

## Cyclometallation of ferrocenyldimines III. Regioselectivity in Hg(II) cyclometallated complexes

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### Abstract

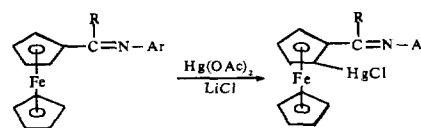
The synthesis and mercuration of a series of Schiff bases 1'-benzoyl-1-[(arylimino)phenylmethyl]ferrocene (aryl: a variety of substituted phenyls) have been studied. In all cases the mercuration occurred at the 2-position of the ferrocene ring. Oxygen → mercury coordinated products were not obtained. The X-ray crystal structure of [2-chloromercurio-1-[(phenylimino)phenylmethyl]-1'-benzoyl]ferrocene **5c** has been determined; this crystallizes in the monoclinic, space group  $P2_1/c$  with  $a = 10.168(3)$ ,  $b = 16.105(3)$ ,  $c = 15.463(4)$  Å,  $\beta = 103.61(2)^\circ$  and  $Z = 4$ . Refinement of atomic parameters gave an  $R$  factor of 0.038 ( $R_w = 0.055$ ) for 2440 unique reflections having  $I > 3\sigma(I)$ . The structure confirms the formation of a five-membered metallocycle on the ferrocene moiety. © 1997 Elsevier Science S.A.

**Keywords:** Mercury; Ferrocene; Crystal structure

### 1. Introduction

Cyclometallated compounds have attracted much attention because of their potential utility in organic synthesis, catalysis, asymmetric synthesis and photochemistry [1]. While most cyclometallation reactions are closely associated with transition metals, there are a few examples dealing with the reactions of non-transition metals, such as mercury. More recently, we have studied the mercurations of ferrocenylaldimines **1** and ferrocenylketimines **2**, **3** and found that in all cases the imino nitrogen directed mercury into the ortho-position of the substituted Cp ring [2]. The nature of the substituent at the iminic carbon atom and on the *N*-phenyl ring is an important factor influencing the cyclometallation reac-

tion, the structure and the properties of the ligands and their cyclomercurated products.



R = H(**1**), CH<sub>3</sub>(**2**), Ph(**3**)

Kovar and Rausch [3] reported that mercuration of a series of mono acylferrocenes produced appreciable amounts of 1,2- as well as 1,1'-mercurated products. If the *N*-donor and *O*-donor groups are simultaneously contained in one molecule, the mercuration would be competitive. In order to understand better the influence of coordinating atoms on the reactivity of mercuration,

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in the present paper we describe the synthesis, structure and properties of [1-[(arylimino)phenylmethyl]-1'-benzoyl]ferrocene and their cyclomercurated products.

## 2. Results and discussion

The imines **4** were prepared by refluxing 1,1'-dibenzoylferrocene and the corresponding amines in toluene solutions in the presence of freshly activated  $\text{Al}_2\text{O}_3$  [4] for 2–7 days. Every day, addition of small quantities of the amines and activated  $\text{Al}_2\text{O}_3$  were needed to complete the reaction. This was found even when the starting amines/1,1'-dibenzoylferrocene ratio was up to 4:1

the mono Schiff base was still the major product. Small amounts of bis Schiff bases were obtained only for  $\text{Ar} = m\text{-CH}_3\text{C}_6\text{H}_4$ ,  $m\text{-BrC}_6\text{H}_4$ .

Cyclomercurations of **4a–4i** were carried out according to the published procedure [2], which involved the initial coordination of the mercury to the imino nitrogen and subsequent electrophilic attack at the 2-carbon atom. Isolation of the pure compounds **5** is easily achieved by chromatography of the reaction mixture on silica gel, since the compounds **5** exhibited much higher  $R_f$  values than those of the corresponding starting materials and the other mercurated products, whose TLC bands move more slowly. In all cases the chloromercurio group was directed by imino nitrogen to the substituted Cp ring.

