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Studies on the synthesis and structural characterization of cyclomercurated ferrocenylimines containing heterocyclic ring

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Abstract

The cyclomercurated ferrocenylimines containing heterocyclic ring can be prepared by the cyclomercuration of acylferrocene, followed by the condensation of the resulting product with the appropriate heterocyclic amine. This procedure provides an efficient method for the synthesis of cyclomerucurated ferrocenylimines containing heterocyclic ring which is difficultly synthesized by the traditional method, i.e. imination and then cyclomercuration. A series of these compounds were synthesized by this new method and characterized. The X-ray crystal structure of [HgCl(η^5-$C_5H_3C(CH_3)$=N-2-C_5H_3N-6-CH_3) Fe(η^5-C_5H_5)] (**3d**) has been determined and the reaction mechanism was proposed.

Keywords: Heterocyclic ring containing cyclomercurated ferrocenylimine; Synthesis; X-ray crystal structure

1. Introduction

The cyclometallation of ferrocenylimines has been systematically studied both in theoretical and applied aspects [1–4]. It was found that some ferrocenylimines containing strong electron-withdrawing group on aryl ring or containing heterocyclic ring, which are the precursors of the corresponding cyclometallated ferrocenylimines, have scarcely been successfully synthesized through the traditional condensation of acylferrocene with aromatic or heterocyclic amines, because the strong electron-withdrawing group on aryl ring or the heteroatom in heterocyclic ring decreased the electron density of the amino group and weakened its nucleophilic attack on the carbon atom of the carbonyl group. Moreover, these ferrocenylimines formed are usually unstable and difficultly separated from the solution. This paper reports a new method for synthesizing some cyclomercurated ferrocenylimines, which could be used as precursor for organic synthesis and transmetallating agent for the synthesis of other cyclometallated ferrocenylimines [5,6]. As far as we know, this synthetic pathway was an efficient method for synthesis of cyclomercurated ferrocenylimines containing heterocyclic ring which could not be successfully synthesized by traditional method.

2. Results and discussion

2.1. Synthesis

There are two pathways for synthesis of cyclomercurated ferrocenylimines, **A** and **B**. The former is a traditional method and the latter is a new method as shown in Scheme 1.

The new pathway **B** is contrary to the previous route **A** in sequence. According to the traditional method, the cyclomercurated ferrocenylimine was synthesized in the following order: imination (condensation) and then cyclomercuration. With the new method, the cyclomercuration was carried out prior to the imination (condensation). The stable intermediate, cyclomercurated acylferrocene **2**, was easily synthesized and separated by preparative TLC [7]. Four cyclomercurated ferrocenylketimines containing pyridyl ring were synthesized via

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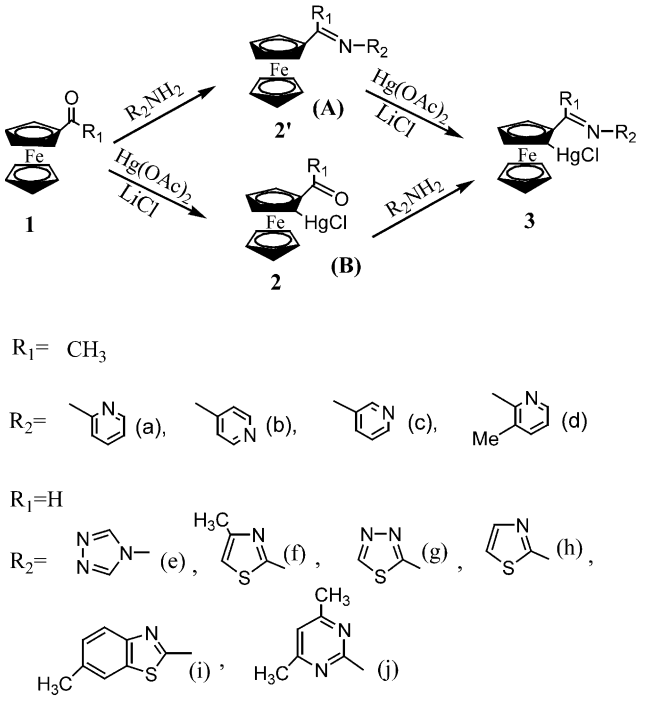


Scheme 1.

new pathway **B** and the results obtained are listed in Table 1.

