A High Pressure Infrared Spectral Study of the Reactions of Dodecacarbonyltetrairidium with Carbon Monoxide and Hydrogen

By **R. Whyman**, Imperial Chemical Industries Limited, Corporate Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire

The reactions of $Ir_4(CO)_{12}$ under pressures of carbon monoxide and hydrogen have been investigated by following i.r. spectral changes in a high pressure spectrophotometric cell in attempts to obtain evidence for the existence of $Ir_2(CO)_8$ and $HIr(CO)_4$. Although no reaction has been observed with carbon monoxide alone, the parent carbonyl is partially converted into $HIr(CO)_4$ by reaction with carbon monoxide and hydrogen (1 : 1 mole ratio) at 430 atm. total pressure and 200 °C; no evidence has been obtained for the formation of $Ir_2(CO)_8$. A convenient synthesis of $Ir_4(CO)_{12}$ in high yield is also described.

THE chemistry of the iridium carbonyls has not been thoroughly explored[1] no doubt partly because of the high cost of iridium salts but also because of apparent difficulties in the synthesis and characterisation of the various species which would be expected to exist.

In 1940, Hieber and Lagally[2] reported the preparation of two iridium carbonyls of empirical formulae $[Ir(CO)_3]$ and $[Ir(CO)_4]$ and of a carbonyl hydride $HIr(CO)_4$. The carbonyls were prepared by the reaction of either anhydrous iridium halides IrX_3 or halogenoiridiates $[IrX_6]^{4-}$ and $[IrX_6]^{3-}$, where X = Cl, Br, and I, with carbon monoxide at 350 atm. pressure and high temperatures (100—200 °C) in the presence of copper or silver as halogen acceptor. The hydridocarbonyl $HIr(CO)_4$ was described as a very volatile compound obtained when water containing iridium trichloride was used in the preparation of the iridium carbonyls. The species $[Ir(CO)_3]$ is now well characterised as the tetrameric $Ir_4(CO)_{12}$ and a crystal structure determination has shown the presence of a tetrahedral Ir_4 cluster supported solely by metal–metal bonds and with three terminal carbonyl groups attached to each iridium atom.[3] In contrast, there has been no further positive evidence to support the existence of either the presumably dimeric $[Ir(CO)_4]$ or $HIr(CO)_4$ since the original publication of Hieber and Lagally. The characterisation of the hexanuclear carbonyl $Ir_6(CO)_{16}$, isomorphous with the well known $Rh_6(CO)_{16}$, has recently been described[4] and the carbonylation of hydrated iridium trichloride in methanol at 40 atm. pressure and 60 °C for 36 h has been shown to provide a 57% yield of $Ir_4(CO)_{12}$.[5]

This paper describes our attempts to clarify the situation concerning the existence of $Ir_2(CO)_8$ and $HIr(CO)_4$ by a direct study of the reactions of $Ir_4(CO)_{12}$ under pressures of carbon monoxide and hydrogen using a high pressure spectrophotometric cell.[6] A high yield synthesis of $Ir_4(CO)_{12}$ is also described. A preliminary account of this work has appeared.[7]

RESULTS AND DISCUSSION

Synthesis of Dodecacarbonyltetrairidium.—During the course of this work a convenient synthesis of $Ir_4(CO)_{12}$ has been devised using a similar method to that of Chaston and Stone[5] but with the advantages that the product is obtained in higher yield and in shorter reaction times than those reported by these workers. The method involves the carbonylation of a chloroiridiate salt, preferably $Na_2IrCl_6,6H_2O$, (K_2IrCl_6 and $Na_3IrCl_6,12H_2O$ are also satisfactory) in 2-methoxyethanol as solvent at 80—100 atm. pressure and 100 °C for 12—16 h in the presence of copper bronze as halogen acceptor. Under these conditions the product may be isolated in 70—80% yield, based on the starting iridium salt. Higher yields (80—90%) of $Ir_4(CO)_{12}$ may be obtained if the carbon monoxide pressure is increased to 200 atm.

Infrared Spectral Studies under Pressure.—A direct study of the formation of the iridium carbonyls under the 'dry' methods of preparation reported by Hieber and Lagally was precluded by the experimental limitations of the high-pressure i.r. spectroscopic technique. The most convenient alternative approach to obtain evidence for the formation of $Ir_2(CO)_8$ and $HIr(CO)_4$ appeared to be an investigation of the reactions of the tetranuclear $Ir_4(CO)_{12}$ under pressures of carbon monoxide and hydrogen, by analogy with the behaviour observed in the corresponding rhodium carbonyl system. In the latter case we were able to show from i.r. spectral measurements that the equilibrium (I) was reversibly displaced towards the right hand side under high pressures of carbon monoxide and low temperatures.[8]

$$M_4(CO)_{12} + 4CO \rightleftharpoons 2M_2(CO)_8 \qquad (I)$$

Spectral studies of the tetranuclear iridium carbonyl, particularly at low temperatures, are hampered by its low solubility in organic solvents and initial measurements were carried out using liquid paraffin mulls of $Ir_4(CO)_{12}$. Figure 1 illustrates examples of the spectra which have been obtained in the range 2200—1800 cm^{-1} on pressurising liquid paraffin mulls of $Ir_4(CO)_{12}$ with carbon monoxide. The initially broad and indistinct bands due to the solid state spectrum [spectrum (a)] sharpen considerably above 150 °C as the suspension of