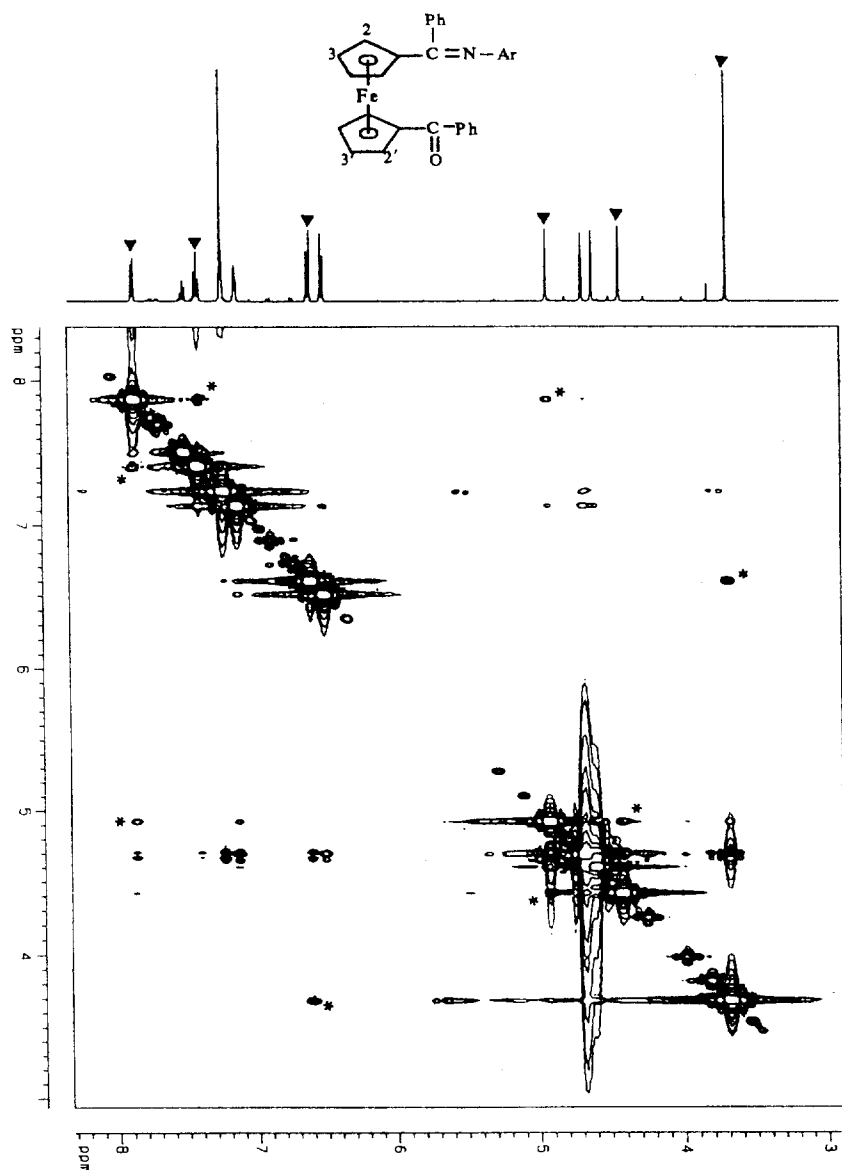
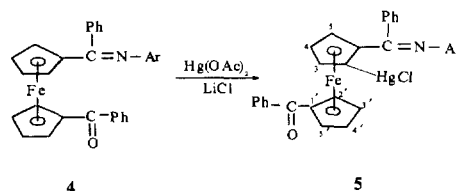


Fig. 1. 2D-NOESY spectrum of **4a**: \* NOE peaks; ▼ correlation lines in the 1D NMR spectrum.

No oxygen-directed mercurated products were obtained, which indicates that the coordination ability of nitrogen to mercury is much stronger than that of oxygen, which is the key step in cyclomercuriation reaction. The results of the mercuriation reactions indicated that the yields were clearly influenced by the position of the substituents in the *N*-phenyl ring, and decreased in the sequence para > meta > ortho. In view of this fact, it seems likely that steric factors are predominant in this reaction, since the large bulk in meta- and ortho-substituted ligands results in a more difficult coordination of nitrogen to mercury. There was no significant increase of the yields of compounds **5** by prolonging the

reaction time from 4.5 h to 40 h, while the parent compounds gradually decomposed.



Ar = *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>(a), *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>(b), C<sub>6</sub>H<sub>5</sub>(c), *p*-ClC<sub>6</sub>H<sub>4</sub>(d), *p*-BrC<sub>6</sub>H<sub>4</sub>(e),  
*m*-ClC<sub>6</sub>H<sub>4</sub>(f), *m*-BrC<sub>6</sub>H<sub>4</sub>(g), *o*-ClC<sub>6</sub>H<sub>4</sub>(h), *o*-BrC<sub>6</sub>H<sub>4</sub>(i).

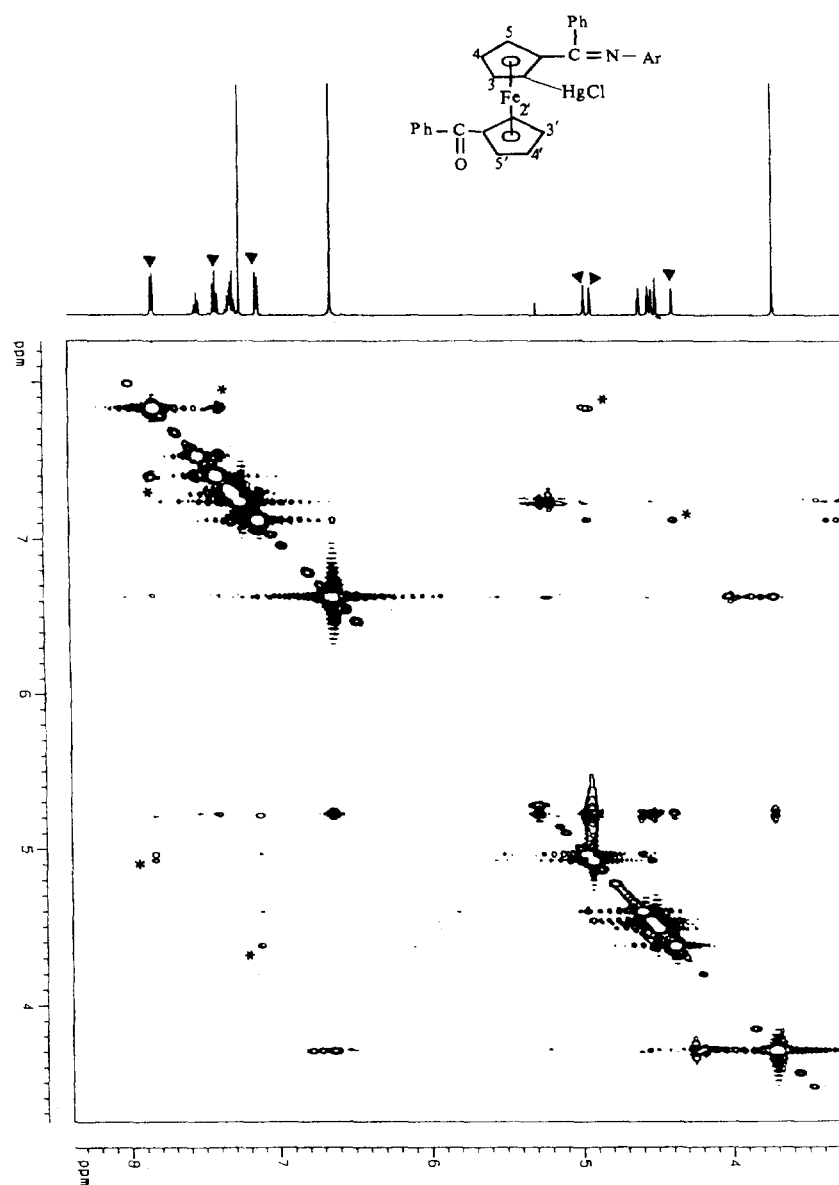
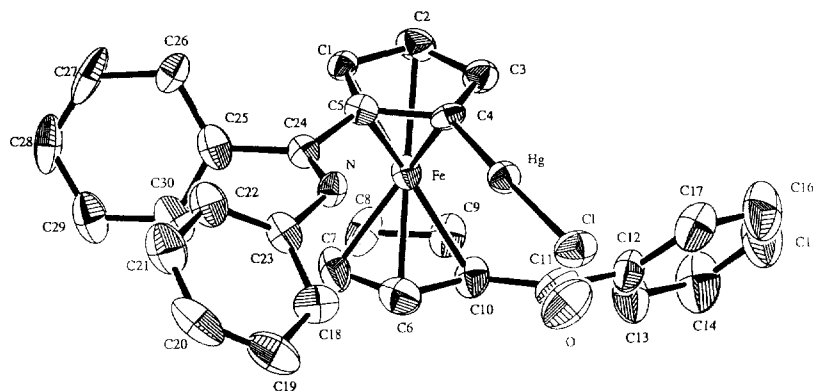


