

FORMATION OF $[\text{Rh}(\text{CO})\text{Cl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ FROM $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ AND CARBON DIOXIDE*

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The formation of the title rhodium-carbonyl compound by reaction of carbon dioxide with $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ in the presence of organosilicon hydrides was further examined. Analogous reactions of related ruthenium-phosphine complexes, $[\text{RuCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ and $[\text{RuClH}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ are discussed and the mechanism of the reaction is proposed.

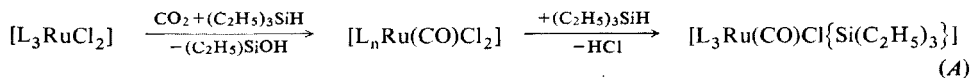
In recent years, reactions of carbon dioxide with transition metal complexes have attracted increasing attention. Several modes of coordination of CO_2 and its insertion reactions to metal-hydrogen or metal-alkyl bonds have been recognised and exemplified¹⁻³. However, until now, there are only a few examples of reactions of CO_2 leading to formation of transition metal-carbonyl complexes. Thus, Belopotapova found⁴ that $[\text{RuH}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_4]$ reacts with CO_2 under pressure and at elevated temperatures (e.g. 130°C , an autoclave, benzene as solvent) to form $[\text{Ru}(\text{CO})\text{H}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$.

In a recent paper⁵ we briefly reported on formation of $[\text{Rh}(\text{CO})\text{Cl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ by reaction of $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ with CO_2 in the presence of silicon hydrides. In continuing the examination of the carbonylation of $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ in the presence of triethylsilane and triethoxysilane we found that in the latter case an excess of the silicon hydride with respect to the rhodium-phosphine complex, which was used previously by us⁵, is not necessary. The reaction proceeds almost quantitatively with essentially equimolar amounts of these substances, giving again $[\text{Rh}(\text{CO})\text{Cl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ as a sole product. From preparative standpoint it is noteworthy that with equimolar amount of triethoxysilane the reaction was complete in the time comparable to that used in experiments with excess silicon hydride (1 hour). Compared to triethoxysilane, triethylsilane gave not only the less pure rhodium-carbonyl complex but also the carbonylation proceeded at slower rate³. When following the progress of the carbonylation in the presence of triethoxysilane by IR spectroscopy we further found that a gradual change in the colouration of the reaction mixture from red to yellow is due to formation of both the rhodium-carbonyl ($\nu(\text{C}=\text{O})$ 1970 cm^{-1}) and the rhodium-silyl complex, $[\text{RhClH}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\{\text{Si}(\text{OC}_2\text{H}_5)_3\}]$, the latter

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compound prevailing in the initial phase of the reaction ($\nu(\text{Rh}-\text{H})$ 2060 cm^{-1} , *cf.*⁶). Identical results as with equimolar mixture of the rhodium-phosphine complex and triethoxysilane were also obtained with the complex⁶ $[\text{RhH}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2 \cdot \{\text{Si}(\text{OC}_2\text{H}_5)_3\}]$ prepared separately. In this case the formation of free triethoxysilane ($\nu(\text{Si}-\text{H})$ 2196 cm^{-1}) due to dissociation of the complex during its reaction with carbon dioxide was not detected by IR spectroscopy. These facts all indicated that the carbonylation by carbon dioxide in the presence of silicon hydrides might generally proceed *via* a silylmetal-hydride complex which is subsequently converted by carbon dioxide to the metal-carbonyl complex. The slower rate of carbonylation observed with triethylsilane relative to triethoxysilane can then be related to the ease with which corresponding silylrhodium-hydride complexes are formed⁶.

