Cyclometallation of ferrocenylimines

Part II. Studies on the cyclomercuration of [1-(arylimino)ethyl] ferrocenes and related structure-reactivity relationships *

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Abstract

A series of 2-chloromercurio-1-[1-(arylimino)ethyl]ferrocenes has been synthesized by direct mercuration of the corresponding ferrocenylketimines. Competitive coordination and protonation processes are proposed and the effect of the structures of ferrocenylketimines on the mercuration reactivities discussed. A relatively strong intramolecular coordination between the imino nitrogen and mercury in the molecules of the 2-mercurated products was indicated by the X-ray crystal structure analysis of 2-chloromercurio-1-[1-[(4-chlorophenyl)imino]ethyl]ferrocene, in which the distance between the mercury and the nitrogen is 2.766 Å, significantly shorter than the sum of the Van der Waals radii of mercury and nitrogen, 3.05–3.15 Å.

Key words: Iron; Mercury; Ferrocenylimine; Cyclometallation; Crystal structure

1. Introduction

We recently reported a reaction between aryliminomethylferrocenes (**1**) and mercuric acetate, which involved the mercuration of the substituted Cp ring at the *ortho*-position, *e.g.* **1** → **2**, and also the crystal structure of 2-chloromercurio-1-[(4-methoxyphenylimino)methyl]ferrocene (**2a**) [1]. This reaction can be included in the general classification of cyclometallation reactions where an organic ligand of a metal complex undergoes intramolecular metallation with the formation of a metal–carbon σ bond [2–7]. In order to examine this reaction further, we have prepared a series of ferrocenylketimines **3** and have investigated the reaction of **3** with mercuric acetate. The present paper describes the syntheses, structures and properties of 2-chloromercurated ferrocenylketimines, including the effects of substituent on the selectivities of the 2-mercurated products and the influence of the conformations of [1-[(1-naphthyl)imino]ethyl]ferrocene on its reactivity as regards mercuration.

2. Results and discussion

Mercuration of **3** with an equimolar quantity of mercuric acetate in methylene chloride and methanol at ambient temperature for about 1 h, followed by

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* For Part I see ref. 1.

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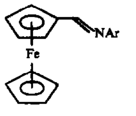
TABLE 1. IR C=N stretching frequencies (cm^{-1}) for the compounds **3** and **4** [a]

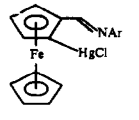
	a	b	c	d	e	f	g	h	i	j	k	l	m
3	1623	1624	1634	1623	1623	1623	1632	1624	1624	1638	1631	1626	1627
4	1613	1615	1610	1615	1614	1610	1623	1614	1614	1616	1606	1620	1615

[a] KBr pellets.

treatment with LiCl, gave 2-chloromercurated ferrocenylketimines (**4**) as major products with the exception of **4a**, **4b**, and **4k**. The isolation of pure compounds **4** is easily achieved by chromatography of the reaction mixture on silica gel, since the compounds **4** exhibited much higher R_f values than those of the corresponding starting materials. All 2-mercurated ferrocenylketimines were characterized by elemental analyses, IR, and ^{1}H NMR spectra. The spectral features of compounds **4** are similar to those of compounds **2**. The C=N absorptions of **4** are shifted to lower energy as shown by the range from 7 to 25 cm^{-1} (Table 1), when compared with the unmercurated parent compounds **3**, which, along with the chromatographic characteristics of compounds **4**, indicates intramolecular N → Hg coordination [1,8].



1



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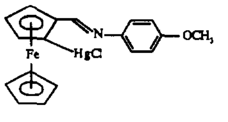
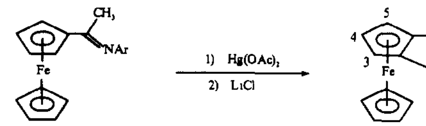


2a



3 4

$\mathrm{Ar} = p\text{-}\mathrm{CH_3OC_6H_4}(\mathbf{a}),\ p\text{-}\mathrm{CH_3C_6H_4}(\mathbf{b}),\ \mathrm{C_6H_5}(\mathbf{c}),$
$p\text{-}\mathrm{ClC_6H_4}(\mathbf{d}),\ p\text{-}\mathrm{BrC_6H_4}(\mathbf{e}),\ p\text{-}\mathrm{IC_6H_4}(\mathbf{f}),$
$p\text{-}\mathrm{NO_2C_6H_4}(\mathbf{g}),\ m\text{-}\mathrm{ClC_6H_4}(\mathbf{h}),$
$m\text{-}\mathrm{BrC_6H_4}(\mathbf{i}),\ m\text{-}\mathrm{NO_2C_6H_4}(\mathbf{j}),$
$1\text{-naphthyl}(\mathbf{k}),\ 2\text{-naphthyl}(\mathbf{l}),\ o\text{-}\mathrm{ClC_6H_4}(\mathbf{m}).$