Fig. 2. 2D-NOESY spectrum of **5a**: \* NOE peaks; ▼ correlation lines in the 1D NMR spectrum.

Fig. 3. Molecular structure of **5c**.

The infrared spectra of free imines show two intense sharp bands in the range  $1631\text{--}1640\text{ cm}^{-1}$  ( $\nu_{\text{C}=\text{O}}$ ) and  $1604\text{--}1620\text{ cm}^{-1}$  ( $\nu_{\text{C}=\text{N}}$ ). For the cyclomercurated complexes the C=N absorptions are shifted to lower energy by 7 to  $39\text{ cm}^{-1}$ , showing an intramolecular  $\text{N} \rightarrow \text{Hg}$  coordination [5]. On the other hand, the carbonyl stretching frequencies of **5** are very close to those of the parent compounds **4**. For free ligands or cyclomercurated products there were no absorption bands found at  $1000$  and  $1100\text{ cm}^{-1}$ , which indicated the substitution of two cyclopentadienyl rings [5].

The 1D NMR spectra of compounds **4** and **5**, and 2D-NOESY spectra of **4a** and **5a** (Figs. 1 and 2) were measured to elucidate the structures in solution. The 2D-NOESY spectrum for compound **4a** shows negative cross-peaks  $2'(5')\text{-H}/\text{C-Ph}(2)\text{-H}$  ( $\text{N}=\text{C}$ -phenyl ring and  $\text{O}=\text{C}$ -phenyl ring are designated as C-Ph(1) ring and C-Ph(2) ring respectively) and  $2'\text{-H}/3'\text{-H}$  due to the ortho interaction; this allowed the assignment of signals at  $\delta 4.93$  and  $\delta 4.42$  to protons  $2'$  and  $3'$  respectively, and the signals at  $\delta 4.68$  and  $\delta 4.60$  to protons 2 and 3 respectively. Other signals include: two doublets at  $\delta 6.51$  and  $\delta 6.60$  for the protons of the *N*-phenyl ring; two complex multiplets at  $\delta 7.14$  and  $\delta 7.24$  for

the five protons of the C-Ph(1) ring; three multiplets at  $\delta 7.41$ ,  $\delta 7.51$  and  $\delta 7.87$  for the protons of C-Ph(2) ring.

The  $^1\text{H}$  NMR spectra of **5** indicated strongly that the starting materials were converted to the corresponding mercurated products. The seven remaining hydrogen atoms in the ferrocenyl region behaved as if in seven different magnetic environments. As a result, seven sets of signals were displayed in this region. With the aid of a 2D-NOESY spectrum of **5a**, the  $2'(5')\text{-H}$  and  $5\text{-H}$  protons were figured out because of the NOE cross-peak  $2'(5')\text{-H}/\text{C-Ph}(2)\text{-H}$  and  $5\text{-H}/\text{C-Ph}(1)\text{-H}$ . The signals of  $3(3')\text{-H}$  and  $4(4')\text{-H}$  can not be distinguished owing to the small chemical shift difference between these protons. The  $^1\text{H}$  NMR spectra patterns in the aromatic region are very similar to those for the starting materials **4**.

