Dirhodium Octacarbonyl

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Summary I.r. spectral evidence for the reversible formation of $Rh_2(CO)_8$ from $Rh_4(CO)_{12}$ under high pressures of carbon monoxide and low temperatures is described.

IN 1943, Hieber and Lagally reported the preparation of dirhodium octacarbonyl by the action of carbon monoxide on freshly prepared rhodium metal at 460 atm. pressure and 200°.[1] There has been no subsequent confirmatory evidence to support the existence of this compound.[2] Indeed, several groups of workers have unsuccessfully attempted to repeat the original preparation.[3]

Recent work on the phosphine-substituted rhodium carbonyls has demonstrated the instability of the dimeric derivatives $[Rh_2(CO)_6L_2]$ in solution with respect to the tetrameric species $[Rh_4(CO)_{10}L_2]$.[4] This behaviour suggests that the parent carbonyl $Rh_2(CO)_8$ might be even less stable with respect to the tetramer $Rh_4(CO)_{12}$. However, there remains the possibility that the equilibrium

$$Rh_4(CO)_{12} + 4CO \rightleftharpoons 2Rh_2(CO)_8$$

may be displaced to the right under high carbon monoxide pressures. Accordingly we have studied the reactions of liquid paraffin–heptane mixed solutions of $Rh_4(CO)_{12}$ with high pressures of carbon monoxide by following i.r. spectral changes directly in a high-pressure spectrophotometric cell.[5] Above 60°, even under high pressures of carbon monoxide (600 atm.), only the formation of $Rh_6(CO)_{16}$ is observed. This is consistent with the temperature-dependence of the preparation of $Rh_4(CO)_{12}$ in solution. Above 50°, appreciable quantities of $Rh_6(CO)_{16}$ are always formed.

However, on cooling a liquid paraffin–heptane (3 : 1) solution of $Rh_4(CO)_{12}$ under 490 atm. pressure of carbon monoxide below room temperature, additional bands are observed in the spectra as illustrated in the Figure. At 20° the normal solution spectrum of $Rh_4(CO)_{12}$ is observed with absorption maxima at 2076 vs, 2071 vs, 2045 s, and 1886 s cm^{-1}; at 4° [spectrum (b)] additional bands are beginning to appear, and at −19° [spectrum (c)] the intensities of the new bands and those due to the starting $Rh_4(CO)_{12}$ are approximately the same. This appears to be the limiting spectrum and little change is observed on further cooling. At −30° all the bands weaken considerably in intensity, presumably because of the insolubility of the compounds at low temperature. The system is completely reversible, and warming to room temperature yields only the starting spectrum of $Rh_4(CO)_{12}$.

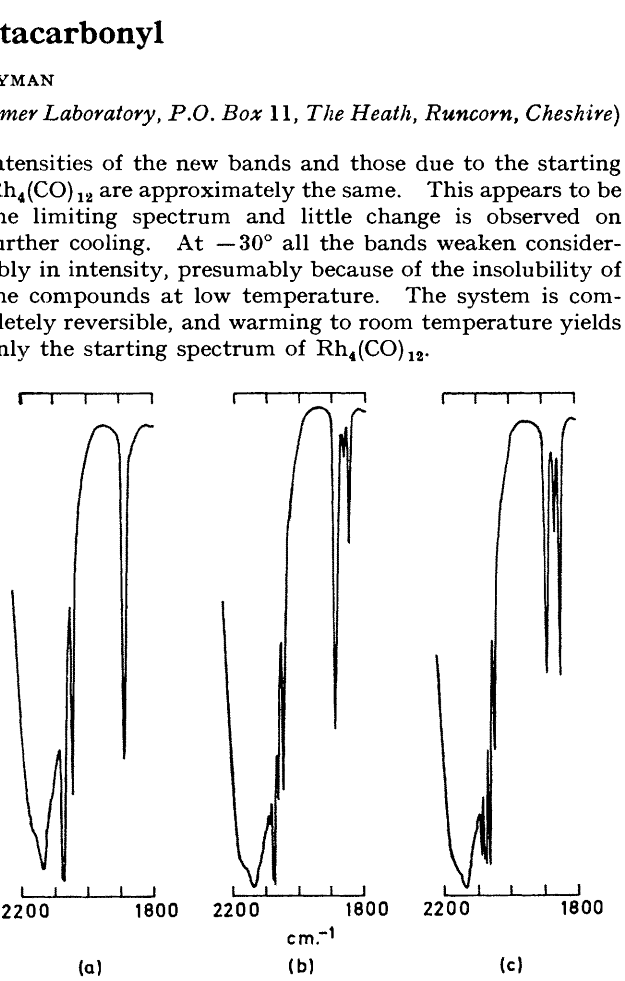

FIGURE. *Reaction of* $Rh_4(CO)_{12}$ *with carbon monoxide in liquid paraffin–heptane*: (a) 490 *atm. pressure and* 20°; (b) 460 *atm. and* 4°; (c) 430 *atm. and* −19°.

The reaction has also been studied at initial carbon monoxide pressures of *ca.* 400, 300, and 200 atm. over the same temperature range (20° to −30°). At the lower pressures the new frequencies still appear, but are proportionally weaker in intensity; they also increase in relative intensity with decreasing temperature. The pressure-dependence of the new bands suggests that the carbon monoxide to rhodium ratio of the species present in solution is increasing with increasing pressure. In addition, the reactions of $Rh_4(CO)_{12}$ in the absence of carbon monoxide, *e.g.* under pressures of nitrogen, show no new absorptions and no band shifts from the starting $Rh_4(CO)_{12}$.

Accurate band maxima for the new species occur at 2086, 2061, 1860, and 1845 cm^{-1}. The frequencies and relative intensities (see Figure) of the new bands are very similar to the stronger bands which have been assigned to the spectrum of the bridged isomer of $Co_2(CO)_8$.[6] For the latter species these occur at 2071 vs, 2044 vs, 2042 vs, 1866 sh, and 1857 s cm^{-1} in heptane. It thus appears likely that the bridged form of $Rh_2(CO)_8$ may be stabilised under high carbon monoxide pressures and low temperatures.

No evidence is obtained for the formation of a non-bridged isomer of $Rh_2(CO)_8$ when the system is allowed to warm to room temperature, in contrast to the $Co_2(CO)_8$ system.[6] However, in the latter case the proportion of isomers was found to be both solvent- and temperature-dependent; the formation of $Rh_2(CO)_8$ has only been studied in paraffin hydrocarbon solvents. Also, increasing the pressure with hydrogen at −19° produces no evidence for the formation of $HRh(CO)_4$, a compound which was also claimed by Hieber and Lagally.[1] However, the spectrum is complicated due to the additional presence of $Rh_4(CO)_{12}$ and this experiment cannot be regarded as conclusive.

The existence of $Rh_2(CO)_8$ only under high carbon monoxide pressures and low temperatures is consistent with the difficulty experienced by various groups of workers in characterising this material[3] and with studies on the phosphine-substituted derivatives.[4]

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