

Crystal and molecular structure of [1-[(4-chlorophenyl)imino]ethyl]ferrocene and a structural comparison with its cyclometallated derivatives

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Abstract

The structure of [1-[(4-chlorophenyl)imino]ethyl]ferrocene (**1**) has been established by X-ray crystal structure analysis. The most striking feature of the molecule is the twist of the N-phenyl ring out of the plane C–C=N–C by 75.1°, and the perpendicular nature of the N-phenyl ring with respect to the ferrocenyl cyclopentadienyl rings. A structural comparison between **1**, its cyclomercurated derivative **2** and cyclopalladated derivative **3** has been made to find out the relationship between the structure and the properties of **1** and its cyclometallated derivatives.

Keywords: Iron; Ferrocenylimine; Crystal structure; Cyclometallated derivative; Mercury; Palladium

1. Introduction

The structures of the substituted benzylideneanilines have been extensively explored [1–3], and the nonplanar nature of two phenyl rings elucidated, but studies on the crystal structures of ferrocenylimines are rare. Recently, we described the crystal and molecular structures of the cyclomercurated ferrocenylaldimine [4] and ferrocenylketimine [5] and the cyclopalladated ferrocenylketimine [6]. Interestingly, it was found that the Cp rings (cyclopentadienyl ring) are almost perpendicular to the N-phenyl ring in the metallated ferrocenylketimines **2** and **3**, dihedral angles being nearly 90°. In contrast, the Cp rings form a smaller dihedral angle with the N-phenyl ring in the compound **4** (ca. 52°). In this paper, we wish to report the crystal and molecular structure of the ferrocenylketimine **1** and make a structural comparison between **1** and its cyclometallated derivatives **2** and **3**, which would be expected to permit a deeper and more extensive under-

standing of the relationship between the structure and the properties of ferrocenylimines.

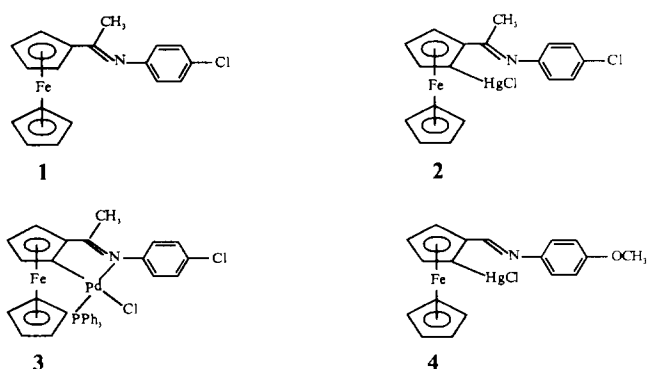
2. Results and discussion

2.1. The structure of **1**

The molecular structure of the compound **1** is shown in Fig. 1. The final atomic coordinates and anisotropic thermal parameters of all nonhydrogen atoms are listed in Table 1, and selected bond lengths and bond angles in Table 2.

The most striking features of the molecule are that the N-phenyl ring is almost perpendicular to the Cp rings, interangles being 87.92° and 90.28° for the substituted and unsubstituted Cp rings respectively, and that the N-phenyl ring forms a dihedral angle with the plane C–C=N–C much larger than that of the substituted Cp ring with the plane (75.11° versus 17.05°). The ferrocenyl moiety adopts a *trans* conformation with the N-phenyl ring, so that the metallation of the ferrocenylketimine **1** and its analogues could be directed to the *ortho*-position of the substituted Cp ring by the

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imino nitrogen and resulted in formation of the cyclometallated compounds [5,6].

2.2. The structural comparison between the ferrocenylketimine **1** and the cyclometallated derivatives **2** and **3**

Selected corresponding bond distances, bond angles and dihedral angles for **1–3** are listed in Tables 3 and 4.