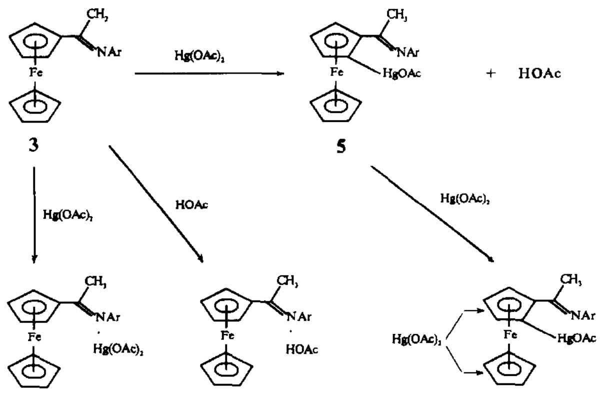
The results of the mercuration reactions are listed in Table 2, and it is to be noted that electron-donating groups present in the aryl ring are quite unfavourable to the mercuration of the substituted Cp ring at the 2-position, while electron-withdrawing groups cause the formation of larger quantities of 2-mercurated products. This is unexpected, since the 2-mercuration of ferrocenylketimines is believed to involve the coordination of mercuric acetate to imino nitrogen with subsequent electrophilic substitution [1]. Donating groups will lead to increased electron density in imino nitrogen, and this means better mercury coordination and faster substitution which would be expected to favour mercuration at the 2-position, whereas withdrawing groups will have the opposite effect.

In order to explain this unexpected effect of substituents on the mercuration, we have proposed that competition may exist between the coordination of mercuric acetate and the bonding of acetic acid liberated in the reaction with imino nitrogen of **3** (Scheme 1). Owing to the strong electron-donating ability of the ferrocenyl system [9] and the electron-donating effect of the α methyl of **3**, ferrocenylketimines are very strong organic bases. When a electron-donating group is present in the aryl ring, the basicity of ferrocenylketimine is so strong that the protonation of the imino nitrogen predominates over the coordination of electrophile to this atom. This can cause a decrease of the

TABLE 2. Mercuration results [a]

3	Conversions [c] (%)	Selectivities [c] of 4 (%)	3	Conversions [b] (%)	Selectivities [c] of 4 (%)
a	36	13	g	60	73
b	40	30	h	63	71
c	55	64	i	65	86
d	53	75	j	70	89
e	62	82	k	45	22
f	56	73	l	58	59
			m	71	84

[a] The results listed here are for the equimolar reaction of ferrocenylimine and mercuric acetate. [b] Conversions refer to the consumed ferrocenylimines. [c] Selectivity = 2 − (mercurated product formed/consumed ferrocenylketimine).



Scheme 1.

TABLE 3. λ_{max} values (nm) of the ferrocene bands for the compounds 3 [a]

	λ_1 [b]	λ_2 [c]	λ_3 [d]	$\Delta\lambda$ ($\lambda_1 - \lambda_2$)
3a	500	451	451	49
3b	492	452	452	40
3c	475	452	451	23
3d	460	453	452	7
3e	458	453	452	5
3f	460	452	452	8
3g	454 [e]	455 [e]	453	−1
3h	456	453	452	3
3i	458	454	452	4
3j	452	455	452	−3
3k	458	452	450	6
3l	470	454	451	16
3m	456	452	452	4

[a] Concentrations of 3 range from 8.04×10^{-4} to 1.14×10^{-3} M. [b] Solvent: $CH_3COOH/CH_2Cl_2/CH_3OH$ (v/v/v) = 1 : 99 : 400. [c] Solvent: CH_2Cl_2/CH_3OH (v/v) = 1 : 4. [d] Solvent: CH_3COOH/CH_2Cl_2 (v/v) = 1 : 499. [e] Estimated values.

yields of the 2-mercurated products. In addition, further mercuration will occur at ferrocenyl rings of **5**, affording polymercurated products, which can also lead to substantial decrease of the yields of monomercurated products **4a** and **4b**.

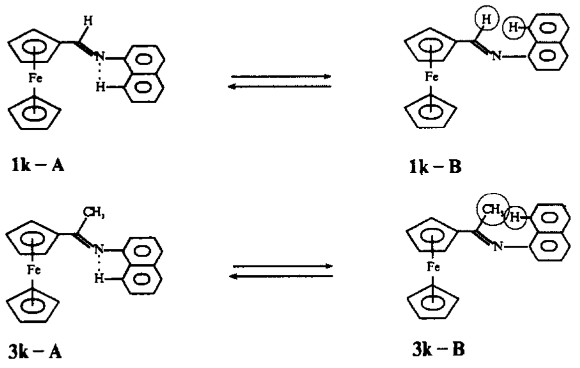
During the study it was found that when a drop of acetic acid was added to the solution of ferrocenylimine in MeOH, the original orange solution quickly turned purple. This is evidence for the above-mentioned protonation, since a protonated imino group might exhibit very strong electron-withdrawing ability, and strong electron-withdrawing groups are known to shift the ferrocene band near 440 nm in the electronic spectra of ferrocene and its derivatives, assigned to the d–d transition of the iron atom [10–12], to long wavelength [13]. In order further to investigate this observation, and to reveal the effect of substituent on the protonation of ferrocenylketimines by acetic acid, we measured the UV spectra of ferrocenylketimines in the presence of a small amount of acetic acid, whose concentration is comparable with that in the mercuration reaction system, and also recorded, for comparison, the UV spectra of **3** in the absence of acetic acid and in different solvents. In Table 3 are listed the λ_{max} values of the ferrocene bands of ferrocenylketimines **3**, which make apparent the following facts. First, the presence of a small amount of acetic acid in the solution of **3** in CH_2Cl_2-CH_3OH leads to the shift of ferrocene bands to long wavelength with the exception of **3g** and **3j** containing a very strongly electron-withdrawing group, indicating the occurrence of protonation in the reaction.

