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^{13}C NMR spectra of cyclomercurated ferrocenylimines: substituent effects and conformations in the ferrocenes

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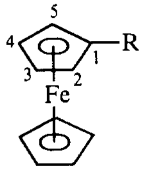
Abstract

Three series of cyclomercurated ferrocenylimines (2-chloromercurio-ferrocenylimines) have been studied using ^{13}C NMR spectroscopy. Good to excellent linear relationships have been found to exist between the chemical shifts of the carbon atoms in the ferrocenyl moiety and normal Hammett substituent constants σ_m and σ_p. The δ values of the iminyl carbon atoms show excellent linear correlations with the σ values. In three series of the ferrocenes, the sensitivity of the carbon atoms to the substituent effect is different, which is discussed in terms of the twist angle between the *N*-phenyl ring and the C–C=N–C plane. The relative sensitivity of the chemical shifts on different positions in ferrocenyl moiety to the substituent effect has also been presented.

Keywords: Iron; Mercury; Ferrocene; Imine; ^{13}C NMR

1. Introduction

^{13}C NMR spectroscopy has been widely used in the study of substituent effects in aromatic systems. In this regard, ferrocene and its derivatives, as a special aromatic system, have received considerable attention over the last two decades or so. Of these, the systematic studies, especially concerning quantitative substituent effect, are most remarkable. Nesmeyanov et al. [1] reported firstly ^{13}C NMR spectra of a large number of monosubstituted ferrocenes and compared the ^{13}C shifts with those of monosubstituted benzene, but without assignment of C(2, 5) and C(3, 4) chemical shifts. Koridze et al. [2–4] reported further ^{13}C NMR studies of the electronic effects in the cyclopentadienyl ring of monosubstituted ferrocenes on the basis of unequivocal assignments of the chemical shifts in the ^{13}C NMR spectra:



^{13}C NMR spectra of aryl-substituted ferrocenes have been extensively studied both for investigating substituent effects in ferrocenes [5] and for analysing the conformation of the arylferrocenes [6]. Recently, the studies of a series of *ortho*-substituted phenyl ferrocenes have revealed the special effect of the *ortho* groups in phenyl ring on the ^{13}C shifts of the Cp ring [7], and more recently, the ^{13}C NMR spectra of some ferrocenyl Schiff bases [8] and some 1,2-diferrocenyl-1,2-diarylethenes and 1,2-diferrocenyl-1,2-diarylethanes [9] have also been reported.

It should be pointed out that the previous studies have dealt with the monosubstituted ferrocenes. ^{13}C NMR data of the disubstituted ferrocenes appear sporadically in the literature but not in any systematic

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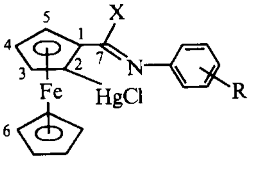
manner. In order to obtain more information about electron effects in ferrocenes and to gain an insight into the transmission of substituent effects in non-planar systems, we report the ^{13}C NMR studies on three series of cyclomercurated ferrocenylimines in this paper.

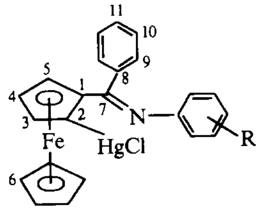
2. Results and discussion

2.1. Assignment of the ^{13}C NMR spectra

The numbering schemes shown as follows have been adopted for the NMR analyses:
The ^{13}C NMR data for **1** and **2** appear in Table 1, and for **3** in Table 2.



X=H(**1**), CH$_3$(**2**)



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The assignments of the spectra were based on the DEPT and C, H-COSY experiments measured for **2k** whose proton NMR spectrum has been assigned previously [10]. Although all the spectra of **1–3** were recorded in CDCl$_3$ solution, the DEPT and COSY-spectra of good quality for **2k** could be obtained in dimethylsulphoxide (DMSO)-d_6 solution. The solubility of this compound in DMSO is better than that in CDCl$_3$ and the signals of ^{13}C NMR spectra showed no overlap with those of DMSO-d_6, but the overlap occurs to some extent in the spectrum obtained by using CDCl$_3$ as solvent. The DEPT and COSY spectra of **2k** in DMSO-d_6 are used for assigning the ^{13}C NMR spectra of the other compounds in CDCl$_3$, this is acceptable because the spectra of **2k** in CDCl$_3$ and DMSO-d_6 were found to be almost identical (Table 1) and the cyclomercurated ferrocenylimines exhibited a similar ^{13}C NMR feature.