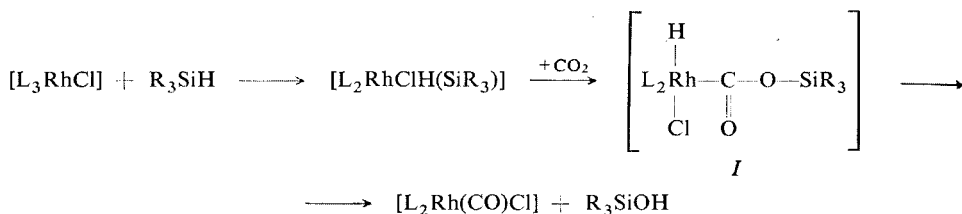
A more complex situation has been found at extending this carbonylation reaction to related ruthenium-phosphine complexes, such as $[\text{RuCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ and $[\text{RuClH}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$, this being in part due to the different course of the reaction of these complexes with different silicon hydrides. Whereas $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ reacts with both triethylsilane and triethoxysilane to give exclusively the corresponding silylrhodium-hydride complex of the structure mentioned above, we recently found⁷ that the reactions of $[\text{RuCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ with triethylsilane and triethoxysilane afford $[\text{RuClH}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ (*cf.*⁸) and $[\text{RuH}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3 \cdot \{\text{Si}(\text{OC}_2\text{H}_5)_3\}]$, respectively. Furthermore, the triethoxysilylruthenium complex is produced by a stepwise reaction involving $[\text{RuClH}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ as an intermediate. Accordingly, the reaction of carbon dioxide with a mixture of $[\text{RuCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ and triethylsilane gave a compound whose IR spectrum showed a strong band at 1926 cm^{-1} indicating the presence of the carbonyl group attached to the metal. This compound was however contaminated by small amounts of $[\text{RuHCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ ($\nu(\text{Ru}-\text{H})$ 2033 cm^{-1} , *ref.*⁷ 2031 cm^{-1}) which we were unable to completely remove. The elemental analysis of this impure product was close to that expected for $[\text{Ru}(\text{CO})\text{Cl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3 \cdot \{\text{Si}(\text{C}_2\text{H}_5)_3\}]$. Attempts at isolating $[\text{Ru}(\text{CO})\text{Cl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$, the formation of which by this reaction was mentioned in a previous work⁷, were unsuccessful. We believe that this mentioned complex is intermediate in the formation of the above silylruthenium compound, which may be depicted in the following way (Eq. (A), $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$).



$[\text{RuClH}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ does not react with carbon dioxide either in the presence or in the absence of triethylsilane. Its formation from $[\text{RuCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ during carbonylation is thus parallel reaction.

With triethoxysilane, the carbonylation of $[\text{RuCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ did not take place. The IR analysis showed that the products arising from this reaction are identical

with those produced by the reaction of the silicon hydride itself, *i.e.* $[\text{RuClH} \cdot \{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ and $[\text{RuH}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3\{\text{Si}(\text{OC}_2\text{H}_5)_3\}]$. Similar to the chlorohydridoruthenium complex, the hydridosilylruthenium complex did not undergo carbonylation reaction under the experimental conditions used (53°C , 2 h). We were further interested in the fate of the reactant, silicon hydride. With $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ and triethylsilane as an example, we found that the silicon hydride is converted to hexaethylidisiloxane, which we believe is the product of subsequent condensation of the initially formed triethylsilanol.



SCHEME 1

On the basis of the results obtained thus far, it is tentatively assumed that the carbonylation proceeds in the way depicted for the rhodium compound in Scheme 1 ($\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$). Formation of metallo-carboxylic acid ester *I*, instead of metallo-carboxylic acid (*via* insertion of CO_2 into the metal-hydrogen bond) is preferred only by analogy with the behaviour of triethylsilyl formate $\text{HCOOSi}(\text{C}_2\text{H}_5)_3$, which can be regarded as an adduct of triethylsilane to carbon dioxide. We found that this compound is easily decarbonylated in stoichiometric reaction with $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ under the conditions which were comparable to those used in the reactions of carbon dioxide, giving identical products, $[\text{Rh}(\text{CO})\text{Cl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ and hexaethylidisiloxane.

EXPERIMENTAL

Compounds used. Triethylsilane and triethoxysilane were prepared in the usual way and their purity was checked by g.l.c. Both silicon hydrides were distilled under argon before use. Benzene was dried by sodium and distilled in an atmosphere of argon. $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ (ref.⁹), $[\text{RuCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ (ref.¹⁰), $[\text{RuClH}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ (ref.¹¹), and $[\text{RhClH}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2 \cdot \{\text{Si}(\text{OC}_2\text{H}_5)_3\}]$ (ref.⁶) were prepared by published methods as indicated. Triethylsilyl formate was obtained¹² by reaction of triethylsilane with formic acid in the presence of NiCl_2 . Carbon dioxide (edible grade purity, from cylinders) was used without further purification.

