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ortho-Mercuration of ferrocenylimines

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Abstract

The mercuration of a series of aryliminomethylferrocenes occurred predominantly in an *ortho*-position of the substituted ferrocenyl ring to yield 2-mercurated ferrocenylimines. The regiospecificity of this reaction suggests that the mercury is directed into the *ortho*-position by coordination of the mercury to imino nitrogen with subsequent electrophilic substitution. The chromatographic and spectral properties of the 2-mercurated products show the presence of an intramolecular N → Hg coordination via the five-membered ring in these molecules, which was further confirmed by the single-crystal structure analysis of 2-chloromercuro-1-[(4-methoxyphenylimino)methyl]ferrocene.

Key words: Mercury; Ferrocene; Imine

1. Introduction

Over the last two decades, there has appeared an increasing number of reports on intramolecular organometallic reactions, in view of their diverse synthetic potential [1]. It is now obvious that the chemistry of *ortho*-metallated complexes has become one of the most advanced areas of modern organometallic chemistry [2]. The reactions of transition metals are most commonly associated with *ortho*-metallation, while only a few reports have dealt with the reactions of nontransition metals, such as mercury. Direct mercurations of substituted azobenzenes, phenylhydrazones, and benzylideneanilines have been reported [3]. Interestingly, it was found that the mercury is directed into an *ortho*-position of the N-phenyl ring in the mercuration of substituted benzylideneanilines, which results in the formation of intramolecular coordination via four-membered ring, but if the *para*-position of the N-phenyl ring is not occupied by a substituent, the mercuration also occurs at this position [3c]. We are attempting to find out whether or not the N → Hg coordination is the main factor in the reaction. In order to understand better the influence of coordinating atoms on reactivity of the aromatic mercuration, we chose aryliminomethylferrocene as the substrate for mercuration. The mercuration of an aryliminomethylferrocene would be expected to occur predominantly on the ferrocenyl rings, since ferrocene is known to be more susceptible to electrophilic substitution than benzene [4]; thus intramolecular coordination via five-membered ring may occur if the imino nitrogen directs mercury into the *ortho*-position of the substituted ferrocenyl ring. In the present paper, we describe the direct *ortho*-mercuration of aryliminomethylferrocene, and elucidate the related intramolecular coordination on the basis of structure analysis. In addition, this mercuration reaction is, to the best of our knowledge, the first example of *ortho*-metallation of ferrocenylimines, and offers a convenient route to the synthesis of 1,2-disubstituted ferrocenylimines.

2. Results and discussion

The mercuration of ferrocenylimines (**1a**–**1k**) proceeded smoothly to produce 2-chloromercurated ferro-

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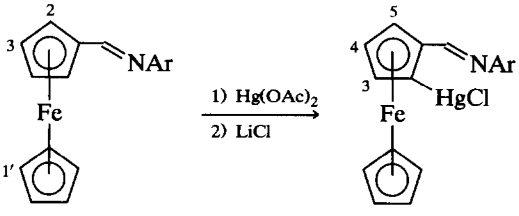
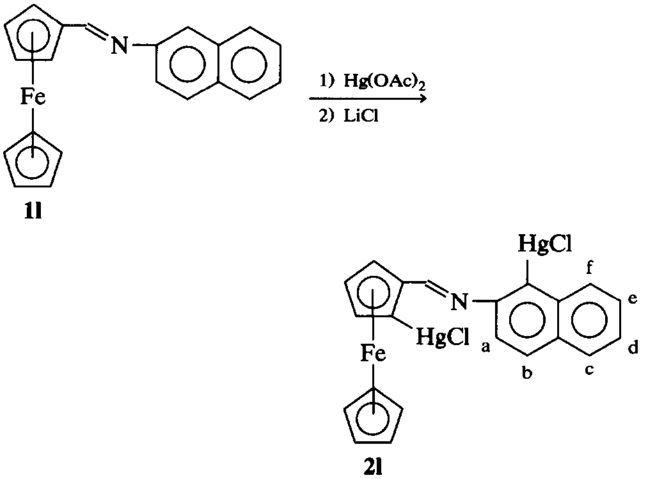
cenylimines (**2a**–**2k**).



