

**Preliminary communication****Hydridotricarbonyliridium—phosphine complexes**

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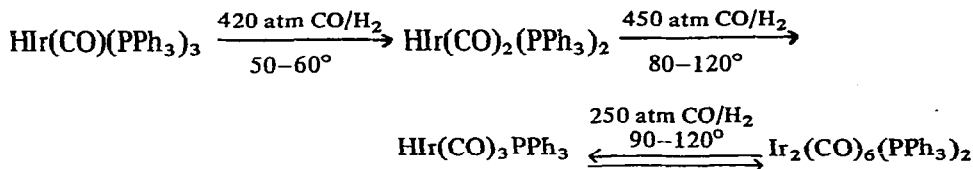
Recently, the formation of dinuclear phosphine-substituted iridium carbonyls from the reactions of tetranuclear phosphine-substituted derivatives with carbon monoxide at high pressures and temperatures has been described<sup>1</sup>. Complexes of the type  $\text{Ir}_2(\text{CO})_6\text{L}_2$ , where  $\text{L} = \text{PPh}_3$  and  $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ , were isolated as yellow, air-stable compounds and the formation of  $\text{Ir}_2(\text{CO})_7\text{L}'$ , where  $\text{L}' = \text{PPh}_3$ ,  $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ ,  $\text{PEt}_3$  and  $\text{P-n-Bu}_3$ , was inferred from IR spectral measurements under pressure. The reactions of the di- and tetra-nuclear phosphine-substituted complexes, e.g.,  $\text{Ir}_2(\text{CO})_6(\text{PPh}_3)_2$  and  $\text{Ir}_4(\text{CO})_8(\text{PEt}_3)_4$  respectively, under pressures of carbon monoxide/hydrogen mixed gases have now been studied by following IR spectral changes in a high pressure spectrophotometric cell<sup>2</sup> and preliminary results are reported here.

When liquid paraffin suspensions of  $\text{Ir}_2(\text{CO})_6(\text{PPh}_3)_2$  are treated with 250 atm of a 1/1 mixture of carbon monoxide and hydrogen new bands are observed in the carbonyl stretching region of the IR spectrum as the temperature is raised above 60°. Thus, peaks at 2046 and 1982  $\text{cm}^{-1}$  increase in intensity as the bands at 1975mw (sh) 1945s and 1900mw (sh)  $\text{cm}^{-1}$  due to the starting material decrease. At 90°, the 1945 and 1982  $\text{cm}^{-1}$  maxima are of equal intensity and conversion to the new species is complete at 125°; no further change is noted on increasing the temperature to 200°. The frequencies and relative intensities of the bands in the spectrum at 125° correspond closely with the IR spectra of monomeric phosphine-substituted derivatives of cobalt tetracarbonyl hydride, e.g.,  $\text{HCo}(\text{CO})_3\text{P-n-Bu}_3$ <sup>3</sup>, and by analogy, the formation of  $\text{HIr}(\text{CO})_3\text{PPh}_3$  is thus inferred. The bands at 2046 and 1982  $\text{cm}^{-1}$  may be assigned as the  $A_1$  and  $E$  vibrations respectively, predicted for a 5-coordinate molecule of this type with  $C_{3v}$  symmetry. The weak peak at 1948  $\text{cm}^{-1}$  could be due either to the presence of small amounts of unreacted starting material or may be assigned as a <sup>13</sup>C<sup>18</sup>O vibration. Since a peak of similar intensity and frequency occurs in the spectra of all the compounds reported here the latter alternative seems more likely.

In liquid paraffin solutions the monomeric species  $\text{HIr}(\text{CO})_3\text{PPh}_3$  is unstable in the absence of carbon monoxide and hydrogen and decomposes on releasing the pressure to re-form the insoluble dimer  $\text{Ir}_2(\text{CO})_6(\text{PPh}_3)_2$ . No replacement of phosphine

occurs on prolonged treatment of  $\text{HIr}(\text{CO})_3\text{PPh}_3$  with carbon monoxide and hydrogen at 450 atm and  $200^\circ$  and we have been unable to obtain any evidence for the formation of  $\text{HIr}(\text{CO})_4$  under these conditions.