Compound **5c** was also characterized crystallographically. A perspective view of the molecular structure of **5c** is shown in Fig. 3. Selected bond lengths and bond angles are listed in Tables 1 and 2, and atomic coordinates in Table 3. This confirms the molecular structure with the chloromercurio group linked directly to the 2-position of the Cp ring. The  $\text{N-Hg}$  distance is  $2.862\text{ \AA}$ , almost identical with that in **3c** ( $2.870\text{ \AA}$ ), which is

Table 1  
Selected bond distances ( $\text{\AA}$ ) for **5c**

Hg-Cl	2.314(3)	C(1)-C(2)	1.42(2)
Hg-C(4)	2.01(1)	C(1)-C(5)	1.46(2)
Fe-C(1)	2.07(1)	C(2)-C(3)	1.41(2)
Fe-C(2)	2.09(1)	C(3)-C(4)	1.45(2)
Fe-C(3)	2.05(1)	C(4)-C(5)	1.46(2)
Fe-C(4)	2.07(1)	C(5)-C(24)	1.48(1)
Fe-C(5)	2.04(1)	C(6)-C(7)	1.40(2)
Fe-C(6)	2.01(1)	C(6)-C(10)	1.42(2)
Fe-C(7)	2.05(1)	C(7)-C(8)	1.41(2)
Fe-C(8)	2.07(1)	C(8)-C(9)	1.40(2)
Fe-C(9)	2.06(1)	C(9)-C(10)	1.44(2)
Fe-C(10)	2.05(1)	C(10)-C(11)	1.46(2)
O-C(11)	1.22(1)	C(11)-C(12)	1.48(2)
N-C(23)	1.43(1)	C(24)-C(25)	1.51(2)
N-C(24)	1.27(1)		

Table 2  
Selected bond angles (deg) for **5c**

Cl-Hg-C(4)	177.2(3)	C(6)-C(10)-C(11)	124(1)
C(23)-N-C(24)	123.4(10)	C(9)-C(10)-C(11)	127(1)
C(1)-C(2)-C(3)	107(1)	O-C(11)-C(10)	119(1)
C(2)-C(3)-C(4)	111.0(10)	O-C(11)-C(12)	121(1)
Hg-C(4)-C(5)	123.2(8)	C(10)-C(11)-C(12)	118(1)
C(3)-C(4)-C(5)	140.5(9)	C(11)-C(12)-C(13)	123(1)
C(1)-C(5)-C(4)	109.0(9)	C(11)-C(12)-C(17)	118(1)
C(1)-C(5)-C(24)	126(1)	N-C(23)-C(18)	115(1)
C(4)-C(5)-C(24)	124(1)	N-C(23)-C(22)	124(1)
C(7)-C(6)-C(10)	108(1)	N-C(24)-C(5)	117(1)
C(6)-C(7)-C(8)	108(1)	N-C(24)-C(25)	126.4(10)
C(7)-C(8)-C(9)	108(1)	C(5)-C(24)-C(25)	116(1)
C(8)-C(9)-C(10)	107(1)	C(24)-C(25)-C(26)	121(1)
C(6)-C(10)-C(9)	106(1)	C(24)-C(25)-C(30)	118(1)

Table 3  
Final positional parameters for C<sub>30</sub>H<sub>22</sub>ClFeHgNO (**5c**)

Atom	x	y	z	B (Å <sup>2</sup> )
Hg	0.08354(4)	0.5688 7(3)	0.12466(3)	2.29(2)
Fe	0.1604(2)	0.7342(1)	0.28607(10)	2.14(4)
Cl	0.0746(3)	0.4290(2)	0.0895(2)	3.36(7)
O	0.072(1)	0.5232(6)	0.3106(6)	4.7(3)
N	0.3408(9)	0.6411(6)	0.1246(6)	2.3(2)
C(1)	0.169(1)	0.8255(7)	0.1936(7)	2.1(3)
C(2)	0.036(1)	0.8222(8)	0.2080(8)	3.1(3)
C(3)	-0.014(1)	0.7406(8)	0.1881(8)	2.6(3)
C(4)	0.084(1)	0.6895(7)	0.1583(7)	2.0(2)
C(5)	0.199(1)	0.7440(7)	0.1628(7)	2.2(3)
C(6)	0.278(1)	0.6481(9)	0.3602(8)	3.5(3)
C(7)	0.337(1)	0.726(1)	0.3826(8)	4.0(4)
C(8)	0.244(1)	0.7761(8)	0.4137(8)	3.5(3)
C(9)	0.128(1)	0.7291(8)	0.4124(7)	3.0(3)
C(10)	0.150(1)	0.6473(8)	0.3807(7)	3.0(3)
C(11)	0.051(1)	0.5800(8)	0.3575(8)	3.1(3)
C(12)	-0.076(1)	0.5851(8)	0.3897(8)	3.1(3)
C(13)	-0.078(1)	0.612(1)	0.4722(8)	4.3(4)
C(14)	-0.198(2)	0.615(1)	0.5008(9)	5.6(5)
C(15)	-0.316(2)	0.595(1)	0.442(1)	6.1(5)
C(16)	-0.317(2)	0.566(1)	0.358(1)	5.6(5)
C(17)	-0.197(2)	0.5631(9)	0.3325(8)	4.0(4)
C(18)	0.485(1)	0.5246(8)	0.1338(8)	3.3(3)
C(19)	0.602(1)	0.483(1)	0.1224(9)	4.5(4)
C(20)	0.688(1)	0.527(1)	0.0813(9)	4.3(4)
C(21)	0.662(1)	0.605(1)	0.0520(10)	4.2(4)
C(22)	0.551(1)	0.6455(8)	0.0675(8)	3.4(3)
C(23)	0.462(1)	0.6055(8)	0.1093(7)	2.7(3)
C(24)	0.332(1)	0.7159(8)	0.1496(6)	2.1(3)
C(25)	0.446(1)	0.7788(8)	0.1698(8)	2.9(3)
C(26)	0.440(1)	0.8514(7)	0.1215(8)	2.7(3)
C(27)	0.552(2)	0.9020(8)	0.140(1)	4.2(4)
C(28)	0.661(1)	0.8885(9)	0.206(1)	3.7(4)
C(29)	0.665(1)	0.8170(9)	0.2530(9)	4.0(4)
C(30)	0.558(1)	0.7607(9)	0.2346(8)	3.4(3)

