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Preliminary communication

Infrared investigation of the reactions of rhodiumcarbonyl halides and carbon monoxide at elevated pressures

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SUMMARY

Infrared spectral results at elevated carbon monoxide pressures suggest that rhodiumdicarbonyl halides and carbon monoxide exist in an equilibrium with the corresponding rhodiumtricarbonyl halides.

Lewis bases such as halides[1], phosphines[2], amines[3], sulphides[4], and nitriles[5] have been reported to split the halide bridges of rhodiumdicarbonyl halides. We have found that carbon monoxide is also capable of bridge-splitting with the rhodiumdicarbonyl halides, albeit at elevated pressures (eqn. 1).

$$[Rh(CO)_2X]_2 + 2CO \rightleftharpoons 2Rh(CO)_3X \qquad (1)$$

$(X = Cl, Br, I)$

We have studied reaction 1 at elevated pressures of carbon monoxide using the high-pressure infrared cell previously described[6]. With X = Cl, Br, or I, an equilibrium[★] is rapidly established at room temperature ($\leqslant$ 10 minutes), the extent of the equilibrium being dependent upon the partial pressure of carbon monoxide, the anion, and the solvent employed.

[★] The infrared spectrum of $[Rh(CO)_2Cl]_2$ in hexane was recorded at 200 psig of carbon monoxide after having been stirred at this pressure for seventeen hours. In addition to the C–O absorptions attributed to $[Rh(CO)_2Cl]_2$, the spectrum contained an absorption at 2052 cm^{-1}. It did not contain absorptions at 2073 and 1886 cm^{-1}. It has previously been reported[7] that prolonged bubbling of a hexane solution of $[Rh(CO)_2Cl]_2$ with carbon monoxide generated a new species having C–O stretching absorptions at 2073 and 1886 cm^{-1}.

The extent of conversion of $[Rh(CO)_2X]_2$ to $Rh(CO)_3X$ increases across the series $Cl < Br < I$ (see Table 1)*. Qualitatively, this is the same direction as has been reported[5] for the reaction of $[Rh(CO)_2X]_2$ ($X = Cl, Br$) with benzonitrile at 20° and 30°. However, the reaction appears to be much more sensitive to the coordinated halide when carbon monoxide is used than when benzonitrile is used.

The solvent has a large influence on the equilibria shown in eq. 1. With $X = Cl$ the conversion of $[Rh(CO)_2Cl]_2$ to $Rh(CO)_3Cl$ is approximately ten times larger in 1,2-dichloroethane than in hexane (Table 1). Again, this same phenomenon was observed[5] with the nitriles when the bridge-splitting occurred to a greater extent in chloroform (more polar) than in benzene (less polar). The reason for this solvent effect is presently not understood.

The products of reaction 1 are unstable in the absence of carbon monoxide and thus were not isolated. However, it has been shown[9] that the di-substituted dimer, $[Rh(CO)(Ph_3P)Cl]_2$, undergoes a similar reversible bridge splitting reaction with carbon monoxide at one atmosphere (eqn. 2)

$$[Rh(CO)(Ph_3P)Cl]_2 + 2CO \rightleftarrows 2Rh(CO)_2(Ph_3P)Cl \qquad (2)$$

This reaction is also reversible and, therefore, the product has not been isolated pure. However, it has been formulated as *cis*-$Rh(CO)_2(Ph_3P)Cl$ on the basis of its infrared spectrum[9], gas evolution experiments[9], and a molecular weight determination performed in a carbon monoxide atmosphere[9c]. Based on the similarity of reactions 1 and 2 it is suggested that the products of reaction 1 are monomeric tricarbonyls, *i.e.*, $Rh(CO)_3X$ where $X = Cl, Br, I$.

TABLE 1

FORMATION OF $Rh(CO)_3X$ FROM $[Rh(CO)_2X]_2$ AND CO[a]

X	*Solvent*	*Conversion (%)*	
		at 200 psig CO	*at 500 psig CO*
Cl	hexane	8	11
Br	hexane	17	44
I	hexane	74	100
Cl	1,2-dichloroethane	88	100
I	1,2-dichloroethane	100[b]	

[a] Performed at 25°. [b] At 50 psig.

Conductivity experiments were carried out to help characterize the products. A 1,2-dichloroethane solution of $[Rh(CO)_2I]_2$ had the same conductivity at 65 psia carbon monoxide as it did at 15 psia nitrogen. In contrast, the infrared spectrum recorded at 65 psia of carbon monoxide shows approximately 100% conversion

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* It has previously been reported[8] that the rates of CO-exchange for the $[Rh(CO)_2X]_2$ compounds decrease with X as follows: $Cl > Br > I$.

