A High-pressure Infrared Spectral Study of the Reactions of Phosphine-substituted Derivatives of Tetrairidium Dodecacarbonyl with Carbon Monoxide and Hydrogen

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The reactions of tetranuclear phosphine-substituted iridium carbonyls of the types $Ir_4(CO)_9L_3$, where L = PPh_3, $P(p\text{-}Me{\cdot}C_6H_4)_3$, PEt_3, and PPr^i_3, and $Ir_4(CO)_8L_4$, where L = PEt_3, PPr^n_3, and PBu^n_3, under pressures of carbon monoxide and hydrogen have been investigated by following i.r. spectral changes in a high-pressure spectrophotometric cell. The tetranuclear arylphosphine- and isopropylphosphine-substituted derivatives are cleaved by reaction with carbon monoxide to give the dinuclear species $Ir_2(CO)_6L_2$, which for L = PPh_3, $P(p\text{-}Me{\cdot}C_6H_4)_3$, and PPr^i_3, have been isolated and characterised. Further reactions of the dinuclear compounds occur under more forcing conditions with the reversible formation of $Ir_2(CO)_7L$. Breakdown of the tetranuclear cluster by carbon monoxide occurs less readily with the n-alkylphosphine-substituted derivatives· instead initial replacement of phosphine by carbon monoxide occurs yielding $Ir_4(CO)_9L_3$, $Ir_4(CO)_{10}L_2$, and finally $Ir_2(CO)_7L$, where L = PEt_3, PPr^n_3, and PBu^n_3. Reactions of both the aryl- and alkyl-phosphine-substituted iridium carbonyls with carbon monoxide and hydrogen mixed gases follow similar courses, finally leading to cleavage of the tetranuclear and dinuclear compounds with the formation of mononuclear hydridocarbonyls of the type $HIr(CO)_3L$, where L = PPh_3, $P(p\text{-}CH_3C_6H_4)_3$, PEt_3, PPr^n_3, PPr^i_3, and PBu^n_3. The significance of the formation of the latter species under high pressures and temperatures is discussed in relation to catalytic species involved in the hydroformylation reaction.

PRELIMINARY studies on the hydroformylation of olefins catalysed by mixtures of phosphines and tetrairidium dodecacarbonyl suggested that tetranuclear, dinuclear, and mononuclear iridium carbonyls or carbonyl hydrides might be present in the reaction mixtures.[1] In an attempt to characterise some of these species spectrally and to determine the reaction conditions under which fission of the Ir_4 cluster occurs, a study of the basic reactions of tetranuclear phosphine-substituted iridium carbonyls under pressures of carbon monoxide and hydrogen in the absence of olefin has been undertaken.

Before the start of this work few polynuclear phosphine-substituted iridium carbonyls had been described but the addition of triphenylphosphine to the carbonyl anions $[Ir_4(CO)_{11}H]^-$ and $[Ir_8(CO)_{20}]^{2-}$ has been shown to yield $Ir_4(CO)_{10}(PPh_3)_2$ and $Ir_4(CO)_9(PPh_3)_3$ respectively.[2] Characterisation of these compounds by *X*-ray analysis [3] has demonstrated that the Ir_4 cluster is supported both by bridging carbonyl groups and metal–metal bonds in both cases. In contrast the structure of the parent carbonyl $Ir_4(CO)_{12}$ consists of an Ir_4 cluster held together solely by metal–metal bonds.[4]

This paper describes the preparation of some tetra- and di-nuclear phosphine-substituted iridium carbonyls and their reactions under pressures of carbon monoxide and hydrogen as studied by use of a high-pressure spectrophotometric cell.[5] Particular interest is focused on i.r. spectral evidence for the existence of the hydridocarbonyl species $HIr(CO)_{4-n}L_n$ under high pressures and temperatures and the potential significance of the results towards the catalytic species present in the hydroformylation reaction is discussed. Preliminary accounts of this work have appeared.[6]

RESULTS AND DISCUSSION

Preparation of the Complexes.—The compounds $Ir_4(CO)_9L_3$, where $L = PPh_3$, $P(p\text{-}Me{\cdot}C_6H_4)_3$, and PPr^i_3, have been prepared by a route similar to that briefly described by Malatesta and Caglio.[2] The products precipitate slowly after the addition of the ligand to a warm solution of $Ir_4(CO)_{12}$ in potassium hydroxide–methanol. The i.r. spectra of the three compounds (Table 1) are very similar and, in the case of $L = PPh_3$, consistent with that reported for $Ir_4(CO)_9(PPh_3)_3$. The complexes are slightly soluble in common organic solvents and are non-electrolytes in nitrobenzene, and a molecular-weight determination of the tri-isopropylphosphine derivative in toluene is consistent with the tetranuclear formulation.