As shown in Table 1, the reaction was completed within 24 h. A longer reaction time could not increase the yield (entry 3 vs. entry 4). Toluene was a suitable solvent for this condensation. The highest yield was obtained when the reaction was carried out in refluxing toluene and using Al_2O_3 as catalyst (entry 10). The yield decreased when the reaction was carried out at lower temperature (entries 5 and 6). When chlorobenzene or xylene was used as the solvent at a higher reaction temperature, the yield was low (entries 7 and 8), which might be due to the cleavage of C–Hg bond. The yields of **3a**, **3b** and **3d** were lower than that of **3c** (entries 3, 9 and 11 vs. 10), because the amino group of 3-aminopyridine has stronger nucleophilicity than those of other aminopyridines. A somewhat higher yield of **3d** comparing with that of **3a** might result from both the electronic effect and steric hindrance of the methyl group. The former facilitated the nucleophilic attack of amino group on the carbonyl group, but the latter hindered it.

A great effort has been made to evaluate the new synthetic method. Some other heterocyclic amines **e**, **f**, **g**, **h**, **i**, **j** were applied to compare the synthetic methods for cyclomercurated ferrocenylimines **3** from formylferrocene **1** via pathway **A** or **B**. According to the traditional method, although **2′e**, **2′f**, **2′g**, **2′h** could be synthesized and were stable in air, in the second step (cyclomercuration), the corresponding mercurated compounds were not obtained probably owing to easy coordination between the mercury atom and various heteroatoms in the heterocyclic ring which resulted in the formation of complicated coordination products.

According to the new method, the first step was a well-known reaction. The condensation of **2** with heterocyclic amines gave **3e**, **3f**, **3g**, **3h**, **3i** and **3j** with moderate yields (47–65%), respectively.

This new synthetic method has also been successfully applied to synthesize a lot of cyclomercurated ferrocenylimines containing aryl moieties. So it can be concluded that this new method may be considered as a useful and indispensable way to synthesize cyclomercurated ferrocenylimines containing heterocyclic ring.

The IR spectra of compounds **3a**–**3d** were consistent with that of 2-chloromercuri-1-[1-(arylimino)ethyl]ferrocenes [8]. The absorptions at 1000 and 1100 cm^{-1} were indicative of an unsubstituted Cp ring. In addition, the C=N absorptions of compounds **3** were appeared in the energy range from 1580 to 1610 cm^{-1} which were somewhat lower than that of 2-chloromercuri-1-[1-(arylimino)ethyl]ferrocenes. This can be explained by the concept concerning the $N_{(C=N)}$–Hg intramolecular coordination [8] and by the stronger electron-withdrawing ability of the heterocyclic ring than that of the aryl

Table 1
The results obtained *via* the new synthetic pathway

Entry	Amine	Product	Solvent	Temp. (°C)	Time (h)	Yield (%)[a]
1	2-aminopyridine	**3a**	Toluene	110	6	45
2	2-aminopyridine	**3a**	Toluene	110	12	56
3	2-aminopyridine	**3a**	Toluene	110	24	72
4	2-aminopyridine	**3a**	Toluene	110	48	72
5	2-aminopyridine	**3a**	THF	66	24	40
6	2-aminopyridine	**3a**	Benzene	80	24	62
7	2-aminopyridine	**3a**	Chlorobenzene	130	24	32
8	2-aminopyridine	**3a**	Xylene	140	24	37
9	4-aminopyridine	**3b**	Toluene	110	24	71
10	3-aminopyridine	**3c**	Toluene	110	24	86
11	6-methyl-2-aminopyridine	**3d**	Toluene	110	24	75

