガスと有機ロジウム化合物との反応生成物はかなり複雑な構造式の化合物となり、ヨウ化メチルとの反応で、メチルアセテートを得るのみであった。

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