Reactions of Mercuric Halides with Some Substituted Iron Carbonyls; Infrared Spectra of the Products and Related Adducts

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The complexes Fe(CO)$_3$L$_2$, (L = Ph$_3$P, Ph$_3$As, Ph$_3$Sb), react with mercuric halides to form 1 : 1 adducts; spectroscopic and conductivity evidence suggests their formulation as metal–donor complexes L$_2$(CO)$_3$Fe $\longrightarrow$ HgX$_2$. A 1 : 2 complex is formed by Fe(CO)$_3${(PhO)$_3$P}$_2$ and consists of a 1 : 1 compound plus a molecule of mercuric halide. Analogous structures are suggested for Fe(CO)$_5$,nHgX$_2$, (n = 1, 2).

Features of the low-frequency spectra of the parent compounds and the adducts are discussed. Mercury–halogen frequencies are correlated with various structural situations.

Reactions of mercuric halides with transition-metal complexes have yielded a number of compounds which contain metal–mercury bonds. The complexes isolated so far have been prepared by three general methods which have been described by Lewis and Wild.[1] In all these reactions the mercuric halide has effectively been split into halogen (X) and mercury–halogen groups (HgX), (X = Cl, Br, or I), and the resulting products contain metal–mercury–halogen bonds, *e.g.*, (Ph$_2$MeAs)$_3$Cl$_2$Rh–HgCl, (Ph$_3$P)$_2$(CO)Cl$_2$Ir–HgCl, W(CO)$_3$(bipy),(HgCl)$_2$.

Recently we [2] have described some reactions of mercuric halides with the d^8 complexes (π-C$_5$H$_5$)ML$_2$ (M = Co or Rh; L = CO; L$_2$ = cyclo-octa-1,5-diene or norbornadiene). The complexes isolated from these reactions are of the type (π-C$_5$H$_5$)ML$_2$,nHgX$_2$ (n = 1 or 2 when M = Co, and L = CO; n = 1 when M = Co, or Rh, and L = CO; L$_2$ = cyclo-octa-1,5-diene or norbornadiene), and it was suggested that the compounds may have similar structures to adducts such as Et$_2$S,2HgCl$_2$ or tetrahydrothiophen,HgCl$_2$. The nature and structure of the complex (π-C$_5$H$_5$)Co(CO)$_2$,HgCl$_2$ has now been determined by a single-crystal *X*-ray analysis [3] which confirms its formulation as a Lewis acid–base adduct. The mercury atom is at the centre of a trigonal bipyramid (Figure 1). The cobalt atom and chlorine atoms of the mercuric chloride occupy the equatorial positions, whilst the axial positions are filled by chlorine atoms of adjacent molecules. The structure is similar to that of tetrahydrothiophen,HgCl$_2$. The isolation of this complex reveals a new type of reaction of mercuric chloride which gives metal-to-mercury bonded compounds without cleavage of the mercury–chlorine bonds. The metal–metal bond formed presumably involves donation of d-electrons of the cobalt into empty σ-orbitals of the mercury. Metal–donor bonds have also been identified in such compounds as nickel dimethylglyoxime and palladium and platinum

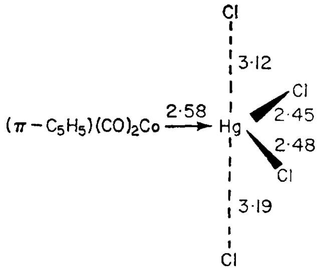

Figure 1 Structure of (π-C$_5$H$_5$)(CO)$_2$CoHgCl$_2$

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[1] J. Lewis and S. B. Wild, *J. Chem. Soc.* (*A*), 1966, 69.

[2] D. J. Cook, J. L. Dawes, and R. D. W. Kemmitt, *J. Chem. Soc.* (*A*), 1967, 1547.

[3] I. N. Nowell and D. R. Russell, *Chem. Comm.*, 1967, 817.

complexes of the type $[M(NH_3)_4][MCl_4]$ which also have the d^8 configuration.[4]

An extension of this work involves the reactions of mercuric halides with d^8 iron complexes and in this paper we describe the reactions of zero-valent iron complexes of the type $Fe(CO)_3L_2$ [L = CO,Ph_3P,$(PhO)_3P$, Ph_3As, and Ph_3Sb] with mercuric halides.[5]