All reactions were catalyzed by Al_2O_3.
[a] Isolated yield, based on cyclomercurated acetylferrocene.

ring. The ^{1}H-NMR spectra of compounds **3** were completely consistent with the structure of 1,2-substituted Cp, exhibiting the AMX system for the three different protons on the 1,2-disubstituted Cp ring, and five protons for the unsubstituted Cp ring resonating at higher field. The chemical shifts of the protons 3, 4 and 5 on the substituted Cp ring of compounds **3** were shifted to downfield ca. 0.1 ppm in comparison with that of compound **2**. This might be due to that the electronic effect of heterocyclic ring has some influence through the C=N bond on the substituted Cp of the ferrocenyl moiety.

For simplicity, compound **3c** was taken as a representative of these cyclomercurated ferrocenylketimine compounds. The broad downfield singlets at 8.38, 8.14 ppm and a quartet at 7.19–7.33 ppm were assigned to the protons 2, 6, 4 and 5 on pyridyl ring, respectively. A five-proton singlet at 4.24 ppm was assigned to the unsubstituted Cp ring. The three apparent multiplets at 4.18, 4.68, 4.86ppm were assigned to protons on the 1,2-disubstituted Cp ring. In IR, an absorption at 1605 cm^{-1}, characteristic of C=N bond and the disappearance of the band at 1635 cm^{-1} corresponding to C=O of complex (**2**) confirmed the formation of the desired product. The bands at 1088 and 1006 cm^{-1} were indicative of the unsubstituted Cp.

2.2. Molecular structure

In order to confirm the formation of the cyclomercurated ferrocenylketimines proposed on the basis of the spectral properties of these compounds, single crystal structure determination of 2-chloromercuri-1-[(6-methylpyridyl-2-imino)ethyl]-ferrocene (**3d**) was undertaken. A red prismatic crystal of **3d** with approximate dimension of $0.30 \times 0.20 \times 0.20$ mm^3 was mounted on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo–K_α radiation. A total of 3519 observed reflections with $I \geq 2\sigma(I)$ was collected in the range of $2.02 < \theta < 27.49°$, and the independent reflections were 3519. The crystal data of **3d** were: $C_{18}H_{19}ClFeHgN_2O$, $M_r = 571.25$, triclinic, $a = 9.2177(18)$ Å, $b = 10.134(2)$ Å, $c = 11.528(2)$ Å, $\alpha = 113.81(3)°$, $\beta = 101.12(3)°$, $\gamma = 100.82(3)°$, $V = 923.5(3)$ $Å^3$, $Z = 2$, $D_{calc} = 2.058$ g cm^{-3}, $F(000) = 546$. The structure was solved by direct method. All calculations were performed using the TEXSAN crystallographic software package. The goodness-of-fit on F^2 was 1.066, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final R was 0.0597 and wR_2 was 0.1663, respectively. The molecular structure of [HgCl(η^5-$C_5H_3C(CH_3)$=N-2-C_5H_3N-6-CH_3)Fe(η^5-C_5H_5)] (**3d**) is shown in Fig. 1. The selected bond lengths and bond angles are listed in Table 2.

It was shown that Hg atom was linked to *ortho* position of the substituted ferrocenyl ring. The distance between $N_{(1)}$ and Hg atom was 2.949 Å, which was slightly shorter than the sum of the van der Waals radii of mercury and nitrogen (3.05–3.15 Å) but significantly longer than that of the 2-chloromercuri-1-[1-(4-methylphenylimino)ethyl]ferrocenes (2.681 Å) [6] and 2-chloromercuri-1-[1-(4-chlorophenylimino)ethyl]ferrocenes (2.766 Å) [9]. The $N_{(2)}$–Hg distance was longer than 3.5 Å, indicating that there was no coordination between the $N_{(2)}$ and Hg. The C=N bond length was 1.282 Å. The chelate cycle was nearly a planar structure and almost parallel with the substituted Cp ring (dihedral angle of 9.5°). The dihedral angle between the pyridyl ring and the chelate cycle is 74.9°.