The ^{13}C NMR and DEPT spectra of **2k** are shown in Fig. 1 and the C,H-COSY spectrum in Fig. 2. The signals at $\delta = 82.74$ and 85.21 ppm were assigned to c(1) and c(2) owing to their disappearance in the DEPT spectrum; thus $\delta = 171.77$ ppm is assigned to C(7) and $\delta = 150.87$ and 148.23 ppm to the carbon atoms bear-

Table 1
^{13}C NMR chemical shifts [a] for **1** and **2**

Compound	R	^{13}C NMR, δ (ppm)												
		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C atoms of the phenyl ring				Me	
1a	p-OCH$_3$	84.84	81.49	76.28	73.61	72.05	69.68	157.42	114.52	122.08	142.69	158.28	55.51	
1b	p-CH$_3$	84.62	81.65	76.46	73.74	72.23	69.73	158.95	120.79	129.92	136.12	147.12	21.05	
1c	H	84.38	81.70	76.67	73.90	72.41	69.77	160.06	120.91	126.19	129.32	149.67		
1d	p-Cl	84.10	81.77	76.84	74.13	72.59	69.83	160.55	122.16	129.43	–	–		
1e	p-Br	84.08	81.79	76.88	74.17	72.62	69.84	160.66	122.54	132.39	119.52	148.64		
1f	p-I	84.06	81.80	–	74.19	72.62	69.84	160.74	122.90	138.38	90.54	149.30		
1g	p-NO$_2$	83.37	82.19	77.71	74.98	73.34	70.08	163.91	121.37	125.26	145.44	155.32		
1i	m-Cl	83.84	81.89	77.08	74.26	72.77	69.88	161.51	120.28 151.05	126.05 –	130.38	134.90		
1j	m-Br	83.79	81.90	77.11	74.28	72.79	69.90	161.55	120.71 151.21	123.01 –	128.99	130.70		
1k	m-NO$_2$	83.41	82.02	–	74.71	73.20	70.04	163.23	114.02 149.11	120.61 150.92	128.87	130.24		
2a	p-OCH$_3$	86.99	82.16	76.31	73.75	70.90	69.92	168.53	114.24	122.18	142.02	156.44	55.54	18.01
2b	p-CH$_3$	86.97	82.17	76.31	73.73	70.89	69.90	168.66	120.70	129.48	133.44	146.33	20.90	17.92
2c	H	86.58	82.20	76.40	73.81	71.00	69.93	169.01	120.69	123.92	128.91	149.03		17.99
2d	p-Cl	86.28	82.26	–	73.98	71.10	69.96	169.93	122.02	129.03	129.28	147.50		17.99
2e	p-Br	86.25	82.28	76.58	73.99	71.11	69.97	169.91	122.44	131.97	116.98	148.02		17.98
2f	p-I	86.23	82.30	–	74.01	71.12	69.98	169.90	122.86	132.94	87.66	148.70		17.98
2g	p-NO$_2$	85.57	82.73	77.13	74.49	71.52	70.16	171.25	120.88	125.10	144.10	155.24		18.43
2i	m-Cl	86.17	82.62	76.80	74.01	71.22	70.02	170.38	118.96 134.52	120.55 150.60	123.93	130.04		18.18
2jk	m-Br	86.12	82.53	76.73	74.04	71.23	70.03	170.38	119.45 122.57	123.37 150.71	126.83	130.34		18.12
2k	m-NO$_2$	–	82.73	–	74.35	71.48	70.14	–	115.29 148.86	118.68 150.42	127.04	129.85		18.20
2k	85.21	82.74	76.77	73.56	71.44	69.92	171.77	114.95	117.98 148.23	127.27 150.88	130.16			18.00

[a] Relative to the solvent CDCl$_3$ ($\delta = 77.00$ ppm).

[b] Using DMSO-d_6 as solvent; chemical shift relative to the solvent ($\delta = 39.50$ ppm).

