Reactions of Mercuric Halides with some Phosphine-substituted Iron Carbonyls

By D. M. ADAM, D. J. COOK, and R. D. W. KEMMITT

(*Department of Chemistry, The University, Leicester*)

MANY covalent molecules AB (*e.g.*, halogens, perfluoroalkyl iodides) add to the five-co-ordinate complexes $M(CO)_3L_2$ (M = Fe; Ru: L = Ph_3P; $L_2 = Ph_2PCH_2CH_2PPh_2$) to form hexa-co-ordinated compounds $M(CO)_2(PPh_3)_2$,AB with elimination of one molecule of carbon monoxide.[1,2] We find that when AB is either mercuric chloride or bromide no carbon monoxide is evolved and 1 : 1 adducts $Fe(CO)_3(PPh_3)_2,HgX_2$ are formed. $Fe(CO)_3\{(PhO)_3P\}_2$ forms a 1 : 2 adduct with mercuric chloride.

The adducts are diamagnetic but insufficiently soluble for molecular-weight determination. ν_{CO} frequencies and conductivities in 10^{-3} M-nitrobenzene solutions are given in the Table. $Fe(CO)_3\{(PhO)_3P\}_2,2HgCl_2$ is clearly a 1 : 1 electrolyte and can be regarded, in solution at least, as $[Fe(CO)_3(HgCl)\{(PhO)_3P\}_2][HgCl_3]$. The low conductivity found for the triphenylphosphine adduct is due to dissociation in solution:

$$[Fe(CO)_3(HgCl)(PPh_3)_2]Cl \rightleftharpoons Fe(CO)_3(PPh_3)_2 + HgCl_2$$

The infrared spectrum of the solution shows carbonyl bands due to both the salt and the starting material. The similarity of the spectra in the carbonyl stretching region for both solids and solutions suggest that our adducts may be salts in both environments.

TABLE

Carbonyl and mercury halogen stretching frequencies

Compound	Solvent	ν_{CO}	ν_{HgCl}	Mol. conductivity 10^{-3} M $PhNO_2$
$Fe(CO)_3(Ph_3P)_2$	Nujol	1885 vs, 1871 vs		
	$PhNO_2$	1883 vs		
$Fe(CO)_3\{(PhO)_3P\}_2$	Nujol	1926 s, 1914 vs, 1884 wsh		
	$PhNO_2$	1917 vs		
$Fe(CO)_3(Ph_3P)_2,HgCl_2$	Nujol	2031 s, 1977 vs, 1954 vs	265·9 vs, 225·5 vs	
	$PhNO_2$	2028 vw, 1971 w, 1883 m[a]		4·4
$Fe(CO)_3(Ph_3P)_2,HgBr_2$	Nujol	2031 s, 1979 vs, 1960 vs	see below[b]	
	$PhNO_2$	2028 w, 1971 m, 1881 m[a]		5·7
$Fe(CO)_3\{(PhO)_3P\}_2,2HgCl_2$	Nujol	2075 s, 2035 s, 2016 s	350 vs, 311·7 m, 245 vs	
	$PhNO_2$	2063 m, 2020 vs		18·6
$[Fe(CO)_3Cl\{(PhO)_3\}_2P]^+AuCl_4^-$	Nujol	2152 s, 2149 s, 2104 vs, 2094 s		25·5
$Mn(CO)_3Cl(Ph_3P)_2$[3]	$CHCl_3$	2049 s, 1954 s, 1917 s		

[a] Band due to $Fe(CO)_3(Ph_3P)_2$.
[b] No bands due to ν_{HgBr} observed above 200 cm.$^{-1}$.

Attempts to precipitate the cationic species with sodium tetraphenylboron, Reinecke's salt, and other large anions were unsuccessful and resulted in recovery of the five-co-ordinate starting materials. However, on addition of potassium tetrachloroaurate to a solution of $[Fe(CO)_3(HgCl)\{(PhO)_3P\}_2][HgCl_3]$, a complex reaction occurred with precipitation of metallic gold. The compound $[Fe(CO)_3Cl\{(PhO)_3P\}_2]$-$[AuCl_4]$ was isolated. Cations of this type, which have not previously been described for iron, are isoelectronic with the known $Mn(CO)_3ClL_2$ ($L = Ph_3P$,[3] $(PhO)_3P$, *etc.*). The extremely high ν_{CO} values for $[Fe(CO)_3Cl\{(PhO_3P\}_2]^+$ show that this cation is not present in the mercuric halide adducts, which themselves have ν_{CO} about 100 cm.$^{-1}$ higher than the five-co-ordinate starting materials, consistent with a decrease in electron density on the iron atom.

The complexes described here were previously formulated as neutral octahedral compounds, $Fe(CO)_2Cl(HgCl)(Ph_3P)_2$.[4]

(*Received, January 25th,* 1966; *Com.* 045.)

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