2.3. Possible mechanism

The possible mechanism of this new synthetic route is shown in Scheme 2.

In the mercurated acylferrocene (**2**), Hg atom withdrew the electron on the oxygen atom of the carbonyl group and led to the electron deficiency of the carbonyl group which facilitated the nucleophilic attack from amino group.

3. Experimental

Melting points were measured on a WC-1 instrument and are uncorrected. Elemental analyses were determined with a Carlo Erba 1160 elemental analyzer. ^{1}H-NMR were recorded on a Bruker DPX 400 instrument using $CDCl_3$ (99.8%) as the solvent and TMS as an internal standard. IR spectra were recorded on a Perkin–Elemer FTIR 1750 spectrophotomer. Preparative TLC was performed on dry silica gel plates developed with methylene chloride. Aminopyridines (**a**, **b**, **c**, **d**) and 2-aminothiazole (**h**) were used as received (Fluka), Al_2O_3 was activated at 120 °C for 2 h before use. All solvents were dried using the appropriate drying agents (toluene, benzene, xylene, THF/Na/benzophenone, MeOH/Mg, CH_2Cl_2/P_2O_5), and freshly distilled prior to use.

4-amino-1,2,4-triazole (**e**), 4-methyl-2-aminothiazole (**f**), 2-amino-1,3,4-thia-dizole (**g**), 6-methylbenzo-2-aminothiazole (**i**) and 4,6-dimethyl-2-aminopyrimidine (**j**) were synthesized according to Refs. [10–14]. Their melting points and IR data were consistent with those of literatures.

3.1. Preparation of compound 2

2-(Chloromercuri)-1-acylferrocene **2** were prepared according to Ref. [7].

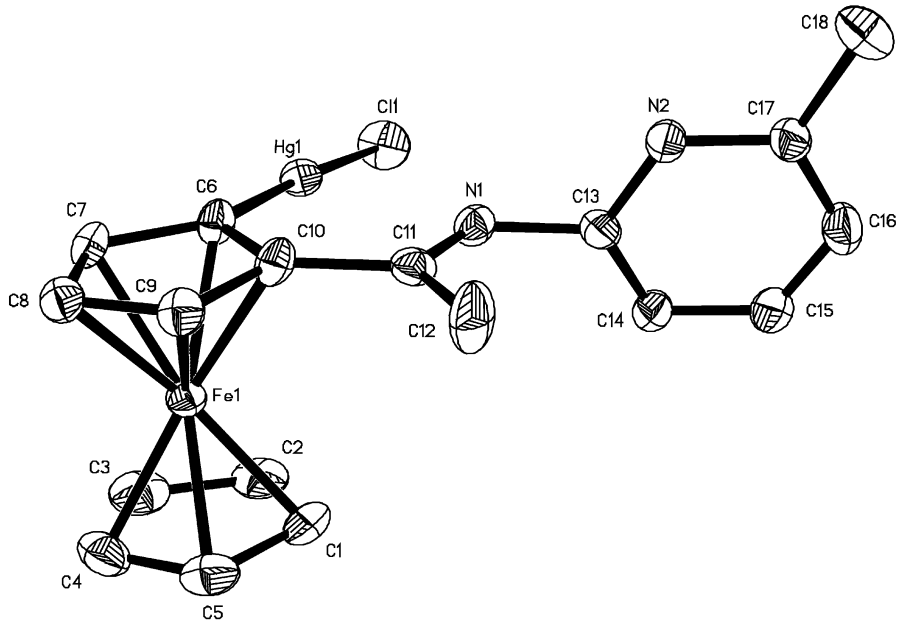


Fig. 1. Molecular structure of **2d**.

