# Tetracarbonyliridium Hydride

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*Summary* I.r. spectral evidence for the existence of tetracarbonyliridium hydride under high pressure is described.

IN 1940, Hieber and Lagally[1] reported the formation of tetracarbonyliridium hydride as a very volatile compound obtained when water-containing iridium trichloride was used in the preparation of the iridium carbonyls. There has been no subsequent published evidence to support the existence of this compound.[2]

We have studied the reaction of $Ir_4(CO)_{12}$ under carbon monoxide and hydrogen (1 : 1 mole ratio) by following i.r. spectral changes directly in a high-pressure spectrophotometric cell.[3] Spectra which have been observed for liquid-paraffin solutions in the range 2200—1800 cm$^{-1}$ are summarised in the Table. Liquid paraffin was used as reaction medium since carbon monoxide under pressure has considerable solubility in lower members of the paraffin hydrocarbon series, *e.g.* heptane, and the absorption due to dissolved CO tends to mask the region of interest. Carbon monoxide is considerably less soluble in liquid paraffin. Under the experimental conditions used, and from the observed sharpness of the spectral bands it is apparent that solution spectra are being studied rather than solid dispersions.

*Carbonyl stretching frequencies (cm.$^{-1}$)*

| Spectrum (a) | Spectrum (b) | Spectrum (c) | Spectrum (d) | |
|---|---|---|---|---|
| $Ir_4(CO)_{12}$ | | | $HIr(CO)_4$ | $HCo(CO)_4$ |
| | | | | 2118vw |
| 2072s | 2072vs | 2072vs | | |
| | | 2054m,sh | 2054m | 2052m |
| 2032m | 2032ms | 2032s | 2031s | 2029s |
| | | | 1999w | 1996vw |

(a) 370 atm. total pressure and 175°; (b) 430 atm. and 200°; c) after 3 hr. at 430 atm. and 200°; (d) 315 atm. and 22°.

Spectrum (a) corresponds with that of $Ir_4(CO)_{12}$. No absorption bands due to bridging carbonyl groups are observed, consistent with the known structure in the solid state.[4] Spectra (b) and (c) were recorded at 430 atm. total pressure and 200°, (c) being measured 3 hr. after (b). During this time the 2032 cm.$^{-1}$ maximum has increased considerably in intensity and a shoulder appeared at 2054 cm.$^{-1}$. $Ir_4(CO)_{12}$ is insoluble in liquid paraffin below 100° and spectrum (d) was obtained after cooling to room temperature when all the unreacted tetramer had crystallised from solution. This spectrum resembles very strongly that of tetracarbonylcobalt hydride [prepared in the high-pressure cell by the reaction of $Co_2(CO)_8$ with 100 atm. total pressure of carbon monoxide and hydrogen at 50°]. The bands at 2054 and 2031 cm.$^{-1}$ may be assigned as the $A_1$ and $E$ vibrations respectively, by analogy with the cobalt analogue,[5] but the presence of the second weak $A_1$ vibration [at 2118 cm.$^{-1}$ in $HCo(CO)_4$] is difficult to confirm because of the absorption band due to dissolved carbon monoxide. None of the observed frequencies is altered significantly on reaction of $Ir_4(CO)_{12}$ with carbon monoxide and deuterium, thus suggesting that the band at 1999 cm.$^{-1}$ is due to a $^{13}C$–O vibration rather than $\nu$(Ir–H). A band in a similar position has been noted previously in the spectrum of $HCo(CO)_4$.[6]

Thus, although the formation of polynuclear carbonyliridium hydrides cannot be excluded, the extreme similarity between spectrum (d) and that of $HCo(CO)_4$ strongly suggests the formation of monomeric tetracarbonyliridium hydride.

Attempts to isolate tetracarbonyliridium hydride have been unsuccessful, rapid decomposition to $Ir_4(CO)_{12}$ occurring on decreasing the pressure to atmospheric. During this decomposition no evidence was obtained for the intermediate formation of $Ir_2(CO)_8$, a compound which was also claimed by Hieber and Lagally.[1] In addition, the liquid paraffin i.r. spectrum of $Ir_4(CO)_{12}$ remains unchanged on prolonged treatment with carbon monoxide alone at 550 atm. and 200°.

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