Chemistry of Polynuclear Compounds. Part IV.[1] Some Amine-substituted Mercury Halide–Iron Carbonyl Compounds

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A number of stable derivatives of bis(chloromercury)–tetracarbonyliron with primary, secondary, and heterocyclic amines have been prepared. Replacement of one or two carbonyl groups may occur, depending upon the amine employed, to give six-co-ordinate complexes of iron. The compounds are non-electrolytes in nitrobenzene, and their infrared spectra are reported.

THE previous Papers in this Series have been concerned with the magnetic interaction in complexes containing two metal ions. The *direct* bonding between the metal ions is often in doubt. We now report work on systems in which direct metal–metal bonding appears to occur without the participation of intermediate bridging groups. The best-known forms of such bonding occur in mercury–transition metal complexes, and we now describe some mercury halide–iron carbonyl complexes and their substitution products with amines.

Complexes containing metal-to-mercury bonds have so far been prepared by three general methods. The first two were employed by Nyholm and Vrieze to prepare complexes containing rhodium-to-mercury[2] and iridium-to-mercury bonds.[3] The rhodium-to-mercury bonded complex was prepared by an *elimination* reaction between a monohydride of tervalent rhodium and a mercuric halide, hydrogen halide being evolved in the reaction, *e.g.*,

$$(\mathrm{Ph_2MeAs})_3\mathrm{Cl_2Rh\ H} + \mathrm{HgCl_2} \longrightarrow (\mathrm{Ph_2MeAs})_3\mathrm{Cl_2Rh{-}HgCl} + \mathrm{HCl}$$

A complex containing an iridium-to-mercury bond was prepared by a similar elimination reaction, *e.g.*,

$$cis\text{-}(\mathrm{Ph_3P})_2(\mathrm{CO})\mathrm{Cl_2IrH} + \mathrm{HgCl_2} \longrightarrow cis\text{-}(\mathrm{Ph_3P})_2(\mathrm{CO})\mathrm{Cl_2Ir{-}HgCl} + \mathrm{HCl}$$

The same complex, however, was also prepared by an "*oxidative*"-*addition* reaction, *e.g.*,

$$trans\text{-}(\mathrm{Ph_3P})(\mathrm{CO})\mathrm{ClIr} + \mathrm{HgCl_2} \longrightarrow cis\text{-}(\mathrm{Ph_3P})_2(\mathrm{CO})\mathrm{Cl_2Ir{-}HgCl}$$

Recently, a seven-co-ordinate complex containing tungsten-to-mercury bonds has been prepared.[4] This appears to follow a third type of reaction which can be described as an "*oxidative*"-*elimination* reaction. This particular reaction yields the complex $W(CO)_3(bipy)(HgCl)_2$ by interaction of $W(CO)_4(bipy)$ with mercuric chloride. The product, in this case, is very similar to the seven-co-ordinate tungsten(II) complex, $W(CO)_3(bipy)I_2$.[5]

In 1928 Hock and Stuhlmann[6] reported the preparation of "double compounds" of the type $Fe(CO)_4Hg,HgX_2$ (where X = Cl, Br, I, OAc, CN, or SCN) and a supposedly polymeric, highly insoluble compound, $Fe(CO)_4Hg$. The double compound, $Fe(CO)_4Hg,HgCl_2$, is prepared by what may now be seen to be an "oxidative"-elimination reaction according to the following equation:

$$\mathrm{Fe(CO)_5} + 2\mathrm{HgCl_2} \longrightarrow \mathrm{Fe(CO)_4Hg,HgCl_2} + \mathrm{COCl_2}$$

We have repeated the preparation of the double compounds, $Fe(CO)_4Hg,HgX_2$ (where X = Cl, Br, or I) and, on the basis of infrared studies, these compounds appear to belong to a general group of iron carbonyl derivatives of the type $Fe(CO)_4L_2$, where L had previously been limited to the halogens Cl, Br, I (and mixtures of these, *e.g.*,[7] L_2 = IBr) and the triphenylphosphinegold group, $Ph_3P \longrightarrow Au$.[8]

