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Preliminary communication

The reactions of carbon monoxide with polynuclear phosphine-substituted iridium carbonyls

R. WHYMAN

Imperial Chemical Industries Limited, Petrochemical & Polymer Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire (Great Britain)

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Malatesta and co-workers have recently reported[1] the reduction of tetrahydrofuran suspensions of tetrairidium dodecacarbonyl with sodium to yield the anions $[Ir_6(CO)_{15}]^{2-}$ and $[Ir(CO)_4]^-$. We have independently prepared the mononuclear species by the same route under a carbon monoxide atmosphere and have also failed to obtain evidence for the formation of $HIr(CO)_4$ or $Ir_2(CO)_8$ by acidification of this anion (with HCl or H_3PO_4 at −78°). IR spectral evidence has however been obtained previously for the formation of $HIr(CO)_4$ from $Ir_4(CO)_{12}$ under high pressures of carbon monoxide and hydrogen[2]. An alternative approach to substantiate the existence of $Ir_2(CO)_8$, first claimed by Hieber and Lagally[3] in 1940, is to investigate the reactions of carbon monoxide with phosphine-substituted derivatives of $Ir_4(CO)_{12}$. The preliminary results of such a study are reported here.

Phosphine-substituted derivatives of $Ir_4(CO)_{12}$ may be prepared[4] by the addition of a phosphine to the polynuclear carbonyl anions $[Ir_4(CO)_{11}H]^-$ and $[Ir_8(CO)_{20}]^{2-}$. Tetranuclear compounds of the formulae $Ir_4(CO)_{10}(PPh_3)_2$ and $Ir_4(CO)_9(PPh_3)_3$ have been characterised by X-ray analysis[5], and the Ir_4 cluster is found to be supported by both bridging carbonyl groups and metal—metal bonds. 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[6].

Treatment of heptane suspensions of the compounds $Ir_4(CO)_9L_3$ (I), where L = PPh_3 and $P(p\text{-}MeC_6H_4)_3$, with 80—100 atm carbon monoxide at 150° affords yellow, air-stable compounds of empirical formula $[Ir(CO)_3L]$ (II), 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 IR spectra of these complexes in the carbonyl stretching region (see Table 1) exhibit one very strong band ca. 1940 cm^{-1} and shoulders ca. 1970 and 1900 cm^{-1}, an absorption pattern which is very similar to that observed for the dimeric non-bridged phosphine-substituted complexes of dicobalt octacarbonyl[7]. The dimeric nature of the latter materials has been confirmed by X-ray analysis for $[Co(CO)_3P(n\text{-}Bu)_3]_2$[8,9]. The iridium complexes (II) are accordingly formulated as dimeric species and are the first formally disubstituted derivatives of $Ir_2(CO)_8$ to be reported. They are only slightly soluble in organic solvents, thus precluding molecular weight measurements, and are non-

TABLE 1

IR SPECTRA (cm^{-1}) IN THE (CO) REGION[a]

$[Ir(CO)_3PPh_3]_2$[b]	$Ir_2(CO)_7PPh_3$	$Ir_4(CO)_8(PEt_3)_4$	$Ir_4(CO)_9(PEt_3)_3$	$Ir_4(CO)_{10}(PEt_3)_2$ + $Ir_2(CO)_7PEt_3$
	2072 ms			2066 s
	2033 m	2035 vw	2035 ms	2038 s
			2012 w	2000 ms (br)
1975 m (sh)	1981 s	1991 m	1992 s	1974 vs
			1985 vs	
		1959 s	1963 ms	
1945 vs		1953 s (sh)		
		1927 w		
1900 m (sh)				
				1830 m
1807 vw				1792 m
			1784 s	
		1772 s	1780 s	

[a] Paraffin hydrocarbon solvents. [b] Nujol mull.

electrolytes in nitrobenzene. The stability of these compounds contrasts with that of dimeric rhodium analogues[10] and there is no apparent tendency for conversion to the tetrameric species in solution as was observed in the latter case.