Table 2
The selected bond lengths (Å) and bond angles (°)

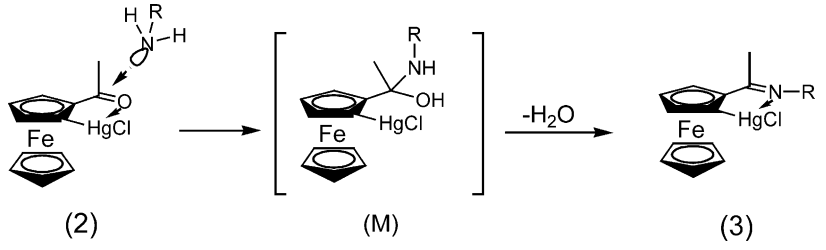
Bond lengths			
Hg(1)–C(6)	2.056(9)	N(1)–C(11)	1.282(14)
Hg(1)–Cl(1)	2.313(3)	N(1)–C(13)	1.410(13)
Fe(1)–C(1)	2.042(12)	N(2)–C(17)	1.364(13)
Fe(1)–C(10)	2.046(12)	N(2)–C(13)	1.365(14)
Fe(1)–C(6)	2.083(11)	Hg(1)–N(1)	2.949
Bond angles			
C(6)–Hg(1)–Cl(1)	176.2(3)	Hg(1)–C(6)–Fe(1)	118.7(5)
C(11)–N(1)–C(13)	121.1(9)	C(6)–C(10)–C(11)	125.5(9)
C(10)–C(6)–C(7)	107.6(9)	N(1)–C(11)–C(10)	117.8(9)
C(10)–C(6)–Hg(1)	124.0(7)	N(1)–C(11)–C(12)	124.0(10)
C(7)–C(6)–Hg(1)	127.4(7)	C(10)–C(11)–C(12)	118.1(10)

3.2. General procedure for synthesis of compounds **3**

To a solution of 2-(chloromercuri)-1-acylferrocene (0.5 mmol) in toluene (30 ml), heterocyclic amines (1.0 mmol) were added, and the mixture was refluxed with stirring in the presence of activated neutral Al_2O_3 overnight under argon. The resulting mixture was then cooled to room temperature (r.t.) and the solid was separated by filtration. The filtrate was evaporated in vacuo to dryness and the residue was dissolved in a minimum amount of methylene chloride and subjected to a short dry column of silica gel, eluted with methylene chloride. The second band was collected and afforded the product after the evaporation of the solvent and recrystallization from methylene chloride–petroleum ether (60–90). The physical, spectroscopic and analytical data are as follows.

3.2.1. 2-Chloromercurio-1-[(pyridyl-2-imino)ethyl]ferrocene (**3a**)

Dark red crystals, yield, 72%; m.p. 210 °C (dec.). Anal. Found: C, 38.03; H, 2.78; N, 5.01. $C_{17}H_{15}ClFeHgN_2$ Calc.: C, 37.87; H, 2.80; N, 5.20%. IR (KBr pellet): 1600, 1588, 1450, 1271, 1099, 990, 801 760, 730 cm^{-1}. ^{1}H-NMR: δ 2.21(s, 3H, CH_3), 4.26 (s, 5H, C_5H_5), 4.46 (t, 1H, $J = 2.4$ Hz, H-3), 4.67 (t, 1H, $J = 2.4$, H-4), 4.87 (q, 1H, $J = 2.4$ Hz, H-5), 6.98 (d, 1H, $J = 7.5$ Hz, Py-H3), 7.06 (dd, 1H, $J = 8.4$ Hz, 7.6 Hz, Py-H4), 7.69 (dd, 1H, $J = 8.4$ Hz, 7.6 Hz, Py-H5), 8.50 (d, 1H, $J = 8.4$ Hz, Py-H6).



Scheme 2. The possible mechanism of the new method.

