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Reaction of rhodium carbonyl chloride with carbon monoxide

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Recent interest in the chemistry of the carbonyls of rhodium has led to the development of several methods[1,2] for the synthesis of $Rh_4(CO)_{12}$, but all involve long reaction times. With a view to producing a facile synthesis of $Rh_4(CO)_{12}$ we have investigated methods utilising carbon monoxide at atmospheric pressure. Previous reports[1] indicated that rhodium carbonyl chloride reacted with carbon monoxide at atmospheric pressure to produce $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$, the proportions depending upon the solvent system. With hexane as solvent and in the presence of sodium bicarbonate, $Rh_4(CO)_{12}$ was reported to be the predominant product. We have found that under anhydrous conditions this reaction does not yield $Rh_4(CO)_{12}$ even with prolonged reaction times. Water is a necessary ingredient for the reaction to occur, and reaction is rapid in its presence. A typical synthesis is summarised as follows:

$$\begin{array}{lccccccc} [Rh(CO)_2Cl]_2 & + \; CO & + & H_2O & + & NaHCO_3 & \xrightarrow[\text{n-hexane (150 cm}^3)]{3\text{ h}} & Rh_4(CO)_{12} \\ 0.35\text{ g} & & & 0.01\text{ g} & & 1.0\text{ g} & & 0.22\text{ g} \end{array}$$

The $Rh_4(CO)_{12}$ can be isolated after filtering the reaction mixture, by evaporating the hexane under reduced pressure to low volume and cooling to –70°. The amount of water added is critical, larger amounts resulting in decomposition of $Rh_4(CO)_{12}$ to the insoluble $Rh_6(CO)_{16}$. It has been shown previously that water is essential for the reaction between rhodium carbonyl chloride and allyl chloride[3]

Further, we find that with a hexane solution of rhodium carbonyl chloride under anhydrous conditions in an atmosphere of carbon monoxide and in the presence of sodium bicarbonate, an equilibrium is set up between the carbonyl chloride and a new species which apparently contains a bridging carbonyl group, as indicated by the appearance of a band at 1886 cm^{-1} in the infrared spectrum of

TABLE 1

ν(C=O)absorptions(cm^{-1})						
$[Rh(CO)_2Cl]_2$ in n-hexane	2105 (sh)[a]	2089 (8)[b]	2080 (sh)	2035 (10)	2005 (3)	
Equilibrium position	2100 (5)	2089 (7)	2073 (10)	2040 (10)	2010 (2)	1886 (7)
Immediately after addition of water	2100 (5)	2077 (10)	2046 (7)	2027 (7)	1886 (9)	
Final solution containing $Rh_4(CO)_{12}$	2077 (9)	2046 (8)	1886 (10)			

[a] (sh), shoulder. [b] Figures in parentheses indicate relative intensities.

the solution. Equilibrium was attained approximately four hours after admission of the carbon monoxide, but in the absence of sodium bicarbonate the rate of attainment of equilibrium was slower and the intensity of the bands attributable to the bridged species was considerably lower. The reaction was followed by infrared spectroscopy and the results are shown in Table 1. Displacement of the carbon monoxide atmosphere by nitrogen resulted in a reduction in intensity of the bands at 2073 and 1886 cm^{-1}. The production of $Rh_4(CO)_{12}$ can be followed by noting the disappearance of the absorptions at 2027 and 2100 cm^{-1}. Work is in progress to elucidate the structure of the bridged species which must be an intermediate in the formation of the rhodium carbonyls.

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