From Table 3, some conclusions can be drawn as follows. Firstly, the shifts of IR absorptions of C=N bonds from high energy to low energy in the order of **1**, **2** and **3** (1623, 1615, 1570 cm^{-1}) observed previously [5,6] are a result of the N \rightarrow M interactions present in the cyclometallated compounds **2** and **3** lead to increases of C=N bond lengths. Moreover, the stronger the N \rightarrow M interaction the longer the C=N bond, since it is well known that mercury (II) has fully filled d orbitals and exhibits a much weaker coordinating ability by reason of its unoccupied 6p orbital than the palladium (II) which has unoccupied d orbitals. Also the N \rightarrow Hg coordination is only a nonbonding interaction, in other words a secondary bond, while N \rightarrow Pd is in fact a coordination bond which thus causes larger IR shifts of the C=N bond (53 cm^{-1}). The C–N bond lengths for **1–3** show the same increasing order as that of the C=N bond lengths.

Secondly, changes concerning the ferrocenyl moiety caused by the substituents are made evident, specifically by the substituents in the Cp ring increasing in

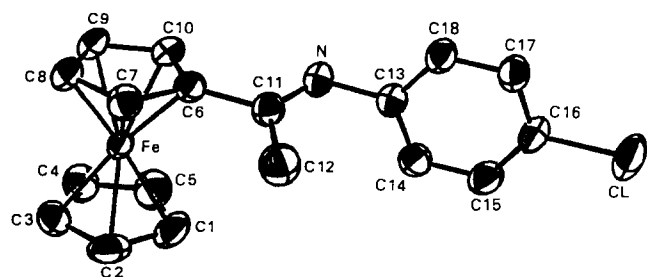


Fig. 1. Molecular structure of **1**.

Table 1

Final atomic coordinates and anisotropic thermal parameters for $\text{C}_{18}\text{H}_{16}\text{ClFeN}$ (**1**)

Atom	x	y	z	B (\AA^2)
Fe	0.99839(8)	0.27757(6)	0.77132(5)	2.58(1)
Cl	1.7025(2)	0.1778(2)	0.1086(1)	5.54(3)
N	1.1117(5)	0.2012(4)	0.4292(3)	3.34(8)
C(1)	1.2669(6)	0.2691(6)	0.8132(5)	4.7(1)
C(2)	1.2257(7)	0.3873(6)	0.9067(5)	4.4(1)
C(3)	1.0764(7)	0.3244(5)	0.9599(4)	3.9(1)
C(4)	1.0286(7)	0.1727(5)	0.8995(4)	4.1(1)
C(5)	1.1453(7)	0.1372(5)	0.8070(4)	4.3(1)
C(6)	0.9629(5)	0.3008(4)	0.5993(4)	2.83(8)
C(7)	0.9178(6)	0.4193(4)	0.6913(4)	3.35(9)
C(8)	0.7698(6)	0.3576(5)	0.7450(4)	3.8(1)
C(9)	0.7250(6)	0.2054(5)	0.6895(4)	3.7(1)
C(10)	0.8445(5)	0.1673(5)	0.5988(4)	3.04(9)
C(11)	1.1162(6)	0.3117(4)	0.5222(4)	2.99(8)
C(12)	1.2561(7)	0.4539(5)	0.5599(5)	4.5(1)
C(13)	1.2580(6)	0.2010(4)	0.3558(4)	3.00(8)
C(14)	1.4295(6)	0.1831(5)	0.3981(4)	3.54(9)
C(15)	1.5678(6)	0.1744(5)	0.3217(4)	3.55(9)
C(16)	1.5296(6)	0.1847(5)	0.2043(4)	3.40(9)
C(17)	1.3612(6)	0.2015(5)	0.1588(4)	3.9(1)
C(18)	1.2231(6)	0.2092(5)	0.2354(4)	3.56(9)

both number and steric repulsion in the order of **1**, **2** and **3**. The average Fe–C distances, C–C distances for the Cp rings and the distances between the Cp rings