*3.2.2. 2-Chloromercurio-1-[(pyridyl-4-imino)ethyl]ferrocene (**3b**)*

Deep red crystals, yield 71%; m.p. 175 °C. Anal. Found: C, 38.13; H, 2.80; N, 5.11. $C_{17}H_{15}ClFeHgN_2$ Calc.: C, 37.87; H, 2.80; N.5.20%. IR (KBr pellet): 1601, 1582, 1420, 1256, 1102, 995, 835, 813, 671 cm^{-1}. ^{1}H-NMR: δ 2.20 (s, 3H, CH_3), 4.24 (s, 5H, C_5H_5), 4.46 (t, 1H, $J = 2.4$ Hz, H-3), 4.66 (t, 1H, $J = 2.4$ Hz, H-4), 4.88 (q, 1H, $J = 2.4$ Hz, H-5), 6.98 (d, 2H, $J = 6.0$ Hz, Py-H3, 5), 8.55 (d, 2H, $J = 6.0$ Hz, Py-H2, 6).

*3.2.3. 2-Chloromercurio-1-[(pyridyl-3-imino)ethyl]ferrocene (**3c**)*

Deep red crystals, yield 86%; m.p. 202 °C. Anal. Found: C, 38.13; H, 2.80; N, 5.25. $C_{17}H_{15}ClFeHgN_2$ Calc.: C, 37.87; H, 2.80; N, 5.20%. IR (KBr pellet): 1605, 1560, 1400, 1353, 1088, 1006, 988, 810, 786, 730, 705, 687 cm^{-1}. ^{1}H-NMR: δ 2.20(s, 3H, CH_3), 4.24 (s, 5H, C_5H_5), 4.48 (t, 1H, $J = 2.4$ Hz, H-3), 4.68 (t, 1H, $J = 2.4$ Hz, H-4), 4.86 (q, 1H, $J = 2.4$ Hz, H-5), 7.21 (d, 1H, $J = 8.0$ Hz, Py-H4), 7.32 (q, 1H, $J = 8.0$ Hz, 7.2 Hz, Py-H5), 8.14 (broad, s, 1H, Py-H6), 8.38 (broad, s, 1H, Py-H2).

*3.2.4. 2-Chloromercurio-1-[(6-methylpyridyl-2-imino)ethyl]ferrocene (**3d**)*

Deep red crystals, yield 75%; m.p. 172 °C. Anal. Found: C, 38.53; H, 2.78; N, 5.01. $C_{18}H_{17}ClFeHgN_2$ Calc.: C, 39.08; H, 3.10; N, 5.06%. IR (KBr pellet): 1601, 1573, 1549, 1278, 1096, 989, 798, 738, 717 cm^{-1}. ^{1}H-NMR: δ 2.23 (s, 3H, CH_3), 2.52 (s, 3H, CH_3 to Py), 4.26 (s, 5H, C_5H_5), 4.45 (q, 1H, $J = 2.4$ Hz, H-3), 4.64 (t, 1H, $J = 2.4$ Hz, H-4), 4.85 (q, 1H, $J = 2.8$ Hz, H-5), 6.73 (d, 1H, $J = 8.0$ Hz, Py-H4), 6.90 (d, 1H, $J = 7.6$ Hz, Py-H6), 7.59 (t, 1H, $J = 8.0$ Hz, 7.6 Hz, Py-H5).

*3.2.5. 2-Chloromercurio-1-[(1,2,4-triazoyl-4-imino)methyl]ferrocene (**3e**)*

Red crystals, yield, 65%; m.p. 184 °C (dec.). Anal. Found: C, 29.86; H, 2.15; N, 11.02. $C_{13}H_{11}ClFeHgN_4$ Calc.: C, 30.31; H, 2.15; N, 10.88%. IR (KBr pellet): 1595, 1520, 1455, 1367, 1178, 1056, 1004, 910, 961, 851, 677 cm^{-1}. ^{1}H-NMR, δ 4.28 (s, 5H, C_5H_5), 4.49 (s, 1H, H-3), 4.68 (s, 1H, H-4), 4.88 (s, 1H, H-5), 8.45 (s, 2H, H–C=N_{cycle}), 8.65 (s, 1H, H–C=N).