Further reactions of (II) with carbon monoxide have been found to occur at higher pressures and temperatures by following IR spectral changes in a high pressure spectrophotometric cell[11]. Thus, additional bands are observed in the carbonyl stretching region when liquid paraffin mulls of $[Ir(CO)_3PPh_3]_2$ are treated with carbon monoxide at 450 atm and 175°. The new bands correspond with the formation of $Ir_2(CO)_7PPh_3$ (III), by analogy with the similarity to the IR spectrum of $Co_2(CO)_7PPh_3$ [12]. Complete conversion to $Ir_2(CO)_7PPh_3$ occurs at 175° and at higher temperatures (200°) further reaction takes place with the formation of $Ir_4(CO)_{12}$ (IV); 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 $Ir_4(CO)_{12}$ [2]. No evidence for the intermediate formation of $Ir_2(CO)_8$ is obtained during the conversion of $Ir_2(CO)_7PPh_3$ into $Ir_4(CO)_{12}$ under these high pressure-high temperature conditions.

Although phosphines are reported to react directly with $Ir_4(CO)_{12}$ only under drastic conditions[13], we have found that alkyl phosphines react readily with suspensions of $Ir_4(CO)_{12}$ in refluxing toluene to yield complexes of the type $Ir_4(CO)_8L_4$ (V), where L = PEt_3 and $P(n\text{-}Bu)_3$. The former is an orange, air-stable compound which has been characterised by elemental analysis. It is a non-electrolyte in nitrobenzene and a molecular weight determination in benzene (found 1300 ± 5%, calcd. 1465) suggests the occurrence of slight dissociation in solution. Mass spectral data is consistent with the presence of an Ir_4 cluster.

The reactions of carbon monoxide with liquid paraffin/heptane (3/1) mixed solutions of (V) have been studied in the high pressure cell. In contrast to the aryl

REACTION SCHEME

$$\underset{\text{(I)}}{Ir_4(CO)_9L_3} \xrightarrow[\substack{80\text{–}100\text{ atm}\\150^\circ}]{CO} \underset{\text{(II)}}{[Ir(CO)_3L]_2} \xrightarrow[\substack{450\text{ atm}\\175^\circ}]{CO} \underset{\text{(III)}}{Ir_2(CO)_7L} \xrightarrow[\substack{450\text{ atm}\\200^\circ}]{CO} \underset{\text{(IV)}}{Ir_4(CO)_{12}}$$

($L = PPh_3, P(p\text{-}MeC_6H_4)_3$

$$\underset{\text{(V)}}{Ir_4(CO)_8L_4} \xrightarrow[\substack{400\text{ atm}\\90\text{–}100^\circ}]{CO} \underset{\text{(VI)}}{Ir_4(CO)_9L_3} \xrightarrow[\substack{450\text{ atm}\\200^\circ}]{CO} \underset{\text{(VII)}}{Ir_4(CO)_{10}L_2} + \underset{\text{(VIII)}}{Ir_2(CO)_7L}$$

($L = PEt_3, P(n\text{-}Bu)_3$)

phosphine derivatives (I), the Ir_4 cluster in $Ir_4(CO)_8(PEt_3)_4$ is not initially cleaved by reaction with carbon monoxide; instead successive replacement of phosphine by carbon monoxide occurs. Thus $Ir_4(CO)_9(PEt_3)_3$ (VI) is formed at 400 atm pressure and 90–100° and $Ir_4(CO)_{10}(PEt_3)_2$ (VII) at 450 atm and 200°. The formation of (VI) and (VII) is inferred from the similarity to the IR spectra of the previously reported triphenylphosphine analogues[4]. However, the spectrum of (VII) exhibits an additional strong band at 1974 cm^{-1}, a peak which may correspond with the formation of $Ir_2(CO)_7PEt_3$ (VIII); other absorptions anticipated for (VIII) may overlap with the 2066 and 2038 cm^{-1} bands due to $Ir_4(CO)_{10}(PEt_3)_2$ [*cf.* the IR spectrum of $Ir_2(CO)_7PPh_3$]. In the case of $L = PBu_3$ the species (VIII) appears to be the predominant final product. There is no further reaction under these conditions (450 atm, 200°) for prolonged periods of time and no evidence for the formation of the elusive $Ir_2(CO)_8$.

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