1 **2**

Ar = p-$CH_3OC_6H_4$ (**a**), p-$CH_3C_6H_4$ (**b**), C_6H_5 (**c**), p-ClC_6H_4 (**d**), p-BrC_6H_4 (**e**), p-IC_6H_4 (**f**), p-$NO_2C_6H_4$ (**g**), m-ClC_6H_4 (**h**), m-BrC_6H_4 (**i**), m-$NO_2C_6H_4$ (**j**), 1-naphthyl (**k**).

The mercuration of **1l** is, however, very different from those of the others. In this case, dimercurated product (**2l**) was obtained in high yield.



2l

Isolation of the pure compounds (**2a**–**2l**) was by rapid chromatography on silica gel; in each separation, the band possessing the highest R_f contained the 2-chloromercurated products, and this phenomenon is similar to that observed in the mercuration of acylferrocenes [5]. A TLC examination of the reaction mixture showed large quantities of the 2-mercurated product and unmercurated parent compound, and very small amounts of the other mercurated products, whose TLC bands move more slowly.

The effect of aryliminomethyl group (ArN = CH–) on ferrocene can be two-fold: steric and electronic. Electronically, this group will deactivate the substituted Cp ring towards electrophilic substitution. The steric hindrance of the group can inhibit the attack at the 2-position of the Cp ring, so the mercuration of aryliminomethylferrocene should have occurred predominantly on the 1'-position due to the higher reactivity of unsubstituted Cp ring. But in fact, the mercuration occurs predominantly on the 2-position, which indicated that intramolecular coordination played an important role in this reaction.

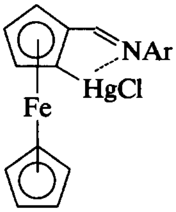
TABLE 1. Mercuration results [a]

1	Conversions [b] (%)	Selectivities [c] of **2** (%)	**1**	Conversions [b] (%)	Selectivities [c] of **2** (%)
a	51	59	**g**	40	25
b	55	64	**h**	64	86
c	62	73	**i**	59	80
d	53	66	**j**	53	60
e	57	70	**k**	56	61
f	64	83	**l**	90	87

[a] The results listed here are for the equimolar reaction of ferrocenylimine and mercuric acetate with the exception of the reaction of **1l** in which two equiv of mercuric acetate was used. [b] Conversions refer to the consumed ferrocenylimines. [c] Selectivity = 2-mercurated product formed/consumed ferrocenylimine.

In Table 1 are listed the results of the mercuration reactions. It can be seen that selectivity towards the 2-position is remarkable, and the selectivities of **2** are 59–87% except that of **2g**, which is mainly due to the serious decomposition of **2g** during the workup. In addition, the strong electron-withdrawing nitro group in *para*-position of phenyl ring is also expected to cause the decrease of electron density on imino nitrogen. This means a weak coordination is present between the imino nitrogen and mercury atom.

The "anomalous" sequence of elution observed for the 2-mercurated ferrocenylimines (**2**) can be explained by the postulation, proposed by M.D. Rausch for the 2-chloromercurated acylferrocenes [5], that coordination occurs between the imino nitrogen and the 2-chloromercuro groups, thereby decreasing electron density in the C = N bond. This result could cause a decrease in the affinity of the *ortho*-mercurated products for the chromatographic substrate.



The IR spectra of compounds **2** showed absorptions at 1000 and 1100 cm^{-1}, indicative of an unsubstituted Cp ring [6]. In addition, the C = N absorptions of **2** are shifted to lower energy by 4 to 15 cm^{-1} (Table 2), which can also be explained by the above-mentioned concept concerning the N → Hg intramolecular coordination.

