Journal of Organometallic Chemistry, 270 (1984) 221–228
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

MÖSSBAUER SPECTROSCOPY OF FERROCENE COMPLEXES

XIII *. CONFORMATIONAL ANALYSIS OF ARYLFERROCENES USING MÖSSBAUER, ^{1}H NMR, AND ^{13}C NMR SPECTROSCOPY

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(Received March 20th, 1984)

Summary

A series of arylferrocenes (FcC_6H_4X) have been studied using ^{1}H and ^{13}C NMR spectroscopy as well as ^{57}Fe Mössbauer spectroscopy. The H_β resonances $\delta(H_\beta)$ gave a biphasic plot against both σ and σ^+, electron-withdrawing groups having about three times the effect of electron releasing substituents. For *ortho*-phenyl derivatives $\delta(H_\beta)$ was relatively insensitive to the nature of the substituent, but $\delta(H_\alpha)$ varied significantly. The effect is discussed in terms of twist angle θ between the phenyl and cyclopentadienyl rings.

From ^{13}C data, average values of the ferrocenyl substituent effect on the chemical shifts (CCS) of the phenyl carbons was evaluated. From a plot of the values for the *para* carbon vs. σ and σ^+ for monosubstituted benzenes, σ and σ^+ values for the ferrocenyl substituent of -0.01 and -0.19, respectively, were found. This indicates that the ferrocenyl substituent is not a particularly strong electron releaser in this system.

Further comparison of CCS data with those for the related biphenyls enabled an assessment to be made of θ for *meta* and *para* substituents. θ values for the *ortho* derivatives were discussed in a qualitative manner.

Mössbauer data reveal a small mesomeric effect on the quadrupole splitting (QS) of the *para* substituted derivatives. These splittings were significantly lower than that of ferrocene. The introduction of an *ortho* substituent of any nature resulted in QS values very close to ferrocene. These results were also discussed in terms of changes in θ.

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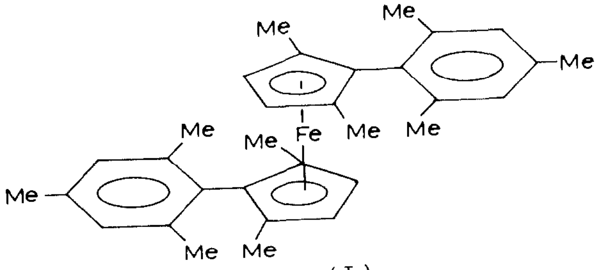
Introduction

In previous papers in this series we have reported a systematic study of ferrocene derivatives by Mössbauer and NMR spectroscopy covering a wide range of structural types [2]. One of the salient features to emerge from this work was that conjugate electron withdrawal via ligand-based orbitals (e_1) resulted in a significant diminution of quadrupole splitting (QS) values, whereas marked increases occurred for electron withdrawal via iron-based orbitals (e_2). Our attention has now turned to the arylferrocenes, which both provide yet another test for the above postulate and also present some interesting stereochemistry redolent of biphenyl derivatives. The structures of the latter have very recently been investigated [3] using ^{13}C NMR in an attempt to estimate interplanar angles θ by methods previously adopted for the ferrocenyl ketones [4]. Arylferrocenes were first synthesised after the discovery of ferrocene itself [5,6] and although some important properties such as redox potentials [7,8,9] amd ^{1}H NMR [10] have been reported there has been little work relevant to their structures. Mössbauer data appears sporadically in the literature [11] but not in any systematic manner. Although a recent ^{13}C NMR study has dealt with some *meta* and *para* substituted derivatives [12], no attempt was made to estimate the effect of ring twist.

Two crystal structures have been reported. 2-Biphenylferrocene [13] has the first phenyl ring twisted 43° out of the cyclopentadienyl (Cp) ring plane. The second makes an angle of 58° with that of the first. Very recently the structure of 1,1′,3,3′-tetramethyl-2,2′-bis(2,4,6-trimethylphenyl)ferrocene (I) has been elucidated.



