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PREPARATION OF CHLOROCARBONYLBIS(TRIPHENYLPHOSPHINE)RHODIUM FROM TRIS(TRIPHENYLPHOSPHINE)CHLORORHODIUM, CARBON DIOXIDE, AND MOLECULAR HYDROGEN

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Chlorocarbonylbis(triphenylphosphine)rhodium was obtained by the reaction of tris(triphenylphosphine)chlororhodium with carbon dioxide and hydrogen. Use of a polar aprotic solvent was effective for the reaction. This reaction indicates carbon dioxide is reduced by molecular hydrogen on a rhodium complex and fixed in the form of a carbonyl complex.

Recent interest in the reaction of carbon dioxide with transition metal complexes has led to the formation of various transition metal complexes which have carbon dioxide or its inserted group as a ligand.$^{1)}$ However, examples of carbonyl complexes prepared from the reaction of transition metal complexes and carbon dioxide are still limited in spite of their potential significance as possible intermediates of catalytic reduction of carbon dioxide on transition metal complexes.$^{2)}$

We found that chlorocarbonylbis(triphenylphosphine)rhodium can be obtained in good yield from tris(triphenylphosphine)chlororhodium, carbon dioxide, and hydrogen when the reaction is carried out in a polar aprotic solvent, such as hexamethylphosphoramide. We consider this is the first reaction in which hydrogen appears to have worked as the reducing agent of carbon dioxide to give an isolable carbonyl complex of rhodium.

$$\mathrm{RhCl(PPh_3)_3} \xrightarrow[\text{in HMPA,}\qquad 100^\circ\mathrm{C}]{\mathrm{H_2}\text{(20 atm),}\qquad \mathrm{CO_2}\text{(20 atm)}} \mathrm{RhCl(CO)(PPh_3)_2}$$

The dark red solution of tris(triphenylphosphine)chlororhodium in hexamethylphosphoramide (HMPA) was placed in an autoclave and constantly stirred at 100°C under pressure of carbon dioxide (20 atm) and hydrogen (20 atm). After reaction for 40 hr., the solution was still homogeneous in appearance, but its color changed to pale yellow. The reaction solution was mixed with a large amount of ethanol or n-hexane to yield yellow crystals which were identified as $RhCl(CO)(PPh_3)_2$: m.p. 195-197°C (ref.[3] 195-200°C) ; ν (C=O) 1965 cm^{-1} (ref.[4a] 1960 cm^{-1}, ref.[4b] 1970 cm^{-1}) ; m.w. 690 (measured by VPO), 691 (calculated for $RhCl(CO)(PPh_3)_2$). Elemental analysis values for the recrystallized complex from benzene solution are C 67.82 % ; H 4.67 % (calculated for $RhCl(CO)(PPh_3)_2 \cdot C_6H_6$, C 67.17 % ; H 4.72 %). Neither by-products nor the unreacted starting complex were isolated from the reaction mixture.

Table 1 lists the results of reactions carried out under various conditions. To avoid the complication of the reaction by the decarbonylation of a reaction medium,[5] no solvent used in the present study had a carbon-oxygen bond except tetrahydrofuran. Although Svoboda et al. recently reported a similar carbonylation reaction of tris(triphenylphosphine)chlororhodium by carbon dioxide in the presence of triethoxysilane,[2d] our reaction is substantially different from theirs since carbon dioxide is the sole reactant with carbon-oxygen bonds and hydrogen is considered to be a weaker reducing agent than triethoxysilane.

Table 1. Formation of $RhCl(CO)(PPh_3)_2$ from $RhCl(PPh_3)_3$, CO_2, and H_2.[a]

Run	Solvent	CO_2 (atm)	H_2 (atm)	Temp. (°C)	Time (hr)	Yield (%)	Remarks[b]
1	HMPA	20	20	100	40	70	H_2O added, yellow
2	HMPA	20	20	100	40	58	Yellow
3	HMPA	20	20	50	17	40	H_2O added, yellow
4	HMPA	20	20	30	40	16	H_2O added, red
5	HMPA	20	0	100	40	0	Red
6	HMPA	0	20	100	40	0	Red
7	Pyridine	20	20	100	18	47	Yellow
8	Benzene	20	20	100	40	20	Red
9	Benzene	20	20	50	17	0	Red
10	Tetrahydrofuran	20	20	100	45	36	H_2O added, red[c]
11	Tetrahydrofuran	0	20	100	45	trace	H_2O added, red
12	Water	20	20	100	40	trace	Heterogeneous reaction
13	HMPA	20	20	80	85	21	a), red
14	HMPA	0	0	100	40	29	Reaction with HCOOH[d]

a) $RhCl(PPh_3)_3$: ca. 370 mg (0.4 mmole) except Run 13 where $RhCl_3 \cdot 3H_2O$ (0.7 mmole) and PPh_3 (3 mmole) were used instead.

b) H_2O : 0.9 ml. Colors are of the solutions after reactions.

c) With yellow precipitate.