In the course of preparative work it was found that these tetranuclear cluster compounds could be fairly readily cleaved by reaction with carbon monoxide. Thus, treatment of heptane suspensions of these compounds with 80—100 atm carbon monoxide at 150 °C affords yellow, air-stable compounds of empirical formula $[Ir(CO)_3L]$, as indicated by elemental analysis. Highest yields are obtained when the reaction is carried out in the presence of a slight excess of L. The i.r. spectra of these complexes in the carbonyl stretching region (see Table 1) exhibit one very strong band at *ca.* 1940 cm^{-1} and shoulders at *ca.* 1970 and 1900 cm^{-1}, an absorption pattern very similar to that observed for the dimeric non-bridged phosphine-substituted complexes of dicobalt octacarbonyl $Co_2(CO)_6L_2$.[7] The compounds are non-electrolytes in nitrobenzene and, for $L = PPh_3$ and $P(p\text{-}Me{\cdot}C_6H_4)_3$, almost insoluble in organic solvents.

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[1] R. Whyman, unpublished results.

[2] L. Malatesta and G. Caglio, *Chem. Comm.*, 1967, 420.

[3] V. Albano, P. L. Bellon, and V. Scatturin, *Chem. Comm.*, 1967, 730.

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

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

[6] R. Whyman, Proc. 3rd. Internat. Symposium on Reactivity and Bonding in Transition Organometallic Compounds, Venice, 8—10th September 1970, Paper E2; *J. Organometallic Chem.*, 1970, **24**, C35; 1971, **29**, C36.

[7] O. Vohler, *Chem. Ber.*, 1958, **91**, 1235.

The tri-isopropylphosphine complex is, however, more soluble and a molecular-weight determination in toluene gave a value of 820, consistent with the dimeric formulation (calc. 872). The three complexes are therefore formulated as dimers. Their stability contrasts markedly with that of the dimeric rhodium analogues,[8] and there is no apparent tendency for conversion into the tetramers in solution as was observed in the latter case.

An alternative synthesis of $Ir_2(CO)_6(PPh_3)_2$ with milder conditions has also been described.[9] However, this suffers from the disadvantage that the complex is formed as a mixture with an equimolar amount of $HIr(CO)(PPh_3)_3$, thus involving either a tedious separation of a mixture of two only slightly soluble compounds or further treatment with carbon monoxide under pressure to convert $HIr(CO)(PPh_3)_3$ into $Ir_2(CO)_6(PPh_3)_2$ (see later).

TABLE 1

ν(CO) Stretching frequencies/cm^{-1} for phosphine-substituted iridium carbonyls [a]

L	PEt_3	PPr^n_3	PBu^n_3	PPr^i_3	PPh_3	$P(p\text{-}Me{\cdot}C_6H_4)_3$
$Ir_4(CO)_8L_4$	2035vw	2032vw	2023vw	*b*	*b*	*b*
	1991m	1988m	1981m			
		1968m,sh				
	1959s	1956vs	1947vs			
	1953s,sh	1950s,sh				
	1927w	1925w	1914w			
	1772s	1772s	1766s			
$Ir_4(CO)_9L_3$	2034ms	2033ms	2033ms	2040s [c]	2042ms [d]	2038ms [d]
	2011w	2011w	2010w		2015sh	2007sh
	1991s	1989s	1990s	1992s		
	1984vs	1982vs	1982vs	1982vs	1982vs	1983vs
				1967w		
	1960ms	1960ms	1960ms	1959w	1962sh	1958sh
	1784s	1784s	1780s,br	1781s	1772s,br	1775s
	1780s	1780s		1774s		1765s
$Ir_4(CO)_{10}L_2$	2066s	2064s	2062s	2068s	*b*	*b*
	2038s	2036s	2035s	2040s		
	2000ms,br	2001ms,br	2001s	2005s		
	1830m	1830m	1829m	1828m		
	1792m	1790m	1782m	1781m		
$Ir_2(CO)_6L_2$	*b*	*b*	*b*	1975mw,sh [e]	1975ms,sh [e]	1970ms,sh [e]
				1954s	1945s	1943s
				1933sh	1900mw,sh	1896mw,sh
$Ir_2(CO)_7L$	2066	2064	2062	2072	2072ms	2071
	2038	2036	2035	2042	2033m	2032
	1974	1975	1976	1973	1981s	1978
	1938	1937	1936	1947	1947w,sh	1946?
$HIr(CO)_3L$	2035mw	2041mw	2039mw	2040mw	2046mw	2043mw
	1973s	1973s	1972s	1970s	1982s	1979s
	1938w	1940w	1937w	1934w	1948w	1946w

[a] Paraffin hydrocarbon solvents. [b] Not isolated. [c] At 75 °C. [d] KBr disc. [e] Nujol mull.

Although direct reaction of $Ir_4(CO)_{12}$ and arylphosphines only occurs under drastic conditions to give mixtures of products in low yields we have found that alkylphosphines react readily with suspensions of $Ir_4(CO)_{12}$ in refluxing toluene to yield complexes of the types $Ir_4(CO)_8L_4$, where L = PEt_3, PPr^n_3, and PBu^n_3, and $Ir_4(CO)_9L'_3$, where L' = PEt_3 and PPr^i_3. In the last case formation of $Ir_4(CO)_9(PPr^i_3)_3$ occurs only very slowly by this route and a preferable preparation is *via* the $[Ir_8(CO)_{20}]^{2-}$ anion. These new compounds are orange or yellow air-stable solids [with the exception of $Ir_4(CO)_8(PBu^n_3)_4$ which is an oil] and have been characterised by elemental analysis. They are non-electrolytes in nitrobenzene and molecular-weight determinations in benzene or toluene correspond approximately with the tetranuclear formulation although the results are rather lower than the calculated values; mass spectra of the triethylphosphine complexes $Ir_4(CO)_8L_4$ and $Ir_4(CO)_9L_3$ show parent ions at *ca.* 1460 and 1370 and breakdown patterns consistent with the presence of a tetranuclear iridium cluster.