Secondly, the substituents in the phenyl ring markedly affect the protonation of **3** by acetic acid. Of all compounds, **3a** and **3b** exhibit the largest shifts $\Delta\lambda$, showing that the electron-donating groups in the *para*-position of the phenyl ring cause the increase of electron density in nitrogen, thus favouring protonation. This result is consistent with the explanation offered above.

Finally, it is noteworthy that, if only methylene chloride is used as the solvent, the addition of a small amount of acetic acid to ferrocenylketimines has almost no effect on the ferrocene bands near 450 nm. This shows that methanol, as a protonic solvent, can facilitate the dissociation of acetic acid thus favouring protonation of ferrocenylketimines. Furthermore, in CH_2Cl_2-CH_3OH solution, the ferrocene bands of compounds **3** show no dependence on strong electron-withdrawing substituents. This may be due to the non-planarity between the ferrocenyl ring and the phenyl ring, which can influence the transmission of the electronic effects of substituents in the phenyl ring through the C=N bond to the ferrocenyl moiety. These preliminary UV data can explain the unusual experimental results.

It is believed that both the coordination of electrophile to imino nitrogen and the protonation of this atom by acetic acid generally exist in the mercuration of imines. Which predominates depends on the basicity of an imine and/or the concentrations of $Hg(OAc)_2$ and HOAc. The competitive coordination and protonation processes are also responsible for the fair yields of 2-mercurated products **2** [1] and **4**. Kovar and Rausch noted that the mercuration of acylferrocenes occurred in the absence of perchloric acid, affording higher conversion to the 2-mercurated acylferrocenes than that in the presence of small amounts of perchloric acid [8]. This result can also be explained by the above-mentioned proposition.

From Table 2, it can be seen that 2-mercurated product **4k** was obtained in very low yield, and especially, the yield of **4k** is far lower than that of **2k** [1]. This result is consistent with the conformation of **1k** and **3k**. Generally, the conformations of **1k** and **3k** can be roughly illustrated as follows (Scheme 2). It can be seen that the conformations **1k-A** and **3k-A** should be the more stable ones, due to the smaller steric requirement and the possible N ··· H interaction. The H–H and CH_3–H repulsions make **1k-B** and **3k-B** less stable, and furthermore, in **3k-B**, the large group CH_3 and the H are too crowded to endure this conformation. In this case, mercury can be directed into the 2-position of the substituted Cp ring by coordination with nitrogen. But the mercuration of the stable conformations **1k-A** and **3k-A** does not occur at the 2-position because the hindrance of H and the possible N ··· H interaction will block the coordination of mer-



Scheme 2.

curic acetate to imino nitrogen. Thus, the compound **4k** was obtained in lower yield, and the yields of **2k** and **4k**, to a certain extent, may be the reflection of the distribution of the stable and unstable conformations of **1k** and **3k**.

The X-ray crystal structure of **4d** was determined in order to elucidate the intramolecular coordination in the molecules of the compounds **4**, as well as for comparison with that of **2a** [1]. The structure is illustrated in Fig. 1. The distances Hg–C (1), 2.037 Å, and Hg–Cl (1), 2.309 Å, are typical of organic derivatives of mercury. The bond angle C(1)–Hg–Cl(1) is 179.1° and is, in fact, almost identical with the ideal in organomercurials, 180° [13].

The distance between the nitrogen atom and the mercury atom is 2.766 Å, and corresponds to the notably strong coordination between N and Hg, since it is 0.38 Å shorter than the sum of the Van der Waals radii of N and Hg [13–17], and also significantly shorter than the corresponding distance in **2a** [1] and those found for other *ortho*-mercurated ferrocene derivatives [18,19]. Due to the coordination between N and Hg, the bond angles Hg–C(1)–C(2) and C(1)–C(2)–C(11) decrease to 121.3° and 124°, respectively, and this is comparable with the feature found for **2a**. A detailed comparison of the structure of **4d** with that of **2a** shows that the angle N–C(11)–C(2), 118.2°, is smaller than the corresponding angle of **2a**, which may be due to the large steric hindrance caused by α methyl group in **4a**. The smaller angle facilitates the N → Hg coordination.

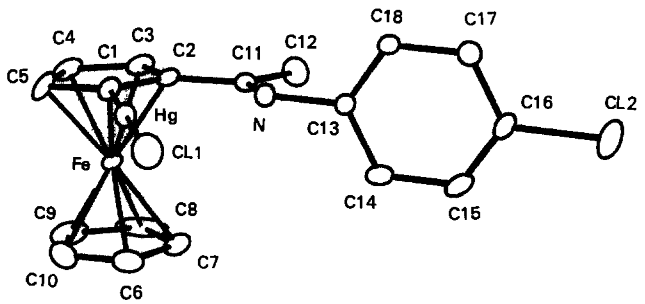


Fig. 1. Molecular structure of **4d** showing the atom numbering scheme.

Average Fe–C(1–5) and Fe–C(6–10) distances are 2.047 and 2.031 Å, respectively and the average C–C distances in the ferrocenyl moiety are 1.390 and 1.426 Å for the unsubstituted and substituted Cp ring, respectively. The chelate cycle Hg–C(1)–C(2)–C(11)–N is nearly planar, and the torsion angles Hg–C(1)–C(2)–C(11) and C(1)–C(2)–C(11)–N are 1.31° and 3.46°, respectively. The Cp rings are almost parallel (dihedral angle 1.29°). The dihedral angle between the substituted Cp ring and the chelate cycle is 2.72°. These features have also been found for **2a**.