shorter than the sum of the Van der Waals radii of N and Hg (3.05–3.15 Å) [6,7] and indicates an intramolecular coordination between N and Hg which forms a weak secondary coordination chemical bond. The bond angle Cl–Hg–C(4) is 177.2°, close to the ideal value of 180° in organic derivatives of mercury [6]. The bond angles of 123.2° for Hg–C(4)–C(5) and 124° for C(4)–C(5)–C(24) are less than the normal value (126°). This can also be explained in terms of the intramolecular coordination between N and Hg. The N–C(24)–C(25) angle is equal to 126.4°, which is larger than that in **3c** (122.7°) owing to the larger steric hindrance between the C-phenyl ring and N-phenyl ring. The chelate cycle Hg–C(4)–C(5)–C(24)–N is nearly planar, with the largest distance deviation 0.035 Å of C(24). The C-phenyl ring and the N-phenyl ring form dihedral angles of 117.9° and 40.34° respectively with the plane of the C=N bond, while the angle between the Cp ring and the plane is only 7.76°, indicating the better conjugation between the Cp ring and the C=N bond.

The geometry of the ferrocenyl fragments in com-

pound **5c** is very similar to that observed for other ferrocene derivatives. The Fe–C (ring) bond distance ranges from 2.01 to 2.09 Å. The average C–C bond length in the two rings is 1.427 Å. The two Cp rings are parallel, with an interplanar angle of 2.23°.

### 3. Experimental section

#### 3.1. General

Melting points were measured on a WC-1 apparatus and are uncorrected. Elemental analyses were determined with a Carlo Erba 1.160 elemental analyser. <sup>1</sup>H NMR spectra were recorded on a Bruker ARX 500, using CDCl<sub>3</sub> as the solvent and TMS as an internal standard. 2D-NOESY spectra were recorded in CDCl<sub>3</sub> at room temperature with a mixing time of 200 ms. IR spectra were recorded on a Perkin Elmer FTIR 1750 spectrophotometer. Chromatographic work was carried out on a short column packed with dry silica gel under reduced pressure.

Ferrocenylketimines (**4a–4i**) were prepared by the published method [4]; new compounds were characterized as follows.

##### 3.1.1. [1-[(4-Methoxyphenyl)imino]phenylmethyl]-1'-benzoylferrocene (**4a**)

Red-brown crystals, yield 38.4%, m.p. 156–157°C. IR (KBr pellet): 1639, 1615, 843, 732, 703 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 3.68 (s, 3H, OCH<sub>3</sub>); 4.68 (t, 2H, J = 1.9 Hz, H-2); 4.60 (t, 2H, J = 2.0 Hz, H-3); 4.93 (t, 2H, J = 2.0 Hz, H-2'); 4.42 (t, 2H, J = 2.0 Hz, H-3'); 6.51 (d, 2H, J = 8.9 Hz, N–Ar–H); 6.60 (t, 2H, J = 6.5 Hz, N–Ar–H); 7.14m, 7.24m (5H, C–Ph(1)–H); 7.87m, 7.41m, 7.51m (5H, C–Ph(2)–H). Found: C, 74.53; H, 4.89; N, 2.65. Calc. for C<sub>31</sub>H<sub>25</sub>FeNO<sub>2</sub>: C, 74.56; H, 5.00; N, 2.80%.

##### 3.1.2. [1-[(4-Methylphenyl)imino]phenylmethyl]-1'-benzoylferrocene (**4b**)

Red-brown crystals, yield 26.7%, m.p. 148–151°C. IR KBr (pellet): 1639, 1613, 837, 734, 707 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 2.17 (s, 3H, CH<sub>3</sub>); 2.68 (t, 2H, J = 2.0 Hz, H-2); 2.61 (t, 2H, J = 2.0 Hz, H-3); 4.93 (t, 2H, J = 2.0 Hz, H-2'); 4.42 (t, 2H, J = 2.0 Hz, H-3'); 6.46 (d, 2H, J = 8.2 Hz, N–Ar–H); 6.85 (d, 2H, J = 7.9 Hz, N–Ar–H); 7.14m, 7.23m (5H, C–Ph(1)–H); 7.41m, 7.51m, 7.87m (5H, C–Ph(2)–H). Found: C, 76.86; H, 5.23; N, 3.00. Calc. for C<sub>31</sub>H<sub>25</sub>FeNO: C, 77.02; H, 5.21; N, 2.90%.

##### 3.1.3. [1-[(Phenyl)imino]phenylmethyl]-1'-benzoylferrocene (**4c**)

Red-brown crystals, yield 34.2%, m.p. 150–151°C. IR KBr (pellet): 1631, 1620, 716, 699 cm<sup>-1</sup>. <sup>1</sup>H NMR:

$\delta$  4.69 (t, 2H,  $J = 1.9$  Hz, H-2); 4.62 (t, 2H,  $J = 1.9$  Hz, H-3); 4.94 (t, 2H,  $J = 2.0$  Hz, H-2'); 4.44 (t, 2H,  $J = 1.9$  Hz, H-3'); 6.57m, 6.85m, 7.06m (5H, N-Ar-H); 7.14m, 7.23m (5H, C-Ph(1)-H); 7.42m, 7.51m, 7.87m (5H, C-Ph(2)-H). Found: C, 76.43; H, 4.94; N, 3.01. Calc. for  $C_{30}H_{23}FeNO$ : C, 76.76; H, 4.94; N, 2.98%.