Table 2

Selected bond distances (\AA) and bond angles (deg) for the compound **1**

Fe–C(1)	2.035(5)	C(3)–C(4)	1.408(7)
Fe–C(2)	2.051(5)	C(4)–C(5)	1.424(7)
Fe–C(3)	2.046(5)	C(6)–C(7)	1.436(6)
Fe–C(4)	2.045(5)	C(6)–C(10)	1.433(6)
Fe–C(5)	2.042(5)	C(6)–C(11)	1.498(6)
Fe–C(6)	2.029(5)	C(7)–C(8)	1.420(7)
Fe–C(7)	2.041(4)	C(8)–C(9)	1.407(7)
Fe–C(8)	2.050(4)	C(9)–C(10)	1.428(6)
Fe–C(9)	2.047(4)	C(11)–C(12)	1.491(6)
Fe–C(10)	2.038(4)	C(13)–C(14)	1.387(7)
Cl–C(16)	1.747(4)	C(13)–C(18)	1.394(6)
N–C(11)	1.263(6)	C(14)–C(15)	1.397(6)
N–C(13)	1.421(5)	C(15)–C(16)	1.373(6)
C(1)–C(2)	1.429(8)	C(16)–C(17)	1.372(6)
C(1)–C(5)	1.411(8)	C(17)–C(18)	1.396(7)
C(2)–C(3)	1.427(8)		
C(1)–C(2)–C(3)	106.3(5)	N–C(11)–C(6)	117.0(4)
C(2)–C(1)–C(5)	109.7(4)	N–C(11)–C(12)	126.1(5)
C(2)–C(3)–C(4)	108.5(5)	N–C(13)–C(14)	121.4(4)
C(3)–C(4)–C(5)	108.9(5)	N–C(13)–C(18)	118.9(4)
C(1)–C(5)–C(4)	106.7(5)	C(14)–C(13)–C(18)	119.5(4)
C(7)–C(6)–C(10)	108.6(4)	C(13)–C(14)–C(15)	120.6(5)
C(7)–C(6)–C(11)	126.5(5)	C(14)–C(15)–C(16)	118.3(5)
C(10)–C(6)–C(11)	124.8(4)	Cl–C(16)–C(15)	118.9(3)
C(6)–C(7)–C(8)	106.9(5)	Cl–C(16)–C(17)	118.3(4)
C(7)–C(8)–C(9)	109.0(5)	C(15)–C(16)–C(17)	122.8(5)
C(8)–C(9)–C(10)	108.8(4)	C(16)–C(17)–C(18)	118.6(4)
C(6)–C(10)–C(9)	106.7(4)	C(13)–C(18)–C(17)	120.1(5)
C(6)–C(11)–C(12)	116.8(4)	C(11)–N–C(13)	120.0(4)

Table 3
Selected bond lengths (Å) for compounds 1–3^{a,b}

	1	2	3
C=N	1.263	1.267	1.296
C–N	1.421	1.431	1.458
Fe–Cs ^c	2.041	2.047	2.055
Fe–Cu ^c	2.044	2.031	2.052
Fe–Cps	1.642	1.651	1.655
Fe–Cpu	1.649	1.650	1.660
Cs–Cs ^c	1.425	1.426	1.431
Cu–Cu ^c	1.420	1.390	1.418
Cs–C	1.498	1.47	1.450
N–M		2.766	2.135

^a Values for compounds 2 and 3 are taken from ref. [5,6].

^b Cs and Cu refer to the carbon atoms of the substituted Cp ring and the unsubstituted Cp ring respectively, Cps and Cpu refer to the substituted and unsubstituted Cp rings respectively.

^c Average values.

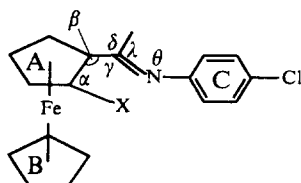
and the iron atom increase progressively, indicating that both the bulky substituent and the multisubstitution loosen the Cp ring structure, and even the whole ferrocene system. In addition, it can also be seen that the substituted Cp ring has a looser structure when compared with the unsubstituted Cp ring for all three compounds. Finally, the distances of the Cs–C single bond for both 2 and 3 are significantly shorter than that of 1. This may be attributed to the more coplanarity between the substituted Cp ring and the plane C–C=N–C for 2 and 3, which implies better conjugation and thus shorter C–C bond distances (see Table 4).