It is of interest that the phenyl ring is almost perpendicular to the Cp ring, the dihedral angle being 91.68° for the substituted Cp ring and the phenyl ring. In the case of **2a**, the corresponding angle is only 51.97° [1]. This can also be due to the greater steric requirement in **4d** than in **2a**.

In conclusion, these studies have shown that the mercuration of ferrocenylimines is markedly affected by the structures of imines, that competition between coordination and protonation can explain the experimental results well, and that its existence in the mercuration of ferrocenylimines as a general phenomenon is beyond doubt, though further evidence would not be amiss. An internal cyclomercuration process responsible for the formation of 2-mercurated products is proved by the existence of an intramolecular N → Hg coordination confirmed by crystal structure analyses in the 2-mercurated products, and that all phenomena resulting from the mercuration can be explained by this cyclomercuration process.

3. Experimental section

Melting points were measured on a WC-microscopic apparatus and are uncorrected. Elemental analyses were determined with a Carlo Erba 1116 Elemental Analyzer. ^{1}H NMR spectra were recorded on a Bruker AM 400 spectrometer and IR spectra on a Shimadzu IR 435 spectrophotometer. UV spectra were measured with a Shimadzu UV-2100 spectrophotometer. Chromatography was on silica gel under reduced pressure.

Ferrocenylketimines (**3a–m**) were prepared by published methods [20], new compounds were characterized as follows.

[1-[(4-methoxyphenyl)imino]ethyl]ferrocene (**3a**). Yellow-brown crystals, yield 50%; m.p. 125–127°C. Anal. Found: C, 68.38; H, 5.70; N, 4.27. $C_{19}H_{19}FeNO$ calc.: C, 68.49; H, 5.75; N, 4.20%. IR (KBr pellet): 1623, 1227, 1100, 1000, 838, 821 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.11 (s, 3H, CH$_3$), 3.81 (s, 3H, OCH$_3$), 4.21

(s, 5H, C_5H_5), 4.42 (broad s, 2H, H-3), 4.81 (broad s, 2H, H-2), 6.73 (d, 2H, $J = 8.5$ Hz, H α to N), 6.89 (d, 2H, $J = 8.8$ Hz, H β to N).

[1-[(4-methylphenyl)imino]ethyl]ferrocene (**3b**). Red-brown crystals, yield 56%; m.p. 127–129°C. Anal. Found: C, 71.82; H, 6.02; N, 4.46. $C_{19}H_{19}FeN$ calc.: C, 71.96; H, 6.04; N, 4.42%. IR(KBr pellet): 1624, 1100, 1000, 840, 822 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.10 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 4.22(s, 5H, C_5H_5), 4.43 (broad s, 2H, H-3), 4.81 (broad s, 2H, H-2), 6.68 (d, 2H, $J = 7.6$ Hz, H α to N), 7.13 (d, 2H, $J = 7.7$ Hz, H β to N).

[1-[(4-chlorophenyl)imino]ethyl]ferrocene (**3d**). Orange crystals, yield 40%; m.p. 146–148°C. Anal. Found: C, 63.94; H, 4.34; N, 4.11. $C_{17}H_{16}ClFeN$ calc.: C, 64.05; H, 4.49; N, 4.16%. IR(KBr pellet): 1623, 1100, 1000, 842, 820 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.08 (s, 3H, CH_3), 4.21 (s, 5H, C_5H_5), 4.44 (broad s, 2H, H-3), 4.79 (broad s, 2H, H-2), 6.70 (d, 2H, $J = 7.3$ Hz, H α to N), 7.28 (d, 2H, $J = 7.2$ Hz, H β to N).

[1-[(4-iodophenyl)imino]ethyl]ferrocene (**3f**). Yellow-brown crystals, yield 43%; m.p. 160–162°C. Anal. Found: C, 50.31; H, 3.78; N, 3.15. $C_{18}H_{16}FeIN$ calc.: C, 50.37; H, 3.17; N, 3.26%. IR(KBr pellet): 1623, 1098, 1000, 840, 820 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.05 (s, 3H, CH_3), 4.21 (s, 5H, C_5H_5), 4.45 (broad s, 2H, H-3), 4.80 (broad s, 2H, H-2), 6.55 (d, 2H, $J = 6.6$ Hz, H α to N), 7.62 (d, 2H, $J = 7.1$ Hz, H β to N).

[1-[(3-nitrophenyl)imino]ethyl]ferrocene (**3j**). Yellow-brown crystals, yield 50%; m.p. 168–170°C. Anal. Found: C, 61.89; H, 4.58; N 8.02. $C_{18}H_{16}FeN_2O_2$ calc.: C, 62.10; H, 4.74; N, 7.89%. IR(KBr pellet): 1638, 1514, 1344, 1100, 1000, 832, 798, 750 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.09 (s, 3H, CH_3), 4.25 (s, 5H, C_5H_5), 4.51 (broad s, 2H, H-3), 4.82 (broad s, 2H, H-2), 7.12 (d, 1H, $J = 8.0$ Hz, H α to imino N), 7.49 (t, 1H, $J = 8.0$ Hz, H β to NO_2), 7.63 (s, 1H, H α to NO_2), 7.94 (d, 1H, $J = 7.4$ Hz, H α to NO_2).