The similarity of the infrared spectra of the compounds $Fe(CO)_4(HgX)_2$ in the metal-carbonyl region to those of $Fe(CO)_4(Au \longleftarrow PPh_3)_2$ and $Fe(CO)_4I_2$ points strongly to an octahedral formulation with a *cis*-arrangement of the two Hg–X groups[9] (see Table 2). As with the $Ph_3P \longrightarrow Au$ group, the Hg–X group may be considered

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[1] Part III, J. Lewis, Y. C. Lin, L. K. Royston, and R. C. Thompson, *J. Chem. Soc.*, 1965, 6464.

[2] R. S. Nyholm and K. Vrieze, *Proc. Chem. Soc.*, **1963**, 138.

[3] R. S. Nyholm and K. Vrieze, *Chem. and Ind.*, 1964, 318.

[4] M. C. Ganorkar and M. H. B. Stiddard, *Proc. Chem. Soc.*, 1965, 22.

[5] M. H. B. Stiddard, *J. Chem. Soc.*, 1962, 4712.

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

[7] W. Hieber and A. Wirsching, *Z. anorg. Chem.*, 1940, **245**, 35.

[8] C. E. Coffey, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1964, 1741.

[9] J. Lewis, *Pure Appl. Chem.*, 1965, **10**, 11.

to be a pseudohalogen so far as the $>Fe(CO)_4$ group is concerned. Treatment of $Fe(CO)_4(HgCl)_2$ with iodine yields $Fe(CO_4I_2$ and a mixture of mercuric iodide and chloride whilst $Fe(CO)_4(Au \leftarrow PPh_3)_2$ gives $Fe(CO)_4I_2$ and $Ph_3P \leftarrow AuI$.[7]

We have investigated the reaction of amines with mercury halide–iron carbonyl complexes (see Table 1).

TABLE 1

Complex	M. p.	Colour	Mol. conductivity in $PhNO_2$	
			$PhNO_2$ Λ_M	Concn. ($\times 10^{-3}$)
$Fe(CO)_2py_2(HgCl)_2$ *	$>340°$	Bright yellow	0·3	1·45
$Fe(CO)_2(\beta\text{-pic})_2(HgCl)_2$ * ...	>340	Bright yellow	0·5	1·03
$Fe(CO)_2(o\text{-phen})(HgCl)_2$ ...	171—173 (decomp.)	Pale pink	1·1	1·7
$Fe(CO)_2(bipy)(HgCl)_2$	148—150 (decomp.)	Pink	1·3	1·3
$Fe(CO)_2(C_6H_{11}NH_2)_2(HgCl)_2$	184—187 (decomp.)	White	2·0	1·7
$Fe(CO)_2(morph)_2(HgCl)_2$ * ...	>340	Yellow	5·0	1·2
$Fe(CO)_3(morph)(HgCl)_2$ ...	—	Pale yellow	0·7	1·6
$Fe(CO)_3(\gamma\text{-pic})(HgCl)_2$ * ...	>340	Pale yellow	0·6	1·5
$Fe(CO)_3(PhNH_2)(HgCl)_2$ * ...	>340	Pale yellow	0·7	1·6
$Fe(CO)_2(C_6H_{11}NH_2)_2(HgBr)_2$	183—186 (decomp.)	White	0·8	1·3

* Complexes generally turn black at *ca.* 130°, then to a translucent brown but do not melt below 340°.