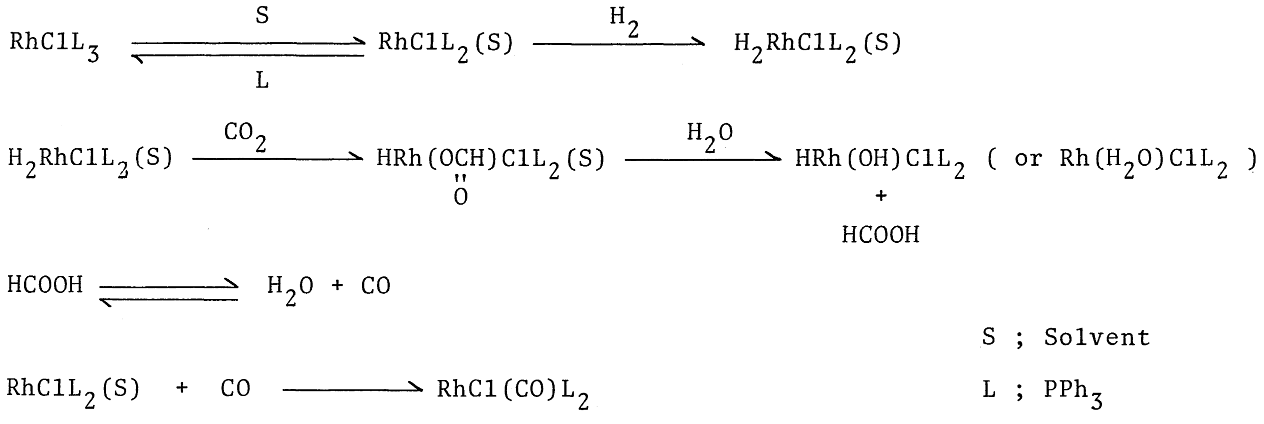
d) Formic acid (1.0 mmole) was used instead of H_2 and CO_2.

Polar solvents like hexamethylphosphoramide and pyridine gave better yields than benzene, in which the initial dark red color of the reaction mixture was almost unchanged after reaction for 40 hr. at 100°C. The reaction in tetrahydrofuran solution also resulted in the formation of $\mathrm{RhCl(CO)(PPh_3)_2}$, and the contribution of carbon monoxide abstraction from the tetrahydrofuran itself should be minor because the carbonyl complex was scarcely obtained under the similar reaction conditions in the absence of carbon dioxide.

From comparison of the results of Run 1 or 2 with those of Runs 5 and 6 in Table 1, it is obvious that carbon dioxide and hydrogen are necessary for this reaction. This fact excludes the possibility that the carbonyl complex was formed by the reaction with carbon monoxide contained as an impurity in the starting materials. Both carbon dioxide and hydrogen used in the present study had purities of more than 99.99 % and carbon monoxide was not detected at all by the gas chromatographic analyses. The phosphine ligand or monovalent rhodium might have reduced carbon dioxide into carbon monoxide as postulated for the reactions of molybdenum complexes,[2c,e] but these possibilities can also be ruled out in our case since the carbonylation did not occur in the absence of hydrogen and no apparent ir absorptions due to the phosphine oxide or rhodium carbonate were detected in the crude products.

Water seems to accelerate the reaction, giving a carbonyl complex under mild conditions (Run 4). However, water itself was not a good reaction medium, probably due to its inability to dissolve the initial complex. Since the yields shown in Table 1 were calculated on the bases of the isolated carbonyl complex, reaction of Run 1 is considered to be nearly quantitative.

In view of the necessity of both carbon dioxide and hydrogen for this reaction and the acceleration effect by water, we tentatively presume that the reaction proceeds as follows.



$$\mathrm{RhClL_3} \underset{L}{\overset{S}{\rightleftharpoons}} \mathrm{RhClL_2(S)} \xrightarrow{H_2} \mathrm{H_2RhClL_2(S)}$$

$$\mathrm{H_2RhClL_2(S)} \xrightarrow{CO_2} \mathrm{HRh(O\underset{\overset{\|}{O}}{C}H)ClL_2(S)} \xrightarrow{H_2O} \mathrm{HRh(OH)ClL_2}\ (\text{ or } \mathrm{Rh(H_2O)ClL_2}\ ) + \mathrm{HCOOH}$$

$$\mathrm{HCOOH} \rightleftharpoons \mathrm{H_2O + CO}$$

$$\mathrm{RhClL_2(S)} + \mathrm{CO} \longrightarrow \mathrm{RhCl(CO)L_2}$$

S ; Solvent

L ; $\mathrm{PPh_3}$

Although the attempt to detect formic acid which should be formed according to this scheme has been unsuccessful, the presence of carbon monoxide was confirmed by gas chromatographic analysis of the gas mixture collected immediately after the reaction. In addition, chlorocarbonylbis(triphenylphosphine)rhodium can be obtained from the reaction between tris(triphenylphosphine)chlororhodium and formic acid in hexamethylphosphoramide solution as exemplified by the result of Run 14 in Table 1. Further investigations are in progress to elucidate the reaction mechanism, to apply this reaction for other transition metal complexes, and to extend this reaction to catalytic fixation of carbon dioxide.

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