RESULTS AND DISCUSSION

In 1928 Hock and Stuhlmann [6] showed that reaction of mercuric chloride with iron pentacarbonyl in aqueous or ethanolic solutions gives the compound $Fe(CO)_4,Hg_2Cl_2$ (I), which was also later prepared from the polymeric $Fe(CO)_4Hg$ and mercuric chloride. We have recently shown (I) to be *cis*-$[Fe(CO)_4(HgCl)_2]$.[7] The same conclusion was reached independently by Lewis and Wild [1] and has since been supported by a single-crystal *X*-ray study of $Fe(CO)_4,(HgBr)_2$ by Baird and Dahl.[8] Hock and Stuhlmann further found that in dry acetone solution at 0° equimolar amounts of mercuric chloride and iron pentacarbonyl react to give the adduct $Fe(CO)_5,HgCl_2$, (II). At room temperature we find that (II) loses iron pentacarbonyl and, when kept *in vacuo* ½ hr., yields a second adduct which analyses approximately as $Fe(CO)_5,2HgCl_2$, (III). There are no structural data on (II) or (III) . We discuss them below.

TABLE 1

Carbonyl stretching frequencies and molar conductivities (10^{-3}M-solutions in nitrobenzene)

	ν(CO), Nujol mull	ν(CO) in nitrobenzene	Conductivity (ohm.$^{-1}$ cm.$^{-1}$)
$Fe(CO)_3L_2$:			
L = PPh_3	1885vs, 1871vs	1883vs	
$AsPh_3$	1885vs, 1873vs	1878vs	
$SbPh_3$	1874vs, 1865vs	1878vs	
$P(OPh)_3$	2008sh, 1915vs	1917vs	
$Fe(CO)_3L_2,HgCl_2$:			
L = PPh_3	2031s, 1979vs, 1960vs	2028vw, 1971w, 1883m *	4·4
$AsPh_3$	2020s, 1970sh, 1963vs	2028m, 1973s, 1878m *	2·6
$SbPh_3$	2028s, 1978vs, 1960vs	2040m, 1979vs, 1878vw *	0·9
$Fe(CO)_3L_2,HgBr_2$:			
L = PPh_3	2031s, 1979vs, 1963vs	2028w, 1971m, 1882m *	5·7
$AsPh_3$	2034s, 1975vs, 1960vs	2032w, 1971m, 1879m *	4·2
$SbPh_3$	2027s, 1982vs, 1966vs	2035m, 1976vs, 1877w *	1·8
$Fe(CO)_3\{P(OPh)_3\}_2,2HgCl_2$	2099s, 2056vs, 2033vs	2094sh, 2023vs, 1923s *	4·6
$Fe(CO)_3\{P(OPh)_3\}_2,2HgBr_2$	2074s, 2034s, 2012vs	2056vw, 2008w, 1918vs *	5·8
$[Fe(CO)_3Cl\{P(OPh)_3\}_2][AuCl_4]$	2152s, 2149s, 2104vs, 2094s		25·5

* Band due to five-co-ordinate starting material.

Reaction of mercuric halides with $Fe(CO)_3L_2$ (L = Ph_3P, Ph_3As, or Ph_3Sb) gives compounds $Fe(CO)_3L_2,HgX_2$, (X = Cl or Br), which are considerably more stable than the iron pentacarbonyl adducts. A slow reaction occurs between mercuric iodide and $Fe(CO)_3(Ph_3P)_2$ but, although ν(CO) values indicate similar compound formation, no analytically pure compound was isolated.

Although only 1 : 1 adducts are formed with phosphine-, arsine-, or stibine-substituted complexes, $Fe(CO)_3\{(PhO)_3P\}_2$ forms only the 1 : 2 adducts, $Fe(CO)_3\{(PhO)_3P\}_2,2HgX_2$, (X = Cl or Br).

For the various adducts ν(CO) values (Table 1) are about 100 cm.$^{-1}$ above those observed in the five-co-ordinate starting materials, consistent with both a change in stereochemistry and decrease in electron density on the iron atom. In nitrobenzene solution, infrared spectra of the 1 : 1 adducts show carbonyl bands due to the adducts and the parent carbonyl complex, due to the dissociation:

$$Fe(CO)_3L_2,HgX_2 \rightleftharpoons Fe(CO)_3L_2 + HgX_2$$

The same solutions (10^{-3}M) have extremely low conductivities (see Table 1), showing that the adducts are only slightly ionized in solution; the above dissociation process would depress any conductivity due to the adducts if they were salts, but probably not to such low levels as we observed.

Two reasonable structures can be suggested for the 1 : 1 adducts: (i) $[L_2(CO)_3Fe{-}HgX]^+X^-$ or, (ii) metal-donor complexes, $L_2(CO)_3Fe \longrightarrow HgX_2$, as in $Co(CO)_2(\pi\text{-}C_5H_5)HgCl_2$.