(I)

This interesting molecule clearly suffers severe steric hindrance between the methyl substituents on the Cp and phenyl rings resulting in the two ring systems adopting an orthogonal disposition to one another. The compressions resulting from the above interaction is alleviated by a distortion of the mesityl–Cp bond 20° out of the Cp plane.

In this paper we report ^{1}H, ^{13}C NMR spectra and Mössbauer data for a range of *ortho*-, *meta*- and *para*-substituted arylferrocenes.

Results and discussion

A series of substituted arylferrocenes (FcC_6H_4X, X = *o*-Me, *m*-Me, *p*-Me; *o*-OMe, *m*-OMe, *p*-OMe; *o*-NO_2, *m*-NO_2, *p*-NO_2) were prepared via the appropriate diazonium salt [6,7,8]. The use of THF as a co-solvent enabled solution of all the reactants and results in rather fewer biproducts, though yields were not substantially improved (10–20%).

^1H NMR and ^{13}C NMR spectroscopy

Table 1 lists the ^{1}H NMR spectra. From this data it is clear that the Cp resonance is not very sensitive to substituent effects in the phenyl ring. The β position has been shown to be analogous to the *para* position in benzene derivatives [15] and might be expected to respond in an analogous manner to substituent effects. Toma et al. [10] have presented ^{1}H NMR data for a series of *meta*- and *para*-monosubstituted derivatives of phenylferrocenes. They found that only a moderately satisfactory Hammett correlation existed using normal σ value ($r = 0.868$ $N = 28$ (data points)) which was improved somewhat by arbitrarily removing three of the data points. On examining the values for δ_β it is clear that the data can be fitted to two separate lines for both σ and σ^+ correlations, one for all the electron releasing substituents ($r = 0.937$, $\rho = 0.071$, $N = 7$ points (σ); $r = 0.904$, $\rho = 0.036$, $N = 10$ (σ^+)) and the other for electron-withdrawing groups ($r = 0.909$, $\rho = 0.225$, $N = 16$ (σ); $r = 0.950$, $\rho = 0.133$, $N = 14$ (σ^+))].

For either σ or σ^+ correlations, the slopes of the two lines are markedly different, the electron-withdrawing series having 3–3.5 times larger slopes. This anomalous behaviour can be rationalised as follows. The Cp ring is an electron-releasing structure (vide infra). Thus electron-releasing substituents in the phenyl ring will be electronically incompatible, resulting in only a weak sensitivity to such aryl-substituent effects. The converse will be true for electron-attracting substituents. Any quantitative assessments of such an effect is hampered by ring twisting between the Cp and phenyl rings. Substituents which are electronically compatible with the Cp ring can gain in resonance energy at the expense of some distortion of the *ortho* hydrogens and hence adopt a lower θ value. One other interesting feature of the data in Table 1 are the δ values for the *ortho*-substituted derivatives. As anticipated, the shifts of the β hydrogens are relatively insensitive to the nature of the *ortho* substituent. However, the α protons show a much wider variation. There is no correlation between the shifts and σ_I values indicating that effects other than inductive processes are operational. The twist angle θ would vary with the sub-

TABLE 1

^{1}H NMR DATA (chemical shift δ in ppm from TMS as internal standard) FOR A SERIES OF SUBSTITUTED PHENYL FERROCENES FcC_6H_4X IN CCl_4

X	C(2,5)	C(3,4)	C	others	
1 *p*-CH_3	4.48	4.18	3.90	CH_3	2.31
				Ph	6.9, 7.03, 7.2, 7.33
2 *m*-CH_3	4.50	4.18	3.90	CH_3	2.32
				Ph	6.8-7.65
3 *o*-CH_3	4.38	4.18	4.04	CH_3	2.30
4 *p*-NO_2	4.64	4.40	3.99	Ph	7.40, 7.58, 8.18, 8.02
5 *m*-NO_2	4.62	4.30	3.99	Ph	7.20–7.80
6 *o*-NO_2	4.41	4.30	3.99	Ph	7.20–7.80
7 *p*-OCH_3	4.42	4.12	3.90	OCH_3	3.75
				Ph	6.65, 6.80, 7.24, 7.39
8 *m*-OCH_3	4.50	4.12	3.89	OCH_3	3.74
				Ph	6.6–7.5
9 *o*-OCH_3	4.67	4.14	3.95	OCH_3	3.87
10 H	4.58	4.22	3.99		

