Insertion of Mercury into Iron–Halogen Bonds. X-Ray Structure of $[(p\text{-MeC}_6\text{H}_4\text{NC})_5\text{Fe}\rightarrow\text{HgI}_2]$†

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The complexes $[\text{FeI}_2(\text{CNR})_4]$ (R = Ph, p-MeC_6H_4 or Bu^t) react with Hg in the presence of CNR to give $[(\text{RNC})_5\text{Fe}\rightarrow\text{HgI}_2]$, and exchange reactions with AgX (X = Br or Cl) lead to the corresponding halogeno-complexes $[(\text{RNC})_5\text{Fe}\rightarrow\text{HgX}_2]$. Treatment with 1 mol of AgClO_4 affords the cationic complexes $[(\text{RNC})_5\text{Fe–HgX}]\text{ClO}_4$ which are unstable towards mercury extrusion. The relative stability of the complexes is discussed in terms of the influence of the ligands co-ordinated to Hg and the steric and electronic characteristics of the RNC ligands. The structure of $[(p\text{-MeC}_6\text{H}_4\text{NC})_5\text{Fe}\rightarrow\text{HgI}_2]$ has been determined: monoclinic, space group $P2_1/a$, $a = 16.680(3)$, $b = 18.031(4)$, $c = 15.256(2)$ Å, $\beta = 116.92(2)°$ and $Z = 4$.

There is a vast chemistry of complexes containing mercury bonded to a transition metal, and complexes $\text{L}_n\text{M}(\text{HgX}_2)$ constitute a well represented type.[1,2] These are usually obtained by direct reaction between a mercury dihalide or pseudohalide acting as a Lewis acid and a transition-metal complex in a low oxidation state (usually a carbonyl complex) acting as a metallic base [(i) in Scheme 1].

$$\text{L}_n\text{M} + \text{HgX}_2 \xrightarrow{(i)} \text{L}_n\text{M}(\text{HgX}_2) \xleftarrow{(ii)} \text{L}_n\text{MX}_2 + \text{Hg}$$

Scheme 1

The same complexes might be accessible by treating transition-metal complexes in a higher oxidation state with mercury [(ii), Scheme 1], but surprisingly this procedure (which formally involves a redox process and the insertion of mercury into a M–X bond) seems to have been reported only rarely. Thus, $[\text{M}(\text{cp})(\text{CO})_3(\text{HgI})]$ (M = Mo or W; cp = η^5-C_5H_5) are cleanly formed from $[\text{M}(\text{cp})(\text{CO})_3\text{I}]$ and mercury under UV irradiation,[3] but only poor yields (< 20%) of inserted products are obtained from $[\text{Fe}(\text{cp})(\text{CO})_2\text{X}]$ (X = Cl, Br or I).[4,5] Mercury insertion is suspected to be involved in the reduction of halogenocarbonyl complexes by sodium amalgam, and mercury-containing compounds have been detected or isolated occasionally in the course of the reduction.[6,7]

In this paper we report the high-yield easy synthesis of $[\text{FeL}_5(\text{HgI}_2)]$ (L = PhNC, p-$\text{MeC}_6\text{H}_4\text{NC}$ or Bu^tNC) by direct reaction of mercury with *cis*- or *trans*-$[\text{FeI}_2\text{L}_4]$ and L at room temperature, in contrast with the poor yields and complications produced in the apparently more straightforward procedure (i) in Scheme 1. The X-ray crystal structure of $[\text{Fe}(\text{CNC}_6\text{H}_4\text{Me-}p)_5(\text{HgI}_2)]$ and the preparation of other neutral and cationic derivatives containing Fe–Hg bonds are also reported.

Results

The complexes *cis*-, *trans*-, or mixtures of *cis*- and *trans*-$[\text{FeI}_2(\text{CNR})_4]$ (R = Ph, p-MeC_6H_4 or Bu^t) in tetrahydrofuran and in the presence of one extra mol of RNC react slowly with metallic mercury at room temperature to give $[\text{Fe}(\text{CNR})_5(\text{HgI}_2)]$ according to equation (1). The complexes are produced

$$[\text{FeI}_2(\text{CNR})_4] + \text{RNC} + \text{Hg} \longrightarrow [(\text{RNC})_5\text{Fe}\rightarrow\text{HgI}_2] \quad (1)$$

	R
1a	Ph
1b	MeC_6H_4
1c	Bu^t

in excellent yields (> 85%) for R = Ph or p-MeC_6H_4, and in modest yield (< 16%) for R = Bu^t. The compounds can also be made in the same yields starting from a mixture of FeI_2, CNR and Hg (1:5:excess), and are even formed when $[\text{FeI}_2(\text{CNR})_4]$ are treated with mercury in the absence of additional RNC, although in this case the yields are noticeably lower (*ca.* 20% for R = Ph or p-MeC_6H_4, not attempted for R = Bu^t). Characterisation data are given in Table 1.

The molecular structure of complex **1b** was determined by X-ray diffraction and is shown in Fig. 1. The iron atom is in an approximately octahedral geometry defined by four 'equatorial' isonitrile ligands, the mercury atom, and the 'apical' isonitrile ligand *trans* to the mercury atom. The four equatorial isonitriles lie out of the equatorial plane, closer to the mercury atom apex of the octahedron; the Fe atom is 0.185 Å out of the plane defined by the four equatorial C atoms.

The mercury atom is in a distorted trigonal plane defined by the two iodines and the iron atom and this plane is staggered from the equatorial isonitriles, so that I(2) lies approximately under the bisector of C(28)–Fe–C(37), and I(1) under the bisector of C(1)–Fe–C(10). The packing forces produce different dihedral angles between the phenyl moieties and the equatorial plane; thus the phenyls of the C(1) and C(10) isonitriles are to 101 and 112° of the equatorial plane, while those of C(28) and C(37) are to 32 and 20°, respectively. This produces a steric hindrance between the I(1) atom and the phenyl moieties of the C(1) and C(10) isonitrile ligands which seems to affect the co-ordination of the Hg atom (see below).