The above evidence supports (ii) rather than (i).

The phosphite mercuric chloride complex was erroneously reported to have a high conductivity in nitrobenzene solution. It has, in fact, a very low conductivity. ν(CO) bands for the solution show that it also dissociates in solution to the parent carbonyl (Table 1); the mercuric bromide complex $Fe(CO)_3\{(PhO)_3P\}_2,2HgBr_2$ behaves similarly. This evidence, together with the infrared data, (see Table 2), suggests that these 1 : 2 adducts should be formulated as

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[4] J. Lewis and R. S. Nyholm, *Sci. Progr.*, 1964, **52**, 557.

[5] D. M. Adams, D. J. Cook, and R. D. W. Kemmitt, *Chem. Comm.*, 1966, 103.

[6] H. Hock and H. Stuhlmann, *Ber.*, 1928, **61**, *B*, 2097; 1929, **62**, *B*, 431.

[7] D. M. Adams, D. J. Cook, and R. D. W. Kemmitt, *Nature*, 1965, **205**, 589.

[8] H. W. Baird and L. F. Dahl, *J. Organometallic Chem.*, 1967, **7**, 503.

1 : 1 adducts plus a molecule of mercuric halide in the lattice.

It is noteworthy that the related complexes $M(CO)_3(Ph_3P)_2,2HgX_2$, (M = Ru, or Os, X = Cl, Br, or I) are 1 : 1 electrolytes in nitrobenzene and must be formulated as salts, $[M(CO)_3(HgX)L_2][HgX_3]$ in solution.[9]

Attempts to precipitate any cationic species present in the adducts with large anions were unsuccessful and resulted in recovery of the five-co-ordinate starting materials consistent with the formulation of the adducts as metal donor–acceptor complexes. Thus addition of sodium tetraphenylboron, sodium perchlorate, sodium hexachloroiridate(IV), or Reinecke's salt to aqueous acetone solutions of $Fe(CO)_3\{(PhO)_3P\}_2,2HgCl_2$ led to the recovery of $Fe(CO)_3\{(PhO)_3P\}_2$. However, from the reaction of potassium tetrachloroaurate and $Fe(CO)_3\{(PhO)_3P\}_2,2HgCl_2$ in aqueous acetone the compound $[Fe(CO)_3Cl\{(PhO)_3P\}_2]^+[AuCl_4]^-$ was isolated. Similar cationic species have recently been isolated by Hieber.[10] The extremely high ν(CO) values for $[Fe(CO)_3Cl\{(PhO)_3P\}_2]^+$ show that this cation is not present in the mercuric chloride adduct.

Miscellaneous Reactions.—No reaction was found to occur between mercuric chloride and the iron complexes, cycloheptatrienetricarbonyliron, norbornadienetricarbonyliron, and tetraphenylcyclopentadienonetricarbonyliron in acetone solutions, illustrating the lower basicity of these complexes. Reaction did occur between mercuric chloride and the compounds $Fe(CO)_4L$ but analytically pure samples could not be isolated.

The low-frequency spectra of adducts of the types $Fe(CO)_{5-m}L_m,nHgX_2$ and of $Co(CO)_2(\pi\text{-}C_5H_5),nHgX_2$, are distinguishable by the number of halogen-sensitive bands present. For $n = 1$ there is a single band (often broad or with a shoulder) in the region 275—240 cm.$^{-1}$. When $n = 2$, there are two *additional* bands in the range 365—310 cm.$^{-1}$. The interpretation of the spectra can be tied to the known structures of $Co(CO)_2(\pi\text{-}C_5H_5),HgCl_2$ [3] and $Et_2S,2HgCl_2$: [11]

(i) For the cobalt complex two ν(Hg–X) bands should be found: only one is present (240 cm.$^{-1}$), but it is very broad and must contain two contributions. Most of the ν(Hg–X) bands of the $n = 1$ series are broad. Their frequencies are low compared with normal Hg^{II}–Cl bond frequencies (*cf.* the range 331—314 cm.$^{-1}$ for RHgCl) [12] but not low enough to be regarded as bridging bonds; *vide infra*.

(ii) Two ν(Hg–Cl) bands are usually associated with $HgCl_2$ in a lattice. In $Et_2S,2HgCl_2$ there is no significant departure from linearity of $HgCl_2$ but the Hg–Cl bond lengths are unequal, probably sufficiently to allow the symmetric stretch to become infrared-active. Low site symmetry is clearly associated with the changes in *D*(Hg–Cl). Values for ν(Hg–Cl) of lattice $HgCl_2$ in our $n = 2$ series vary from a little above those of the sulphide complex to close to the i.r. and Raman values of solid mercuric chloride.