### 3.1.4. [1-[(4-Chlorophenyl)imino]phenylmethyl]-1'-benzoylferrocene (**4d**)

Red-brown crystals, yield 35.6%, m.p. 156–157.5°C. IR KBr (pellet): 1638, 1604, 836, 730, 711  $cm^{-1}$ .  $^1H$  NMR:  $\delta$  4.67 (t, 2H,  $J = 1.9$  Hz, H-2); 4.59 (t, 2H,  $J = 2.0$  Hz, H-3); 4.93 (t, 2H,  $J = 2.0$  Hz, H-2'); 4.44 (t, 2H,  $J = 1.9$  Hz, H-3'); 6.48 (d, 2H,  $J = 8.7$  Hz, N-Ar-H); 7.00 (d, 2H,  $J = 8.6$  Hz, N-Ar-H); 7.13m, 7.24m (5H, C-Ph(1)-H); 7.42m, 7.51m, 7.87m (5H, C-Ph(2)-H). Found: C, 71.06; H, 4.45; N, 2.92. Calc. for  $C_{30}H_{22}ClFeNO$ : C, 71.52; H, 4.40; N, 2.78%.

### 3.1.5. [1-[(4-Bromophenyl)imino]phenylmethyl]-1'-benzoylferrocene (**4e**)

Red-brown crystals, yield 73.3%, m.p. 151.5–153.5°C. IR KBr (pellet): 1640, 1612, 839, 732, 716  $cm^{-1}$ .  $^1H$  NMR:  $\delta$  4.67 (t, 2H,  $J = 1.9$  Hz, H-2); 4.59 (t, 2H,  $J = 1.9$  Hz, H-3); 4.93 (t, 2H,  $J = 1.9$  Hz, H-2'); 4.45 (t, 2H,  $J = 1.9$  Hz, H-3'); 6.43d, 7.13m (4H, N-Ar-H); 7.13m, 7.24m (5H, C-Ph(1)-H); 7.42m, 7.51m, 7.87m (5H, C-Ph(2)-H). Found: C, 65.74; H, 4.13; N, 2.60. Calc. for  $C_{30}H_{22}BrFeNO$ : C, 65.72; H, 4.04; N, 2.56%.

### 3.1.6. [1-[(3-Chlorophenyl)imino]phenylmethyl]-1'-benzoylferrocene (**4f**)

Red-brown crystals, yield 29%, m.p. 115.5–117.5°C. IR KBr (pellet): 1639, 1612, 893, 780, 734, 716  $cm^{-1}$ .  $^1H$  NMR:  $\delta$  4.66 (t, 2H,  $J = 1.8$  Hz, H-2); 4.60 (t, 2H,  $J = 1.8$  Hz, H-3); 4.93 (t, 2H,  $J = 1.8$  Hz, H-2'); 4.46 (t, 2H,  $J = 1.8$  Hz, H-3'); 6.38 (d, 1H,  $J = 7.9$  Hz, N-Ar-H); 6.56 (d, 1H,  $J = 1.9$  Hz, N-Ar-H); 6.83m (1H, N-Ar-H); 6.94m (1H, N-Ar-H); 7.12m, 7.24m (5H, C-Ph(1)-H); 7.42m, 7.52m, 7.87m (5H, C-Ph(2)-H). Found: C, 71.56; H, 4.32; N, 2.62. Calc. for  $C_{30}H_{22}ClFeNO$ : C, 71.52; H, 4.40; N, 2.78%.

### 3.1.7. [1-[(3-Bromophenyl)imino]phenylmethyl]-1'-benzoylferrocene (**4g**)

Red-brown crystals, yield 27.5%, m.p. 97–98°C. IR KBr (pellet): 1636, 1613, 888, 777, 733, 702  $cm^{-1}$ .  $^1H$  NMR:  $\delta$  4.66 (t, 2H,  $J = 2.0$  Hz, H-2); 4.60 (t, 2H,  $J = 2.0$  Hz, H-3); 4.93 (t, 2H,  $J = 2.0$  Hz, H-2'); 4.46 (t, 2H,  $J = 2.0$  Hz, H-3'); 6.72 (d, 1H,  $J = 1.9$  Hz, N-Ar-H); 6.42m, 6.89m, 6.99m (3H, N-Ar-H); 7.13m, 7.24m (5H, C-Ph(1)-H); 7.42m, 7.52m, 7.87m (5H, C-

Ph(2)-H). Found: C, 65.74; H, 4.05; N, 2.59. Calc. for  $C_{30}H_{22}BrFeNO$ : C, 65.72; H, 4.04; N, 2.56%.

### 3.1.8. [1-[(2-Chlorophenyl)imino]phenylmethyl]-1'-benzoylferrocene (**4h**)

Red-brown crystals, yield 12.6%, m.p. 85–87°C. IR KBr (pellet): 1639, 1608, 764, 730, 703  $cm^{-1}$ .  $^1H$  NMR:  $\delta$  4.73m (4H, H-2(3)); 4.97 (t, 2H,  $J = 2.0$  Hz, H-2'); 4.47 (t, 2H,  $J = 1.9$  Hz, H-3'); 6.63m, 6.80m, 6.87m (4H, N-Ar-H); 7.13m, 7.21m (5H, C-Ph(1)-H); 7.40m, 7.51m, 7.82m (5H, C-Ph(2)-H). Found: C, 71.25; H, 4.42; N, 2.80. Calc. for  $C_{30}H_{22}ClFeNO$ : C, 71.52; H, 4.40; N, 2.78%.