Bond distances and angles are given in Table 2. It is well known that the distances Fe–C and C–N, and the bending of a co-ordinated isonitrile ligand, are sensitive to the extent of back bonding from the metal into the antibonding orbitals of the

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† Diiodo-2κ*I*-pentakis(p-tolyl isocyanide)-1κ^5*C*-iron mercury (*Fe–Hg*).
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp, xviii–xxii.

Table 1 Analytical (calculated values in parentheses), molar conductivities and ^{1}H NMR (δ, $CDCl_3$, reference $SiMe_4$) data

		Analysis (%)					
Complex		C	H	N	$\Lambda_M{}^a/\Omega^{-1}$ cm^2 mol^{-1}	^{1}H NMR	
1a	$[Fe(CNPh)_5(HgI_2)]$	41.35 (40.95)	2.40 (2.45)	6.50 (6.80)	4^b		7.50 (m)
1b	$[Fe(CNC_6H_4Me\text{-}p)_5(HgI_2)]$	43.95 (43.85)	3.25 (3.20)	6.55 (6.40)	5^b	2.24 (s), 2.35 (s)	7.31 (m)
1c	$[Fe(CNBu^t)_5(HgI_2)]$	32.45 (32.40)	4.90 (4.85)	7.40 (7.55)	21^b	1.58 (s), 1.50 (s)	
2a	$[Fe(CNPh)_5(HgBr_2)]$	44.85 (45.15)	2.45 (2.70)	7.20 (7.50)	9^b		7.39 (m)
2b	$[Fe(CNC_6H_4Me\text{-}p)_5(HgBr_2)]$	47.10 (47.95)	3.40 (3.50)	6.75 (7.00)	10^b	2.16 (s), 2.25 (s)	7.11 (m)
2c	$[Fe(CNBu^t)_5(HgBr_2)]$	35.75 (36.10)	5.25 (5.40)	8.00 (8.45)	25^b	1.51 (s)	
3a	$[Fe(CNPh)_5(HgCl_2)]$	49.65 (49.90)	2.85 (2.95)	8.25 (8.30)	12^b		7.54 (m)
3b	$[Fe(CNC_6H_4Me\text{-}p)_5(HgCl_2)]$	52.20 (52.65)	3.65 (3.85)	7.45 (7.70)	14^b	2.23 (s), 2.32 (s)	7.24 (m)
3c	$[Fe(CNBu^t)_5(HgCl_2)]$	40.10 (40.45)	5.65 (6.05)	9.30 (9.45)	27^b	1.48 (s)	
4a	$[Fe(CNPh)_5(HgI)]ClO_4$	41.80 (42.15)	2.35 (2.50)	6.95 (7.00)	117^c		7.48 (m)
4b	$[Fe(CNC_6H_4Me\text{-}p)_5(HgI)]ClO_4$	45.65 (44.95)	3.50 (3.25)	6.30 (6.55)	118^c	1.96 (s)	6.81 (m)
4c	$[Fe(CNBu^t)_5(HgI)]ClO_4$	33.45 (33.45)	5.40 (5.00)	7.95 (7.80)	150^c	1.61 (s)	
5a	$[Fe(CNPh)_5(HgBr)]ClO_4$	43.80 (44.20)	2.50 (2.65)	7.25 (7.35)	128^c		7.38 (m)
5b	$[Fe(CNC_6H_4Me\text{-}p)_5(HgBr)]ClO_4$	46.80 (47.05)	3.25 (3.45)	6.70 (6.85)	117^c	2.11 (s)	7.11 (m)
5c	$[Fe(CNBu^t)_5(HgBr)]ClO_4$	35.15 (35.30)	5.00 (5.30)	8.00 (8.25)	133^c	1.64 (s)	
6a	$[Fe(CNPh)_5(HgCl)]ClO_4$	46.15 (46.40)	2.55 (2.75)	7.55 (7.75)	127^c		7.08 (m)
6b	$[Fe(CNC_6H_4Me\text{-}p)_5(HgCl)]ClO_4$	49.75 (49.15)	3.40 (3.60)	7.15 (7.15)	114^c	2.26 (s)	7.24 (m)
6c	$[Fe(CNBu^t)_5(HgCl)]ClO_4$	36.85 (37.25)	5.30 (5.60)	8.30 (8.70)	143^c	1.34 (s)	

^{a} $c = 0.5 \times 10^{-4}$ mol dm^{-3}. ^{b} In nitrobenzene. ^{c} In acetone.

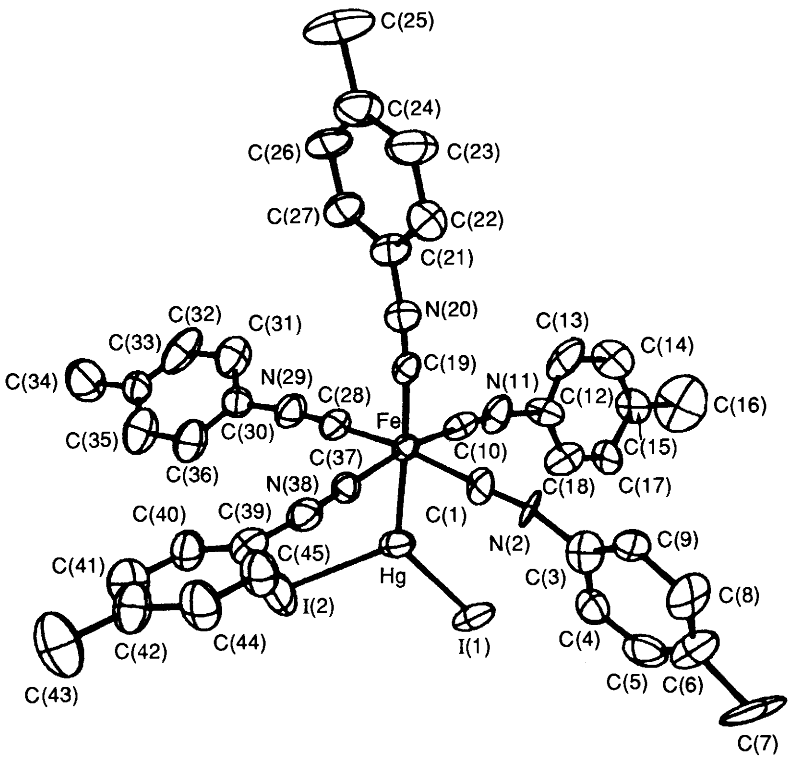
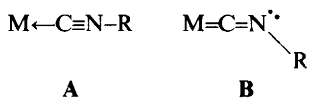


Fig. 1 Molecular structure of $[Fe(CNC_6H_4Me\text{-}p)_5(HgI_2)]$ showing the atom numbering scheme

isonitrile ligand; back bonding will increase the contribution of the bent canonical form **B**.