Reaction of amines with the parent carbonyl, in general, leads to a disproportionation reaction to produce derivatives of iron(II) and a carbonyl anion, *viz.*,

$$3Fe(CO)_5 + 6\ \text{amine} \longrightarrow [Fe(\text{amine})_6][Fe_2(CO)_8] + 7CO$$

This reaction appears to be typical of the behaviour of other metal carbonyls, with the possible exception of Group VI metals, and is in contrast to their behaviour with phosphines where substitution of carbon monoxide of the metal carbonyl appears to occur. The difference in behaviour of these two classes of reagents may be associated with their relative π-bonding capacity. Because of their greater affinity for π-bonding the phosphines normally involve a higher tendency to stabilise the metal in the zerovalent state, whereas amines favour co-ordination to higher oxidation states and disproportionation of the carbonyl. We have investigated the interaction of amines with the mercury halide–iron carbonyl adducts, as they may be considered to be similar to the compound $Fe(CO)_4I_2$ and we anticipated stable carbonyl–amine products. The reaction occurs with displacement of either one or two carbon monoxide molecules depending upon the amine employed. This is in contrast to the behaviour of mercury–cobalt carbonyl,[10] $Hg[Co(CO)_4]_2$, which disproportionates with amines, *e.g.*,

$$3Hg[Co(CO)_4]_2 + 12NH_3 \longrightarrow 3Hg + 2[Co(NH_3)_6][Co(CO)_4]_2 + 8CO$$

Whereas di-iodo-tetracarbonyliron forms a very unstable dark green derivative $[Fe(CO)_2py_2I_2]$,[7] bis(chloromercury)tetracarbonyliron dissolves in hot pyridine–chloroform solutions to yield, on cooling, bright yellow, stable crystals of the bispyridine derivative, $Fe(CO)_2py_2(HgCl)_2$. This compound is moderately unstable to light and is insoluble in non-polar solvents. The β-picoline analogue, $Fe(CO)_2(\beta\text{-pic})_2(HgCl)_2$, can be prepared similarly. Both of these complexes have similar infrared spectra in chloroform solutions of the corresponding heterocyclic base (Table 2). In mixed solvents [*e.g.*, py–$CHCl_3$ for the complex $Fe(CO)_2(\beta\text{-pic})_2(HgCl)_2$], or polar solvents (*e.g.*, CH_3NO_2), shoulders and splitting of bands occur which is possibly associated with solvolysis reactions. General solvent effects of the type reported previously also occur; thus, the carbonyl bands of $Fe(CO)_2(\beta\text{-pic})_2(HgCl)_2$ shift to higher frequencies by *ca.* 30 cm.$^{-1}$ when nitromethane is used as a solvent.

Bidentate chelates were also found to react readily with the mercury–iron complexes. Thus, bis(chloromercury)tetracarbonyliron dissolves in a hot solution of 2,2′-bipyridyl–chloroform to yield, on cooling, very fine pale pink crystals of $Fe(CO)_2(bipy)(HgCl)_2$. The primary amine, cyclohexylamine, reacts instantaneously in the cold with a suspension of bis(chloromercury)-tetracarbonyliron in chloroform to form a voluminous, white, crystalline precipitate; analytical data for this compound correspond with the formula $Fe(CO)_2(C_6H_{11}NH_2)_2(HgCl)_2$.

We were successful in isolating both the mono- and di-substituted products from the reaction between bis(chloromercury)tetracarbonyliron and the cyclic secondary amine, morpholine. The monosubstituted product, $Fe(CO)_3(morph)(HgCl)_2$, has three strong groups of bands in the metal-carbonyl stretching region [2080 (doublet), 2030 (doublet), and 2005 cm.$^{-1}$ (triplet)] whilst the disubstituted product, $Fe(CO)_2(morph)_2(HgCl)_2$, has two strong sets of bands at 2065 and 1980 cm.$^{-1}$ (triplet).

Evidence for complexes in which only one carbonyl group was replaced was also observed in other systems. Thus, bis(chloromercury)tetracarbonyliron dissolves in an excess of γ-picoline in hot chloroform to form a bright yellow solution from which, on cooling, a yellow crystalline compound, $Fe(CO)_3(\gamma\text{-pic})(HgCl)_2$ separates. The infrared spectrum of this compound (Nujol) shows strong bands at 2068 (triplet), 2025 (doublet) and 2000 cm.$^{-1}$ (singlet). The infrared spectrum of this compound in γ-picoline–chloroform solution, however, is very similar to that of the β-picoline derivative, $Fe(CO)_2(\beta\text{-pic})_2(HgCl)_2$, and shows two strong bands at 2064 and 1996 cm.$^{-1}$ (Table 2). This is in agreement with the formation of the disubstituted product in solution.