The ^1H NMR spectra of the compounds **2a**-**2l** were completely consistent with the proposed structure (1,2-disubstituted). For example, the ^1H NMR spectrum of **2c** exhibited a singlet at δ 4.26 integrating for the five protons for the unsubstituted Cp ring, and the

TABLE 2. IR C=N stretching frequencies (cm^{-1}) for the compounds **1** and **2** [a]

	a	b	c	d	e	f	g	h	i	j	k	l
1	1618	1618	1619	1617	1615	1615	1614	1618	1617	1621	1628	1628
2	1609	1613	1610	1605	1606	1605	1610	1609	1604	1615	1612	1620

[a] KBr pellets.

expected two doublets at δ 4.51 and δ 4.80 and a triplet at δ 4.68 for the three different protons on the substituted Cp ring, among which the downfield doublet at δ 4.80 with $J = 2.2$ Hz can be assigned to the proton α to phenyliminomethyl group (proton 5) due to the deshielding effect by this group, and the triplet with $J = 2.4$ Hz assigned to the proton 4. The other doublet with $J = 2.3$ Hz is then assigned to the proton 3. Interestingly, the relative positions of the doublets and triplet indicate that a chloromercuro group present in these molecules tends to shield the proton α to this group to a greater extent than the proton β to it. The other signals include two triplets at δ 7.23 and 7.39, a doublet at δ 7.29 integrating for the five protons on the phenyl ring, and a downfield singlet at δ 8.74 for the proton of methine. The ^{1}H NMR spectra of the other 2-mercurated products were analogous. The structure of compound **2l** was confirmed unambiguously by elemental analysis, IR, ^{1}H NMR and ^{13}C NMR spectra.

In order to confirm the existence of intramolecular N → Hg coordination in the 2-mercurated ferrocenylimines proposed on the basis of the chromatographic and spectral properties of these compounds, single crystal structure determination of 2-chloromercuro-1-[(4-methoxyphenylimino)methyl]ferrocene (**2a**) was undertaken. Atomic parameters for the crystal structure are given in Table 3 and a view of the molecule illustrating the numbering scheme is shown in Fig. 1. Bond distances and selected bond angles are noted in Tables 4 and 5, respectively.

TABLE 3. Final positional parameters for the compound **2a**

	x	*y*	*z*	*B* (Å^2)
Hg	0.15676(5)	0.06056(2)	0.88952(5)	2.337(9)
Fe	0.2743(2)	0.10039(9)	1.2876(2)	2.15(4)
Cl	0.1668(4)	0.0821(2)	0.6676(4)	4.11(8)
O	−0.369(1)	0.4083(5)	0.587(1)	4.3(3)
N	−0.035(1)	0.1666(5)	0.918(1)	2.8(2)
C(1)	0.415(2)	0.1696(8)	1.260(2)	4.1(3)
C(2)	0.481(2)	0.115(1)	1.360(3)	6.9(7)
C(3)	0.450(2)	0.117(1)	1.475(3)	7.1(6)
C(4)	0.352(2)	0.1792(9)	1.449(2)	8.3(4)
C(5)	0.330(2)	0.2122(8)	1.309(2)	5.1(5)
C(6)	0.074(1)	0.0930(6)	1.137(1)	2.1(2)
C(7)	0.091(1)	0.0661(6)	1.281(1)	2.7(2)
C(8)	0.187(1)	0.0036(7)	1.324(2)	3.0(3)
C(9)	0.223(1)	−0.0086(6)	1.205(1)	2.4(3)
C(10)	0.158(1)	0.0449(6)	1.090(1)	2.0(2)
C(11)	−0.013(1)	0.1562(6)	1.046(1)	2.4(2)
C(12)	−0.123(1)	0.2280(6)	0.836(1)	2.5(2)
C(13)	−0.117(1)	0.3015(6)	0.896(1)	2.8(3)
C(14)	−0.200(1)	0.3589(7)	0.811(2)	3.4(3)
C(15)	−0.291(1)	0.3460(6)	0.664(2)	3.1(3)
C(16)	−0.303(1)	0.2735(7)	0.603(2)	3.1(3)
C(17)	−0.216(1)	0.2155(7)	0.689(2)	2.9(3)
C(18)	−0.464(2)	0.3979(9)	0.439(2)	5.1(5)