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[1] F. Calderazzo, R. Ercoli, and G. Natta, 'Organic Syntheses *via* Metal Carbonyls,' ed. I. Wender and P. Pino, Interscience–Wiley, New York, 1968, vol. 1.

[2] W. Hieber and H. Lagally, *Z. anorg. Chem.*, 1940, **245**, 321.

[3] C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 4792.

[4] L. Malatesta, G. Caglio, and M. Angoletta, *Chem. Comm.*, 1970, 532.

[5] S. H. H. Chaston and F. G. A. Stone, *Chem. Comm.*, 1967, 964; *J. Chem. Soc.* (*A*), 1969, 500.

[6] W. Rigby, R. Whyman, and K. Wilding, *J. Phys.* (*E*), 1970, **3**, 572.

[7] R. Whyman, *Chem. Comm.*, 1969, 1381.

[8] R. Whyman, *Chem. Comm.*, 1970, 1194; *J.C.S. Dalton*, 1972, 1375.

$Ir_4(CO)_{12}$ dissolves. The solution spectrum [spectrum (b)] is extremely simple with band maxima at 2072s and 2032m cm^{-1}; no peaks are observed in the bridging carbonyl region, consistent with the known structure of $Ir_4(CO)_{12}$ in the solid state. The only detectable change in the liquid paraffin solution spectrum even after treatment for 16 h at 550 atm. of carbon monoxide and 200 °C [spectrum (d)] is a slight increase in the intensity of the 2032 cm^{-1} band which approximately parallels the increased intensity of the broad band centred at *ca.* 2150 cm^{-1} arising from additional carbon monoxide dissolved in solution at high temperatures. The apparent intensity increase of the 2032 cm^{-1} band may also be explained by the formation of a small amount of $HIr(CO)_4$ (see later) from reaction with carbon monoxide and the small amount of hydrogen (*ca.* 0·5%) normally present in our supply of this gas.

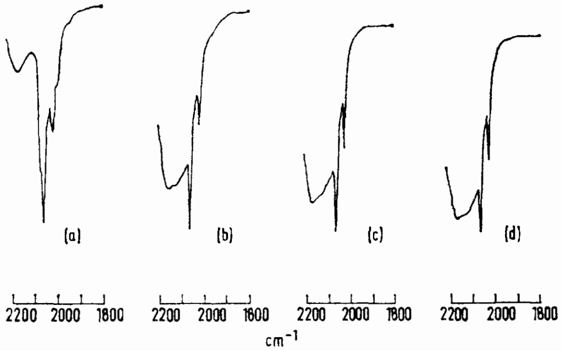

FIGURE 1 Reaction of $Ir_4(CO)_{12}$ with carbon monoxide in liquid paraffin: (a), 340 atm. pressure and 40 °C; (b), 400 atm. and 175 °C; (c), 410 atm. and 200 °C; and (d), 550 atm. and 200 °C

Cleavage of the tetranuclear cluster by carbon monoxide alone thus appears very difficult under the high pressure–high temperature conditions described above. Again, by analogy with behaviour observed in the $Rh_4(CO)_{12}$ system, there remains the possibility that breakdown of the cluster might occur at low rather than high temperatures, and to investigate this possibility the reaction of $Ir_4(CO)_{12}$ with carbon monoxide has been studied in carbon tetrachloride and tetrahydrofuran (THF) solutions using a long pathlength (1 mm) between the windows of the high pressure cell. No significant spectral changes have been observed either in CCl_4 at 300 atm. pressure over the temperature range −10° to 110 °C or in THF at 280 atm. pressure and 20—180 °C. Lower carbon monoxide pressures have been used with CCl_4 and THF than when liquid paraffin was used as reaction medium because the greater solubility of carbon monoxide in the first two solvents gives rise to such a strong peak at *ca.* 2150 cm^{-1} that the significant part of the carbonyl stretching region (2100—2000 cm^{-1}) becomes obscured. At temperatures below −10 °C in CCl_4 the metal carbonyl stretching frequencies become even weaker in intensity, presumably because of the almost complete insolubility of $Ir_4(CO)_{12}$ at these temperatures.