Although the high insolubility of these amine–iron–mercury bonded complexes precludes molecular-weight determinations they may be considered as monomeric octahedral iron complexes. The oxidation state of

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[10] W. Hieber and R. Breu, *Chem. Ber.*, 1957, **90**, 1259.

0 for the iron atom and +1 for the mercury atom is in agreement with the definition of oxidation state described by Lewis and Nyholm.[11] Clearly, the oxidation states in metal–metal bonded systems are arbitrary, as exemplified in the iridium-to-mercury bonded complex, $(Ph_3P)_2(CO)Cl_2Ir{-}HgCl$, where the oxidation state of the iridium will necessarily vary from +1 to +3 as that of the mercury varies from +2 to 0. Complexes of the type $Fe(CO)_2(X)_2(HgY)_2$ (where X = CO or N-bases and Y = Cl, Br, or I) are therefore considered to be typical $d^{10}s^1$–d^8 metal-to-metal bonded complexes and are members of the general group of complexes, $Fe(CO)_4L_2$, mentioned previously.

TABLE 2

Infrared bands due to CO stretching (cm.$^{-1}$)

Complex	Solvent		Mean (cm.$^{-1}$)
$Fe(CO)_4(HgCl)_2$	Nujol	2088sh, 2083s, 2023s, 2008s	2051
$Fe(CO)_4(HgBr)_2$	Nujol	2095ms, 2090s, 2030s, 2020s	2059
$Fe(CO)_4(HgI)_2$	Nujol	2092s, 2020s, 2015s	2042
$Fe(CO)_4(Au \leftarrow PPh_3)_2$	CCl_4	2004ms, 1934s, 1894s	1944
$Fe(CO)_4I_2$	$CHCl_3$	2071, 2091, 2136	2099
$Fe(CO)_2py_2(HgCl)_2$	$CHCl_3$–py	2068s, d, 2000s	
	Nujol	2060s, 1986s, d	
	CH_3NO_2	2096s, d, 2026s	
$Fe(CO)_2(\beta\text{-pic})_2(HgCl)_2$	$CHCl_3$–β-pic	2064s, 1990s	
	Nujol	2060s, 1985s, d	
	CH_3NO_2	2096s, d, 2026s	
$Fe(CO)_2(o\text{-phen})(HgCl)_2$	$CHCl_3$	Insufficiently soluble	
	Nujol	2065s, d, 1990s, m	
$Fe(CO)_2(bipy)(HgCl)_2$	$CHCl_3$	Insufficiently soluble	
	Nujol	2076s, 1996s	
$Fe(CO)_2(C_6H_{11}NH_2)_2(HgCl)_2$	$CHCl_3$	2080s, 2010s	
	Nujol	2060s, d, 2006s, d, 1968s	
$Fe(CO)_2(morph)_2(HgCl)_2$	$CHCl_3$–morph	2060s, 1990s	
	Nujol	2065s, 1980s, t	
$Fe(CO)_3(morph)(HgCl)_2$	$CHCl_3$–morph	2060s, 1990s	
	Nujol	2080s, d, 2030s, d, 2005s, t	
$Fe(CO)_3(\gamma\text{-pic})(HgCl)_2$	$CHCl_3$–γ-pic	2064s, 1996s	
	Nujol	2068s, t, 2025s, d, 2000s	
$Fe(CO)_3(PhNH_2)(HgCl)_2$	$CHCl_3$–$PhNH_2$	2086s, 2020s	
	Nujol	2088s, d, 2000s, m	
	CH_3NO_2	2106s, 2026s, d	
$Fe(CO)_2(C_6H_{11}NH_2)_2(HgBr)_2$	$CHCl_3$	2085s, 2025s	

d, Doublet; t, triplet; m, multiplet.