The distance between the nitrogen and the mercury is 2.897(2) Å, which is shorter than the sum of Van der Waals radii of N and Hg (3.05–3.15 Å) [7] and corresponds to the intramolecular coordination. The decrease of the angle Hg–C(10)–C(6) and angle C(10)–C(6)–C(11) to 120.7° and 123.4° from the normal value (126°), respectively, is also an indication of the interaction between the mercury and the nitrogen. The Hg–Cl distance 2.296 Å is similar to those found for typical organic derivatives of mercury [7a], but the Hg–C(6) distance 2.016 Å is somewhat shorter than those found for other mercurials [7a]. The angle C(10)–Hg–Cl is 176.84°, narrower than the ideal value of 180° in organic derivatives of mercury. The average Fe–C(1–5) and Fe–C(6–10) distances are 2.032 and 2.048 Å, respectively, and the average C–C distances in the ferrocenyl moiety are 1.402 and 1.433 Å for unsubstituted and substituted rings, respectively.

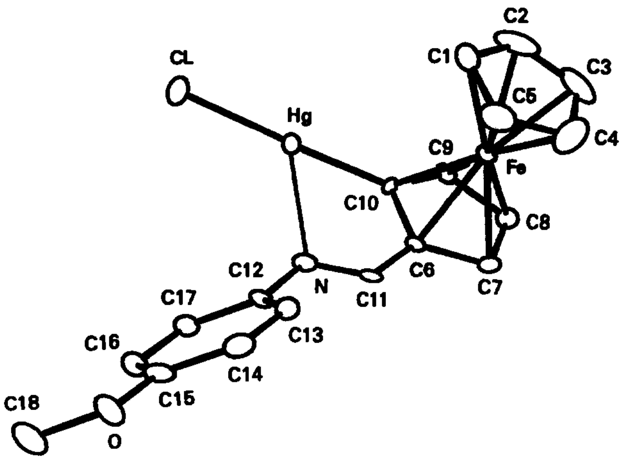


Fig. 1. A view of the X-ray crystal structure of **2a** showing the atom numbering scheme.

TABLE 4. Bond distances (Å) for the compound **2a**

Hg-Cl	2.2959(9)	Hg-N	2.897(2)
Hg-C(10)	2.016(3)	Fe-C(1)	2.062(4)
Fe-C(2)	2.051(5)	Fe-C(3)	2.019(6)
Fe-C(4)	2.002(3)	Fe-C(5)	2.026(3)
Fe-C(6)	2.030(3)	Fe-C(7)	2.057(3)
Fe-C(8)	2.050(3)	Fe-C(9)	2.049(3)
Fe-C(10)	2.055(3)	O-C(15)	1.384(4)
O-C(18)	1.391(6)	N-C(11)	1.204(4)
N-C(12)	1.427(4)	C(1)-C(2)	1.344(8)
C(2)-C(3)	1.33(2)	C(3)-C(4)	1.47(2)
C(4)-C(5)	1.428(8)	C(1)-C(5)	1.436(7)
C(6)-C(7)	1.439(5)	C(6)-C(10)	1.459(4)
C(7)-C(8)	1.438(4)	C(8)-C(9)	1.421(5)
C(9)-C(10)	1.406(4)	C(6)-C(11)	1.476(4)
C(12)-C(13)	1.404(5)	C(12)-C(17)	1.386(5)
C(13)-C(14)	1.361(5)	C(14)-C(15)	1.381(6)
C(15)-C(16)	1.387(5)	C(16)-C(17)	1.393(5)

The Cp rings are almost parallel (dihedral angle 2.01°). The chelate cycle Hg-C(10)-C(6)-C(11)-N is nearly planar. The dihedral angle between the substituted Cp ring and the chelate cycle is 2.29°, and that between the Cp ring and phenyl ring is 38.58°.

3. Experimental details

Melting points were measured on a WC-1 microscopic apparatus and are uncorrected. Elemental analyses were determined with a Carlo Erba 1106 elemental analyzer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer, using $CDCl_3$ as the solvent and TMS as an internal standard. IR spectra were recorded on a Shimadzu IR 435 spectrophotometer. Chromatographic work was carried out using silica gel under reduced pressure. Ferrocenylimines (**1a–1l**) were prepared according to the literature procedure [8].