Table 2
^{13}C NMR chemical shifts [a] for **3**

Compound	R	^{13}C NMR, δ (ppm)																	
		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C atoms of the *N*-phenyl ring						Me
3a	*p*-CH_3O	87.03	82.56	76.70	73.88	73.31	70.03	169.63	136.85	128.30	128.15	128.69	113.85	123.80	141.44	156.48			55.33
3b	*p*-CH_3	86.80	82.74	76.82	73.94	73.39	70.08	170.32	136.67	129.08	128.18	128.67	–	122.23	133.48	145.73			20.82
3c	H	86.48	82.86	–	74.11	73.57	70.15	171.15	136.42	128.46	128.18	128.77	–	122.18	123.87	148.48			
3d	*p*-Cl	86.18	82.87	–	74.29	73.69	70.20	172.10	136.06	128.32	128.14	129.02	123.50	128.63	129.26	147.02			
3e	*p*-Br	86.18	82.88	–	74.30	73.70	70.19	172.10	136.00	128.33	128.11	129.02	123.87	131.58	117.09	147.48			
3f	*p*-I	86.18	82.94	77.18	74.31	73.70	70.21	172.10	135.99	128.33	128.11	129.03	124.26	137.53	87.95	148.16			
3h	*m*-CH_3	86.56	82.76	–	74.06	73.54	70.14	170.81	136.52	–	128.15	128.71	119.16	123.08	124.73	–	138.18	148.33	21.33
3i	*m*-Cl	85.95	82.93	77.22	74.34	73.81	70.25	172.74	135.85	128.25	128.09	129.07	120.37	122.09	123.85	129.48	134.06	149.89	
3j	*m*-Br	85.93	82.97	77.24	74.33	73.78	70.21	172.78	135.85	128.25	128.10	129.08	120.83	124.98	126.74	129.75	122.10	150.06	
3k	*m*-NO_2	85.36	83.18	77.55	74.62	74.00	70.33	174.58	135.32	128.41	127.98	129.21	116.69	118.43	128.24	129.31	148.95	149.95	

[a] Chemical shift relative to the solvent $CDCl_3$ ($\delta = 77.00$ ppm).

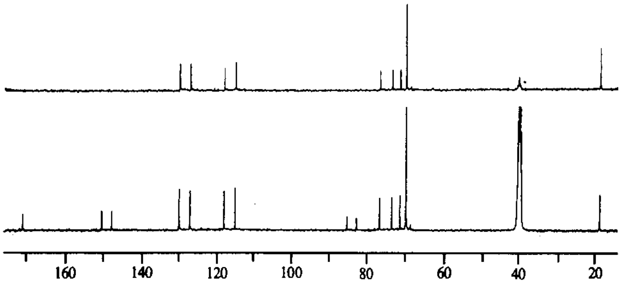

Fig. 1. ^{13}C NMR and DEPT spectra of **2k**.

ing the nitro group and the imino group respectively. Although these quaternary carbon atoms may be identified by their relatively low intensity, the DEPT spectrum provided strict proof. From the C,H-COSY spectrum, the signals at $\delta = 71.44$, 73.56 and 76.77 ppm can be assigned to c(5), c(4) and c(3) respectively because of their correlations with the corresponding protons. It is of interest that the order of the shifts of the carbon atoms 3, 4 and 5 is just opposite to that of protons 3, 4 and 5. In the same manner, the signals at $\delta = 69.92$ and 18.00 ppm were assigned to the carbon atoms of the unsubstituted Cp ring and of methyl respectively. These results can be applied to the assignments of the other compounds as mentioned above. The signals in the range 110–140 ppm can also be assigned unequivocally to the carbon atoms in the *N*-phenyl ring of **2k**, but the corresponding carbon atoms in the other compounds have not been assigned, because our interest in this paper is essentially in the effects of substituents in the *N*-phenyl ring on the ^{13}C chemical shifts of the carbons of Cp rings; furthermore, there have been many reports on the substituent effects in the substituted benzene.

2.2. Correlation analysis of chemical shifts with Hammett constants

It can be seen from the ^{13}C NMR data that the substituent effects on the carbon atoms of Cp rings are not very significant but exhibit obvious regularity. The electron-donating groups cause the upfield shift of the chemical shifts, whereas the electron-withdrawing groups have the opposite effect. However, the substituent effect on the carbon atom corresponding to the downfield shift of the two signals in the range 81–87 ppm (c(1) or c(2)) is in the opposite direction. In aryl-substituted ferrocenes and ferrocenyl Schiff bases studied previously [5–8], the same direction of substituent effect was found for the carbon atoms connected directly with the aryl or aryliminomethyl groups. In the light of this, the downfield signal can be assigned to c(1) and the other at a higher field thus assigned to c(2). Correlation of the chemical shifts δ with the normal Hammett substituent constants σ_m or σ_p [11] revealed good to excellent linear relationships for carbon atoms of different positions (Table 3).