The infrared spectra of the compounds are summarised in Table 2. The positions of the bands associated with the carbonyl stretching vibration are higher than those observed in iron pentacarbonyl[12] (2022 and 2000 cm.$^{-1}$ in cyclohexane), however, although this is in agreement with the concept of higher formal charge on the iron group, the change in stereochemistry and effects of substituents are probably more significant in accounting for this small variation in energy. The spectra observed for the compounds, in Nujol mulls, were usually complex and ould be related to the existence of more than one of the possible geometric isomers, but the complexity is more probably associated with the local symmetry of the molecules in the solid being lower than the point-group symmetry of the individual molecule. In agreement with this the solution spectra were simpler, being consistent with the presence of only one major isomer with a C_{2v} distribution of the carbonyl groups in the molecule. Owing to the insolubility of the compounds it was often necessary to measure the spectra in mixed solvents. Some spectra were determined in nitromethane. In general these were more complex and indicated isomerisation in solution or reaction with solvent.

In so far as average stretching frequencies are meaningful the values of these for the sequence $Fe(CO)_4Br_2$ (mean 2116 cm.$^{-1}$), $Fe(CO)_4I_2$ (mean 2099 cm.$^{-1}$), $Fe(CO)_4(HgX)_2$ (mean 2051 cm.$^{-1}$), and $Fe(CO)_4(Au \leftarrow PPh_3)_2$ (mean 1944 cm.$^{-1}$) suggest that the Hg–X group has an effective electronegativity intermediate between iodine and the $(Ph_3P \rightarrow Au)$ group. This lowering of C–O stretching frequency in passing from $Fe(CO)_4I_2$ to $Fe(CO)_4(HgX)_2$ (*ca.* 40 cm.$^{-1}$) is consistent with the lowering of the frequency observed in passing from $W(CO)_3(bipy)I_2$ to $W(CO)_3(bipy)(HgCl)_2$ (*ca.* 30 cm.$^{-1}$) and consequent lowering of electronegativity in passing from iodine to the mercury halide group. It appears that the $(HgCl)^+$ group in many ways behaves as a pseudohalogen. This is in agreement with the data given by Nyholm[13] for the sum of the first ionisation potential and of electron affinity of the halogens and transition elements in Table 3.

TABLE 3

Sum of ionisation potential and electron affinity

Atom	F	Cl	Br	I	Hg	Au
I.P. + E.A. (e.u.)	20·9	16·7	15·3	13·6	10·4	11·9

EXPERIMENTAL

Analysis.—All C, H, Hg, N, and O analyses were carried out by Alfred Bernhardt, Max Planck Institute, Mülheim, Germany. Although the samples were recrystallised many times, we were unable to get good carbon analyses for some of these compounds.

Bis(chloromercury)–Tetracarbonyliron.—This compound was prepared by the method of Hock and Stuhlmann.[6] Iron pentacarbonyl (5 ml.) was added to a solution of mercuric chloride (9 g.) in absolute ethanol (200 ml.) and the resultant solution was stirred under nitrogen for 3 hr. The pale yellow, insoluble product (5·65 g.) was filtered off and washed thoroughly with absolute ethanol and ether (Found: C, 7·5; Fe, 8·7; O, 10·4. Calc. for $C_4Cl_2FeHg_2O_4$: C, 7·5; Fe, 8·7; O, 10·0%).

Bis(bromomercury)–Tetracarbonyliron.—Iron pentacarbonyl (2·5 ml.) was added to a solution of mercuric bromide (5·6 g.) in absolute ethanol (100 ml.) and the resultant solution was stirred under nitrogen for 1 hr. The pale yellow insoluble product (1·9 g.) was filtered off and washed thoroughly with absolute ethanol and ether (Found: C, 6·1;

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[11] J. Lewis and R. S. Nyholm, *Sci. Progr.*, 1964, **52**, 557.
[12] K. Noack, *Helv. Chim. Acta*, 1962, **45**, 1847.
[13] R. S. Nyholm, *Proc. Chem. Soc.*, 1961, 273.