### 3.1.9. [1-[(2-Bromophenyl)imino]phenylmethyl]-1'-benzoylferrocene (**4i**)

Red-brown crystals, yield 17.36%, m.p. 97–100°C. IR KBr (pellet): 1639, 1604, 764, 731, 703  $cm^{-1}$ .  $^1H$  NMR:  $\delta$  4.75m (4H, H-2(3)), 4.97 (t, 2H,  $J = 2.0$  Hz, H-2'), 4.47 (t, 2H,  $J = 2.0$  Hz, H-3'), 6.26 (d, 1H,  $J = 7.9$  Hz, N-Ar-H), 6.70m, 7.00m (3H, N-Ar-H), 7.13m, 7.21m (5H, C-Ph(1)-H), 7.40m, 7.51m, 7.80m (5H, C-Ph(2)-H). Found: C, 65.76; H, 4.29; N, 2.69. Calc. for  $C_{30}H_{22}BrFeNO$ : C, 65.72; H, 4.04; N, 2.56%.

## 3.2. Mercuration of ferrocenylkelimines (**5a–5i**)

The details of the mercuration reaction, the separation of reaction mixture and the purification procedures are similar to those described previously [2].

### 3.2.1. [2-Chloromercurio-1-[(4-methoxyphenyl)imino]phenylmethyl]-1'-benzoylferrocene (**5a**)

Orange crystals, yield 39.1%, m.p. > 200°C (dec.). IR KBr (pellet): 1628, 1605, 805, 719  $cm^{-1}$ .  $^1H$  NMR:  $\delta$  3.71 (s, 3H,  $OCH_3$ ); 4.38 (bs, 1H, H-5); 4.97t, 4.93t (2H, H-2'(5')); 4.49t, 4.52t, 4.54t, 4.60t (4H, H-3(4) and 3'(4')); 6.63 (s, 4H, N-Ar-H); 7.12m, 7.30m (5H, C-Ph(1)-H); 7.41m, 7.52m, 7.84m (5H, C-Ph(2)-H). Found: C, 51.03; H, 3.25; N, 2.03. Calc. for  $C_{31}H_{24}ClFeHgNO_2$ : C, 50.76; H, 3.29; N, 1.91%.

### 3.2.2. [2-Chloromercurio-1-[(4-methylphenyl)imino]phenylmethyl]-1'-benzoylferrocene (**5b**)

Orange crystals, yield 43.6%, m.p. 182–184°C. IR KBr (pellet): 1628, 1591, 822, 717  $cm^{-1}$ .  $^1H$  NMR:  $\delta$  2.20 (s, 3H,  $CH_3$ ); 4.40 (bs, 1H, H-5); 4.97t, 4.92t (2H, H-2'(5')); 4.51m, 4.54d, 4.61bs (4H, H-3(4) and 3'(4')); 6.54d, 6.88d (4H, N-Ar-H); 7.13m, 7.27m (5H, C-Ph(1)-H); 7.42m, 7.52m, 7.84m (5H, C-Ph(2)-H). Found: C, 51.74; H, 3.35; N, 1.95. Calc. for  $C_{31}H_{24}ClFeHgNO$ : C, 51.89; H, 3.37; N, 1.95%.

### 3.2.3. [2-Chloromercurio-1-(((phenyl)imino)phenylmethyl)-1'-benzoyl]ferrocene (5c)

Orange crystals, yield 44.4%, m.p. > 200 °C (dec.). IR KBr (pellet): 1630, 1593, 727, 702 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 4.42 (bs, 1H, H-5); 4.98t, 4.93t (2H, H-2'(5')); 4.53m, 4.55d, 4.61d (4H, H-3(4) and 3'(4')); 6.63m, 6.95m, 7.08m (5H, N-Ar-H); 7.12m, 7.25m (5H, C-Ph(1)-H); 7.42m, 7.51m, 7.84m (5H, C-Ph(2)-H). Found: C, 51.08; H, 3.03; N, 2.01. Calc. for C<sub>30</sub>H<sub>22</sub>ClFeHgNO: C, 51.22; H, 3.02; N, 1.99%.

### 3.2.4. [2-Chloromercurio-1-(((4-chlorophenyl)imino)phenylmethyl)-1'-benzoyl]ferrocene (5d)

Orange crystals, yield 43.6%, m.p. > 200 °C (dec.). IR KBr (pellet): 1642, 1595, 817, 726, 700 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 4.42 (bs, 1H, H-5); 4.97t, 4.93t (2H, H-2'(5')); 4.53m, 4.60d (4H, H-3(4) and 3'(4')); 6.56m, 7.03d (4H, N-Ar-H); 7.11m, 7.28m (5H, C-Ph(1)-H); 7.42m, 7.51m, 7.86m (5H, C-Ph(2)-H). Found: C, 48.59; H, 2.84; N, 1.96. Calc. for C<sub>30</sub>H<sub>21</sub>Cl<sub>2</sub>FeHgNO: C, 48.83; H, 2.87; N, 1.96%.

### 3.2.5. [2-Chloromercurio-1-(((4-bromophenyl)imino)phenylmethyl)-1'-benzoyl]ferrocene (5e)

Orange crystals, yield 30.1%, m.p. > 200 °C (dec.). IR KBr (pellet): 1628, 1596, 827, 723, 699 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 4.42 (bs, 1H, H-5); 4.97t, 4.93t (2H, H-2'(5')); 4.53m, 4.56bs, 4.60d (4H, H-3(4) and 3'(4')), 6.50d, 7.11d (4H, N-Ar-H), 7.18m, 7.28m (5H, C-Ph(1)-H), 7.42m, 7.51m, 7.84m (5H, C-Ph(2)-H). Found: C, 45.73, H, 2.67, N, 1.65. Calc. for C<sub>30</sub>H<sub>21</sub>BrFeHgNO: C, 46.06; H, 2.70; N, 1.79%.