A **B**

These parameters suggest that the extent of back donation in **1b** is in the order of that in a iron(II) complex and much less than that in a iron(0) complex. Thus, the CNC angles in **1b** (average 171.2°) are far from the angles found for $[Fe(CNBu^t)_5]$ (average 135°),[8] and in the range found for iron(II) complexes such as *trans*-$[Fe(CN)_2(CNMe)_4]$ (average 166°)[9] or $[Fe(CNMe)_6][FeCl_4]$ (average 178.8°).[10] In addition, short C–N and long Fe–C distances are found and these effects are particularly noticeable in the 'apical' isonitrile ligand (*trans* to the dative bond). All these data indicate that the formation of the Fe→Hg bond produces a significant decrease in the electron density at the iron centre.

The co-ordination of mercury deserves further comment. Its co-ordination number in complex **1b** is three and the shortest non-bonding intermolecular Hg···I distances are above 6 Å. This three-co-ordination contrasts with the situation found for other related complexes $[M(CO)_m(HgX_2)_n]$[11-13] where, without exception, the mercury atom increases its co-ordination number establishing intermolecular Hg···X bonds or contacts. Such a possibility is excluded in **1b** due to the steric

Table 2 Bond lengths (Å) and angles (°) for complex **1b**

I(1)–Hg	2.747(1)	C(6)–C(5)	1.346(19)	N(20)–C(19)	1.139(14)	C(34)–C(33)	1.549(18)
I(2)–Hg	2.850(1)	C(7)–C(6)	1.562(18)	C(21)–N(20)	1.386(14)	C(35)–C(33)	1.360(20)
Fe–Hg	2.551(1)	C(8)–C(6)	1.417(18)	C(23)–C(22)	1.379(18)	C(36)–C(35)	1.369(16)
C(1)–Fe	1.880(8)	C(9)–C(8)	1.399(12)	C(24)–C(23)	1.430(15)	N(38)–C(37)	1.155(13)
C(10)–Fe	1.848(9)	N(11)–C(10)	1.186(11)	C(25)–C(24)	1.531(18)	C(39)–N(38)	1.423(13)
C(19)–Fe	1.883(11)	C(12)–N(11)	1.418(12)	C(26)–C(24)	1.347(19)	C(40)–C(39)	1.358(15)
C(28)–Fe	1.841(9)	C(13)–C(12)	1.348(20)	C(27)–C(26)	1.351(17)	C(45)–C(39)	1.370(14)
C(37)–Fe	1.855(10)	C(18)–C(12)	1.346(15)	N(29)–C(28)	1.166(12)	C(41)–C(40)	1.424(16)
N(2)–C(1)	1.151(10)	C(14)–C(13)	1.444(16)	C(30)–N(29)	1.401(13)	C(42)–C(41)	1.356(17)
C(3)–N(2)	1.383(10)	C(15)–C(14)	1.364(17)	C(31)–C(30)	1.409(18)	C(43)–C(42)	1.564(17)
C(4)–C(3)	1.454(18)	C(16)–C(15)	1.533(18)	C(36)–C(30)	1.370(19)	C(44)–C(42)	1.380(17)
C(9)–C(3)	1.382(16)	C(17)–C(15)	1.429(20)	C(32)–C(31)	1.375(18)	C(45)–C(44)	1.358(17)
C(5)–C(4)	1.349(14)	C(18)–C(17)	1.328(16)	C(33)–C(32)	1.361(22)		
I(2)–Hg–I(1)	104.7(1)	C(9)–C(3)–C(4)	120.7(8)	C(17)–C(15)–C(16)	121.2(12)	C(34)–C(33)–C(32)	120.4(12)
Fe–Hg–I(1)	137.3(1)	C(5)–C(4)–C(3)	118.1(11)	C(18)–C(17)–C(15)	119.4(11)	C(35)–C(33)–C(32)	117.3(11)
Fe–Hg–I(2)	118.0(1)	C(6)–C(5)–C(4)	123.6(12)	C(17)–C(18)–C(12)	121.8(13)	C(35)–C(33)–C(34)	122.3(13)
C(10)–Fe–C(1)	85.2(4)	C(7)–C(6)–C(5)	122.4(13)	N(20)–C(19)–Fe	174.6(7)	C(36)–C(35)–C(33)	123.0(14)
C(19)–Fe–C(1)	99.7(4)	C(8)–C(6)–C(5)	118.3(9)	C(21)–N(20)–C(19)	174.0(9)	C(35)–C(36)–C(30)	119.0(13)
C(19)–Fe–C(10)	96.4(4)	C(8)–C(6)–C(7)	118.4(12)	C(24)–C(23)–C(22)	120.8(13)	N(38)–C(37)–Fe	176.5(9)
C(28)–Fe–C(1)	169.5(5)	C(9)–C(8)–C(6)	121.9(11)	C(25)–C(24)–C(23)	119.3(13)	C(39)–N(38)–C(37)	176.2(8)
C(28)–Fe–C(10)	93.8(4)	C(8)–C(9)–C(3)	117.4(11)	C(26)–C(24)–C(23)	118.2(12)	C(40)–C(39)–N(38)	118.5(9)
C(28)–Fe–C(19)	90.8(4)	N(11)–C(10)–Fe	176.0(7)	C(26)–C(24)–C(25)	122.5(10)	C(45)–C(39)–N(38)	119.0(10)
C(37)–Fe–C(1)	92.1(4)	C(12)–N(11)–C(10)	167.9(8)	C(27)–C(26)–C(24)	122.9(10)	C(45)–C(39)–C(40)	122.4(10)
C(37)–Fe–C(10)	167.4(5)	C(13)–C(12)–N(11)	115.4(9)	N(29)–C(28)–Fe	175.0(8)	C(41)–C(40)–C(39)	117.3(10)
C(37)–Fe–C(19)	96.1(4)	C(18)–C(12)–N(11)	120.4(11)	C(30)–N(29)–C(28)	173.4(13)	C(42)–C(41)–C(40)	120.2(12)
C(37)–Fe–C(28)	86.6(4)	C(18)–C(12)–C(13)	124.1(10)	C(31)–C(30)–N(29)	121.2(11)	C(43)–C(42)–C(41)	119.5(11)
N(2)–C(1)–Fe	177.2(10)	C(14)–C(13)–C(12)	114.2(11)	C(36)–C(30)–N(29)	119.1(10)	C(44)–C(42)–C(41)	120.1(12)
C(3)–N(2)–C(1)	164.0(11)	C(15)–C(14)–C(13)	123.1(13)	C(36)–C(30)–C(31)	119.6(11)	C(44)–C(42)–C(43)	120.4(11)
C(4)–C(3)–N(2)	118.2(10)	C(16)–C(15)–C(14)	121.7(14)	C(32)–C(31)–C(30)	117.9(14)	C(45)–C(44)–C(42)	120.4(11)
C(9)–C(3)–N(2)	121.1(10)	C(17)–C(15)–C(14)	117.1(10)	C(33)–C(32)–C(31)	122.8(13)	C(44)–C(45)–C(39)	119.4(11)