Fe, 7·6; O, 8·4. Calc for $C_4Br_2FeHg_2O_4$: C, 6·6; Fe, 7·7; O, 8·8%).

Bis(iodomercury)–Tetracarbonyliron.—Iron pentacarbonyl (1·5 ml.) was added to a solution of mercuric iodide (1·8 g.) in absolute ethanol (125 ml.). The resultant solution was stirred under nitrogen for 13 hr. to yield the product (0·37 g.) as an insoluble orange powder (Found: C, 4·2. Calc. for $C_4I_2FeHg_2O_4$: C, 3·7%).

Bish(chloromercury)–Bis(pyridine)dicarbonyliron. — Bis-(chloromercury)–tetracarbonyliron (1 g.) was refluxed in 10% pyridine–chloroform (50 ml.) for 0·5 hr. The bright yellow solution was filtered hot and cooled to yield the crude product (0·95 g.), which was recrystallised from 20% pyridine–chloroform (50 ml.) to yield the pure product as bright yellow prisms (0·64 g.), m. p. >340° (Found: C, 20·9; H, 1·35; Fe, 7·1; Hg, 53·5; N, 3·8. Calc. for $C_{12}H_{10}Cl_2FeHg_2N_2O_2$: C, 19·4; H, 1·35; Fe, 7·5; Hg, 53·9; N, 3·8%).

Bis(chloromercury)–Bis(β-picoline)dicarbonyliron. — Bis-(chloromercury)–tetracarbonyliron (0·5 g.) was refluxed in 12·5% β-picoline–chloroform (50 ml.) for 0·25 hr. The bright yellow solution was filtered hot and allowed to cool to 0° overnight. The crude product (0·46 g.) was filtered off, washed well with chloroform and ether, and recrystallised from 6% β-picoline–chloroform (30 ml.). It was obtained as bright yellow prisms (0·39 g.), m. p. >340° (Found: C, 22·5; H, 1·9; Fe, 7·3; N, 3·7. Calc. for $C_{14}H_{14}Cl_2FeHg_2N_2O_2$: C, 21·8; H, 1·8; Fe, 7·3; N, 3·6%).

Bis(chloromercury)–(1,10-Phenanthroline)dicarbonyliron.—A solution of 1,10-phenanthroline (0·2 g.) in chloroform (40 ml.) was shaken with bis(chloromercury)–tetracarbonyl-iron (0·5 g.) for 0·5 hr. The insoluble starting material dissolved to produce a flocculent pale pink precipitate. The crude product (0·58 g.) was collected, washed well with chloroform, and was obtained pure from boiling methylene dichloride (200 ml.) as very fine pale pink prisms (0·41 g.), m. p. 171—173° (decomp.) (Found: C, 23·8; H, 0·9; N, 3·2. Calc. for $C_{14}H_8Cl_2FeHg_2N_2O_2$: C, 23·6; H, 1·1; N, 3·8%).

Bis(chloromercury)–(2,2′-Bipyridyl)dicarbonyliron. — A solution of 2,2′-bipyridyl (0·5 g.) in chloroform (80 ml.) was heated under reflux with bis(chloromercury)–tetracarbonyliron (1 g.) for 5 min. The solution was filtered hot and cooled to give the desired product as fine pink prisms (0·13 g.), m. p. 148—150° (decomp.) (Found: C, 20·2; H, 1·2; Fe, 7·9; N, 3·0. Calc. for $C_{12}H_8Cl_2FeHg_2N_2O_2$: C, 19·5; H, 1·1; Fe, 7·6; N, 3·8%).