TABLE 2

C–O STRETCHING FREQUENCIES OF $Rh(CO)_3X$ [a]

X	*Solvent*	*$[Rh(CO)_2X]_2$*	*$Rh(CO)_3X$*
Cl	1,2-dichloroethane	2108 (sh), 2093 s, 2059 w, 2036 s	2100 s, 2060 s
Cl	hexane	2107 m, 2091 s, 2080 w, 2052 w 2036 s	2098 s, 2052 s
Br	hexane	2103 m-w, 2087 s, 2076 vw, 2033 s	2093 s, 2054 s
I	hexane	2096 m, 2080 s, 2070 w, 2054 w, 2028 s	2084 s, 2054 s
I	1,2-dichloroethane	2098 m, 2080 s, 2028 s	2087 s, 2061 m
OAc	hexane	2098 s, 2076 m, 2024 s	2076 s, 2071 s, 2045 m, 2004 vs, 1888 m [b]

[a] s, strong; m, medium; w, weak; (sh), shoulder. [b] These five bands are attributed to $Rh_4(CO)_{12}$

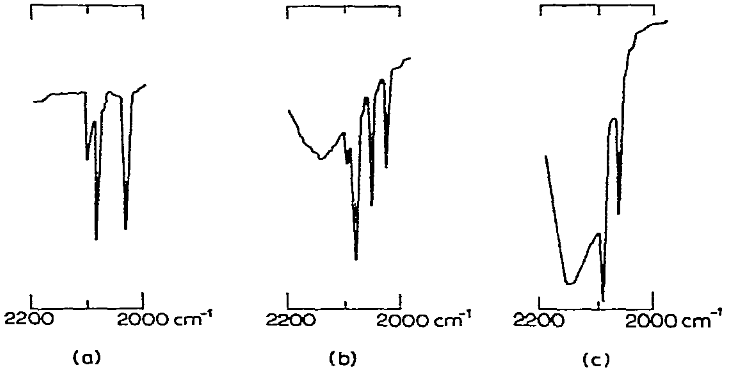

Fig.1. Equilibration of $[Rh(CO)_2I]_2$ with carbon monoxide in hexane: (a) 100 psig of N_2; (b) 100 psig of CO; (c) 500 psig of CO. Dissolved CO responsible for large band at ca. 2140 cm^{-1}.

of $[Rh(CO)_2I]_2$ to the product having bands at 2087 and 2061 cm^{-1} in this solvent. This precludes the possibility of iodide (halide) displacement by carbon monoxide at elevated pressures.

The products of reaction 1 all exhibit two strong C–O stretching frequencies (see Table 2) in the infrared which is consistent with a square-planar $Rh(CO)_3X$ structure. The higher energy band of each of these compounds shows a progressive shift to lower energies as the halide is varied from $Cl > Br > I$. Figure 1 illustrates the dependence of the infrared spectrum of $[Rh(CO)_2I]_2$ upon the carbon monoxide pressure at room temperature. Under 100 psig of nitrogen [spectrum (a)] the normal solution spectrum of $[Rh(CO)_2I]_2$ is observed with absorption maxima at 2096 m, 2080 s, and 2028 s cm^{-1}; under 100 psig of carbon monoxide [spectrum (b)] an additional band has appeared at 2054 cm^{-1}; and, under 500 psig of carbon monoxide [spectrum (c)] the original bands have completely disappeared and two strong bands at 2084 and 2054 cm^{-1} remain which we attribute to $Rh(CO)_3I$. The reaction is completely reversible and removing the carbon monoxide pressure generates the original $[Rh(CO)_2I]_2$ spectrum.

The equilibria appear to be reversed at higher temperatures. For example, the spectrum of $[Rh(CO)_2Cl]_2$ in 1,2-dichloroethane at 100° is unchanged on going from 0 to 500 psig of carbon monoxide.

The infrared spectrum of $[Rh(CO)_2OAc]_2$ at elevated carbon monoxide pressures did not yield any evidence for the formation of $Rh(CO)_3OAc$. Instead, there was a slow irreversible conversion of $[Rh(CO)_2OAc]_2$ to $Rh_4(CO)_{12}$ as shown by the appearance of C–O stretching frequencies at 2076, 2071, 2045, 2004, and 1888 cm^{-1} (eqn. 3)[10].

$$2[Rh(CO)_2OAc]_2 + 6CO + 2H_2O \rightarrow Rh_4(CO)_{12} + 2CO_2 + 4HOAc \qquad (3)$$

Both carbon dioxide and acetic acid have been identified (GLC and mass spectroscopy) as the other products of the reaction*. It is possible, however, that $Rh(CO)_3OAc$ is an intermediate in reaction 3 which, in contrast to the analogous $Rh(CO)_3X$ species (X = Cl, Br, or I), is unstable towards reduction to $Rh_4(CO)_{12}$.

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* The analogous reaction has been reported[11] for $[Rh(CO)_2Cl]_2$.