We see therefore that the ν(Hg–X) bands are consistent with the formulations given above for the 1 : 1 and 1 : 2 adducts. The spectra of the compounds $Fe(CO)_5,nHgCl_2$, ($n = 1, 2$), also clearly fall into the two classes defined for the $Fe(CO)_{5-m}L_m,nHgX_2$ and $Co(CO)_2(\pi\text{-}C_5H_5),nHgX_2$ series and can be formulated as $(CO)_5Fe \longrightarrow HgCl_2$ ($n = 2$) or without ($n = 1$) a mole of 'lattice' mercuric chloride.

In contrast to the above types of absorption associated with 'lattice $HgCl_2$' and co-ordinated $HgCl_2$, ν(Hg–Cl) for the chloromercurate ligand, HgCl, is found at positions which are mostly intermediate between the above types. *cis*-$[Fe(CO)_4(HgCl)_2]$ [6] and $W(CO)_3(bipy),(HgCl)_2$ [13] each has two halogen-sensitive bands (292, 273 and 276, 266 cm.$^{-1}$ respectively) between 292 and 266 cm.$^{-1}$.

Mercury–Halogen Frequencies.—In connection with our studies of the adducts, we have had to extend the spectroscopic work on mercury–halogen frequencies.

The structural chemistry of mercury is particularly complicated;[14] a wide range of mercury–halogen bond lengths, *D*(Hg–X), are known. For the solids $HgCl_2$, NH_4HgCl_3, and K_2HgCl_4,H_2O Poulet and Mathieu [15] found an inverse correlation between *D*(Hg–Cl) for the two shortest colinear Hg–Cl bonds and their totally symmetric stretching frequencies. ν(Hg–Cl) for aqueous solutions of $KCl + HgCl_2$ and for solid Hg_2Cl_2 also fitted this series. The infrared active $\nu(HgX_2)as.$ frequencies for the same compounds [12,15-17] also follow this trend; see Figure 2.

ν(Hg–X) for several types of mercury compound have been reported by Coates and Ridley.[12] For compounds of stoicheiometry HgX_2L, presumed to be halogen-bridged dimers, a band due to terminal Hg–Cl stretching was found in the region 307—273 cm.$^{-1}$, but no bridge stretching frequencies, $\nu(Hg\text{–}Cl)_b$, were found to 200 cm.$^{-1}$. We have now located these (Table 3). $(HgCl_2)_2,Et_2S$, which consists of $[Cl\text{–}Hg\text{–}SEt_2]^+,Cl^-$ and neutral $HgCl_2$, shows three halogen-sensitive bands. *D*(Hg–Cl) is is 2·35 Å for the cation and 2·33, 2·30 Å for the $HgCl_2$ molecule. Assuming that the above correlation of *D*(Hg–Cl) and ν(Hg–Cl) holds we assign the bands as in Table 3. These figures are substantially lower than the values 374 (X = Cl); 251 (X = Br) cm.$^{-1}$ found for solid mercuric halides in the i.r. spectra, and clearly show that although the bonds between the HgX_2 molecules and other components in $(HgCl_2)_2,Et_2S$ are considerably greater than the radius sums, they are sufficient to cause significant changes in *D*(Hg–X)

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[9] J. P. Collman and W. R. Roper, *Chem. Comm.*, 1966, 244.

[10] W. Hieber, V. Frey, and P. John, *Chem. Ber.*, 1967, **100**, 1961.

[11] C. I. Branden, *Arkiv Kemi*, 1963, **22**, 83.

[12] G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1964, 166.

[13] M. C. Ganorkar and M. H. B. Stiddard, *Chem. Comm.*, 1965, 22.

[14] D. Grdenić, *Quart. Rev.*, 1965, **19**, 303.

[15] H. Poulet and J. P. Mathieu, *J. Chim. phys.*, 1963, **61**, 442.

[16] D. M. Adams, M. Goldstein, and E. F. Mooney, *Trans. Faraday Soc.*, 1963, **59**, 2228.

[17] D. M. Adams, 'Metal Ligand and Related Vibrations,' Arnold, London, 1967.

and consequently in ν(Hg–X). The values for the sulphide complex fit into the D(Hg–X)/ν(Hg–X) correlation.

We have also recorded the low-frequency spectra of the other compounds shown in Table 3. The terminal Hg–X bond stretching frequencies, $\nu(\text{Hg–X})_t$, are found as reported by Coates and Ridley.[12] In addition, two other bands can be associated with the bridge-bonds. In comparison with halogen bridges formed by other metals, these are very low, and suggest the presence of rather long bonds.