requirement of the CNC_6H_4Me-*p* ligands. The irregular geometry found in the $FeHgI_2$ triangle (nearly planar but with three very different angles: 104.7, 118.0 and 137.3°) seems to be a compromise of the best packing with the four 'equatorial' CNC_6H_4Me-*p* ligands of the same molecule and the 'apical' CNC_6H_4Me-*p* group of a neighbouring molecule invading the same space. Thus, I(1) has short intramolecular distances to C(4) [4.095(7) Å] and C(18) [4.351(7) Å] and a short intermolecular distance to C(25i) (4.287 Å) (*i* 1 + *x*, *y*, *z*), in a neighbouring molecule, whereas I(2) shows only short intramolecular distances to C(28) [4.105(7) Å] and N(38) [4.058(7) Å].

Although the assignment of oxidation states in compounds containing M–Hg bonds is a controversial matter and there is no general agreement,[11] the easiest way to describe the molecular structure found in the crystal is as an adduct of HgI_2 with the metallic base $[Fe(CNR)_5]$. Reaction (1) can thus be looked at as an oxidation of Hg^0 to Hg^{II} by Fe^{II} involving insertion of mercury into an iron–iodine bond. This insertion occurs also in the corresponding Br or Cl derivatives but the rate of the reaction decreases markedly in the series I > Br > Cl. A much more convenient way to obtain the halogeno derivatives **2a**–**2c** and **3a**–**3c** is the exchange reaction at low temperature (ice-bath) shown in equation (2).

$$[(RNC)_5Fe\rightarrow HgI_2] + 2AgX \longrightarrow [(RNC)_5Fe\rightarrow HgX_2] + 2AgI \quad (2)$$

2a–**2c** X = Br
3a–**3c** X = Cl

The nature of compounds **1**–**3** suggests that they should be obtained easily in a more direct process, shown in equation (3),

$$[Fe(CNR)_5] + HgX_2 \longrightarrow \underset{\mathbf{1\text{–}3}}{[(RNC)_5Fe\rightarrow HgX_2]} \quad (3)$$

involving the addition of $[Fe(CNR)_5]$ to HgX_2. Surprisingly, this turns out to be a very undesirable procedure; while the spectra of the reaction solutions suggest that they contain only the corresponding compounds **1**–**3**, they show dark rather than yellow-orange colours, **1**–**3** do not precipitate spontaneously as had been expected, and evaporation affords tars from which only modest yields (< 20%) of **1**–**3** can be isolated after difficult working up.

Table 1 collects the analytical data for the complexes (in good agreement with the proposed stoicheiometries) and the ^1H NMR data, which are in accordance with the presence of two types of isonitrile (4:1 ratio), as expected for any $[Fe(CNR)_5(HgX_n)]$ octahedral arrangement; even in the cases where no well separated resonances are observed the shape of the signals suggests that this is due to lack of resolution of two very close resonances and not to exchange of isonitriles.

The IR spectra (Table 3) of complexes **1**–**3** in Nujol mulls (where we assume for all the complexes the structure found for **1b** show three ν(C≡N) absorptions (C_{4v}, $2A_1 + E$). Their average wavenumbers are higher than for the corresponding complexes $[Fe(CNR)_5]$ (R = *p*-MeC_6H_4, see Experimental section; R = Bu^t, see ref. 8; and R = Ph, see ref. 14) reflecting the decrease in electron density in the iron atom when the $Fe(CNR)_5$ moiety is co-ordinated to HgX_2, as observed previously for the related $[Fe(CO)_3L_2(HgX_2)]$ systems.[15]

The IR spectra in CH_2Cl_2 solution usually show two bands (one weak and one strong) but this is deceptive and has to be considered in conjunction with the molar conductivity values for the complexes (Table 1). These reveal that complexes **1**–**3** dissociate in solution according to equation (4), and consequently their conductivities are concentration-dependent giving values approaching those for 1:1 electrolytes with increasing dilution (Λ_M for 1:1 electrolytes 20–30 $ohm^{-1}\ cm^2\ mol^{-1}$ in nitrobenzene and 100–140 $ohm^{-1}\ cm^2\ mol^{-1}$ in acetone[16]); in addition the conductivities are found to be dependent on the isonitrile ($Bu^t \gg p$-MeC_6H_4 > Ph) and the halogen (Cl > Br > I).