I.r. spectra (Table 1) of the trisubstituted derivatives $Ir_4(CO)_9L_3$ are all virtually identical and very similar to those previously described, suggesting the presence of similar structural isomers in each case; spectra of the tetrasubstituted complexes $Ir_4(CO)_8L_4$ are relatively simple for molecules of this complexity, indicating fairly highly symmetrical structures. Halogen oxidation of the triethylphosphine derivative $Ir_4(CO)_8(PEt_3)_4$ causes fission of the cluster with the formation of the species $Ir(CO)_2(PEt_3)X_3$, where X = Cl or I. This evidence suggests that in the starting compound one phosphine ligand is attached to each iridium atom.

With the exception of $Ir_4(CO)_9(PPr^i_3)_3$ these alkylphosphine-substituted compounds are much more resistant to cleavage by carbon monoxide than the arylphosphine derivatives. Thus similar treatment of the

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[8] R. Whyman, *Chem. Comm.*, 1970, 230; *J.C.S. Dalton*, 1972, 1375.

[9] L. Malatesta, M. Angoletta, and G. Caglio, Proc. XIIIth Internat. Conf. Coordinat. Chem., Cracow-Zakopane, 1970, p. 397; L. Malatesta, M. Angoletta, and F. Conti, *J. Organometallic Chem.*, 1971, **33**, C43.

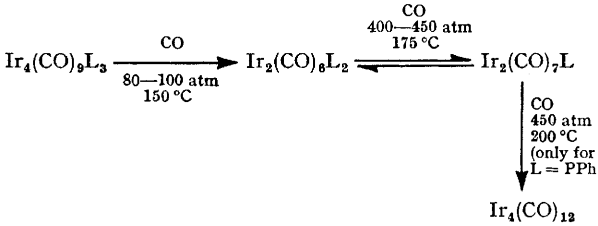
compounds $Ir_4(CO)_8L_4$, where L = PEt_3, $PPr^n{}_3$, and $PBu^n{}_3$, with carbon monoxide at 100 atm and 150 °C results in the replacement of one molecule of phosphine and the formation of $Ir_4(CO)_9L_3$. This species, even when separated from the excess of phosphine by isolation, does not react further with carbon monoxide under these conditions.

I.r. Spectroscopic Studies under High Pressure.—The reactions of complexes of the general formulae $Ir_2(CO)_6L_2$, $Ir_4(CO)_9L_3$, and $Ir_4(CO)_8L_4$ with carbon monoxide and hydrogen at pressures above 100 atm and temperatures higher than 150 °C appeared to give unstable products and these reactions have been studied in detail in the high-pressure i.r. cell. The general courses of these reactions may be indicated by a discussion of two typical examples, namely $Ir_2(CO)_6(PPh_3)_2$ and $Ir_4(CO)_8(PEt_3)_4$.

$Ir_2(CO)_6(PPh_3)_2$. When liquid paraffin suspensions of $Ir_2(CO)_6(PPh_3)_2$ are treated with carbon monoxide at an initial pressure of 410 atm little change is observed in the spectrum until the temperature is increased to 160 °C whereupon new absorptions appear at 2072, 2033, and 1981 cm^{-1} together with a concomitant decrease in intensity of the band at 1945 cm^{-1}. The new peaks correspond to the replacement of one molecule of triphenylphosphine by carbon monoxide and the formation of $Ir_2(CO)_7PPh_3$, by analogy with the similarity to the i.r. spectrum[10] of $Co_2(CO)_7PPh_3$ [ν(CO) 2079, 2026, 1996, and 1964 cm^{-1}]. The fourth peak which might be expected to appear at *ca.* 1950 cm^{-1} is at this stage obscured by the spectrum of the starting material. However, complete conversion into $Ir_2(CO)_7PPh_3$ apparently occurs at 175 °C, when the shoulder at 1947 cm^{-1} is observed unchanged during several hours at this temperature. This shoulder probably corresponds with the fourth band observed in the spectrum of $Co_2(CO)_7PPh_3$ although its intensity is less than would be expected on the same analogy. At higher temperatures (200 °C) further reaction takes place with the formation of $Ir_4(CO)_{12}$; the band at 1981 cm^{-1} decreases in intensity as the 2072 cm^{-1} maximum increases. Finally, the spectrum consists of two bands at 2072 and 2032 cm^{-1}, characteristic of the solution spectrum of $Ir_4(CO)_{12}$.[11] No evidence for the intermediate formation of $Ir_2(CO)_8$ [12] is obtained during the conversion of $Ir_2(CO)_7PPh_3$ into $Ir_4(CO)_{12}$ under these conditions of high pressure and high temperature.

The compound $Ir_2(CO)_7PPh_3$ is unstable and attempts at its isolation from preparative-scale reactions have been unsuccessful. Although i.r. spectra measured immediately after depressurising the autoclave indicate that the compound is present in solution, rapid recombination with the excess of phosphine occurs leading to the precipitation of the starting material, $Ir_2(CO)_6(PPh_3)_2$. Attempts at scavenging the excess of phosphine with methyl iodide led to the isolation of a mixture of $Ir_4(CO)_{12}$ and $Ir_2(CO)_6(PPh_3)_2$.