ν(Hg–X) frequencies for our new complexes of the metal–donor type have been mentioned above. For $Co(CO)_2(\pi\text{-}C_5H_5),HgCl_2$ the correlation of ν(Hg–Cl) with D(Hg–Cl) is apparently not obeyed (see Figure 2). However, there is no doubt that the infrared ν(Hg–Cl) frequency of mercurous chloride is lower than that of the cobalt complex. We suggest therefore that the published value of D(Hg–Cl) in mercurous chloride may be substantially in error (it was estimated from unit-cell size), probably also (to a lesser extent) those of K_2HgCl_4,H_2O.

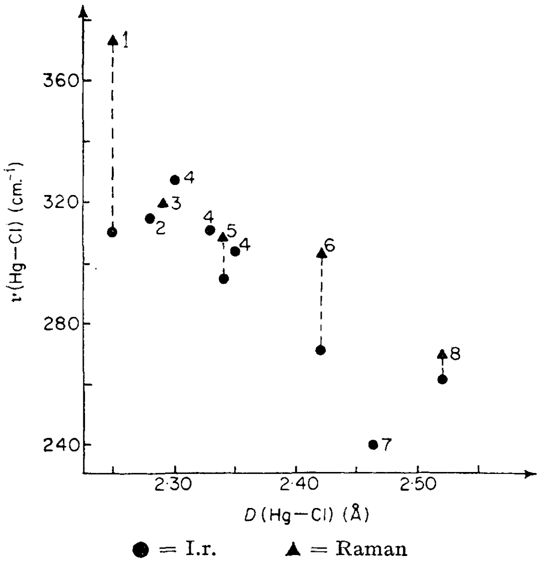

FIGURE 2 Correlation between ν(Hg–Cl) and Hg–Cl bond length. (1, $HgCl_2$; 2, MeHgCl; 3, $CsHgCl_3$; 4, $Et_2S,2HgCl_2$; 5, NH_4HgCl_3; 6, K_2HgCl_4,H_2O; 7, $(\pi\text{-}C_5H_5)(CO)_2CoHgCl_2$; 8, Hg_2Cl_2)

The variations of ν(Hg–X) may be rationalised in terms of oxidation state, co-ordination number, and ligand properties. Difference in oxidation state causes *ca.* 100 cm.$^{-1}$ differences between ν(Hg–Cl) in mercuric and mercurous chlorides. However, in a metal–metal bonded complex such as *cis*-$[Fe(CO)_4(HgCl)_2]$ the concept of oxidation state is not particularly useful. It is more fruitful to consider the electronegativity of the ligands. Thus, in mercuric chloride, Cl–HgCl, chlorine has a high electronegativity lowering D(Hg–Cl) in the (HgCl) moeity, whilst in ClHg–HgCl the (HgCl) ligand has much lower electronegativity and D(Hg–Cl) is consequently longer. The following series can be set up: Cl–HgCl (375 cm.$^{-1}$); C_6F_5–HgCl (344 cm.$^{-1}$); C_6H_5–HgCl (331 cm.$^{-1}$); C_2H_5–HgCl (314 cm.$^{-1}$); ClHg–HgCl (260 cm.$^{-1}$). Comparison with ν(Hg–Cl) for $Fe(CO)_4(HgCl)_2$; $Fe(CO)_2(\pi\text{-}C_5H_5)(HgCl)$, (278vs), etc., places the electronegativities of the metal groups between those of the ethyl group and (ClHg) in mercurous chloride.

TABLE 2

Absorption frequencies (cm.$^{-1}$) of $Fe(CO)_3L_2HgX_2$ (L = Ph_3P, Ph_3As, Ph_3Sb), 800—200 cm.$^{-1}$ Nujol mulls

L = Ph_3P		L = Ph_3As		L = Ph_3Sb		
X = Cl	X = Br	X = Cl	X = Br	X = Cl	X = Br	
759m	755m	749m	749m	743m	747m	
747s	745w	740sh	739s	732s	742m	
	740m	736s		728s	737m	
706s	707s				733sh	
702s	701s				729s	
695s	694s	689s	693s	690s	722s	
				658w	691s	
					678w	
					661w	
620m	619m	617m	618m	616sh	627s	ν(Fe–C) + δ(FeCO)
613s	613s	613s	613s	611s		
590s	589s	582s	579s	585s	580vs	
576vs	572vs	565vs	562vs	570vs		
517w	517w	522w	517w	528w	527w	
492w	492w		491w	490w	490w	
455w	454w	473sh	478sh	460m	453s	
442w	441w	468s	470s	449s	449s	
426m	426m					
	396w	392w		304sh		
	279w	344sh	341vs	300s	299vs	
266vs	267m	339vs	334s	277m	276s	
257sh *		328s	326s	270s *	271m	
235s	232s	275m *		242s	240s	
				237sh		
225s	224s	266vs *		231sh	227w	
201w	201m	261sh	258m	223w		
		245s	243m	216w	215m	
				212w		
		217m	216m	204w	203m	
				200w		

* ν(Hg–Cl).