We have thus been unable to obtain any evidence for the formation of $Ir_2(CO)_8$ from the reaction of $Ir_4(CO)_{12}$ under high pressures of carbon monoxide at either high or low temperatures. This contrasts with results obtained in the corresponding cobalt and rhodium systems and the ease with which equilibrium (I) is displaced to the right obviously lies in the order Co $>$ Rh $\gg$ Ir. In the case of M = Co, hexane solutions of $Co_4(CO)_{12}$ may readily be converted into $Co_2(CO)_8$ by treatment with carbon monoxide at 100 atm. pressure and 75 °C; indeed this conversion has even been reported to occur under ambient conditions in isopropyl alcohol as solvent.[9] This dramatic difference in reactivity of $M_4(CO)_{12}$ towards carbon monoxide in the series Co, Rh, and Ir may simply be a reflection of the generally accepted view that the tendency to form metal–metal bonded cluster compounds (and presumably the stability of such compounds relative to mononuclear species) increases on progressing down a given triad of elements.[1] However, it should also be borne in mind that different structural species are present in the compounds under study. Thus in $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ three of the four metal atoms in the tetrahedral clusters are supported by both bridging carbonyl groups and metal–metal bonds [3,10] whereas in $Ir_4(CO)_{12}$ all four metal atoms, as mentioned previously, are joined solely by metal–metal bonds.[3]

The reactions of liquid paraffin mulls of $Ir_4(CO)_{12}$ under pressures of carbon monoxide and hydrogen mixed gas (1 : 1 mole ratio) have also been studied and examples of the spectra which have been obtained in the region 2200—1800 cm^{-1} are illustrated in Figure 2.

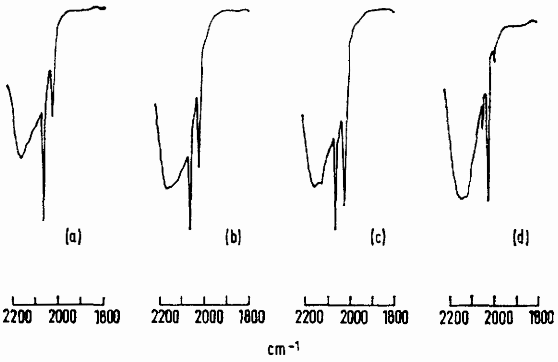

FIGURE 2 Reaction of $Ir_4(CO)_{12}$ with carbon monoxide and hydrogen (1 : 1) mixed gas in liquid paraffin: (a), 370 atm. pressure and 175 °C; (b), 430 atm. and 200 °C; (c), 430 atm. and 200 °C; and (d), 315 atm. and 22 °C

Spectrum (a) corresponds with the solution spectrum of $Ir_4(CO)_{12}$. Spectra (b) and (c) were measured at 430 atm. total pressure and 200 °C, (c) being recorded 3 h after (b). During this time the peak at 2031 cm^{-1} has increased considerably in intensity and a shoulder appeared at 2054 cm^{-1}. After the recording of spectrum (c) the cell was allowed to cool. Below 100 °C $Ir_4(CO)_{12}$

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[9] P. Chini, *Inorg. Chim. Acta Rev.*, 1968, **2**, 31.
[10] C. H. Wei, *Inorg. Chem.*, 1969, **8**, 2384.

is insoluble in liquid paraffin and commences to crystallise out on the base of the cell. Spectrum (d) was obtained after cooling to room temperature when all the unreacted tetramer had crystallised from solution. This spectrum is very similar to that of cobalt tetracarbonyl hydride which was recorded in the high pressure cell on treatment of a hexane solution of $Co_2(CO)_8$ with 300 atm. total pressure of carbon monoxide and hydrogen at 75 °C.

Metal carbonyl stretching frequencies (cm^{-1}) *

$Ir_4(CO)_{12}$	$HIr(CO)_4$	$HCo(CO)_4$
		2118vw
2072s		
	2054m	2052m
2032m	2031s	2029s
	1999w	1996vw

* Paraffin hydrocarbon solvents.

Band maxima for the various species are summarised in the Table. By analogy with the spectrum of $HCo(CO)_4$ [11] the bands at 2054 and 2031 cm^{-1} may be assigned as the A_1 and E vibrations respectively, but the presence of a 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 a ^{13}C–O vibration rather than ν(Ir–H). A band in a similar position has been noted previously in the spectrum of $HCo(CO)_4$.[12] Thus, although the formation of polynuclear iridium carbonyl hydrides cannot be excluded, the extreme similarity between spectrum (d) and that of $HCo(CO)_4$ strongly suggests that the tetranuclear cluster of $Ir_4(CO)_{12}$ has been cleaved by carbon monoxide and hydrogen under the high pressure–high temperature conditions with the formation of monomeric iridium tetracarbonyl hydride.