[1-[(1-naphthyl)imino]ethyl]ferrocene (**3k**). Red-brown crystals, yield 40%; m.p. 193–195°C. Anal. Found: C, 74.62; H, 5.44; N, 3.88. $C_{22}H_{19}FeN$ calc.: C, 74.82; H, 5.15; N, 3.96%. IR(KBr pellet): 1626, 1100, 1000, 802, 780 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.06 (s, 3H, CH_3), 4.30 (s, 5H, C_5H_5), 4.49 (broad s, 2H, H-3), 4.93 (broad s, 2H, H-2), 6.76–7.87 (m, 7H, protons for the naphthyl ring).

[1-[(2-naphthyl)imino]ethyl]ferrocene (**3l**). Brown crystals, yield 45%; m.p. 169–171°C. Anal. Found: C, 74.61; H, 5.38; N, 4.09. $C_{22}H_{19}FeN$ calc.: C, 74.82; H, 5.15; N, 3.96%. IR(KBr pellet): 1631, 1100, 998, 818, 760 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.13 (s, 3H, CH_3), 4.26 (s, 5H, C_5H_5), 4.46 (broad s, 2H, H-3), 4.85 (broad s, 2H, H-2), 7.00–7.83 (m, 7H, protons for the naphthyl ring).

[1-[(2-chlorophenyl)imino]ethyl]ferrocene (**3m**). Yellow-brown crystals, yield 63%; m.p. 135–136°C. Anal. Found: C, 63.87; H, 4.68; N, 4.16. $C_{18}H_{16}ClFeN$ calc.: C, 64.05; H, 4.49; N, 4.16%. IR (KBr pellet): 1627, 1102 1000, 820, 760 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.05 (s, 3H, CH_3), 4.27 (s, 5H, C_5H_5), 4.46 (broad s, 2H, H-3), 4.84 (broad s, 2H, H-2), 6.77 (d, 1H, $J = 6.7$ Hz, H α to N), 7.00 (t, 1H, $J = 7.6$ Hz, H γ to N), 7.22 (t, 1H, $J = 6.4$ Hz, H γ to Cl and β to N), 7.40 (d, 1H, $J = 8.0$ Hz, H α to Cl).

3.1. Mercuration of ferrocenylketimines (3a–m)

The details of the mercuration reactions, the separation of reaction mixtures and the purification procedures by rapid column chromatography on silica gel have been described previously [1].

2-chloromercurio-1-[1-[(4-methoxyphenyl)ethyl]ferrocene (**4a**). Orange crystals, yield 5%; m.p. 145–147°C. Anal. Found: C, 40.15; H, 3.16; N, 2.29. $C_{19}H_{18}ClFeHgNO$ calc.: C, 40.17; H, 3.20; N, 2.47%. IR (KBr pellet): 1613, 1245, 1102, 1000, 824, 810 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.20 (s, 3H, CH_3), 3.61 (s, 3H, OCH_3), 4.22 (s, 5H, C_5H_5), 4.42 (broad s, 1H, H-3), 4.62 (broad s, 1H, H-4), 4.81 (broad s, 1H, H-5), 6.80 (d, 2H, $J = 8.0$ Hz, H α to N), 6.90 (d, 2H, $J = 8.0$ Hz, H β to N).

2-chloromercurio-1-[1-[(4-methylphenyl)imino]ethyl]ferrocene (**4b**). Orange crystals, yield 12%; m.p. 166–167°C. Anal. Found: C, 41.08; H, 3.09; N, 2.57. $C_{19}H_{18}ClFeHgN$ calc.: C, 41.33; H, 3.29; N, 2.54%. IR (KBr pellet): 1615, 1606, 1102 1000, 840, 812 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.18 (s, 3H, $CH_3\text{-}C=N$), 2.34 (s, 3H, CH_3), 4.22 (s, 5H, C_5H_5), 4.43 (broad s, 1H, H-3), 4.62 (broad s, 1H, H-4), 4.81 (broad s, 1H, H-5), 6.73 (d, 2H, $J = 7.7$ Hz, H α to N), 7.15 (d, 2H, $J = 7.7$ Hz, H β to N).

2-chloromercurio-1-[1-(phenylimino)ethyl]ferrocene (**4c**). Orange crystals, yield 35%; m.p. 172–174°C. Anal. Found: C, 40.01; H, 3.10; N, 3.01. $C_{18}H_{16}ClFeHgN$ calc.: C, 40.17; H, 3.00; N, 2.60%. IR (KBr pellet): 1609, 1100, 1000, 808, 770, 704 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.17 (s, 3H, CH_3), 4.23 (s, 5H, C_5H_5), 4.44 (broad s, 1H, H-3), 4.63 (broad s, 1H, H-4), 4.82 (broad s, 1H, H-5), 6.61 (d, 2H, $J = 7.7$ Hz, H α to N), 7.10 (t, 1H, $J = 7.4$ Hz, H γ to N), 7.35 (t, 2H, $J = 7.5$ Hz, H β to N).

2-chloromercurio-1-[1-[(chlorophenyl)imino]ethyl] ferrocene (**4d**). Orange crystals, yield 40%; m.p. 208–210°C (dec.). Anal. Found: C, 37.44; H, 2.41; N, 2.61. $C_{18}H_{15}Cl_2FeHgN$ calc.: C, 37.76; H, 2.65; N, 2.45%. IR (KBr pellet): 1616, 1100, 1000, 842, 822 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.16 (s, 3H, CH_3), 4.23 (s, 5H, C_5H_5), 4.45 (d, 1H, $J = 1.9$ Hz, H-3), 4.65 (t, 1H, $J = 2.3$ Hz, H-4), 4.83 (d, 1H, $J = 2.3$ Hz, H-5), 6.75 (d, 2H, $J = 8.6$ Hz, H α to N), 7.31 (d, 2H, $J = 8.6$ Hz, H β to N).