The IR absorption spectra of solid samples in pressed KBr discs were measured on a double-beam spectrometer Zeiss (Jena), model UR-20. The region of wavenumbers around 2000 cm^{-1} (LiF-prism) was calibrated with the 1944 cm^{-1} band of polystyrene film.

Carbonylation of $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ in the presence of $(\text{C}_2\text{H}_5)_3\text{SiH}$ and $\text{HSi}(\text{OC}_2\text{H}_5)_3$ (room temperature). A) A 10 ml. reaction flask equipped with reflux condenser was charged with 790 mg (0.85 mmol) of the rhodium compound, 160 μl (0.85 mmol) of $\text{HSi}(\text{OC}_2\text{H}_5)_3$, and 3 ml of

benzene and then carbon dioxide was introduced into this mixture at a rate of 5 ml per min. During initial 15 min initiated solution turned yellow. The reaction was continued for another 3/4 hours. The yellow precipitate was separated by filtration. A total of 570 mg (96.5%) of $[\text{Rh}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ were obtained ($\nu(\text{CO})$ 1970 cm^{-1} ; calculated: 5.13% Cl, 8.96% P; found: 4.84% Cl, 9.20% P, 0.0% Si). B) Carbon dioxide was introduced into a mixture of 790 mg (0.85 mmol) of $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$, 140 μl (0.88 mmol) of $(\text{C}_2\text{H}_5)_3\text{SiH}$, and 5 ml of benzene at a rate of 5 ml per min for 3 hours. The rhodium-carbonyl complex was obtained less pure (as checked by IR comparison with an authentic sample and by elemental analysis) in 72% yield.

Carbonylation of $[\text{RhClH}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\{\text{Si}(\text{OC}_2\text{H}_5)_3\}]$. A stream of carbon dioxide (5 ml per min) was introduced at ambient temperature into a mixture of 500 mg (0.60 mmol) of the rhodium complex and 5 ml of benzene for 1 hour. The reaction afforded 363 mg (87%) of $[\text{Rh}(\text{CO})\text{Cl}\cdot\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ whose properties were identical with those of the product of the reaction (A) described in the preceding paragraph.

Reaction of $[\text{RuCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ with CO_2 and $(\text{C}_2\text{H}_5)_3\text{SiH}$. Carbon dioxide (5 ml per min) was introduced at room temperature into a mixture of 500 mg (0.52 mmol) of the ruthenium compound, 3 ml (19 mmol) of $(\text{C}_2\text{H}_5)_3\text{SiH}$, and 10 ml of benzene for 5 hours. The product obtained (420 mg) was a brownish substance whose IR spectrum showed characteristic bands at 1926 cm^{-1} ($\nu(\text{CO})$) and 2033 cm^{-1} ($\nu(\text{Ru}-\text{H})$).

Reaction of $[\text{RuCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ with CO_2 and $\text{HSi}(\text{OC}_2\text{H}_5)_3$. Two test tubes, one containing 500 mg (0.21 mmol) of the ruthenium compound, 1 ml (5.3 mmol) of $\text{HSi}(\text{OC}_2\text{H}_5)_3$, and 3 ml of benzene and the other filled with 3 g of dry ice, were placed in an autoclave. After sealing, the autoclave was heated at 53°C for 2.5 hours. The reaction gave 180 mg of a pale violet product whose IR spectrum showed characteristic bands at 1970 cm^{-1} and 2033 cm^{-1} ($\nu(\text{Ru}-\text{H})$) in $[\text{RuH}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3\{\text{Si}(\text{OC}_2\text{H}_5)_3\}]$ and $\nu(\text{Ru}-\text{H})$ in $[\text{RuClH}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$, respectively; cf.⁷.

Carbonylation of $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ by $\text{HCOOSi}(\text{C}_2\text{H}_5)_3$. A mixture of 50 mg (0.05 mmol) of the rhodium compound, 0.1 ml (0.55 mmol) of $\text{HCOOSi}(\text{C}_2\text{H}_5)_3$, and 5 ml of benzene was stirred at ambient temperature for 4 hours. After removal of volatile compounds by evaporation *in vacuo* and recrystallisation, the pure $[\text{Rh}(\text{CO})\text{Cl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ was obtained in 84% yield.

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