Bis(chloromercury)–(γ-Picoline)tricarbonyliron. — Bis-(chloromercury)–tetracarbonyliron (0·5 g.) was refluxed in 6% γ-picoline–chloroform (50 ml.) for 10 min. The yellow solution was filtered hot and cooled to 0° overnight to yield the crude product (0·23 g.). The filtrate was diluted with ether (5 ml.) and cooled to 0° overnight to yield a further crop of pale yellow crystals (0·17 g.). The combined product (0·41 g.) crystallised from hot 5% γ-picoline–chloroform (40 ml.) as pale yellow prisms (0·28 g.), m. p. >340° (Found: C, 16·5; H, 0·9; Fe, 7·7; N, 2·0. Calc. for $C_9H_7Cl_2FeHg_2NO_3$: C, 15·3; H, 1·0; Fe, 7·9; N, 2·0%).

Bis(chloromercury)–(Aniline)tricarbonyliron.—Bis(chloromercury)–tetracarbonyliron (0·8 g.) was dissolved in AnalaR aniline (10 ml.). After 5 min., the mixture was diluted with ether (20 ml.) to precipitate the crude product (0·6 g.). The pure product crystallised from 40% aniline–chloroform (50 ml.) as fine yellow prisms (0·47 g.), m. p. >340° (Found: C, 14·8; H, 0·8; Fe, 7·9; Hg, 55·5; N, 1·8. Calc. for $C_9H_7Cl_2FeHg_2NO_3$: C, 15·0; H, 1·0; Fe, 8·0; Hg, 56·9; N, 2·0%).

Bis(chloromercury)–Bis(cyclohexylamine)dicarbonyliron.—Cyclohexylamine (0·5 ml.) was added slowly to bis(chloromercury)–tetracarbonyliron (0·5 g.) in chloroform (40 ml.). The starting material dissolved immediately and the solution, within several seconds, set solid with a voluminous white precipitate of the product (0·63 g.). The crude product was twice recrystallised from chloroform (30 ml.) and was obtained pure as very fine white needles (0·5 g.), m. p. 184—187° (decomp.) (Found: C, 22·6; H, 3·3; Fe, 6·8; N, 3·4. Calc. for $C_{14}H_{26}Cl_2FeHg_2N_2O_2$: C, 21·5; H, 3·4; Fe, 7·1; N, 3·6%).

Bis(chloromercury)–(Morpholine)tricarbonyliron. — Morpholine (1 ml.) was added to bis(chloromercury)–tetracarbonyliron (0·5 g.) in chloroform (50 ml.). The reaction vessel was gently shaken to dissolve the starting material and the solution rapidly filtered. After cooling the solution to 0° overnight, the pale yellow crystals (0·22 g.) were filtered off and washed thoroughly with chloroform and ether (Found: C, 11·5; H, 1·0; Fe, 7·8; N, 1·7. Calc. for $C_7H_9Cl_2FeHg_2NO_4$: C, 12·0; H, 1·3; Fe, 8·0; N, 2·0%).

Bis(chloromercury)–Bis(morpholine)dicarbonyliron. — Bis-(chloromercury)–(morpholine)tricarbonyliron (0·18 g.) was refluxed in 8% morpholine–chloroform (25 ml.) for 10 min. The solution was filtered hot, concentrated (to *ca.* 15 ml.), and cooled to 0° overnight. The product was filtered off (0·08 g.) and washed well with chloroform and ether, m. p. >340° (Found: C, 16·4; H, 2·2; Fe, 7·3; N, 3·4. Calc. for $C_{10}H_{18}Cl_2FeHg_2N_2O_4$: C, 15·8; H, 2·4; Fe, 7·4; N, 3·7%).

[*Note added in proof. Bis(bromomercury)–Bis(cyclohexylamine)dicarbonyliron.*—This compound was prepared in a similar manner to the corresponding *chloro*-compound and obtained pure from boiling chloroform as white needles, m. p. 183–186°(decomp.) (Found: C, 20·3; H, 2·9; Fe, 6·4; N, 3·3. Calc. For $C_{14}H_{26}Br_2FeHg_2N_2O_2$: C, 19·3; H, 3·0; Fe, 6·4; N, 3·2%.]

Infrared Spectra.—These were recorded on a Perkin-Elmer 237 grating infrared spectrometer.

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