TABLE 5. Selected bond angles (deg) for the compound **2a**

Cl-Hg-N	109.47(6)	Cl-Hg-C(10)	176.84(8)
N-Hg-C(10)	71.2(1)	C(1)-C(2)-C(3)	111.6(5)
C(2)-C(1)-C(5)	109.2(5)	C(2)-C(3)-C(4)	108.0(5)
C(3)-C(4)-C(5)	105.8(5)	C(1)-C(5)-C(4)	105.6(5)
C(7)-C(6)-C(10)	108.1(2)	C(7)-C(6)-C(11)	128.5(3)
C(10)-C(6)-C(11)	123.4(3)	C(6)-C(7)-C(8)	107.7(3)
C(7)-C(8)-C(9)	106.9(3)	C(8)-C(9)-C(10)	111.0(2)
C(6)-C(10)-C(9)	106.2(2)	N-C(11)-C(6)	122.9(3)
N-C(12)-C(13)	123.3(3)	N-C(12)-C(17)	118.7(3)
C(13)-C(12)-C(17)	118.1(3)	C(12)-C(13)-C(14)	121.0(3)
C(13)-C(14)-C(15)	120.4(3)	O-C(15)-C(14)	115.9(3)
O-C(15)-C(16)	123.9(4)	C(14)-C(15)-C(16)	120.2(3)
C(15)-C(16)-C(17)	119.1(3)	C(12)-C(17)-C(16)	121.3(3)
C(15)-O-C(18)	118.2(3)	C(11)-N-C(12)	119.6(3)

3.1. Mercuration of ferrocenylimines: general procedure

Into a 100 ml flask equipped with a magnetic stirrer and an equilibrated addition funnel were added 0.002 mol of ferrocenylimine and 10 ml of methylene chloride. Meanwhile, 0.002 mol of mercuric acetate was dissolved in a sufficient amount of methanol. This solution was then added dropwise to the flask over a period of 30 min. Subsequently, 0.003 mol of lithium chloride dissolved in methanol was added, and the mixture stirred for 15 min. The contents of the flask were transferred to a separatory funnel, and an additional 20 ml of methylene chloride was added. The solution was washed with two 50 ml portions of water, filtered to remove some polymercurated products which are insoluble in methylene chloride, and then dried over Na_2SO_4. The resulting solution was evaporated *in vacuo* to a minimum amount and subjected to a short dry column of silica gel, eluted with methylene chloride. The first band was collected and afforded the 2-chloromercurated product after the evaporation of the solvent and recrystallization from methylene chloride-petroleum ether (60-90). The second band contained unmercurated starting material. The third band contained very small amounts of the other mercurated products, which were not isolated for further investigation.

*3.2. 2-chloromercuro-1-[(4-methoxyphenylimino)methyl]ferrocene (**2a**)*

Deep red crystals, yield 30%; m.p. 165–167°C. Anal. Found: C, 38.81; H, 2.91; N, 2.53. $C_{18}H_{16}ClFeHgNO$ calc.: C, 39.00; H, 2.91; N, 2.53%. IR (KBr pellet): 1609, 1237, 1100, 992, 814 cm^{-1}. ^{1}H NMR: δ 3.82 (s, 3H, OCH_3), 4.24 (s, 5H, C_5H_5), 4.49 (d, 1H, $J = 2.2$ Hz, H-3), 4.65 (t, 1H, $J = 2.4$ Hz, H-4), 4.77 (d, 1H, $J = 2.6$ Hz, H-5), 6.92 (d, 2H, $J = 8.8$ Hz, H α to OCH_3), 7.31 (d, 2H, $J = 8.8$ Hz, H β to OCH_3), 8.71 (s, 1H, CH=N).

*3.3. 2-chloromercuro-1-[(4-methylphenylimino)methyl] ferrocene (**2b**)*

Deep red crystals, yield 35%; m.p. 132–134°C. Anal. Found: C, 39.93; H, 2.85; N, 2.43. $C_{18}H_{16}ClFeHgN$ calc.: C, 40.16; H, 2.99; N, 2.60%. IR (KBr pellet): 1613, 1100, 993, 811 cm^{-1}. ^{1}H NMR: δ 2.36 (s, 3H, CH_3), 4.24 (s, 5H, C_5H_5), 4.49 (d, 1H, $J = 1.7$ Hz, H-3), 4.66 (t, 1H, $J = 2.5$ Hz, H-4), 4.78 (d, 1H, $J = 2.6$ Hz, H-5), 7.19 (d, 2H, $J = 8.6$ Hz, H α to CH_3), 7.22 (d, 2H, $J = 8.6$ Hz, H β to CH_3), 8.71 (s, 1H, CH=N).