$$[(RNC)_5Fe\rightarrow HgX_2] \rightleftharpoons [(RNC)_5Fe\text{–}HgX]X \quad (4)$$

Table 3 IR data (cm^{-1})

		ν(C≡N)(Nujol)			ν(C≡N)(CH_2Cl_2)		
Complex	X	R = Ph	C_6H_4Me-*p*	Bu^t	R = Ph	C_6H_4Me-*p*	Bu^t
[Fe(CNR)$_5$(HgX$_2$)]	I	2181m	2175m	2188m	2183w	2178w	2189w
		2115s	2110s	2130s	2123s	2125s	2145s
		1992w	2035w	2070w(sh)			
	Br	2185m	2180m	2175m	2170m(sh)	2185w	2200m
		2115vs	2105vs	2125vs	2125s	2127s	2150s
		1995w	2040w	2060w(sh)			
	Cl	2195m	2175m	2202m	2185w	2200w	2195w
		2125s	2115vs	2135s	2125s	2142s	2150s
		1997w	2035w	2055w(sh)			
[Fe(CNR)$_5$(HgX)]ClO$_4$	I	2190m	2195m	2215m	2195w	2195w	2195w
		2125s	2135s	2155s	2140s	2145s	2145s
		1975w	2030w	2070w			
	Br	2200m	2200m	2205m	2195w	2197w	2196w
		2137vs	2145vs	2155s	2145s	2147s	2147s
		1985vw	2030vw	2065w(sh)			
	Cl	2202m	2200m	2210m	2195w	2198w	2200w
		2140s	2145vs	2155s	2145s	2149s	2155s
		1985vw	2030vw	2055vw			

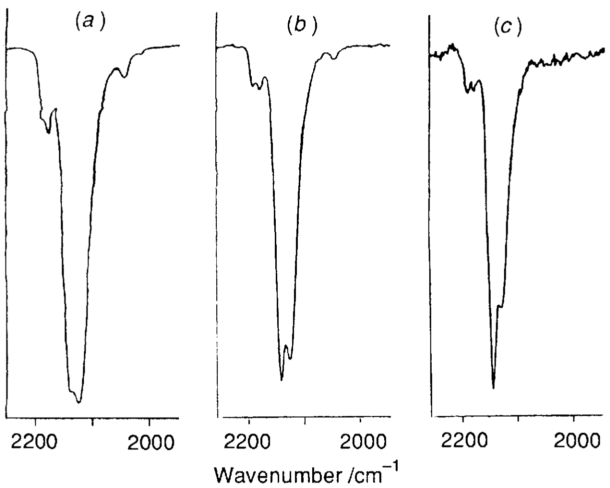


Fig. 2 The ν(C≡N) absorptions of [Fe(CNC$_6$H$_4$Me-*p*)$_5$(HgCl$_2$)] in CH_2Cl_2 solution at different concentrations: (*a*) 8.6 × 10^{-3}; (*b*) 1.7 × 10^{-3} and (*c*) 0.4 × 10^{-3} mol dm^{-3}

The cationic species proposed in equation (4) can be isolated with perchlorate as the counter ion according to equations (5) and (6). Complexes **4–6** behave as 1:1 electrolytes in acetone (Table 1). Their IR spectra in solution (Table 3) show a shift of ν(C≡N) towards higher wavenumbers compared to their parent complexes [(RNC)$_5$Fe→HgX$_2$]. This reflects the fact that removal of a X$^-$ ligand from mercury (and change from sp^2 to sp hybridisation) increases its orbital electronegativity and consequently its demand of electron density from iron. We have represented this conventionally by using a Fe→Hg notation for the neutral species and Fe–Hg for the cationic species.

$$[(RNC)_5Fe{\rightarrow}HgI_2] + AgClO_4 \longrightarrow [(RNC)_5Fe{-}HgI]ClO_4 + AgI \quad (5)$$

4a–4c

$$[(RNC)_5Fe{-}HgI]ClO_4 + AgX \longrightarrow [(RNC)_5Fe{-}HgX]ClO_4 + AgI \quad (6)$$

5a–5c X = Br
6a–6c X = Cl

In the solid state (Nujol mulls) the IR spectra of complexes **4–6** reveal a ν(C≡N) shift toward higher wavenumbers by about 30–20 cm^{-1} on going from [(RNC)$_5$Fe→HgX$_2$] to [(RNC)$_5$Fe–HgX]$^+$. Considering this, it is clear that the solution IR spectra of the complexes **1** and **3** must be the overlap of bands arising from the two species in solution [equation (4)]; since these bands are not always resolved and the proportion of the two species is concentration dependent, different spectra can be observed. Fig. 2 shows this variation for complex **3b**.

The 'neutral' complexes **1–3** are fairly stable in solution in the absence of light and only traces of mercury are formed even after a few days. In contrast, the cationic complexes **4–6** are very unstable in solution at room temperature and extrusion of mercury occurs easily [equation (7)], so that they

$$[(RNC)_5Fe{-}HgX]ClO_4 \longrightarrow [FeX(CNR)_5]ClO_4 + Hg \quad (7)$$

must be prepared in an ice-bath. Consistently, the complexes [FeI(CNR)$_5$]ClO$_4$ do not insert mercury to give [(RNC)$_5$Fe–HgI]ClO$_4$, neither does [FeI(CNR)$_5$][HgI$_3$] (R = *p*-MeC$_6$H$_4$) which is easily obtained according to equation (8).