The sequence of reactions with carbon monoxide starting from $Ir_4(CO)_9L_3$ may therefore be summarised as in Scheme 1. For L = $P(p\text{-Me}\cdot C_6H_4)_3$ and $PPr^i{}_3$ the reactions follow a similar trend but in the former case $Ir_2(CO)_7L$ formation does not go to completion and in the latter a small amount of an additional species, probably $Ir_4(CO)_{11}L$, is also formed.



L = PPh_3, $P(p\text{-Me}\cdot C_6H_4)_3$, or $PPr^i{}_3$
SCHEME 1

When liquid paraffin suspensions of $Ir_2(CO)_6(PPh_3)_2$ are treated with 250 atm of a 1 : 1 mixture of carbon monoxide and hydrogen new bands are observed in the spectra as the temperature is increased above 60 °C. Thus peaks at 2046 and 1982 cm^{-1} increase in relative intensity as the bands at 1975mw,sh, 1945s, and 1900mw cm^{-1} due to the starting material decrease. At 90 °C the 1945 and 1982 cm^{-1} maxima are of equal intensity and conversion into the new species is complete at 125 °C; no further change is noted on increasing the temperature to 200 °C. The frequencies and relative intensities of the bands in the spectrum at 125 °C correspond closely with the i.r. spectra of monomeric phosphine-substituted derivatives of cobalt tetracarbonyl hydride, *e.g.*, $HCo(CO)_3PBu^n{}_3$,[13] and, by analogy, the formation of $HIr(CO)_3PPh_3$ is thus inferred. The bands at 2046 and 1982 cm^{-1} may be assigned as the A_1 and E vibrations respectively, predicted for a 5-co-ordinate molecule of this type with C_{3v} symmetry. The weak peak at 1948 cm^{-1} could be due either to the presence of small amounts of unchanged starting material or may be assigned as a ^{13}CO 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 $HIr(CO)_3PPh_3$ is unstable in the absence of carbon monoxide and hydrogen and decomposes on releasing the pressure to re-form the insoluble dimer $Ir_2(CO)_6(PPh_3)_2$. No replacement of phosphine occurs on prolonged treatment of $HIr(CO)_3PPh_3$ with carbon monoxide and hydrogen at 450 atm and 200 °C and we have been unable to obtain any evidence for the formation of $HIr(CO)_4$ under these conditions.

This spectral evidence for the formation of $HIr(CO)_3PPh_3$ means that all the members of the series of

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[10] G. Bor and L. Markó, *Chem. and Ind.*, 1963, 912; P. Szabó, L. Fekete, G. Bor, Z. Nagy-Magos, and L. Markó, *J. Organometallic Chem.*, 1968, **12**, 245.

[11] R. Whyman, *Chem. Comm.*, 1969, 1381; *J.C.S. Dalton*, 1972, 2294.

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

[13] F. Piacenti, M. Bianchi, and E. Benedetti, *Chimica e Industria*, 1967, **49**, 245.

compounds $HIr(CO)(PPh_3)_3$,[14] $HIr(CO)_2(PPh_3)_2$,[15] $HIr(CO)_3PPh_3$, and $HIr(CO)_4$ [11] are now known. Indeed, the same final spectrum, corresponding with the formation of $HIr(CO)_3PPh_3$, can be observed (from the successive replacement of phosphine by carbon monoxide) starting from liquid paraffin suspensions of $HIr(CO)(PPh_3)_3$ under the reaction conditions summarised in Scheme 2. Again no further reaction is observed up to 200 °C.

$$\begin{tikzcd}
HIr(CO)(PPh_3)_3 \arrow[r, "400\text{—}450\text{ atm CO-H}_2", "50\text{—}60\text{ °C}"'] & {} & \\
HIr(CO)_2(PPh_3)_2 \arrow[rr, "400\text{—}450\text{ atm CO-H}_2", "80\text{—}120\text{ °C}"'] & & HIr(CO)_3PPh_3 \arrow[d, shift left, "250\text{ atm CO-H}_2", "90\text{—}120\text{ °C}"'] \\
& & Ir_2(CO)_6(PPh_3)_2 \arrow[u, shift left]
\end{tikzcd}$$

SCHEME 2

Additional complexes of the type $HIr(CO)_3L$ can 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 $L = P(p\text{-}MeC_6H_4)_3$ reaction occurs at 430 atm and 140—175 °C whereas for $L = PPr^i_3$ the reaction is particularly rapid and takes place at 300 atm and room temperature. Indeed, in the latter case, i.r. evidence suggests that the hydrido-species $HIr(CO)_3PPr^i_3$ is the initial product formed in the reaction of $Ir_4(CO)_9(PPr^i_3)_3$ and PPr^i_3 with carbon monoxide. Only on evaporation of the solvent under reduced pressure does the colourless solution turn yellow and deposit yellow crystals of $Ir_2(CO)_6(PPr^i_3)_2$. The origin of the hydride is of interest in this particular system. It is unlikely to arise from hydrogen impurities in the gas stream since the same product is obtained when specially purified carbon monoxide is used. We conclude therefore that the most likely source of hydrogen appears to be from some decomposition of the excess of tri-isopropylphosphine ligand under the reaction conditions.