TABLE 2

^{13}C SHIFTS [a] (ppm from TMS) FOR SUBSTITUTED PHENYLFERROCENES FcC_6H_4X IN SOLVENT CS_2

X	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C′(1)	C′(3,4) [b]	C′(2,5) [b]	Cp	Me
p-Me	136 38	126.45	129.44	135.39	129.44	126.45	86.01	69.37	66.89	70.17	21.82
	(136.8)	(125.5)	(128.9)	(134.9)	(128.9)	(125.5)	–	–	–	–	–
m-Me	139.30	127.17	137.62	127.17	128.67	123.81	85.86	69.48	67.04	70.19	22.04
	(139.6)	(126.3)	(137.1)	(126.7)	(128.1)	(122.8)	–	–	–	–	–
o-Me	136.75	134.86	130.07	125.79	125.14 [c]	129.93 [c]	86.94	69.48	67.80	69.30	21.05
	(140.4)	(134.5)	(128.9)	(125.9)	(125.3)	(125.5)	–	–	–	–	–
p-NO_2	146.07	126.18	123.94	147.73	123.94	126.18	82.28	71.17	67.82	70.68	–
	(145.5)	(126.0)	(123.4)	(146.0)	(123.4)	(126.0)	–	–	–	–	–
m-NO_2	142.44	120.67	148.98	120.67	129.35	131.48	82.86	70.57	67.43	70.48	–
	(140.6)	(120.8)	(148.2)	(121.2)	(129.1)	(131.4)	–	–	–	–	–
o-NO_2	133.28	150.06	123.42	130.72	132.03	126.65	81.31	70.01	69.43	70.55	–
	(134.9)	(145.6)	(123.4)	(126.9)	(134.0)	(126.5)	–	–	–	–	–
p-OMe	131.38	127.42	114.27	158.35	114.27	127.42	86.17	69.15	67.83	70.07	55.07
	(132.0)	(126.6)	(114.2)	(157.4)	(114.2)	(126.6)	–	–	–	–	–
m-OMe	140.84	111.50	159.90	112.53	129.53	119.17	85.63	69.55	67.19	70.24	54.97
	(140.7)	(111.2)	(159.6)	(111.6)	(129.2)	(117.9)	–	–	–	–	–
o-OMe	127.76	156.85	111.42	129.41	121.13	127.31	82.95	69.44	68.98	69.99	55.29
	(127.2)	(157.0)	(113.8)	(127.0)	(120.5)	(126.6)	–	–	–	–	–
H	139.40	126.35	128.68	126.45	128.68	126.35	85.72	69.59	67.07	70.22	–
	(139.7)	(125.6)	(128.2)	(126.0)	(128.2)	(125.6)	–	–	–	–	–

[a] Calculated values in parentheses. [b] Assignments according to ref 23 and 24. [c] Assignments tentative.

stituent and would depend on its steric bulk. Thus θ should increase in the order $H < OMe < NO_2 < CH_3$ [16,17]. Since the anisotropy of the phenyl ring varies as a $\cos^2\theta$ function of the interplanar angle, the higher θ the lower the deshielding [18]. This trend would give the sequence of chemical shifts as $H > OMe > NO_2 > CH_3$ which compares fairly well with the observed trend of $OMe > H > NO_2 > CH_3$ and is not in accord with the inductive sequence $NO_2 > OMe > H > Me$. ^{13}C chemical shifts (δ(C)) appear in Table 2. Apart from the *ortho*-substituted derivatives, there is good agreement between the calculated values (obtained using additivity rules [19]) and those observed. By comparing the data for the phenylferrocenes [12] with those of the corresponding monosubstituted benzenes [20] (Table 3) it is possible to evaluate the effect of a ferrocenyl substituent on the δ(C) values for the phenyl ring. The following average effects were found: Cl ($N = 11$), 11.1 ± 1.0; *ortho* ($N = 16$), -3.0 ± 0.8; *meta* ($N = 15$), -0.4 ± 0.4; *para* ($N = 11$), -2.6 ± 0.9.