For **2** and **3**, δ was relatively insensitive to the nature of the substituent (smaller slopes), but the δ values for the cyclomercurated ferrocenylaldimines **1** varied significantly (larger slopes), and it appears that δ for **3** is slightly more sensitive to the substituent effect when compared with **2**. This interesting behaviour can be rationalized as follows. The crystal structures of cyclomercurated ferrocenylimines showed that the non-planar nature between the *N*-phenyl ring and the C–C=N–C plane is the most striking feature for these compounds and the twist angle θ varies with different imines to a great extent [10,12]; for example, in **2d** the twist angle of the *N*-phenyl ring out of the

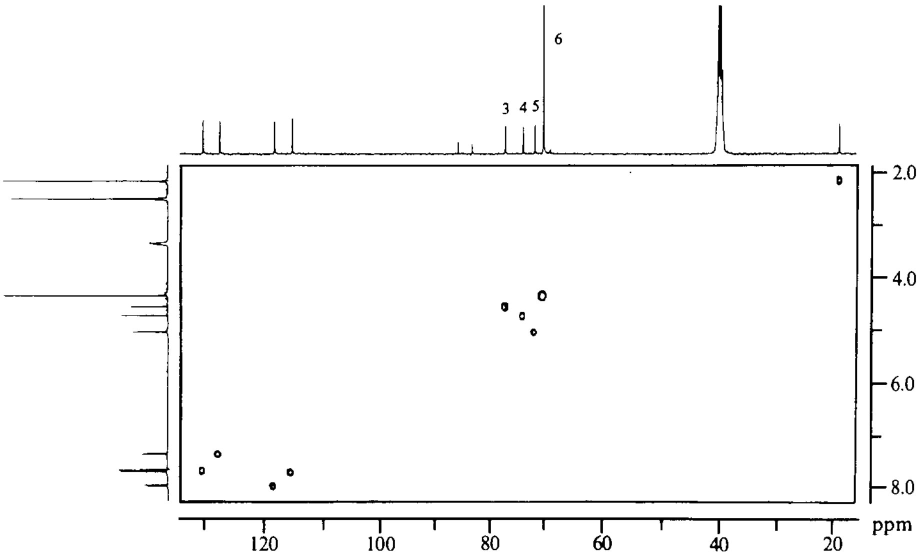

Fig. 2. C,H-COSY spectrum of **2k**.

Table 3
Results of linear correlations for ^{13}C chemical shifts δ with Hammett constants σ

$\delta_1(C(1)) = 84.40 - 1.39\sigma$	$N = 10$	$r = 0.995$
$\delta_1(C(2)) = 81.68 + 0.56\sigma$	$N = 10$	$r = 0.975$
$\delta_1(C(3)) = 76.63 + 1.29\sigma$	$N = 8$	$r = 0.993$
$\delta_1(C(4)) = 73.89 + 1.19\sigma$	$N = 10$	$r = 0.987$
$\delta_1(C(5)) = 72.37 + 1.15\sigma$	$N = 10$	$r = 0.994$
$\delta_1(C(6)) = 69.77 + 0.36\sigma$	$N = 10$	$r = 0.987$
$\delta_1(C(7)) = 159.46 + 5.45\sigma$	$N = 10$	$r = 0.985$
$\delta_2(C(1)) = 86.63 - 1.37\sigma$	$N = 9$	$r = 0.993$
$\delta_2(C(2)) = 82.24 + 0.62\sigma$	$N = 10$	$r = 0.916$
$\delta_2(C(3)) = 76.45 + 0.81\sigma$	$N = 7$	$r = 0.984$
$\delta_2(C(4)) = 73.84 + 0.70\sigma$	$N = 10$	$r = 0.972$
$\delta_2(C(5)) = 71.00 + 0.62\sigma$	$N = 10$	$r = 0.984$
$\delta_2(C(6)) = 69.94 + 0.25\sigma$	$N = 10$	$r = 0.953$
$\delta_2(C(7)) = 169.20 + 2.75\sigma$	$N = 9$	$r = 0.990$
$\delta_3(C(1)) = 86.54 - 1.60\sigma$	$N = 10$	$r = 0.994$
$\delta_3(C(2)) = 82.78 + 0.53\sigma$	$N = 10$	$r = 0.958$
$\delta_3(C(3)) = 76.94 + 0.83\sigma$	$N = 6$	$r = 0.995$
$\delta_3(C(4)) = 74.09 + 0.74\sigma$	$N = 10$	$r = 0.992$
$\delta_3(C(5)) = 73.53 + 0.68\sigma$	$N = 10$	$r = 0.989$
$\delta_3(C(6)) = 70.13 + 0.28\sigma$	$N = 10$	$r = 0.976$
$\delta_3(C(7)) = 171.02 + 4.75\sigma$	$N = 10$	$r = 0.996$
$\delta_3(C(8)) = 136.42 - 1.54\sigma$	$N = 10$	$r = 0.998$
$\delta_3(C(10)) = 128.15 - 0.17\sigma$	$N = 10$	$r = 0.883$
$\delta_3(C(11)) = 128.82 + 0.64\sigma$	$N = 10$	$r = 0.969$