The formation of $HIr(CO)_3PPh_3$ from the reaction of a benzene suspension of $Ir_2(CO)_6(PPh_3)_2$ with hydrogen under ambient conditions has also been reported.[9] We have found that when liquid paraffin suspensions of $Ir_2(CO)_6(PPh_3)_2$ are treated with hydrogen alone no reaction occurs until 75 °C is reached. Above this temperature several new bands are observed in the spectra. Two of these are consistent with the formation of $HIr(CO)_3PPh_3$ and they decrease in intensity at 100 °C, finally leaving a spectrum showing maxima at 2125m,sh, 2111m,br, 2046w, 2025m, and 1997s cm^{-1}. This is very similar to the spectrum reported for the species $H_3Ir(CO)_2PPh_3$.[9] No further change in the spectrum is noted on heating to 175 °C. The reason for the apparent difference in reactivity of $Ir_2(CO)_6(PPh_3)_2$ towards hydrogen in benzene [9] and liquid paraffin may lie simply in the relative solubilities of hydrogen in the two reaction media.

$Ir_4(CO)_8(PEt_3)_4$. The reactions of $Ir_4(CO)_8(PEt_3)_4$ have been studied in liquid paraffin–heptane (3 : 1) mixed solutions. In contrast to the arylphosphine derivatives, as mentioned previously, the Ir_4 cluster in $Ir_4(CO)_8(PEt_3)_4$ is not initially cleaved by reaction with carbon monoxide even at 400 atm; instead successive replacement of phosphine by carbon monoxide occurs. Thus $Ir_4(CO)_9(PEt_3)_3$ is formed at 400 atm and 90—100 °C, and $Ir_4(CO)_{10}(PEt_3)_2$ at 505 atm and 200 °C. The former has been isolated and characterised and the formation of the latter is inferred from the similarity to the i.r. spectra of the previously reported triphenylphosphine analogues.[2] However, the spectrum of $Ir_4(CO)_{10}(PEt_3)_2$ exhibits an additional strong band at 1974 cm^{-1} and a weaker one at 1938 cm^{-1}, peaks which may correspond with the formation of $Ir_2(CO)_7PEt_3$; other absorptions expected for this species may overlap with the 2066 and 2038 cm^{-1} bands due to $Ir_4(CO)_{10}(PEt_3)_2$ [*cf.* the i.r. spectrum of $Ir_2(CO)_7PPh_3$]. In the case of $L = PBu^n_3$ the species $Ir_2(CO)_7PBu^n_3$ appears to be the predominant final product. There is no further reaction under these conditions (505 atm, 200 °C) for prolonged periods and no evidence for the formation of $Ir_2(CO)_8$.

The reaction of $Ir_4(CO)_8(PEt_3)_4$ with 1 : 1 mixtures of carbon monoxide and hydrogen follows a similar course to that with carbon monoxide alone and the initial product, $Ir_4(CO)_9(PEt_3)_3$, is formed at 460 atm and 100 °C, no further change occurring until 190 °C is reached. At this temperature the spectrum simplifies considerably as the absorptions at 1992, 1985, 1784, and 1780 cm^{-1} slowly disappear and a new peak appears at 1973 cm^{-1}. The final spectrum measured at 435 atm and 200 °C shows bands at 2035mw, 1973s, and 1938w cm^{-1}, a band pattern which appears characteristic of species of the type $HM(CO)_3L$; the formation of $HIr(CO)_3PEt_3$ is thus inferred. No further reaction of $HIr(CO)_3PEt_3$ is observed during prolonged periods at 450 atm and 200 °C. Again the monomeric hydrido-species appears to be unstable in the absence of carbon monoxide and hydrogen pressures.

The reactions of the complexes $Ir_4(CO)_8L_4$ with carbon monoxide and CO–H_2 mixed gases are summarised in Scheme 3.

$$Ir_4(CO)_8L_4 \xrightarrow[90\text{—}100\text{ °C}]{300\text{—}400\text{ atm CO}}$$

$$Ir_4(CO)_9L_3 \xrightarrow[200\text{ °C}]{400\text{—}450\text{ atm CO}} Ir_4(CO)_{10}L_2 + Ir_2(CO)_7L$$

$$Ir_4(CO)_8L_4 \xrightarrow[90\text{—}100\text{ °C}]{300\text{—}400\text{ atm CO-H}_2}$$

$$Ir_4(CO)_9L_3 \xrightarrow[200\text{ °C}]{400\text{—}450\text{ atm CO-H}_2} HIr(CO)_3L$$

$$L = PEt_3,\ PPr^n_3,\ PBu^n_3$$

SCHEME 3

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[14] S. S. Bath and L. Vaska, *J. Amer. Chem. Soc.*, 1963, **85**, 3500.

[15] J. P. Collman, F. Vastine, and W. R. Roper, *J. Amer. Chem. Soc.*, 1968, **90**, 2282; G. Yagupsky and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 725.