The values in Table 4 indicate the effect of the intramolecular coordination between the imino nitrogen and the metals on the related angles. It can be noted that, owing to the N → M coordination, the angles α for both compounds 2 and 3 decrease and

Table 4
Selected bond angles (deg) and dihedral angles (deg) for 1–3^a

	1 (X = H)	2 (X = Hg)	3 (X = Pd)
α	125.7	121.3	112.1
β	124.8	124	117.8
γ	117.0	118.2	113.8
θ	120.0	120.6	120.4
δ	116.8	116.8	120.7
λ	126.1	125.0	125.5
A–D	17.05	5.47	8.81
C–D	75.11	94.62	75.51
A–B	2.42	1.29	7.04
A–C	87.92	91.68	82.01

^a D = the plane C–C=N–C, and the other planes and angles are indicated as follows:



that the angles β and γ for 3 also decrease substantially in comparison with 1, while the angles β and γ for 2 and the angles θ and λ for both 2 and 3 show no obvious change. It is remarkable that the N → Pd coordination influences the angles to a much larger extent than the N → Hg interaction and this is consistent with the stronger N → Pd interaction.

The structural feature shared by all three compounds, as shown in Table 4, is that the N-phenyl ring forms a dihedral angle with the plane C–C=N–C that is much larger than that of the substituted Cp ring and the N-phenyl ring is almost perpendicular to the substituted Cp ring. This may be a general characteristic of the ferrocenylimines, and only the deviations of the dihedral angles from 90° may differ for the various ferrocenylimines. The coplanarity of the substituted Cp ring with the plane C–C=N–C for the cyclometallated derivatives is better than that of compound 1, and this means a better conjugation between the two planes, which is in accord with the result obtained from the comparison of the related bond distances. This may be because the intramolecular coordination between imino nitrogen and metals is expected to hold the substituted Cp ring and the plane C–C=N–C in coplanar geometry. Additionally, the ferrocenyl moiety has planar Cp rings for both the compounds 1 and 2 which are nearly parallel to each other, while in the compound 3, the Cp rings are not completely parallel, the interplanar angle being 7.04°, which can be ascribed to the steric repulsion caused by the crowded triphenylphosphine ligand.

3. Experimental section

The synthesis of 1 has been described [5]. Single crystals were formed by slow evaporation of a methylene chloride-petroleum ether solution, and a crystal of approximate dimensions 0.20 × 0.18 × 0.13 mm was used for data collection.

Crystal data: C₁₈H₁₆ClFeN, $M_r = 337.63$, triclinic, $P\bar{1}$, $a = 7.428(1)$, $b = 9.919(2)$, $c = 11.310(1)$ Å, $\alpha = 107.47(1)$, $\beta = 94.82(1)$, $\gamma = 101.65(1)^\circ$, $V = 769.1$ Å³, $Z = 2$, $D_c = 1.458$ g cm⁻³, $F(000) = 348$, $\mu = 94.53$ cm⁻¹, λ (Cu K α) = 1.5418 Å.

Data collection: Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Cu K α radiation and an $\omega - 2\theta$ scan mode in the range of $1 < \theta < 70^\circ$ at room temperature. 3061 reflections were measured, 2567 of which had $I > 3\sigma(I)$ and were used in all calculations. The intensities of the standard reflections monitored at regular interval 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.

Structure solution and refinement: The structure was solved by Patterson methods using the Enraf-Non-

ius SDP program package [7] on a PDD 11/44 computer. All non hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included in calculated positions. The final residuals R and R_w were 0.056 and 0.059, respectively.

4. Supplementary material available

Full tables of bond lengths and angles, hydrogen coordinates, thermal parameters and structure factors are available from the authors.

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