2-chloromercurio-1-[1-[(4-bromophenyl)imino]ethyl] ferrocene (**4e**). Red crystals, yield 51%; m.p. 207–209°C (dec.). Anal. Found: C, 35.01; H, 2.61; N, 2.33. $C_{18}H_{15}BrClFeHgN$ calc.: C, 35.04; H, 2.45; N, 2.27%. IR (KBr pellet): 1614, 1100, 1000, 842, 822 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.16 (s, 3H, CH_3), 4.23 (s, 5H, C_5H_5), 4.45 (d, 1H, $J = 1.8$ Hz, H-3), 4.65 (t, 1H, $J = 2.5$ Hz, H-4), 4.83 (d, 1H, $J = 2.3$ Hz, H-5), 6.69 (d, 2H, $J = 8.6$ Hz, H α to N), 7.45 (d, 2H, $J = 8.6$ Hz, H β to N).

2-chloromercurio-1-[1-[(4-iodophenyl)imino]ethyl] ferrocene (**4f**). Red crystals, yield 41%; m.p. 209–211°C (dec.). Anal. Found: C, 32.20; H, 1.99; N, 2.25. $C_{18}H_{15}ClFeHgIN$ calc.: C, 32.56; H, 2.28; N, 2.11%. IR (KBr pellet): 1610, 1100, 1000, 840, 816 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.16 (s, 3H, CH_3), 4.23 (s, 5H, C_5H_5), 4.45 (d, 1H, $J = 2.0$ Hz, H-3), 4.65 (t, 1H, $J = 2.5$ Hz, H-4), 4.82 (d, 1H, $J = 2.5$ Hz, H-5), 6.58 (d, 2H, $J = 8.5$ Hz, H β to I), 7.64 (d, 2H, $J = 8.4$ Hz, H α to I).

2-chloromercurio-1-[1-[(4-nitrophenyl)imino]ethyl] ferrocene (**4g**). Deep red crystals, yield 44%; m.p. 220–222°C (dec.). Anal. Found: C, 36.99; H, 2.33; N, 4.70. $C_{18}H_{15}ClFeHgN_2O_2$ calc.: C, 37.01; H, 2.59; N, 4.80%. IR (KBr pellet): 1623, 1336, 1100, 1000, 854, 810 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.18 (s, 3H, CH_3), 4.26 (s, 5H, C_5H_5), 4.51 (d, 1H, $J = 2.1$ Hz, H-3), 4.71 (t, 1H, $J = 2.6$ Hz, H-4), 4.87 (d, 1H, $J = 2.4$ Hz, H-5), 6.90 (d, 2H, $J = 8.7$ Hz, H β to nitro group), 8.24 (d, 2H, $J = 8.7$ Hz, H α to nitro group).

2-chloromercurio-1-[1-[(3-chlorophenyl)imino]ethyl] ferrocene (**4h**). Red crystals, yield 45%; m.p. 215–217°C (dec.). Anal. Found: C, 37.47; H, 2.55; N, 2.30. $C_{18}H_{15}Cl_2FeHgN$ calc.: C, 37.76; H, 2.65; N, 2.45%. IR (KBr pellet): 1614, 1102, 996, 867, 790, 721 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.16 (s, 3H, CH_3), 4.24 (s, 5H, C_5H_5), 4.46 (broad s, 1H, H-3), 4.66 (broad s, 1H, H-4), 4.84 (broad s, 1H, H-5), 6.69 (d, 1H, $J = 7.8$ Hz, H α to N and γ to Cl), 6.79 (s, 1H, H α to N and Cl), 7.09 (d, 1H, $J = 8.5$ Hz, H α to Cl and γ to N), 7.28 (t, 1H, $J = 8.0$ Hz, H β to Cl and N).

2-chloromercurio-1-[1-[(3-bromophenyl)imino]ethyl] ferrocene (**4i**). Red crystals, yield 56%; m.p. 212–214°C (dec.). Anal. Found: C, 34.89; H, 2.41; N, 2.25. $C_{18}H_{15}BrClFeHgN$ calc.: C, 35.04; H, 2.45; N, 2.27%. IR (KBr pellet): 1614, 1102, 996, 825, 785 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.16 (s, 3H, CH_3), 4.24 (s, 5H, C_5H_5), 4.46 (d, 1H, $J = 1.9$ Hz, H-3), 4.66 (t, 1H, $J = 2.4$ Hz, H-4), 4.84 (d, 1H, $J = 2.4$ Hz, H-5), 6.74 (d, 1H, $J = 6.9$ Hz, H α to N and γ to Br), 6.94 (s, 1H, H α to N and Br), 7.22 (t, 1H, $J = 7.9$ Hz, H β to N and Br), 7.23 (d, 1H, $J = 6.9$ Hz, H α to Br and γ to N).