TABLE 3

Mercury–halogen frequencies (cm.$^{-1}$)

	$[HgCl_2,PPh_3]_2$	$[HgCl_2,AsPh_3]_2$
$\nu(\text{Hg–Cl})_t$	288vs	291vs
$\nu(\text{Hg–Cl})_b$	190s, 172s	202s, 183s
$\delta(\text{Hg–Cl})_t$	150s	139s
	$[X\text{–}Hg\text{–}SEt_2]^+$	HgX_2 *
ν(Hg–Cl)	304m	328sh, 311s
ν(Hg–Br)	247w	282w, 255m
ν(Hg–S)	336s (X = Cl) 339w (X = Br)	

* In $(HgX_2)_2,Et_2S$.

Low-frequency Spectra of Substituted Carbonyl Compounds.—Although the spectra (4000—200 cm.$^{-1}$) of the mercuric chloride adducts are complicated, comparison with the ligand and starting material spectra enables the origin of all the observed bands to be specified. The ν(M–CO), δ(MCO) pattern in the adduct series $Fe(CO)_3L_2,HgX_2$ is different from that of the starting materials, consistent with a change of stereochemistry. ν(M–CO) and δ(MCO) modes have not been reported previously for five-co-ordinate complexes other than

$CoH(CO)_4$ and $[FeH(CO)_4]^-$, although quite a lot is known about these modes in octahedrally and tetrahedrally co-ordinate systems.[17]

For $Fe(CO)_4L$ and $Fe(CO)_3L_2$ ν(CO) patterns show that the two series have axially substituted L groups. Treating L as a monatomic group, the point symmetries require the numbers of bands shown in Table 4: these

TABLE 4

Selection rules for some substituted carbonyl complexes

		ν(M–C)		δ(MCO)		
		I.r.	Raman	I.r.	Raman	Inact.
$Fe(CO)_4L$	C_{3v}	$2a_1 + e$	$2a_1 + e$	$a_1 + 3e$	$a_1 + 3e$	a_2
$Fe(CO)_3L_2$	D_{3h}	e'	$a_1' + e'$	$a_2'' + e'$	$e' + e''$	a_2'

are the minimum expected. Additional bands can arise because (i) the ligands L will generally lower the point symmetry and, (ii) there may be intermolecular interaction.

For the $Fe(CO)_3L_2$ series three regions of absorption are found in accord with D_{3h} point symmetry, but there is more than one band in each region in one or more cases due to the above reasons. We assign them as shown in Table 5.

TABLE 5

Absorption frequencies (cm.$^{-1}$) of $Fe(CO)_3,L_2$, 800—200 cm.$^{-1}$ as Nujol mulls

L = Ph_3P	L = Ph_3As	L = Ph_3Sb
751m	745sh	738sh
744sh	739s	730s
721vw		
703s	696sh	696s
696s	693s	
682m	672w	658w
634s	**631s**	**626s**
619w	**619w**	**616w**
593sh	**575sh**	
586vs	**570vs**	**567vs**
521m	*519m*	*523m*
508w	*478m*	*513m*
501w	474m	451s
448m	469m	442sh
436m	464m	322s
403w		
395sh	396w	317s
292m	391sh	304w
262m	374sh	273s
255m	358vs	266sh
240w	334s	246s
	328s	221m
	322s	
	271s	
	209m	

[Figures in bold type refer to δ(FeCO); figures in italic refer to ν(Fe–CO)].

The C_{3v} point symmetry of $Fe(CO)_4L$ will probably be less disturbed by L than in the above series. Seven infrared-active bands are found as predicted (Table 6), although assignments to each symmetry species cannot be proven without further evidence. Comparison with $[FeH(CO)_4]^-$ shows that the hydride has ν(CO) lower and ν(M–CO), δ(MCO) higher than the $Fe(CO)_4L$ series,[17] in agreement with current views of the bonding in these compounds.