*3.2.6. 2-Chloromercurio-1-[(4-methylthiazyl-2-imino)methyl]ferrocene (**3f**)*

Deep purple crystals, yield, 57%; m.p. 143 °C (dec.). Anal. Found: C, 32.88; H, 2.41; N, 5.04. $C_{15}H_{13}ClFeHgN_2S$ Calc.: C, 33.04; H, 2.40; N, 5.14%. IR (KBr pellet): 1580, 1432, 1395, 1096, 1010, 917, 790, 730, 710, 642 cm^{-1}. ^{1}H-NMR, δ 2.41(s, 3H, CH_3), 4.29 (s, 5H, C_5H_5), 4.50 (s, 1H, H-3), 4.71 (s, 1H, H-4), 4.86 (s, 1H, H-5), 8.44 (s, 1H, H–C=C), 8.91 (s, 1H, H–C=N).

*3.2.7. 2-Chloromercurio-1-[(1,3,4-thiadiazoyl-2-imino)methyl]ferrocene (**3g**)*

Purple crystals, yield, 48%; m.p. 190 °C. Anal. Found: C, 29.40; H, 1.90; N, 7.92. $C_{13}H_{10}ClFeHgN_3S$ Calc.: C, 29.34; H, 1.89; N, 7.90%. IR (KBr pellet): 1598, 1422, 1249, 1116, 1005, 909, 890, 831, 814, 648 cm^{-1}, ^{1}H-NMR, δ 4.35 (s, 5H, C_5H_5), 4.57 (s, 1H, H-3), 4.79 (s, 1H, H-4), 4.82 (s, 1H, H-5), 8.90 (s, 1H, H–C=N_{cycle}), 9.40 (s, 1H, H–C=N).

*3.2.8. 2-Chloromercurio-1-[(thiazyl-2-imino)methyl]ferrocene (**3h**)*

Deep purple crystals, yield, 52%; m.p. 203 °C. Anal. Found: C, 31.39; H, 2.00; N, 5.48. $C_{14}H_{11}ClFeHgN_2S$ Calc.: C, 31.66; H, 2.09; N, 5.27%. IR (KBr pellet): 1600, 1432, 1380, 1111, 995, 890, 801, 715, 656 cm^{-1}. ^{1}H-NMR, δ 4.28 (s, 5H, C_5H_5), 4.56 (s, 1H, H-3), 4.75 (s, 1H, H-4), 4.89 (s, 1H, H-5), 7.0 (d, 1H, $J = 8.8$ Hz, C=C–H), 7.2 (d, 1H, $J = 8.8$ Hz, H–C=C), 9.01 (s, 1H, H–C=N).

*3.2.9. 2-Chloromercurio-1-[(6-methylbenzothiazolyl-2-imino)methyl]ferrocene (**3i**)*

Purple crystals, yield, 47%; m.p. 158 °C. Anal. Found: C, 38.14; H, 2.64; N, 4.90. $C_{19}H_{15}ClFeHgN_2S$ Calc.: C, 38.34; H, 2.54; N, 4.71%. IR (KBr pellet): 1603, 1544, 1460, 1076, 1001, 910, 799 cm^{-1}. ^{1}H-NMR, δ 2.45 (s, 3H, CH_3), 4.28 (s, 5H, C_5H_5), 4.47 (s, 1H, H-3), 4.66 (s, 1H, H-4), 4.89 (s, 1H, H-5), 8.05 (d, 1H, $J =$ 8.0 Hz, C=C–H), 8.51 (d, 1H, $J = 8.0$ Hz, H–C=C), 8.34 (s, 1H, H–C=C), 8.99 (s, 1H, H–C=N).