*3.4. 2-chloromercuro-1-[(phenylimino)methyl]ferrocene (**2c**)*

Red platelets, yield 45%; m.p. 149–150°C. Anal. Found: C, 38.66; H, 2.67; N, 2.50. $C_{17}H_{14}ClFeHgN$

calc.: C, 38.96; H, 2.70; N, 2.67%. IR (KBr pellet): 1610, 1100, 1000, 767, 688 cm^{-1}. ^1H NMR: δ 4.26 (s, 5H, C_5H_5), 4.51 (d, 1H, $J = 2.3$ Hz, H-3), 4.68 (t, 1H, $J = 2.4$ Hz, H-4), 4.80 (d, 1H, $J = 2.2$ Hz, H-5), 7.23 (t, 1H, $J = 7.3$ Hz, H γ to N), 7.29 (d, 2H, $J = 7.7$ Hz, H α to N), 7.39 (t, 2H, $J = 7.7$ Hz, H β to N), 8.74 (s, 1H, CH=N).

*3.5. 2-chloromercuro-1-[(4-chlorophenylimino)methyl]ferrocene (**2d**)*

Red crystals, yield 35%; m.p. 163–165°C. Anal. Found: C, 36.51; H, 2.47; N, 2.38. $C_{17}H_{13}Cl_2FeHgN$ calc.: C, 36.54; H, 2.34; N, 2.50%. IR (KBr pellet): 1605, 1101, 1008, 820 cm^{-1}. ^1H NMR: δ 4.25 (s, 5H, C_5H_5), 4.53 (d, 1H, $J = 1.8$ Hz, H-3), 4.69 (t, 1H, $J = 2.4$ Hz, H-4), 4.79 (d, 1H, $J = 2.4$ Hz, H-5), 7.22 (d, 2H, $J = 8.4$ Hz, H α to N), 7.34 (d, 2H, $J = 8.5$ Hz, H β to N), 8.70 (s, 1H, CH=N).

*3.6. 2-chloromercuro-1-[(4-bromophenylimino)methyl]ferrocene (**2e**)*

Deep red crystals, yield 40%; m.p. 195–197°C. Anal. Found: C, 33.84; H, 2.28; N, 2.23. $C_{17}H_{13}BrClFeHgN$ calc.: C, 33.85; H, 2.17; N, 2.32%. IR (KBr pellet): 1606, 1100, 1000, 820 cm^{-1}. ^1H NMR: δ 4.25 (s, 5H, C_5H_5), 4.53 (broad s, 1H, H-3), 4.70 (t, 1H, $J = 2.4$ Hz, H-4), 4.80 (d, 1H, $J = 2.1$ Hz, H-5), 7.16 (d, 2H, $J = 8.6$ Hz, H α to N), 7.49 (d, 2H, $J = 8.5$ Hz, H β to N), 8.71 (s, 1H, CH=N).

*3.7. 2-chloromercuro-1-[(4-iodophenylimino)methyl]ferrocene (**2f**)*

Red crystals, yield 53%; m.p. 204–205°C. Anal. Found: C, 31.55; H, 2.10; N, 2.11. $C_{17}H_{13}ClFeHgIN$ calc.: C, 31.41; H, 2.02; N, 2.16%. IR (KBr pellet): 1605, 1103, 1000, 818 cm^{-1}. ^1H NMR: δ 4.25 (s, 5H, C_5H_5), 4.54 (broad s, 1H, H-3), 4.70 (t, 1H, $J = 2.4$ Hz, H-4), 4.80 (d, 1H, $J = 2.3$ Hz, H-5), 7.03 (d, 2H, $J = 8.6$ Hz, H α to N), 7.69 (d, 2H, $J = 8.4$ Hz, H β to N), 8.71 (s, 1H, CH=N).