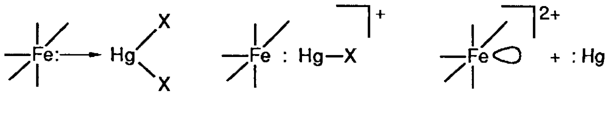
$$[(RNC)_5Fe{\rightarrow}HgI_2] + I_2 \longrightarrow [FeI(CNR)_5][HgI_3] \quad (8)$$

Finally, if the second halide is also removed extrusion of mercury occurs immediately according to equation (9).

$$[(RNC)_5Fe{\rightarrow}HgI_2] + 2AgClO_4 \longrightarrow [Fe(OClO_3)(CNR)_5]ClO_4 + Hg + 2AgI \quad (9)$$

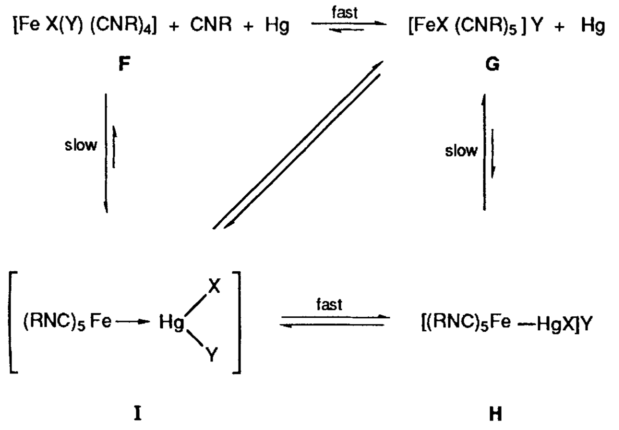
Discussion

The complexes in this work can be regarded as illustrating different stages (**C–E**) in the electron transfer from iron to mercury ending up with extrusion (reduction of mercury). In **C**



C **D** **E**

we represent the 'neutral' complexes as mercury(II) complexes where the mercury is co-ordinated by two halide ligands and by an iron(0) complex acting as a metallic base. Removal of a halide ligand from mercury, as in the cationic complexes, will increase the donation of electron density from iron; this can be repre-



Scheme 2

sented as in **D** where the complex can be seen formally as a Fe^{I}–Hg^{I} species. The cationic complexes **D** are thermodynamically unstable and undergo extrusion of mercury to give **E**; removal of the second halide from mercury [equation (9)] increases the rate of extrusion.

It has been reported that $[FeCl_2(CNR)_4]$ (R = *p*-MeOC$_6$H$_4$NC) partially disociates in solution [equation (10)] and it is reasonable that this equilibrium will lie more to the right in the presence of an extra mole of RNC [equation (10), solv = CNR]. In fact $[FeCl(CNR)_5]Cl$, $[FeCl(CNR)_5]ClO_4$ and $[FeCl(CNR)_5][HgCl_3]$ have been isolated and characterised.[17]

$$[FeCl_2(CNR)_4] \xrightarrow{\text{solvent(solv)}} [FeCl(solv)(CNR)_4]^+Cl^- \quad (10)$$

Taking this into consideration, the reactivity described in this paper can be discussed in terms of a cyclic equilibrium between possible states (**F**–**I**) whose thermodynamic stabilities are determined by the nature of the anionic ligands X and Y, and by the isonitrile attached to iron (Scheme 2).

Starting from any point in the cycle, when the system is allowed to reach equilibrium the only species detected in solution are **I** and/or **G**. This is due to the fact that **F** is displaced towards **G** (and equilibration is fast) and **H** is also displaced towards **G** or **I**, depending on Y. Thus, for Y = ClO$_4$, **H** is displaced towards **G**, although equilibration is slow allowing isolation of **H**. In other words, both **F** and **H** are thermodynamically very disfavoured compared with **G** and **I** and consequently the result of equilibration can be discussed simply in terms of the displacement of the hypothetical equilibrium $\mathbf{I} \rightleftharpoons \mathbf{G}$, *i.e.* in terms of the thermodynamic stabilities of these two species. Whereas our results strongly suggest that **H** is an intermediate in the extrusion of mercury ($\mathbf{I} \longrightarrow \mathbf{H} \longrightarrow \mathbf{G}$), nothing can be said about the slow insertion process when Y = I, Br or Cl, which could occur at the scarce neutral **F** or at the dominant cationic species **G**; in other words $\mathbf{G} \longrightarrow \mathbf{I}$ or $\mathbf{F} \longrightarrow \mathbf{I}$, or both could be operating.

For R = Ph or *p*-MeC$_6$H$_4$ and X = Y = I the equilibria are displaced towards **I** (*i.e.* the fast equilibrium $\mathbf{I} \rightleftharpoons \mathbf{H}$ is displaced towards **I**), the corresponding complexes show low conductivities, and consequently they are formed in good yield and are stable in solution (*i.e.* **I** is in equilibrium with only low concentrations of the extrusion product **G**). The relative stability of **I** decreases for X = Br or Cl as the co-ordinating ability of the halide to mercury decreases; it is known, for instance, that the stability of halogenomercurate ions in solution decreases in the order I > Br > Cl.[18] Consistently, we observe an increase in conductivity and a decrease in stability of $[(RNC)_5Fe{\rightarrow}HgX_2]$ in the series I, Br, Cl. The isolation of the species **I** is, of course, facilitated by working in solvents in which it precipitates.

For R = Bu^t the steric demand of the bulky CNBu^t ligands will disfavour three- over two-co-ordination of mercury (and the higher basicity of the iron fragment will co-operate in the same sense). For this reason the complexes $[(Bu^tNC)_5Fe{\rightarrow}HgX_2]$ are markedly more conducting and less stable. In the slow synthesis of these complexes, owing to their high solubility when R = Bu^t the complexes do not precipitate and an equilibrium is actually reached between **I** and **G**, in which **G** is dominant, which explains the difficulties and lower yields met in the preparation of the CNBu^t complexes.

Obviously, when Y = ClO$_4$ and even more when X = Y = ClO$_4$, the poor ability of the hard ClO$_4^-$ to co-ordinate to a soft mercury(II) centre makes species **I** unstable and the equilibria shift markedly towards **G**. Working at low temperature, the complexes **H** (X = Cl, Br or I; Y = ClO$_4$) can be isolated by taking advantage of the slow rate of the extrusion process $\mathbf{H} \longrightarrow \mathbf{G}$.

Experimental

General.—Infrared spectra were obtained on a Perkin-Elmer 593 or 883 instrument as KBr disks or Nujol mulls, ^{1}H NMR spectra on a Varian T60 instrument at 60 MHz. Elemental analyses were carried out by Centro de Investigación y Desarrollo-C.S.I.C. de Barcelona (Spain). Conductivities were measured with a Crison 522 conductivimeter.