Attempts to isolate iridium tetracarbonyl hydride have been unsuccessful, decomposition to $Ir_4(CO)_{12}$ occurring on decreasing the pressure to that of the atmosphere. During this decomposition no evidence was obtained for the intermediate formation of $Ir_2(CO)_8$. Also, pressurising the solution apparently containing $HIr(CO)_4$ at room temperature with carbon monoxide alone results in the slow transformation to $Ir_4(CO)_{12}$ rather than the formation of $Ir_2(CO)_8$.

Recently, the construction of a second high pressure cell for use in the reference beam of the spectrometer has enabled the apparatus to be used in the conventional double beam manner, thus affording considerably greater versatility with respect to choice of solvents. Using this double beam technique the actual preparative procedure for $Ir_4(CO)_{12}$ from sodium chloroiridate has been followed in 2-methoxyethanol to check for the intermediate formation of either $HIr(CO)_4$ or $Ir_2(CO)_8$. Spectra observed are consistent with the successive formation of the carbonyl anions $[Ir(CO)Cl_4,ROH]^-$, $[Ir(CO)_2Cl_4]^-$, and $[Ir(CO)_2Cl_2]^-$, the reaction following a similar course to that reported for the carbonylation of iridium trichloride, $IrCl_3,xH_2O$.[13] Finally the peaks at 2057 and 1970 cm^{-1} corresponding to $[Ir(CO)_2Cl_2]^-$ slowly decrease in intensity with a concomitant increase in intensity of a band at 2095 cm^{-1}, but without any evidence for the formation of $HIr(CO)_4$, $Ir_2(CO)_8$, or $Ir_4(CO)_{12}$. The peak at 2095 cm^{-1} may correspond with the formation of Cu(CO)Cl in solution.* At the conclusion of the reaction examination of the dismantled cell showed that the area of the cell walls which had been immersed in solvent was coated with a layer of $Ir_4(CO)_{12}$. This is normally insoluble in 2-methoxyethanol at 100 °C and must have crystallised out immediately on formation from, presumably, $[Ir(CO)_2Cl_2]^-$.

In conclusion, although no evidence has been obtained for the existence of $Ir_2(CO)_8$, either during the preparation of $Ir_4(CO)_{12}$ or from the reactions of $Ir_4(CO)_{12}$ with carbon monoxide at various pressures and temperatures, treatment of $Ir_4(CO)_{12}$ with carbon monoxide and hydrogen at high pressures and temperatures strongly suggests the formation of the mononuclear hydridocarbonyl $HIr(CO)_4$.

EXPERIMENTAL

The iridium salts $Na_2IrCl_6,6H_2O$, K_2IrCl_6, and $Na_3IrCl_6,12H_2O$ were obtained from Johnson–Matthey Chemicals Ltd., copper bronze (organic synthesis grade) and 2-methoxyethanol were obtained from B.D.H. Ltd.; the latter was used without further purification. The design, construction, and mode of operation of the high-pressure i.r. cell have been described previously;[6] i.r. spectra were recorded on a Perkin-Elmer model 257 spectrophotometer.

Dodecacarbonyltetrairidium.—Copper bronze (2·54 g) was added to sodium chloroiridate, $Na_2IrCl_6,6H_2O$ (5·59 g) in carbon monoxide-saturated 2-methoxyethanol (70 ml) contained in a glass liner. The liner and contents were transferred to a stainless steel autoclave (150 ml capacity) and treated with carbon monoxide at 100 atm. pressure and 100 °C for 16 h. After cooling and venting the excess pressure the dark yellow precipitated solid was filtered and washed with nitric acid (one part conc. HNO_3 to one part water) to dissolve the unreacted copper bronze. The product was then washed with water and acetone and finally dried *in vacuo* to give $Ir_4(CO)_{12}$ (*ca.* 2·0—2·2 g, 72—80%) as a light yellow powder, identified by comparison of its i.r. spectrum with that of an authentic sample. Further purification, if necessary, may be effected by Soxhlet extraction in carbon tetrachloride.

The use of higher pressures (200 atm.) for the same reaction time affords up to 90% yields of $Ir_4(CO)_{12}$.

The use of $Na_3IrCl_6,12H_2O$ and K_2IrCl_6 as starting materials gives $Ir_4(CO)_{12}$ yields of *ca.* 60—70% which vary somewhat with the particular batch of iridium salt used.

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* A solution of Cu(CO)Cl in tetrahydrofuran exhibits a single ν(CO) stretching frequency at 2096 cm^{-1}.

[11] G. Bor, *Inorg. Chim. Acta*, 1967, **1**, 81.

[12] G. Bor and L. Markó, *Spectrochim. Acta*, 1960, **16**, 1105.

[13] D. Forster, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 433; *Synth. Inorg. Metal-Org. Chem.*, 1971, **1**, 221.