The reaction of liquid paraffin–heptane solutions of $Ir_4(CO)_8(PEt_3)_4$ with hydrogen alone (400 atm) have also been studied. No reaction occurs below 85 °C at which temperature new bands appear in the spectrum at 2008 and 1984 cm^{-1}. These increase in intensity with time and increasing temperature as the maxima due to the starting material decrease. At 150 °C the bridging carbonyl frequencies disappear completely and the spectrum consists of bands at 2107w,br, 2043w, 2033mw, 2008m, and 1984ms cm^{-1}. This presumably corresponds with the formation of a polynuclear phosphine-substituted hydridocarbonyl species. The relative intensities of the bands in the final spectrum compared with those of the starting material suggest that some decomposition has taken place.

In conclusion, the i.r. evidence has indicated that, in a variety of phosphine-substituted iridium carbonyls, the tetranuclear cluster may be split by reactions with either carbon monoxide or carbon monoxide–hydrogen mixed gas at high pressures and temperatures yielding $Ir_2(CO)_7L$ and $HIr(CO)_3L$ respectively. In one case, that of $Ir_2(CO)_7PPh_3$, further reaction occurs at higher temperature to give $Ir_4(CO)_{12}$. These observations are of particular significance to the question of the catalytic species involved in hydroformylations catalysed by iridium carbonyl–phosphine systems. With iridium catalysts it is generally believed that high pressures and temperatures[16,17] are necessary to obtain the desired activity, although stoicheiometric hydroformylation in the presence of $Ir_2(CO)_6(PPh_3)_2$ under ambient conditions has been mentioned.[18] The evidence described here is the first to show that hydrido-species of the type $HIr(CO)_3L$ are formed and are stable under pressures and temperatures approaching those conventionally used in hydroformylation. Additionally, in the absence of phosphines it has previously been shown that $Ir_4(CO)_{12}$ is partially converted into $HIr(CO)_4$ at high pressures of carbon monoxide and hydrogen and high temperatures.[11] These results suggest that it is unlikely that the polynuclear compounds themselves can be the active catalysts in the hydroformylation reaction.

TABLE 2

Analytical, molecular weight, and conductivity data

Compound	Found (%) C	H	P	Hal	Required (%) C	H	P	Hal	*M* Found	Reqd.	Conductivity[b] Ω^{-1} cm² mol⁻¹
$Ir_2(CO)_6(PPh_3)_2$	46·6	2·8	6·15		46·8	2·8	5·8		Insol.	1076	0·12
$Ir_2(CO)_6[P(p\text{-}Me{\cdot}C_6H_4)_3]_2$	49·2	4·5	5·7		49·8	4·6	5·4		Insol.	1160	0·04
$Ir_4(CO)_9[P(p\text{-}Me{\cdot}C_6H_4)_3]_3$	43·7	3·25	4·8		44·7	3·3	4·7		1640	1932	0·09
$Ir_2(CO)_6(PPr^i_3)_2$	32·9	4·9	7·2		33·0	4·8	7·1		820	872	0·12
$Ir_4(CO)_9(PPr^i_3)_3$	28·8	4·4	5·9		28·8	4·2	6·2		1550	1501	0·05
$Ir_4(CO)_8(PPr^n_3)_4$	31·9	5·3	8·0		32·3	5·1	7·6		1450	1633	0·15
$Ir_4(CO)_9(PEt_3)_3$	23·6	3·3	6·6		23·6	3·3	6·8		1300	1375	0·04
$Ir_4(CO)_8(PEt_3)_4$	26·4	4·3	8·6		26·2	4·1	8·5		1300	1465	0·11
$Ir(CO)_2(PEt_3)I_3,\frac{1}{3}C_6H_6$	15·4	2·2	4·0	48·0	15·5	2·2	4·0	49·3			
$Ir(CO)_2(PEt_3)Cl_3$	19·5	3·2	6·2	22·3	20·3	3·2	6·6	22·5			

[a] Determined osmometrically in either benzene or toluene. [b] For *ca.* 10^{-3}M in nitrobenzene at 25 °C.

In studies of hydroformylations catalysed by cobalt and rhodium carbonylphosphine analogues it has been suggested that the active catalysts are $HCo(CO)_3L$ [together with an increasing amount of $HCo(CO)_4$ at higher carbon monoxide pressures][19] and $HRh(CO)_2L_2$[20] respectively. We have shown that $HCo(CO)_3PBu^n_3$ is the major species present under optimum hydroformylation conditions as described by Slaugh and Mullineaux.[1] Our results suggest therefore that iridium parallels cobalt rather than rhodium in behaviour during hydroformylation.

EXPERIMENTAL

All manipulations were performed under dry nitrogen except where stated otherwise. Solid ligands were normally recrystallised before use and solvents dried over sodium and presaturated with dry nitrogen. Microanalyses for carbon, hydrogen, phosphorus, and halogen were performed by Mr. C. E. O'Brien; molecular weight and conductivity data were determined by Messrs. A. Nevin and L. H. Bell respectively; mass spectra were measured by Mr. D. Winstanley. Analytical data for the new compounds are in Table 2.