*3.8. 2-chloromercuro-1-[(4-nitrophenylimino)methyl]ferrocene (**2g**)*

Dark red crystals, yield 10%, m.p. 193–195°C. Anal. Found: C, 35.82; H, 2.30; N, 4.95. $C_{17}H_{13}ClFeHgN_2O_2$ calc.: C, 35.87; H, 2.30; N, 4.95%. IR (KBr pellet): 1610, 1567, 1334, 1104, 998, 808 cm^{-1}. ^1H NMR: δ 4.30 (s, 5H, C_5H_5), 4.62 (d, 1H, $J = 2.1$ Hz, H-3), 4.79 (t, 1H, $J = 2.4$ Hz, H-4), 4.86 (d, 1H, $J = 2.6$ Hz, H-5), 7.33 (d, 2H, $J = 8.7$ Hz, H β to NO_2), 8.26 (d, 2H, $J = 8.5$ Hz, H α to NO_2), 8.77 (s, 1H, CH=N).

*3.9. 2-chloromercuro-1-[(3-chlorophenylimino)methyl]ferrocene (**2h**)*

Deep red crystals, yield 55%; m.p. 124–125°C. Anal. Found: C, 36.89; H, 2.50; N, 2.50. $C_{17}H_{13}Cl_2FeHgN$ calc.: C, 36.54; H, 2.34; N, 2.50%. IR (KBr pellet): 1609, 1102, 998, 774, 682 cm^{-1}. ^1H NMR: δ 4.26 (s, 5H, C_5H_5), 4.54 (broad s, 1H, H-3), 4.71 (broad s, 1H, H-4), 4.81 (broad s, 1H, H-5), 7.18 (d, 1H, $J = 9.7$ Hz, H α to N and γ to Cl), 7.20 (d, 1H, $J = 9.9$ Hz, H α to Cl and γ to N), 7.24 (s, 1H, H α to Cl and N), 7.31 (t, 1H, $J = 7.9$ Hz, H β to Cl and N), 8.71 (s, 1H, CH=N).

*3.10. 2-chloromercuro-1-[(3-bromophenylimino)methyl]ferrocene (**2i**)*

Red crystals, yield 47%; m.p. 126–127°C. Anal. Found: C, 33.77; H, 2.23; N, 2.19. $C_{17}H_{13}BrClFeHgN$ calc.: C, 33.85; H, 2.17; N, 2.32%. IR (KBr pellet): 1604, 1102, 996, 779, 680 cm^{-1}. ^1H NMR: δ 4.26 (s, 5H, C_5H_5), 4.54 (broad s, 1H, H-3), 4.71 (t, 1H, H-4), 4.81 (broad s, 1H, H-5), 7.24–7.39 (m, 4H, protons on phenyl ring), 8.70 (s, 1H, CH=N).

*3.11. 2-chloromercuro-1-[(3-nitrophenylimino)methyl]ferrocene (**2j**)*

Deep red rods, yield 32%; m.p. 184–186°C. Anal. Found: C, 35.95; H, 2.31; N, 4.90. $C_{17}H_{13}ClFeHgN_2O_2$ calc.: C, 35.87; H, 2.30; N, 4.95%. IR (KBr pellet): 1615, 1516, 1340, 1102, 1000, 736, 674 cm^{-1}. ^1H NMR: δ 4.30 (s, 5H, C_5H_5), 4.60 (broad s, 1H, H-3), 4.77 (t, 1H, $J = 2.4$ Hz, H-4), 4.87 (d, 1H, $J = 1.9$ Hz, H-5), 7.56 (t, 1H, $J = 7.8$ Hz, H β to NO_2 and imino N), 7.63 (d, 1H, $J = 8.1$ Hz, H α to imino N and γ to NO_2), 8.08 (s, 1H, H α to imino N and NO_2), 8.90 (d, 1H, H γ to imino N and α to NO_2), 8.82 (s, 1H, CH=N).