2-chloromercurio-1-[1-[(3-nitrophenyl)imino]ethyl] ferrocene (**4j**). Red crystals, yield 62%; m.p. 190–192°C. Anal. Found: C, 37.11; H, 2.54; N, 4.75. $C_{18}H_{15}ClFeHgN_2O_2$ calc.: C, 37.01; H, 2.59; N, 4.80%. IR (KBr pellet): 1616, 1518, 1343, 1100, 997, 802, 748, 716 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.19 (s, 3H, CH_3), 4.28 (s, 5H, C_5H_5), 4.51 (d, 1H, $J = 2.3$ Hz, H-3), 4.71 (t, 1H, $J = 2.4$ Hz, H-4), 4.88 (d, 1H, $J = 2.6$ Hz, H-5), 7.16 (d, 1H, $J = 7.8$ Hz, H α to N and γ to NO_2), 7.52 (t, 1H, $J = 8.0$ Hz, H β to N and NO_2), 7.63 (s, 1H, H α to N and NO_2), 7.99 (d, 1H, $J = 8.0$ Hz, H α to NO_2 and γ to N).

2-chloromercurio-1-[1-[(1-naphthyl)imino]ethyl]ferrocene (**4k**). Orange crystals, yield 10%; m.p. 215–217°C (dec.). Anal. Found: C, 44.43; H, 2.93; N, 2.63. $C_{22}H_{18}ClFeHgN$ calc.: C, 44.92; H, 3.09; N, 2.38%. IR (KBr pellet): 1620, 1102, 998, 818 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.08 (s, 3H, CH_3), 4.32 (s, 5H, C_5H_5), 4.51 (d, 1H, H-3), 4.70 (t, 1H, H-4), 4.88 (d, 1H, $J = 1.9$ Hz, H-5), naphthyl protons appear at: 6.73 (d, 1H, $J = 7.1$ Hz), 7.44 (t, 1H, $J = 7.6$ Hz), 7.46 (t, 1H, $J = 6.8$ Hz), 7.50 (t, 1H, $J = 6.7$ Hz), 7.61 (d, 1H, $J = 8.2$ Hz), 7.71 (d, 1H, $J = 8.1$ Hz), 7.86 (d, 1H, $J = 8.0$ Hz).

2-chloromercurio-1-[1-[(2-naphthyl)imino]ethyl]ferrocene (**4l**). Orange red crystals, yield 34%; m.p. 214–216°C (dec.). Anal. Found: C, 44.80; H, 2.95; N 2.43. $C_{22}H_{18}ClFeHgN$ calc.: C, 44.92; H, 3.09; N, 2.38%. IR (KBr pellet): 1606, 1102, 998, 818 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.21 (s, 3H, CH_3), 4.27 (s, 5H, C_5H_5), 4.46 (d, 1H, H-3), 4.66 (t, 1H, H-4), 4.86 (d, 1H, $J = 1.7$ Hz, H-5), naphthyl protons appear at: 7.04 (d, 1H, $J = 8.3$ Hz), 7.17 (s, 1H), 7.41 (t, 1H, $J = 7.2$ Hz), 7.47 (t, 1H, $J = 7.1$ Hz), 7.79 (d, 1H, $J = 8.1$ Hz), 7.82 (d, 1H, $J = 7.2$ Hz), 7.84 (d, 1H, $J = 8.2$ Hz).

2-chloromercurio-1-[1-[(2-chlorophenyl)imino]ethyl] ferrocene (**4m**). Yellow crystals, yield 60%; m.p. 180–181°C. Anal. Found: C, 37.54; H, 2.75; N, 2.31. $C_{18}H_{15}Cl_2FeHgN$ calc.: C, 37.76; H, 2.65; N, 2.45%. IR (KBr pellet): 1615, 1102, 996, 810, 762 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.09 (s, 3H, CH_3), 4.28 (s, 5H, C_5H_5), 4.47 (d, 1H, $J = 2.0$ Hz, H-3), 4.66 (t, 1H, $J = 2.4$ Hz, H-4), 4.85 (d, 1H, $J = 2.3$ Hz, H-5), 6.72 (d, 1H, $J = 7.7$ Hz, H α to N), 7.04 (t, 1H, $J = 7.5$ Hz, H γ to N), 7.22 (t, 1H, $J = 7.6$ Hz, H γ to Cl), 7.43 (d, 1H, $J = 8.0$ Hz, H α to Cl).

3.2. The structure of 2-chloromercurio-1-[1-[(4-chlorophenyl)imino]ethyl]ferrocene (4d)

Crystal data: $C_{18}H_{15}Cl_2FeHgN$, $M_r = 572.67$, triclinic, $P1$, $a = 9.308(1)$, $b = 12.580(1)$, $c = 9.189(1)$ Å, $\alpha = 102.05(1)$, $\beta = 116.59(1)$, $\gamma = 99.90(1)°$, $V = 906.4$ Å^3, $Z = 2$, $D_c = 2.098$ gcm^{-3}, $F(000) = 540$, λ 1.5418Å, μ(Cu Kα) = 253.29 cm^{-1}.