Plots of *para*-substituent effects Δ_p [$\delta(C(4)) - \delta(C(1))$] (using data in ref. 21) in monosubstituted benzenes show a better correlation with σ^+ ($r = 0.976$, $N = 21$) than with σ ($r = 0.929$, $N = 25$) yielding eq. 1 and 2 (benzenes):

$$\Delta_p = 11.42\sigma - 2.46 \tag{1}$$

$$\Delta_p = 6.31\sigma^+ - 1.43 \tag{2}$$

Using the value of Δ_p of -2.6 ppm for a ferrocenyl substituent σ and σ^+ values of -0.01 and -0.19 are found. This indicates that, at least for these ferrocenylarenes, the ferrocene moiety does not act as a very powerful electron-releasing substituent, behaving in fact very like a phenyl substituent ($\sigma = 0.01$, $\sigma^+ = -0.18$). This in turn mean that the electrons in the Cp rings are held by the central iron atom. Such an effect is in keeping with the preferred stabilisation of ferrocenylcarbenium ions by e_2 rather than Cp-based e_1 orbitals. The carbenium ions would have a similar stereochemistry to the phenylferrocenes in terms of steric hindrance to coplanarity.

Δ_p[i.e. $\delta(C(1)^X) - \delta(C(1)^H)$] for the phenyl ferrocenes also correlates much better with σ^+ ($r = 0.978$, $N = 15$, [12]) than with σ ($r = 0.897$, $N = 16$) leading to the relationships 3 and 4 (phenylferrocenes).

$$\Delta_p = 12.3\sigma - 1.64 \tag{3}$$

$$\Delta_p = 7.51\sigma^+ - 0.64 \tag{4}$$

Similar treatment of data for monosubstituted biphenyls [20] again shows better correlation with σ^+ ($r = 0.982$, $N = 13$) than σ ($r = 0.944$, $N = 13$) yielding the equations 5 and 6 (biphenyls).

$$\Delta_p = 12.66\sigma - 2.67 \tag{5}$$

$$\Delta_p = 7.35\sigma^+ - 0.64 \tag{6}$$

The agreement in behaviour between the phenylferrocenes (eq. 3, 4) and the corresponding biphenyls (eq. 5, 6) is remarkable, indicating a very similar geometry. We thus conclude that the interplanar angle (θ) is about the same in both systems (~ 30°, [3]) since the anisotropic ring current effect from the neighbouring ring is a function of θ.

The biphasic nature of the Hammet plots of $\delta(H_\beta)$ has already been noted above. $\delta(C_\beta)$ shows similar behaviour. Thus for σ^+ correlations for electron-donating groups ($r = 0.943$, $N = 6$), a ρ value of 0.39 is found compared with that of 1.40 for electron-releasing substituents ($r = 0.967$, $N = 12$). For σ correlation electron-donating substituents show a ρ value of 0.84 ($r = 0.930$, $N = 7$), whilst electron withdrawing groups give a ρ value of 2.25 ($r = 0.859$, $N = 12$). Just as for H_β correlations, the ρ values for the electron-withdrawing groups are about three times those of the electron releasers. There is, therefore, a very good correlation between the ^1H and ^{13}C chemical shifts for the β position ($r = 0.971$, $N = 18$).

ortho-Phenyl substituents have a marked effect on the Δ values largely as a result of large differences in $\delta(C'(1))$. This must be due to both changes in θ and in the inductive effect of the *ortho* substituent. Although the data is very limited, there appears to be a reasonably good correlation of $\delta(C'(1))$ with σ_I values ($r = 0.95$, $N = 4$). It is difficult to make estimates of θ for the *ortho*-substituted compounds by the method of Dhami and Stothers [22] since ^{13}C chemical shifts for the cases where $\theta = 0$ and 90° are not known and the shift data itself is rather scanty.

One other point of interest is that there is a better correlation of the shifts of the unsubstituted Cp ring [12] for *meta* and *para* derivatives with σ^+ ($r = 0.942$, $N = 14$, $\rho = 0.44$) than with σ ($r = 0.917$, $N = 14$). For the *ortho* series again an excellent correlation is found with σ^+ ($r = 0.998$, $N = 4$) but with a significantly lower slope (0.28).