Syntheses.—Literature methods were used to prepare CNR (R = Ph, *p*-MeC$_6$H$_4$ or Bu^t),[19] $[FeI_2(CNR)_4]$[17,20] and $[Fe(CNPh)_5]$.[14]

$[Fe(CNC_6H_4Me\text{-}p)_5]$. This compound was prepared following the method described for other $[Fe(CNR)_5]$ complexes by Stone and co-workers.[8] To a solution of FeI$_2$[21] (1.278 g, 4.452 mmol) and CNC$_6$H$_4$Me-*p* (2.800 g, 23.931 mmol) in tetrahydrofuran (50 cm^3) under a nitrogen atmosphere was added 1% Na/Hg (120 g). After stirring for 12 h the solvent was pumped off and the residue extracted with Et$_2$O (4 × 30 cm^3) to give a deep red solution. Addition of hexane (50 cm^3) and evaporation to vacuum afforded $[Fe(CNC_6H_4Me\text{-}p)_5]$ (1.400 g, 51% yield) (Found: C, 73.95; H, 5.85; N, 10.50. Calc.: C, 74.95; H, 5.50; N, 10.95%). ν(C≡N) (Nujol): 2080s, 2030s and 1937(sh) cm^{-1}.

$[Fe(CNPh)_5(HgI_2)]$ **1a**. *Method A*. To a solution of $[FeI_2(CNPh)_4]$ (0.680 g, 0.942 mmol) and CNPh (0.109 g, 1.058 mmol) in tetrahydrofuran (40 cm^3) was added metallic mercury (10 g). Over 12 h of stirring an orange precipitate appeared. The solvent was removed and the orange precipitate extracted in CH$_2$Cl$_2$ (30 cm^3) and crystallised by partial evaporation and addition of hexane (0.830 g, 86% yield). Complexes **1b** (96% yield) and **1c** (16% yield) were prepared similarly.

Method B. A solution of $[Fe(CNPh)_5]$ (0.775 g, 1.209 mmol) in tetrahydrofuran (20 cm^3) was added dropwise under nitrogen to a solution of HgI$_2$ (0.549 g, 1.208 mmol) in tetrahydrofuran (10 cm^3). After 1 h of stirring the solvent was pumped off and the residue extracted in CH$_2$Cl$_2$ (15 cm^3) and filtered to remove traces of Hg and HgI$_2$. The CH$_2$Cl$_2$ solution was partially evaporated. Addition of tetrahydrofuran (10 cm^3), evaporation to 5 cm^3 and cooling afforded orange crystals of complex **1b** (0.384 g, 29% yield).

$[Fe(CNPh)_5(HgBr_2)]$ **2a**. Freshly prepared wet AgBr (0.200 g, 1.065 mmol) was added to a suspension of complex **1a** (0.300 g, 0.292 mmol) in acetone (20 cm^3). The mixture was stirred in the dark for 12 h and the solvent was then pumped off. The residue was extracted with CH$_2$Cl$_2$ (2 × 15 cm^3) and the silver salts were filtered off. The CH$_2$Cl$_2$ solution was dried with MgSO$_4$ and concentrated to *ca.* 5 cm^3. Addition of toluene afforded complex **2a** as a yellow crystalline solid (0.229 g, 84% yield).

The following complexes (yields in parentheses) were obtained similarly, using the corresponding silver halide: **2b** (82), **3a** (64) and **3b** (68%). Since **2c** and **3c** and their precursors are soluble and owing to their lower stability the reactions were

Table 4 Final atomic coordinates (Hg, I and Fe × 10^5, others × 10^4) for complex **1b**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Hg	17 265(2)	15 244(2)	42 689(3)
I(1)	35 036(4)	18 779(4)	54 052(6)
I(2)	15 506(8)	13 602(9)	23 319(7)
Fe	3 404(7)	12 925(6)	45 292(8)
C(1)	1 144(6)	779(6)	5 660(6)
N(2)	1 621(4)	480(4)	6 374(5)
C(3)	2 359(7)	143(5)	7 121(8)
C(4)	3 247(8)	334(6)	7 231(7)
C(5)	3 966(8)	1(7)	7 955(8)
C(6)	3 906(7)	−499(6)	8 578(9)
C(7)	4 731(10)	−964(11)	9 302(14)
C(8)	3 039(8)	−705(5)	8 449(8)
C(9)	2 257(7)	−385(5)	7 719(6)
C(10)	717(5)	2 128(5)	5 313(7)
N(11)	997(5)	2 639(4)	5 859(6)
C(12)	1 490(7)	3 151(6)	6 619(8)
C(13)	1 003(9)	3 541(7)	6 964(9)
C(14)	1 528(8)	4 038(6)	7 760(9)
C(15)	2 435(8)	4 121(6)	8 121(8)
C(16)	2 976(12)	4 629(7)	8 998(12)
C(17)	2 862(7)	3 710(9)	7 649(7)
C(18)	2 378(7)	3 246(6)	6 925(8)
C(19)	−734(6)	1 154(4)	4 631(6)
N(20)	−1 416(5)	1 104(4)	4 627(5)
C(21)	−2 286(6)	1 053(5)	4 518(7)
C(22)	2 524(7)	4 449(6)	5 097(7)
C(23)	1 647(8)	4 503(7)	4 949(10)
C(24)	953(7)	4 061(7)	4 220(9)
C(25)	−18(7)	4 155(9)	4 055(12)
C(26)	1 182(7)	3 584(6)	3 692(9)
C(27)	2 034(7)	3 504(6)	3 823(8)
C(28)	−264(6)	1 826(5)	3 386(7)
N(29)	−679(6)	2 116(5)	2 630(6)
C(30)	−1 106(7)	2 430(6)	1 689(7)
C(31)	−1 618(9)	3 084(8)	1 512(9)
C(32)	−2 046(10)	3 344(8)	563(10)
C(33)	−1 926(8)	3 038(7)	−185(8)
C(34)	−2 371(12)	3 391(10)	−1 223(10)
C(35)	−1 418(9)	2 412(9)	18(8)
C(36)	−985(9)	2 113(7)	941(8)
C(37)	200(6)	476(5)	3 732(6)
N(38)	112(5)	−7(5)	3 200(6)
C(39)	−57(6)	−587(5)	2 505(7)
C(40)	−308(7)	−403(6)	1 553(7)
C(41)	−482(8)	−994(7)	873(9)
C(42)	−413(9)	−1 708(7)	1 178(9)
C(43)	−639(11)	−2 351(7)	413(9)
C(44)	−124(9)	−1 865(7)	2 161(8)
C(45)	57(8)	−1 308(6)	2 823(8)

carried out in an ice-bath and stirring was only for 30 min. Yields were 78% for **2c** and 74% for **3c**.

