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Preliminary communication

CATALYSIS BY METAL COMPLEXES

XXIII*. FORMATION OF TRANSITION METAL—CARBONYL COMPLEXES FROM CARBON DIOXIDE

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Summary

$RhCl(PPh_3)_3$ reacts under mild conditions with CO_2 in the presence of $HSi(OEt)_3$ to give $Rh(CO)Cl(PPh_3)_2$ in a quantitative yield. A similar carbonylation was observed with some ruthenium—phosphine complexes.

The formation of transition metal—carbonyl complexes on reaction with CO_2 was reported by Vol'pin et al. [2], who observed that $RuH_2(PPh_3)_4$ reacted with CO_2 under rather drastic conditions (an autoclave, 130°, benzene as solvent) to form $Ru(CO)H_2(PPh_3)_3$. An analogous reaction of $RhCl(PPh_3)_3$ did not yield a carbonyl complex, but under milder conditions a red dimeric rhodium complex with coordinated CO_2 was obtained [3] $[Rh_2(CO_2)Cl_2(PPh_3)_5]$.

We now report the first example of the carbonylation of transition metal—phosphine complexes by CO_2 under mild conditions. We observe that in the presence of silicon hydrides $RhCl(PPh_3)_3$ reacts with CO_2 at room temperature to form $Rh(CO)Cl(PPh_3)_2$. The reaction proceeds smoothly and a high yield of the rhodium—carbonyl complex is obtained. In a typical example, CO_2 was passed through a solution of $RhCl(PPh_3)_3$ (0.2 mmol) and $HSi(OEt)_3$ (4 mmol) in benzene (5 ml) at room temperature over a period of 1 h. In the initial phase of the reaction a yellow soluble silyl—rhodium complex, $RhH[Si(OEt)_3]Cl(PPh_3)_2$ (cf. [4]), was rapidly formed, which was subsequently converted to $Rh(CO)Cl(PPh_3)_2$ (93% yield, ν(C=O) 1970 cm^{-1} (ref. [5] 1965 cm^{-1}). Found: Cl, 4.83; P, 9.24; calcd.: Cl, 5.13; P, 8.96; Si, 0.0%). With other silicon hydrides,

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[*] For Part XXII see ref. 1.

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such as Et_3SiH and Pr_2SiH_2, the rhodium—carbonyl complex was obtained less pure and in a lower yield. The use of complex hydrides, e.g. $LiAlH_4$ and $NaAlH_2(OCH_2CH_2OCH_2)_3$, led, together with carbonylation, to a partial chlorine—hydrogen exchange, and a mixture of rhodium—carbonyl species containing Rh—Cl and Rh—H bonds was obtained. The nature of these compounds is not yet clear but they are presumably $Rh(CO)Cl(PPh_3)_2$ and $Rh(CO)H(PPh_3)_2$.

Preliminary experiments with some ruthenium—phosphine complexes indicated that this reaction is not limited to rhodium complexes. Thus, for example, the carbonylation of $RuCl_2(PPh_3)_3$ with CO_2 gave $Ru(CO)Cl_2(PPh_3)_3$. The extention of this carbonylation reaction to phosphine complexes of other transition metals and a study of the mechanism of the reaction are in progress.

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