I.r. spectra were recorded with a Perkin-Elmer model 257 spectrophotometer with ×10 scale expansion and calibration with either gaseous carbon monoxide or water vapour. Details of the high-pressure spectrophotometric cell have been described.[5]

Figures illustrating i.r. spectra of the reactions of $Ir_2(CO)_6(PPh_3)_2$ and $Ir_4(CO)_8(PEt_3)_4$ with carbon monoxide and 1 : 1 carbon monoxide-hydrogen mixtures are deposited with the N.L.L. as Supplementary Publication No. SUP 20584 (6 pp.).

Nonacarbonyltris(triphenylphosphine)tetrairidium.— This complex was prepared according to the brief details given by Malatesta and Caglio.[2] $Ir_4(CO)_{12}$ (0·40 g) was added to a solution of potassium hydroxide (1·0 g) in methanol (40 ml) saturated with carbon monoxide at 50 °C. A clear yellow-orange solution was obtained after *ca.* 10 min; triphenylphosphine (0·40 g) in methanol (20 ml) was added, and the mixture stirred at 50 °C for 2 h during which orange-yellow *crystals* of $Ir_4(CO)_9(PPh_3)_3$ (0·53 g) separated from solution;

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[16] B.P. 1,202,779/1970.

[17] L. Benzoni, A. Andreetta, C. Zanzottera, and M. Camia, *Chimica e Industria*, 1966, **48**, 1076.

[18] A. Viviani, Thesis, University of Milan, 1969, quoted in ref. 9.

[19] L. H. Slaugh and R. D. Mullineaux, *J. Organometallic Chem.*, 1968, **13**, 469; F. Piacenti, M. Bianchi, E. Benedetti, and P. Frediani, *ibid.*, 1970, **23**, 257; E. R. Tucci, *Ind. and Eng. Chem.* (*Prod. Res. and Development*), 1970, **9**, 516.

[20] D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 3133; C. K. Brown and G. Wilkinson, *ibid.*, 1970, 2753.

these were filtered off, washed with methanol and heptane, and dried *in vacuo*.

*Nonacarbonyltris(tri-*p*-tolylphosphine)tetrairidium*.— Tri-*p*-tolylphosphine (0·40 g) in methanol (25 ml) was added to the clear orange solution obtained from the mixture of $Ir_4(CO)_{12}$ (0·40 g) with potassium hydroxide (1·0 g) and methanol (40 ml) at 50 °C. The yellow-orange *compound* $Ir_4(CO)_9[P(p\text{-}Me{\cdot}C_6H_4)_3]_3$ (0·34 g) separated slowly on stirring for *ca*. 2 h; it was washed with methanol and heptane and dried *in vacuo*.

Nonacarbonyltris(tri-isopropylphosphine)tetrairidium.— Tri-isopropylphosphine (2·3 ml) in methanol (30 ml) was added to a mixture of $Ir_4(CO)_{12}$ (1·0 g) with potassium hydroxide (2·5 g) in methanol (80 ml) at 50 °C. The mixture was stirred for *ca*. 2 h during which the *compound* $Ir_4(CO)_9[P(Pr^i)_3]_3$ (1·21 g) separated as bright yellow crystals; it was washed with methanol and heptane and dried *in vacuo*.

Hexacarbonylbis(triphenylphosphine)di-iridium.—(a) *From* $Ir_4(CO)_9(PPh_3)_3$. A mixture of $Ir_4(CO)_9(PPh_3)_3$ (0·50 g) and triphenylphosphine (0·20 g) in heptane (70 ml) in a glass liner was treated with carbon monoxide (80—100 atm) in a small autoclave at 150 °C for 6 h. After rapid cooling and venting the excess of pressure the contents of the glass liner were filtered and yellow crystals of the *compound* $Ir_2(CO)_6(PPh_3)_2$ (0·46 g) washed with heptane and dried *in vacuo*.

(b) *From* $HIr(CO)(PPh_3)_3$. A suspension of $HIr(CO)(PPh_3)_3$ (4·50 g) in heptane (100 ml) was treated with carbon monoxide (300 atm) at 150 °C for 15 h. After cooling, the contents of the autoclave were filtered and the yellow *product* $Ir_2(CO)_6(PPh_3)_2$ (3·40 g) was washed with heptane and dried *in vacuo*.

Attempted Preparation of Heptacarbonyl(triphenylphosphine) di-iridium.—(*a*) A suspension of $Ir_2(CO)_6(PPh_3)_2$ (1·0 g) in heptane (100 ml) was treated with carbon monoxide (210 atm) at 175 °C for 14 h. After cooling and venting the excess of pressure an i.r. spectrum of the yellow solution was consistent with the presence of $Ir_2(CO)_7PPh_3$. The solution was reduced in volume to *ca*. 20 ml whereupon a yellow solid (0·9 g) precipitated; it was washed with heptane and dried *in vacuo*. An i.r. spectrum of this solid demonstrated that the starting material $Ir_2(CO)_6(PPh_3)_2$ had been recovered.

(*b*) $Ir_2(CO)_6(PPh_3)_2$ in heptane was treated with carbon monoxide as in (*a*). After cooling, methyl iodide (5 ml) was added followed by treatment with carbon monoxide (200 atm) at 100 °C for a further 7 h. After cooling the reaction mixture was filtered to remove a small amount of white solid (triphenylmethylphosphonium iodide) and the filtrate evaporated to dryness on the rotary evaporator. An i.r. spectrum of the yellow solid obtained was consistent with the presence of a mixture of $Ir_4(CO)_{12}$ and the starting material $Ir_2(CO)_6(PPh_3)_2$.