Electronic effects therefore appear to be transmitted through the metal atom, the reduced ρ value for the *ortho* series being due to the increased angle of twist.

Mössbauer Spectroscopy

Mössbauer data for the arylferrocenes used in this study appear in Table 3. Isomer shifts did not vary significantly in this series and quadrupole splittings (*QS*) were temperature independent. For the *para* derivatives there is some evidence that mesomeric effects are operative cf. *QS* values of 2.26 and 2.36 mm s^{-1} for *p*-NO_2 and *p*-Me substituents (*QS* of phenylferrocene is 2.30 mm s^{-1}). The order is that expected since conjugated electron-withdrawing groups are known to decrease *QS*

TABLE 3

^{57}Fe MOSSBAUER PARAMETERS (isomer shifts, *IS* mm s^{-1} and quadrupole splittings, *QS* mm s^{-1}) FOR SUBSTITUTED PHENYLFERROCENES FcC_6H_4X

X	*T*(K)	*QS*	*IS*
H	80	2.30(2)	0.52(2)
p-Me	80	2.36(2)	0.50(2)
m-Me	80	2.38(2)	0.50(2)
o-Me	80	2.42(2)	0.50(2)
p-OMe	80	2.31(2)	0.53(2)
	298	2.32(2)	0.50(2)
m-OMe	80	2.31(2)	0.53(2)
o-OMe	80	2.37(2)	0.54(2)
	298	2.35(1)	0.50(1)
p-NO_2	80	2.26(2)	0.53(2)
	298	2.27(2)	0.50(2)
m-NO_2	80	2.31(2)	0.53(2)
	298	2.31(1)	0.50(1)
o-NO_2	80	2.37(2)	0.53(2)

values relative to ferrocene itself [2] (*QS* 2.38 mm s^{-1}). With the exception of the methyl substituent, the *meta* derivatives have identical *QS* to phenylferrocene within experimental error. This is the expected result since the *meta* position is not involved in mesomeric resonance so that the aryl group as a whole would be electronically similar to the parent unsubstituted derivative. *m*-Tolylferrocene is anomalous in this respect and it is not easy to account for its rather high *QS*.

The *ortho* derivatives all show *QS* values very close to ferrocene itself. This may be interpreted as being due to a large twist angle θ (> 40 °?) which disrupts the conjugation. The fact that *o*-OMe and *o*-NO_2 derivatives have identical *QS* values indicates that the now dominant inductive effect (via σ bonds) does not alter the electric field gradient, unlike the mesomeric effect. This is in keeping with the small contribution of the σ orbitals to metal ligand binding [25].

Conclusions

For the arylferrocenes it has been shown that ^1H and ^{13}C NMR give some information concerning the angle of twist. The Mössbauer data show some correlation with mesomeric effects for *para* substituents and the expected lack of change with *meta* substituents. It gives only qualitative evidence for the effect of change of θ for the *ortho* derivatives, in that large angles are indicated causing σ bond (inductive) effects to dominate and which have very minor effects on the Mössbauer parameters.

Experimental

The arylferrocenes were prepared by literature methods [6–8], with the modification that THF was used as a co-solvent instead of acetic acid or CH_2Cl_2. The crude mixtures were chromatographed and the first bands subjected to steam distillation to remove the rather large quantities of unreacted ferrocene. The residues were rechromatographed on alumina to give the pure arylferrocenes. The most troublesome derivative was the *ortho*-nitrophenylferrocene which had to be chromatographed several times before a pure sample was obtained.

^1H NMR were run on a Varian EM 360 instrument and ^{13}C NMR on a Bruker WP 80 FT spectrometer.

Mössbauer spectra were obtained as described previously [2].

Acknowledgements

The authors wish to thank Mr. C. Frampton, Mr. B. Lukas and Mr. A.S. Wells for running some of the Mössbauer spectra. Thanks are also due to Mrs. J.F. Warmsley for recording the ^{13}C NMR spectra.

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