TABLE 4. Final positional parameters for $C_{18}H_{15}Cl_2FeHgN$ (**4d**)

	x	y	z	B (Å^2)
Hg	0.25183(5)	0.09866(4)	0.20215(6)	2.94(1)
Fe	0.4159(2)	0.2451(1)	0.6459(2)	2.71(4)
Cl(1)	0.8676(4)	0.9053(3)	0.0776(4)	4.67(9)
Cl(2)	1.0389(5)	0.3980(3)	0.1245(4)	5.54(9)
N	0.597(1)	0.1929(8)	0.358(1)	2.8(2)
C(1)	0.359(1)	0.105(1)	0.450(1)	3.2(3)
C(2)	0.534(1)	0.1494(9)	0.560(1)	2.8(2)
C(3)	0.571(2)	0.146(1)	0.726(1)	3.9(3)
C(4)	0.416(2)	0.100(1)	0.716(2)	4.8(3)
C(5)	0.281(2)	0.076(1)	0.550(1)	4.4(3)
C(6)	0.341(2)	0.370(1)	0.550(2)	5.2(4)
C(7)	0.506(2)	0.410(1)	0.670(2)	5.2(4)
C(8)	0.523(3)	0.401(1)	0.827(2)	9.3(6)
C(9)	0.349(2)	0.350(1)	0.787(2)	7.8(4)
C(10)	0.249(2)	0.335(1)	0.617(2)	6.3(5)
C(11)	0.654(1)	0.1970(9)	0.511(1)	2.6(2)
C(12)	0.835(2)	0.245(1)	0.647(2)	4.5(4)
C(13)	0.707(1)	0.2419(9)	0.304(1)	2.8(2)
C(14)	0.740(2)	0.357(1)	0.320(2)	4.1(3)
C(15)	0.845(2)	0.405(1)	0.266(2)	4.0(3)
C(16)	0.911(1)	0.339(1)	0.195(1)	3.1(3)
C(17)	0.877(1)	0.223(1)	0.176(1)	3.5(3)
C(18)	0.774(1)	0.1760(9)	0.230(1)	3.0(2)

An orange crystal of the title compound, measuring 0.33 × 0.22 × 0.22 mm^3, was mounted on the end of a glass fibre. The diffraction intensities were collected using graphite-monochromated Cu Kα radiation and an ω–2θ scan mode within the range of $0 \leqslant 2\theta \leqslant 120°$ on an Enraf-Nonius CAD-4 diffractometer, in a room temperature environment. Of the 3665 unique reflections, 3287 had $I > 3\sigma(I)$ and were used in all calculations. The intensities of the standard reflections monitored at regular intervals showed no crystal decomposition over the data collection period. Data were corrected for Lorentz and polarization effects. An empirical absorption correction on the basis of ψ scans was applied.

TABLE 5. Selected bond distances (Å) for **4d**

Hg–Cl(1)	2.390(3)	C(1)–C(2)	1.40(2)
Hg–C(1)	2.037(9)	C(1)–C(5)	1.48(1)
Fe–C(1)	2.045(9)	C(2)–C(3)	1.43(2)
Fe–C(2)	2.03(1)	C(3)–C(4)	1.41(2)
Fe–C(3)	2.06(1)	C(4)–C(5)	1.41(2)
Fe–C(4)	2.06(1)	C(6)–C(7)	1.35(1)
Fe–C(5)	2.04(1)	C(6)–C(10)	1.33(1)
Fe–C(6)	2.039(7)	C(7)–C(8)	1.43(1)
Fe–C(7)	2.027(8)	C(8)–C(9)	1.47(1)
Fe–C(8)	2.03(1)	C(9)–C(10)	1.37(2)
Fe–C(9)	2.029(8)	C(13)–C(14)	1.395(9)
Fe–C(10)	2.031(7)	C(13)–C(18)	1.367(9)
Cl(2)–C(16)	1.740(7)	C(14)–C(15)	1.38(2)
N–C(11)	1.267(8)	C(15)–C(16)	1.35(2)
N–C(13)	1.431(8)	C(16)–C(17)	1.39(1)
C(2)–C(11)	1.47(2)	C(17)–C(18)	1.37(1)
C(11)–C(12)	1.49(1)		

TABLE 6. Selected bond angles (deg) for **4d**

Cl(1)–Hg–C(1)	179.1(3)	N–C(11)–C(12)	125.0(6)
Hg–C(1)–C(2)	121.3	N–C(11)–C(2)	118.2(7)
C(1)–C(2)–C(3)	109(1)	C(2)–C(11)–C(12)	116.8(7)
C(2)–C(3)–C(4)	107(1)	N–C(13)–C(14)	119.4(6)
C(3)–C(4)–C(5)	111(1)	N–C(13)–C(18)	121.0(6)
C(1)–C(5)–C(4)	105.5(8)	C(14)–C(13)–C(18)	119.7(6)
C(2)–C(1)–C(5)	108(2)	C(13)–C(14)–C(15)	119.5(7)
C(6)–C(7)–C(8)	108.3(7)	C(14)–C(15)–C(16)	120.1(6)
C(7)–C(8)–C(9)	104.7(8)	C(15)–C(16)–C(17)	121.1(6)
C(8)–C(9)–C(10)	105.6(7)	C(16)–C(17)–C(18)	119.0(7)
C(6)–C(10)–C(9)	111.3(7)	C(13)–C(18)–C(17)	120.7(6)
C(7)–C(6)–C(10)	110.3(7)	Cl(2)–C(16)–C(15)	119.9(5)
C(1)–C(2)–C(11)	124(1)	Cl(2)–C(16)–C(17)	119.1(6)
C(3)–C(2)–C(11)	127(1)		

The structure was solved by Patterson methods using the Enraf-Nonius SDP program package [21] on a PDD 11/44 computer. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included in their calculated positions; final $R = 0.063$, $R_w = 0.070$. The final positional parameters and equivalent isotropic temperature factors are listed in Table 4, and selected bond and angle data are given in Table 5 and 6, respectively. A complete table of bond lengths and angles and lists of thermal parameters and structure factors are available from the authors.

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