### 3.2.6. [2-Chloromercurio-1-(((3-chlorophenyl)imino)phenylmethyl)-1'-benzoyl]ferrocene (5f)

Red-brown crystals, yield 29.7%, m.p. 192–195 °C. IR KBr (pellet): 1631, 1580, 882, 788, 729, 716 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 4.42 (bs, 1H, H-5); 4.96m (2H, H-2'(5')); 4.54m, 4.58d, 4.61d (4H, H-3'(4')), 6.54m, 6.99m, 6.84m (4H, N-Ar-H), 7.10m, 7.28m (5H, C-Ph(1)-H); 7.42m, 7.51m, 7.85m (5H, C-Ph(2)-H). Found: C, 49.06; H, 2.68; N, 1.71. Calc. for C<sub>30</sub>H<sub>21</sub>Cl<sub>2</sub>FeHgNO: C, 48.83; H, 2.87; N, 1.90%.

### 3.2.7. [2-Chloromercurio-1-(((3-bromophenyl)imino)phenylmethyl)-1'-benzoyl]ferrocene (5g)

Red-brown crystals, yield 22.8%, m.p. 195–197 °C. IR KBr (pellet): 1630, 1574, 900, 787, 729, 715 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 4.42 (bs, 1H, H-5); 4.96m (2H, H-2'(5')); 4.54m, 4.58bs, 4.61d (4H, H-3(4) and 3'(4')); 6.58m, 6.69m, 6.94m, 7.00m (4H, N-Ph-H); 7.11m, 7.28m

(5H, C-Ph(1)-H); 7.43m, 7.51m, 7.86m (5H, C-Ph(2)-H). Found: C, 45.62; H, 2.67; N, 1.99. Calc. for C<sub>30</sub>H<sub>21</sub>BrClFeHgNO: C, 46.09; H, 2.69; N, 1.79%.

### 3.2.8. [2-Chloromercurio-1-(((2-chlorophenyl)imino)phenylmethyl)-1'-benzoyl]ferrocene (5h)

Red-brown crystals, yield 6.14%, m.p. 195–197 °C. IR KBr (pellet): 1630, 1574, 787, 729, 715 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 4.45 (bs, 1H, H-5); 5.07t, 4.87t (2H, H-2'(5')); 4.63d, 4.70d, 4.52bs, 4.63d (4H, H-3(4) and 3'(4')); 6.84m, 7.11m, 7.24m (4H, N-Ph-H); 7.24 (5H, C-Ph(1)-H); 7.43m, 7.51m, 7.79m (5H, C-Ph(2)-H). Found: C, 48.58; H, 2.75; N, 2.08. Calc. for C<sub>30</sub>H<sub>21</sub>Cl<sub>2</sub>FeHgNO: C, 48.72; H, 2.84; N, 1.90%.

### 3.2.9. [2-Chloromercurio-1-(((2-bromophenyl)imino)phenylmethyl)-1'-benzoyl]ferrocene (5i)

Red-brown crystals, yield 22.8%, m.p. 195–197 °C. IR KBr (pellet): 1637, 1597, 762, 729, 701 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 4.45(bs, 1H, H-5); 4.87t, 5.07t (2H, H-2'(5')); 4.46bs, 4.61d, 4.65d, 4.72d (4H, H-3(4) and 3'(4')); 6.18m, 6.77m, 6.89m (4H, N-Ar-H); 7.11m, 7.25m (5H, C-Ph(1)-H); 7.44m, 7.54m, 7.79m (5H, C-Ph(2)-H). Found: C, 45.61; H, 2.78; N, 1.95. Calc. for C<sub>30</sub>H<sub>21</sub>BrClFeHgNO: C, 46.09; H, 2.69; N, 1.79%.

## 3.3. X-ray crystal structure determination for 5c

### 3.3.1. Crystal data

C<sub>30</sub>H<sub>22</sub>ClFeHgNO, *M<sub>r</sub>* = 704.40, monoclinic, *P*2<sub>1</sub>/*c* (No. 14), *a* = 10.168(3), *b* = 16.105(3), *c* = 15.463(4) Å, β = 103.61(2)°. *V* = 2461.0(9) Å<sup>3</sup>. *Z* = 4, *D<sub>c</sub>* = 1.901 g cm<sup>-3</sup>, *F*(000) = 1360, λ = 0.71069 Å, μ(Mo Kα)<sup>3</sup> = 69.69 cm<sup>-1</sup>.

### 3.3.2. Data collection

A red crystal of 5c with approximate dimensions 0.20 × 0.20 × 0.30 mm<sup>3</sup> was mounted on a Rigaku AFC7R diffractometer. Unit cell parameters were determined from the angular setting of 21 reflections with 2θ angles in the range 23.32–26.64°. Intensities were collected with graphite-monochromated Mo Kα radiation, using the ω–2θ scan technique. A total of 3576 reflections were measured, 2440 reflections were considered with *I* > 3σ(*I*). The intensities of three representative reflection were measured after every 200 reflections. Over the course of data collection, the standards decreased by –1.0%. A linear correction factor was applied to the data to account for this phenomenon. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. Some non-hydrogen

atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined. The final  $R$  factor was 0.038 ( $R^w = 0.055$ ). The maximum and minimum peaks on the final difference Fourier map corresponded to 1.61 and  $-1.44 e^{-\text{\AA}^3}$ , respectively. All calculations were performed using the TEXSAN program package [8].

### 3.3.3. Supplementary material

Tables of atomic coordinates and thermal parameters, bond lengths and angles, anisotropic thermal parameters and hydrogen atom coordinates for **5c** are available.

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