This spectral evidence for the formation of  $\text{HIr}(\text{CO})_3\text{PPh}_3$  means that all the members of the series of compounds  $\text{HIr}(\text{CO})(\text{PPh}_3)_3$ <sup>4</sup>,  $\text{HIr}(\text{CO})_2(\text{PPh}_3)_2$ <sup>5</sup>,  $\text{HIr}(\text{CO})_3\text{PPh}_3$  and  $\text{HIr}(\text{CO})_4$ <sup>6</sup> are now known. Indeed, the same final spectrum, corresponding with the formation of  $\text{HIr}(\text{CO})_3\text{PPh}_3$ , may be observed (from the successive replacement of phosphine by carbon monoxide) starting from liquid paraffin suspensions of  $\text{HIr}(\text{CO})(\text{PPh}_3)_3$  under the reaction conditions summarised in the scheme:



Again no further reaction is observed up to  $200^\circ$ .

Additional complexes of the type  $\text{HIr}(\text{CO})_3\text{L}$  may be prepared by treatment of analogous dimeric derivatives with carbon monoxide and hydrogen under similar conditions. However, the temperature at which the formation of the hydrido species occurs is apparently dependent upon the nature of the phosphine. Thus for  $\text{L} = \text{P}(p\text{-MeC}_6\text{H}_4)_3$  reaction occurs at 430 atm and  $150-175^\circ$  whereas for  $\text{L} = \text{P-}i\text{-Pr}_3$  the reaction is particularly rapid and takes place at 300 atm and room temperature.

Tetranuclear phosphine-substituted iridium carbonyl derivatives of the types  $\text{Ir}_4(\text{CO})_8\text{L}_4$ , where  $\text{L} = \text{PEt}_3$  and  $\text{P-n-Bu}_3$ , and  $\text{Ir}_4(\text{CO})_9(\text{P-}i\text{-Pr}_3)_3$  also react with carbon monoxide and hydrogen under pressure in liquid paraffin/heptane solutions to give the monomeric hydrido derivatives as the predominant final products:

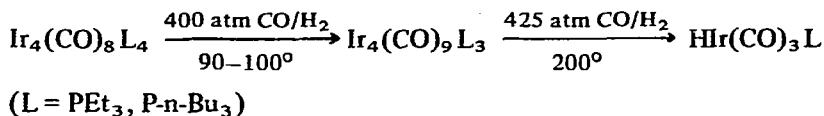


TABLE 1

IR SPECTRA ( $\text{cm}^{-1}$ ) IN THE  $\nu(\text{CO})$  REGION<sup>a</sup>

$\text{Ir}_2(\text{CO})_6(\text{PPh}_3)_2$		1975 mw(sh)	1945 s	1900 mw(sh)
$\text{HIr}(\text{CO})_3\text{PPh}_3$	2046 mw	1982 s	1948 w	
$\text{HIr}(\text{CO})_3\text{P}(p\text{-MeC}_6\text{H}_4)_3$	2043 mw	1979 s	1946 w	
$\text{HIr}(\text{CO})_3\text{PEt}_3$	2035 mw	1973 s	1938 w	
$\text{HIr}(\text{CO})_3\text{P-}i\text{-Pr}_3$	2040 mw	1970 s	1934 w	
$\text{HIr}(\text{CO})_3\text{P-n-Bu}_3$	2039 mw	1972 s	1937 w	
$\text{HCo}(\text{CO})_3\text{P-n-Bu}_3$ <sup>3</sup>	2050 mw	1970 s	1933 w	

<sup>a</sup> Paraffin hydrocarbon solvents.

As in the reaction with carbon monoxide alone<sup>1</sup> the initial product,  $\text{Ir}_4(\text{CO})_9\text{L}_3$ , is formed at 100° and no further change occurs until 190° is reached. At this temperature the spectrum simplifies considerably with the formation of the monomeric species (the absorptions at 1992, 1985, 1784 and 1780  $\text{cm}^{-1}$  slowly disappear and a new peak appears at ca. 1970  $\text{cm}^{-1}$ ). Again no further reaction of  $\text{HIr}(\text{CO})_3\text{L}$  is observed over prolonged periods at 450 atm pressure and 200°. Again, the monomeric hydrido species appear to be unstable in the absence of carbon monoxide and hydrogen pressures.

IR spectra of the hydridotricarbonyliridium–phosphine complexes are summarised in Table 1.

#### ACKNOWLEDGEMENT

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