*3.12. 2-chloromercuro-1-[(1-naphthylimino)methyl]ferrocene (**2k**)*

Orange crystals, yield 34%; m.p. 182–184°C. Anal. Found: C, 43.74; H, 2.82; N, 2.38. $C_{21}H_{16}ClFeHgN$ calc.: C, 43.93; H, 2.81; N, 2.44%. IR (KBr pellet): 1612, 1106, 1000, 815, 770 cm^{-1}. ^1H NMR: δ 4.32 (s, 5H, C_5H_5), 4.55 (d, 1H, $J = 2.0$ Hz, H-3), 4.72 (t, 1H, $J = 2.5$ Hz, H-4), 4.84 (d, 1H, $J = 2.6$ Hz, H-5), 6.97 (d, 1H, $J = 7.2$ Hz), 7.44 (t, 1H, $J = 7.6$ Hz), 7.53 (t, 1H, $J = 8.3$ Hz), 7.58 (t, 1H, $J = 8.8$ Hz), 7.71 (d, 1H, $J = 8.3$ Hz), 7.85 (d, 1H, $J = 7.8$ Hz), 8.25 (d, 1H, $J = 8.1$ Hz), 8.67 (s, 1H, CH=N).

*3.13. 2-chloromercuro-1-[(2-(1-chloromercurionaphthyl)imino)methyl]ferrocene (**2l**)*

Red crystals, yield 78%. This compound decomposes above 220°C. Anal. Found: C, 31.04; H, 1.92; N, 1.67. $C_{21}H_{15}Cl_2FeHg_2N$ calc. C, 31.17; H, 1.87; N, 1.73%. IR (KBr pellet): 1620, 1103, 1000, 815 cm^{-1}. ^1H NMR: δ 4.36 (s, 5H, C_5H_5), 4.60 (broad s, 1H, H-3), 4.77 (t, 1H, $J = 2.2$ Hz, H-4), 4.87 (broad s, 1H, H-5), 7.32 (d, 1H, $J = 8.6$ Hz, H-a), 7.48 (t, 1H, $J = 7.5$ Hz, H-d), 7.58 (t, 1H, $J = 7.2$ Hz, H-e), 7.88 (m, 3H, H-b, c, and f), 8.84 (s, 1H, CH=N). The ^{13}C NMR spectrum of this compound exhibited four quaternary carbon atoms at δ 132.6, 135.3, 137.5, and 151.9, and six hydrogen-bearing carbon atoms at δ 117.8, 125.9, 127.6, 128.5, 130.2 and 131.2, which indicates that there are two substituents on the naphthyl ring.

*3.14. The structure of 2-chloromercuro-1-[(4-methoxyphenylimino)methyl]ferrocene (**2a**)*

Crystal data: $C_{18}H_{16}ClFeHgNO$, $M_r = 554.2$, monoclinic, $P2_1/c$, $a = 10.880(1)$, $b = 17.453(1)$, $c = 9.979(1)$ Å, $\beta = 116.21(1)^\circ$, $Z = 4$, $V = 1700.1$ Å^3, $D_c = 2.165$ gcm^{-3}, $F(000) = 1048$, λ 1.5418 Å, μ (Cu Kα) = 255.635 cm^{-1}.

Crystals were grown by slow evaporation of a methylene chloride/petroleum ether solution, and a crystal of approximate dimensions $0.13 \times 0.10 \times 0.08$ mm^3 was used for data collection. Data were collected using graphite-monochromatized Cu Kα radiation and an $\omega - 2\theta$ scan mode in the range of $2 \leqslant 2\theta \leqslant 140^\circ$ at room temperature on an Enraf-Nonius CAD-4 diffractometer. Throughout data collection the intensities of the standard reflections were monitored at regular intervals and this showed no systematic decay. In all, 2869 unique observed reflections $[I > 3\sigma(I)]$ were collected, data were corrected for Lorentz and polarisation effects, and also for absorption by an empirical method on the basis of ψ scans. The structure was solved by Patterson methods using the Enraf-Nonius SDP program package (Frenz, 1984) on a PDD 11/44 computer. All non hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included in calculated positions with isotropic thermal parameters equal to the isotropic of their carrier atoms. The final residuals R and R_w were 0.064 and 0.073 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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