[Fe(CNPh)$_5$(HgI)]ClO$_4$ **4a**. A solution of AgClO$_4$ (0.414 g, 1.999 mmol) in acetone (20 cm^3) was added to complex **1a** (2.049 g, 1.999 mmol) in acetone (30 cm^3). After 1 h of stirring in an ice-bath and in the dark the yellow precipitate of AgI was filtered off and the solution was evaporated to dryness to give yellow solid **4a** which was recrystallised from CH$_2$Cl$_2$–hexane (1.861 g, 93% yield). Complexes **4b** (93%) and **4c** (55%) were prepared similarly.

[Fe(CNPh)$_5$(HgBr)]ClO$_4$ **5a**. To a solution of complex **4a** (0.250 g, 0.250 mmol) in acetone (40 cm^3) was added freshly prepared AgBr (0.100 g, 0.532 mmol). The mixture was stirred in the dark in an ice-bath for 1 h, and the silver salts were filtered off. The resulting solution was evaporated to dryness and the residue extracted in CH$_2$Cl$_2$. Concentration to small volume, addition of toluene and cooling afforded complex **5a** as a yellow solid (0.146 g, 61%). Complexes **5b** (61), **5c** (91), **6a** (60), **6b** (97) and **6c** (59%) were prepared similarly, using the corresponding silver halide.

Reaction of Complexes **1a–c** *with* AgClO$_4$ *in* 1:2 *Ratio*.—To a suspension of complexes **1a–1c** (0.270 mmol) in acetone (30 cm^3) was added AgClO$_4$ (0.126 g, 0.607 mmol). After 4 h of stirring in the dark the solvent was pumped off and the residue extracted with CH$_2$Cl$_2$ (2 × 10 cm^3). The filtered solution was evaporated to *ca.* 5 cm^3 and Et$_2$O was added, affording a yellow solid identified as [Fe(OClO$_3$)(CNR)$_5$]ClO$_4$.[22] Yields were 67 (R = Ph), 80 (R = *p*-MeC$_6$H$_4$) and 68% (R = Bu^t).

Reaction of [Fe(CNC$_6$H$_4$Me-*p*)$_5$(HgI$_2$)] **1b** *with* I$_2$.—A solution of I$_2$ (0.047 g, 0.185 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added dropwise to a stirred solution of complex **1b** (0.200 g, 0.183 mmol) in CH$_2$Cl$_2$ (15 cm^3). After 30 min of stirring, toluene (10 cm^3) was added and the CH$_2$Cl$_2$ was pumped off to give brown crystals of [FeI(CNC$_6$H$_4$Me-*p*)$_5$][HgI$_3$] (0.190 g, 79% yield) (Found: C, 35.70; H, 2.60; N, 5.25. Calc.: C, 35.60; H, 2.60; N, 5.20%). ν(C≡N) (CH$_2$Cl$_2$): 2205w and 2160s cm^{-1}. Λ_M (acetone, 5×10^{-4} mol dm^{-3}) = 105 Ω^{-1} cm^2 mol^{-1}.

Safety Note.—Perchlorate complexes are potentially shock-sensitive and may explode or ignite on contact with organic material. They should be handled with care and prepared only on a small scale. Mercury and many mercury compounds are known to be poisonous and appropriate care in their handling should be taken.

X-Ray Crystal Structure Determination of Complex **1b**.—Orange crystals were obtained by diffusion from dichloromethane–hexane. A prismatic crystal of dimensions 0.07 × 0.07 × 0.1 mm was used.

Crystal data. C$_{40}$H$_{35}$FeHgI$_2$N$_5$, *M* = 1096.00, monoclinic, space group $P2_1/a$, a = 16.680(3), b = 18.031(4), c = 15.256(2) Å, β = 116.92(2)°, *U* = 4091(2) Å^3, D_c = 1.779 g cm^{-3}, *Z* = 4, *F*(000) = 2088.0, λ(Mo-Kα) = 0.710 69 Å, μ(Mo-Kα) = 57.48 cm^{-1}, 298 K.

Structure determination and refinement. Data were collected with an Enraf-Nonius CAD-4 diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($8 \leqslant \theta \leqslant 12°$) and refined by the least-squares method. Intensities were collected with graphite-monochromatised Mo-Kα radiation, using the ω–2θ scan technique. 6045 Reflections were measured in the range $2 \leqslant \theta \leqslant 25°$, 5393 being assumed as observed [$I \geqslant 2.5\sigma(I)$]; R_{int} on *F* was 0.033. Three reflections were measured every 2 h as orientation and intensity control, but significant intensity decay was not observed. Lorentz polarisation and absorption corrections (using DIFABS)[23] were made.

The structure was solved by Patterson synthesis, using the SHELX 86[24] and DIRDIF 84[25] computer programs and refined by the full-matrix least-squares method with SHELX 76.[26] The function minimised was $\Sigma w \| F_o | - | F_c \|^2$, where $w = |\sigma^{-2}(F_o) + 0.0146(F_o)^2|^{-1}$; f, f' and f'' were taken from ref. 27. The H-atom positions were computed and refined with an overall isotropic thermal parameter and using a riding model. The final *R* factor was 0.054 (*R′* = 0.067) for all observed reflections. Number of refined parameters 444; maximum shift/e.s.d. = 0.1; maximum and minimum peaks in final difference synthesis 0.4 and −0.4 e Å^{-3}. Atomic coordinates are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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