TABLE 6

Absorption frequencies of $Fe(CO)_4,L$, 800—200 cm.$^{-1}$, as Nujol mulls

L = Ph_3P	L = Ph_3As	L = Ph_3Sb
750m	743m	736w
746m	738m	729m
709m		
693s	693s	696s
627vs	**626vs**	**624vs**
617vs	**618vs**	**618vs**
532sh		
526m	**520m**	**521m**
511s		
507m	*496m*	*495m*
485w	*487m*	*485m*
	471s	452s
	464s	449sh
442w	*438w*	*442w*
428w	*427w*	*418w*
415w	397w	392w
401m	385w	284vs
394m	358w	272vs
387m	339vs	259m
273w	332s	255m
266m	328s	223m
253m	249w	
235m-s	240m	
230m-s	217m	
219m	212m	
(199w)	204w	

[Figures in bold type refer to δ(FeCO); figures in italic refer to ν(Fe–CO).]

EXPERIMENTAL

I.r. spectra were obtained with a Perkin-Elmer Model 225 (4000—200 cm.$^{-1}$), a Unicam SP 100 (4000—400 cm.$^{-1}$), and an RIIC FS-520 interferometer (360—70 cm.$^{-1}$) with Nujol mulls unless otherwise stated. Conductivities were measured on a Wayne Kerr conductivity bridge. All solvents were purified before use. M.p.s were taken on a Kofler hot-stage block and are uncorrected. All petroleum used had a b.p. 40—60°. Starting materials were prepared by standard literature methods.

Reaction of Mercuric Chloride with Pentacarbonyliron.—Pentacarbonyliron (4 g., 3 ml., 20 mmoles) was added quickly to mercuric chloride (2·7 g., 10 mmoles) in dry acetone with stirring at below 0°. The pale yellow precipitate was filtered quickly under nitrogen and washed with cold acetone and cold petroleum. The compound was stored at $-30°$ [Found: Hg, 43·7. $Fe(CO)_5,HgCl_2$ requires Hg, 42·9%]. On pumping under reduced pressure for 30 min. at room temperature, the adduct loses pentacarbonyliron to give $Fe(CO)_5,2HgCl_2$ [Found: Hg, 53·1. $Fe(CO)_5,2HgCl_2$ requires Hg, 54·3%].

Under similar conditions mercuric bromide formed a similar pale yellow adduct at $-78°$. However, above $-30°$ the compound rapidly decomposes with loss of pentacarbonyliron.

Bistriphenylphosphinetricarbonyliron Mercuric Chloride.—Mercuric chloride (0·4 g., 5 mmoles) in a 1 : 2 ethyl methyl ketone–benzene mixture (20 ml.) was added with stirring to $Fe(CO)_3(Ph_3P)_2$ (1 g., 1·5 mmoles) in the same solvent (30 ml.) at room temperature. The pale yellow precipitate (1·3 g.) was collected and washed with the solvent mixture (10 ml.) and with petroleum (b.p. <40°, 10 ml.). The compound was dissolved in acetone and reprecipitated by careful addition of petroleum to the filtered solution. During purification considerable loss of the product (*ca.*

50%) occurs due to the dissociation of the product to mercuric chloride and bistriphenylphosphinetricarbonyliron. This can be minimised by the addition of a small amount of mercuric chloride to the acetone solution. M.p.: darkens at 116°, decomposes 212—214° (Found: C, 50·1; H, 3·4; P, 6·5. Calc. for $C_{39}H_{30}Cl_2FeHgO_3P_2$: C, 50·0; H, 3·3; P, 6·6%).

The following compounds were prepared similarly in a 1 : 2 ethyl methyl ketone–benzene mixture (hereafter abbreviated EMK/B).

Bistriphenylphosphinetricarbonyliron Mercuric Bromide.—Mercuric bromide (0·5 g., 1·5 mmoles) in EMK/B (20 ml.) and $Fe(CO)_3(Ph_3P)_2$ (1 g., 1·5 mmoles) in EMK/B (30 ml.) gave the yellow adduct (1·4 g.) which was recrystallised from methylene chloride–petroleum. M.p.: decomposes from 125 to 190° (Found: C, 45·9; H, 3·1; P, 6·2. Calc. for $C_{39}H_{30}Br_2FeHgO_3P_2$: C, 45·8; H, 3·1; P, 6·2%).

Bistriphenylarsinetricarbonyliron Mercuric Chloride.—Mercuric chloride (0·14 g., 0·5 mmole) in EMK/B (10 ml.) and $Fe(CO)_3(Ph_3As)_2$ (0·35 g., 0·5 mmole) in EMK/B (20 ml.) gave the yellow adduct which was recrystallised from acetone–petroleum. Yield 0·2 g. (Found: C, 45·8; H, 3·0; As, 14·7. $C_{39}H_{30}As_2Cl_2FeHgO_3$ requires C, 45·9; H, 2·9; As, 14·8%).