N, number of substituents in regression analysis; *r*, correlation coefficient.

plane is 88.0°, almost perpendicular to each other, which is much higher than that for **1a** (51.97°) [10]. Recent determination of the crystal structure for **3c** revealed a twist angle of 72.28° [13], larger than that for **1a** but smaller than that for **2d**. The non-planar nature between the *N*-phenyl ring and the C–C=N–C plane must influence the operation of the resonance processes in the transmission of the substituent effects and, obviously, as the θ value increases, the fewer resonance processes operate; as a result, the δ value is less sensitive to the substituent effects. The good to excellent linear correlations between δ and σ indicate that besides the polar effects of substituents the resonance effects are more or less operational in these non-planar systems.

Another interesting feature of the data in Table 3 is that the sensitivity for the different positions of the same kind of compound to the substituent effects shows a small but obvious variation, the order of the sensitivity being c(1) > c(3) > c(4) > c(5) > c(2) and it is noteworthy that c(1) is much more sensitive than the other carbon atoms in **2** and **3**, while c(2) is much less sensitive in comparison with the other carbon atoms in 1; this may be because of the different types of the two carbon atoms from that of the other carbon atoms and thus the different manners in which the substituents affect the two carbon atoms. Of all the carbon atoms considered (Table 3), c(7) is most sensitive to the substituent effects and c(6) is least sensitive; the former is attributed to the fact that c(7) is nearest to the substituent and thus very susceptible to changes in the substituent; the latter is therefore because c(6) is farthest from the substituent and probably also because of the difficulty with which the substituent effect is transmitted heteroannularly. Even so, it can be seen from the good correlations between shifts of c(6) and the σ values that the electronic effect appears to be transmitted through the iron atom.

In **3**, as anticipated, c(8) shows a sensitivity to the nature of the substituent comparable with c(1) (with the slope of −1.54 vs. −1.60, the ^{13}C NMR behaviours of the two carbon atoms are the same. When compared with c(3), c(4) and c(5), the shifts of c(9), c(10) and c(11) show a narrower variation. There is no correlation between the shifts of c(9) and the σ values and only a moderately satisfactory Hammett correlation exists between the shifts of c(10) and the σ values. A good correlation between the shifts of c(11) and σ has been found. It can be noted that the substituent effects on the carbons of the *C*-phenyl ring in **3** are quite complex, which may be due to the large twist angle of the *C*-phenyl ring out of the C–C=N–C plane [13], and furthermore the angle could vary with substituents. The *para*-methoxy group showed overall the effect of an electron-withdrawing group in **3a** but not the usual electron-donating group. This indicates that the effects other than resonance are predominant.

In conclusion, for the cyclomercurated ferrocenylimines it has been shown that ^{13}C NMR gives some information concerning the twist angle of the *N*-phenyl ring out of the C–C=N–C plane and the transmission of the substituent effects in the non-planar systems. The present study shows that the order of sensitivity of different positions in the substituted Cp ring to the electronic effects is c(1) > c(3) > c(4) > c(5) > c(2) and electronic effects appear to be transmitted through the metal atom but not very efficiently.

3. Experimental section

The cyclomercurated ferrocenylimines were prepared by methods given in the literature [10,12,14]. The ^{13}C NMR spectra of **1** and **2** were recorded on a Bruker AM 400 spectrometer, and those of **3** on a Bruker AC-80 spectrometer, using $CDCl_3$ as solvent. For all spectra the proton noise decoupling technique was used. The DEPT and C,H-COSY spectra of **2k** were obtained with the Bruker AM 400 spectrometer and using DMSO-d_6 as solvent.

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