*3.2.10. 2-Chloromercurio-1-[(4,6-dimethylpyrimidyl-2-imino)methyl]ferrocene (**3j**)*

Red crystals, yield, 47%; m.p. 188 °C. Anal. Found: C, 36.44; H, 2.92; N, 7.58. $C_{17}H_{16}ClFeHgN_3$ Calc.: C, 36.84; H, 2.91; N, 7.58%. IR (KBr pellet): 1602, 1590, 1457, 1389, 1103, 1000, 953, 915, 792 cm^{-1}. ^{1}H-NMR, δ 2.45 (s, 6H, $2CH_3$), 4.29 (s, 5H, C_5H_5), 4.55 (s, 1H, H-3), 4.76 (s, 1H, H-4), 4.90 (s, 1H, H-5), 8.10 (s, 1H, H–C=C), 8.85 (s, 1H, H–C=N).

*3.2.11. 1,2,4-Triazoyl-4-iminomethylferrocene (**2′e**)*

Deep red crystals, yield, 42%; m.p. 219 °C. Anal. Found: C, 55.38; H, 4.29; N, 20.16. $C_{13}H_{12}FeN_4$ Calc.: C, 55.74; H, 4.32; N, 20.00%. IR (KBr pellet): 1597, 1498, 1150, 1045, 1008, 911, 810, 790 cm^{-1}. ^{1}H-NMR, δ 4.28 (s, 5H, C_5H_5), 4.61 (s, 2H, H-3,4), 4.77 (s, 2H, H-2,5), 8.51 (s, 3H, H–C=N).

*3.2.12. 4-Methylthiazyl-2-iminomethylferrocene (**2′f**)*

Purple crystals, yield, 37%; m.p. 90 °C. Anal. Found: C, 57.96; H, 4.49; N, 9.11. $C_{15}H_{14}FeN_2S$ Calc.: C, 58.08; H, 4.55; N, 9.03%. IR (KBr pellet): 1581, 1503, 1430, 1104, 1010, 913, 695 cm^{-1}. ^{1}H-NMR, δ 2.43 (s, 3H, CH_3), 4.26 (s, 5H, C_5H_5), 4.59 (s, 2H, H-3,4), 4.86 (s,

2H, H-2,5), 6.69 (s, 1H, H–C=C), 8.88 (s, 1H, H–C=N).

*3.2.13. 1,3,4-Thiadiazoyl-2-iminomethylferrocene (**2′g**)*

Purple crystals, yield, 66%; m.p. 138 °C. Anal. Found: C, 52.24; H, 3.31; N, 14.08. $C_{13}H_{11}FeN_3S$ Calc.: C, 52.55; H, 3.37; N, 14.14%. IR (KBr pellet): 1599, 1412, 1167, 1030, 1001, 890, 821, 802, 790 cm^{-1}, ^{1}H-NMR, δ 4.31 (s, 5H, C_5H_5), 4.90 (s, 2H, H-3,4), 4.69 (s, 2H, H-2,5), 8.99 (s, 1H, H–C=N), 8.95 (s, 1H, H–C=N).

*3.2.14. Thiazyl-2-iminomethyl ferrocene (**2′h**)*

Purple crystals, yield, 52%; m.p., 182 °C. Anal. Found: C, 56.67; H, 4.18; N, 9.56. $C_{14}H_{12}FeN_2S$ Calc.: C, 56.78; H, 4.08; N, 9.46%. IR (KBr pellet): 1595, 1500, 1453, 1111, 1009, 913, 690 cm^{-1}. ^{1}H-NMR, δ 4.27 (s, 5H, C_5H_5), 4.61 (s,2H, H-3,4), 4.86 (s, 2H, H-2,5), 6.90 (s, 1H, H–C=C), 7.10 (s, 1H, C=C–H), 8.98 (s, 1H, H–C=N).

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