Bistriphenylarsinetricarbonyliron Mercuric Bromide.—Mercuric bromide (0·25 g., 0·7 mmole) in EMK/B (15 ml.) and $Fe(CO)_3(Ph_3As)_2$ in EMK/B (10 ml.) gave the yellow adduct which was recrystallised from methylene chloride. Yield 0·25 g. M.p.: decomposes 96—98° (Found: C, 42·2; H, 2·8; As, 13·4. $C_{39}H_{30}As_2Br_2FeHgO_3$ requires C, 42·1; H, 2·7; As, 13·5%).

Bistriphenylstibinetricarbonyliron Mercuric Chloride.—Mercuric chloride (0·16 g., 0·6 mmole) in EMK/B (10 ml.) and $Fe(CO)_3(Ph_3Sb)_2$ (0·5 g., 0·6 mmole) in EMK/B (20 ml.) gave the adduct which was recrystallised once from acetone and once from methylene chloride. Yield 0·3 g. The adducts can be prepared more quickly in ethanol as a solvent. M.p.: darkens at 87°, decomposes 118—120° (Found: C, 41·9; H, 2·9; Hg, 17·7. $C_{39}H_{30}Cl_2FeHgO_3Sb_2$ requires C, 41·9; H, 2·7; Hg, 17·9%).

Bistriphenylstibinetricarbonyliron Mercuric Bromide.—Mercuric bromide (0·2 g., 0·6 mmole) in EMK/B (15 ml.) and $Fe(CO)_3(Ph_3Sb)_2$ (0·5 g., 0·6 mmole) in EMK/B (10 ml.) gave the adduct which was recrystallised from methylene chloride. Yield 0·3 g. M.p.: decomposes 118—125° (Found: C, 38·7; H, 2·3; Hg, 16·7. $C_{39}H_{30}Br_2FeHgO_3Sb_2$ requires C, 38·8; H, 2·5; Hg, 16·6%).

Bis(triphenyl Phosphite)tricarbonyliron Bis(mercuric Chloride).—Mercuric chloride (1 g., 4 mmoles) in EMK/B (20 ml.) and $Fe(CO)_3\{(PhO)_3P\}_2$ (1·5 g., 2 mmoles) in EMK/B (10 ml.) gave the pale yellow adduct which was recrystallised from acetone–petroleum. Yield 2·3 g. M.p. 103—105° (Found: C, 36·0; H, 2·4; P, 4·8; Hg, 31·1. Calc. for $C_{39}H_{30}Cl_4FeHg_2O_9P_2$: C, 36·0; H, 2·3; P, 4·8; Hg, 30·5%).

Bis(triphenyl phosphite)tricarbonyliron Bis(mercuric bromide).—Mercuric bromide (0·5 g., 1·4 mmole) in 1 : 2 acetone–benzene mixture (15 ml.) and $Fe(CO)_3\{(PhO)_3P\}_2$ (0·5 g., 0·7 mmole) gave the adduct, which was recrystallised from acetone–petroleum. Yield 0·8 g. M.p.: decomposes 129° (Found: C, 31·5; H, 2·4; P, 4·2; Hg, 27·2. $C_{39}H_{30}Br_4FeHg_2O_9P_2$ requires C, 31·6; H, 2·0; P, 4·1; Hg, 27·1%).

Bis(triphenyl phosphite)tricarbonylchloroiron Tetrachloroaurate.—$Fe(CO)_3\{(PhO)_3P\}_2,2HgCl_2$ (0·7 g., 0·5 mmole) in a minimum of aqueous acetone was added to $KAuCl_4$ (0·6 g., 1·5 mmoles) in the same solvent. The purple-brown precipitate was filtered off, and on standing for several hours the yellow filtrate deposited a yellow precipitate which was recrystallised from ethyl methyl ketone–petroleum. M.p.: decomposes 109—110° (Found: C, 42·0; H, 2·6; Cl, 15·7. Calc. for $C_{39}H_{30}AuCl_5FeO_9P_2$: C, 41·4; H, 2·7; Cl, 15·6%).

We thank Albright and Wilson Ltd. for triphenylphosphine; International Nickel Ltd. for pentacarbonyliron; Johnson Matthey Ltd. for the loan of platinum-metal salts; and Mr. J. L. Dawes for measurement of some carbonyl frequencies. We also thank the S.R.C. for a grant (to D. J. C.).

[7/1189 *Received, September 14th,* 1967]