*Hexacarbonylbis(tri-*p*-tolylphosphine)di-iridium*.—A mixture of $Ir_4(CO)_9[P(p\text{-}Me{\cdot}C_6H_4)_3]_3$ (0·34 g) and tri-*p*-tolylphosphine (0·05 g) in heptane (70 ml) was treated with carbon monoxide (80 atm) at 150 °C for 6 h. After cooling the *compound* $Ir_2(CO)_6[P(p\text{-}Me{\cdot}C_6H_4)_3]_2$ (0·22 g) was isolated by filtration as a yellow solid; it was washed with heptane and dried *in vacuo*.

Hexacarbonylbis(tri-isopropylphosphine)di-iridium.— Tri-isopropylphosphine (0·1 ml) was added to a suspension of $Ir_4(CO)_9[P(Pr^i)_3]_3$ (0·74 g) in heptane (70 ml) and the mixture treated with carbon monoxide (80 atm) at 150 °C for 6 h. After cooling and venting the excess of pressure an almost colourless solution was obtained, the i.r. spectrum of which suggested the presence of $HIr(CO)_3P(Pr^i)_3$ [ν(CO) bands at 2040mw, 1970s, and 1934w cm^{-1}]. On reducing the volume of the solution on a rotary evaporator it became increasingly yellow and finally yellow crystals of the *compound* $Ir_2(CO)_6[P(Pr^i)_3]_2$ (0·43 g) separated from solution; they were washed with heptane and dried *in vacuo*.

Octacarbonyltetrakis(triethylphosphine)tetrairidium.— Triethylphosphine (0·45 ml) was added to a suspension of $Ir_4(CO)_{12}$ (0·75 g) in toluene (140 ml) and the mixture refluxed in a carbon monoxide atmosphere for 2 h. After *ca*. 30 min the $Ir_4(CO)_{12}$ had dissolved to give an orange-red solution. Evaporation of the solvent yielded an orange-red oil which, on addition of ethanol (20 ml) crystallised to give the *compound* $Ir_4(CO)_8(PEt_3)_4$ (0·88 g) as orange crystals; it was washed with ethanol and dried *in vacuo*.

Nonacarbonyltris(triethylphosphine)tetrairidium.— This product was obtained under the previous reaction conditions when smaller quantities of triethylphosphine [0·30 ml, *i.e.*, $Et_3P : Ir_4(CO)_{12} = 3 : 1$] were used. A yellow solid (0·74 g) was obtained which on recrystallisation from heptane yielded the *compound* $Ir_4(CO)_9(PEt_3)_3$ as bright orange-yellow crystals.

Octacarbonyltetrakis(tri-n-propylphosphine)tetrairidium.— Tri-n-propylphosphine (0·65 ml) and $Ir_4(CO)_{12}$ (0·75 g) were refluxed for 2 h in toluene (140 ml) under carbon monoxide. Removal of the solvent yielded an orange-red oil which crystallised on addition of ethanol (25 ml) to give the *compound* $Ir_4(CO)_8(PPr^n{}_3)_4$ (0·69 g) as orange crystals; it was washed with ethanol and dried *in vacuo*.

Octacarbonyltetrakis(tri-n-butylphosphine)tetrairidium.— Tri-n-butylphosphine (0·80 ml) and $Ir_4(CO)_{12}$ (0·75 g) were refluxed for 2 h in toluene (140 ml) under carbon monoxide. Removal of the solvent gave an orange-yellow oil which resisted all efforts at crystallisation. The oil displayed an i.r. spectrum which was very similar to that of $Ir_4(CO)_8(PEt_3)_4$ and $Ir_4(CO)_8(PPr^n{}_3)_4$.

Halogenation of Octacarbonyltetrakis(triethylphosphine)tetrairidium.—(a) *With chlorine*. A slow stream of chlorine was bubbled through a solution of $Ir_4(CO)_8(PEt_3)_4$ (0·20 g) in benzene (50 ml) for 1 min, during which the colour changed from orange to pale yellow. The yellow solid obtained on removal of the solvent was recrystallised from 1,2-dichloroethane–hexane to give the *compound* $Ir(CO)_2(PEt_3)Cl_3$ (0·14 g) as yellow crystals [ν(CO) 2150w, 2110w, and 2080s cm^{-1} (Nujol mull)]; it was washed with hexane and dried *in vacuo*.

(b) *With iodine*. Resublimed iodine (0·40 g) in benzene (15 ml) was slowly added to a stirred solution of $Ir_4(CO)_8(PEt_3)_4$ (0·36 g) (*i.e.*, I : Ir = 3 : 1) in benzene (40 ml) during 10 min during which the colour of the solution rapidly deepened from orange to dark red. After reduction in volume of the reaction mixture to *ca*. 20 ml, ethanol (20 ml) was added and the *compound* $Ir(CO)_2(PEt_3)I_3,\frac{1}{3}C_6H_6$ (0·41 g) separated as a red solid [ν(CO) 2060s and 2042sh cm^{-1} (Nujol mull)]; it was washed with ethanol and dried *in vacuo*.

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