

# Probing the magnetizability distribution of ferrocene as determined via anisotropic contributions to the NMR shielding and its application to several substituted ferrocenes

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Received (in Montpellier, France) 20th October 1999, Accepted 12th November 1999

Molecular magnetic anisotropies of ferrocene derivatives are derived from solution-state measurements of the Cotton–Mouton and Kerr constants. A calculation is presented of chemical shifts induced at the hydrogen and carbon nuclei, arising from the experimental magnetic anisotropy. Ferrocene, ruthenocene and analogously substituted benzenes were also examined. Comparisons of the chemical shifts were used to probe the effects of metal–carbon bonding in the metallocenes. The experimental chemical shifts for pentamethylferrocene have been interpreted, allowing for magnetic anisotropy contributions, to give carbon atom charges that are in close agreement with predictions from the measured electric dipole moment.

Following recent work<sup>1</sup> in this series,<sup>1–6</sup> the mean magnetizability (or susceptibility),  $\chi$ , for a number of substituted ferrocenes was investigated in terms of a perturbation,  $\lambda$ , to the metal–ring bonding introduced to bring the experimental and predicted results into agreement. It was considered that a more sensitive probe of the magnetic environment of the ferrocenyl nucleus would be the *anisotropy* in the magnetizability,  $\Delta\chi$ , rather than the  $\lambda$  corrections to the isotropic value. Considerable electron reorganization is known to occur along the metal–ring axis in ferrocene and ruthenocene,<sup>6</sup>  $M(\eta^5\text{-C}_5\text{H}_5)_2$ ,  $M = \text{Fe}$  or  $\text{Ru}$ , respectively, following coordination. The purpose of this paper is to explore the magnetic anisotropy and other physical properties of both free and complexed rings in these systems. One such property is the NMR chemical shift, which for the ring nuclei of the cyclopentadienyl rings, displays a significant shielding contribution compared to equivalently substituted benzenes. This shielding can arise from a number of causes, including diamagnetic shielding from the metal or diminution of the classic aromatic ring current.

## Experimental

The solute molar Cotton–Mouton constant at infinite dilution,  ${}_{\infty}(\text{m}C_2)$ , from which the solute magnetizability anisotropy can be derived, is obtained from experimental observables by eqn. (1).<sup>6,7</sup>

$${}_{\infty}(\text{m}C_2) = {}_sC_1(1 - \beta - F\gamma + \delta^\perp)M_2 \quad (1)$$

where subscripts 1 and 2 refer in turn to solvent and solute;  ${}_sC_1$  is the specific Cotton–Mouton constant of the solvent;  $\beta$

and  $\gamma$  are derived from the incremental densities and refractive indices of the solutions of graded concentration,<sup>8</sup> which have been presented earlier;<sup>6,9</sup>  $\delta^\perp$  derives from the incremental Cotton–Mouton constants for the solutions;<sup>10</sup>  $F$  is a solvent constant;<sup>11</sup> and  $M_2$  is the molecular weight of the solute. Some of these parameters for the metallocenes studied here are collected in Table 1.

The substituted ferrocenes were purified<sup>2</sup> by vacuum sublimation and/or recrystallization. Solutions were prepared and manipulated under nitrogen. Cyclohexane, an inert solvent for such studies, was purified and dried by distillation under nitrogen from phosphorus pentoxide.

The NMR chemical shifts of the metallocenes were recorded on either a Joel FX-60Q, XLFT-100 or a Bruker WM-400 spectrometer; all chemical shifts are referenced to TMS. The measured shifts ( $\delta$ ) for the metallocenes and reference benzene compounds are given in Table 2.

## Theoretical

For the axially symmetric molecules investigated, each of which has a threefold or higher-order rotation axis (subscripted  $z$ ), the classical statistical mechanical expression for the Cotton–Mouton constant reduces to:<sup>10,12</sup>

$${}_{\text{m}}C_2 = \frac{N_A\mu_0^2}{270\epsilon_0} \left\{ \Delta\eta + \frac{2}{3k_B T} \Delta\alpha\Delta\chi \right\} \quad (2)$$

where  $N_A$ ,  $k_B$ ,  $\epsilon_0$ ,  $\mu_0$  and  $T$  have their usual meanings,<sup>2</sup>  $\Delta\alpha (= \alpha_{zz} - \alpha_{xx})$  and  $\Delta\chi (= \chi_{zz} - \chi_{xx})$  are the anisotropies in the optical polarizability and susceptibility, respectively. The

**Table 1** Infinite-dilution molar Cotton–Mouton constant,  ${}_{\infty}(\text{m}C_2)$ , and the magnetizability anisotropy,  $\Delta\chi$ , of metallocenes as solutes in cyclohexane<sup>a</sup> at 298 K and 632.8 nm

Metallocene	$10^{15}(\Delta C_{12}/w_2)_{w_2=0}$ / m A <sup>-2</sup>	$\delta^\perp$	$10^{27} {}_{\infty}(\text{m}C_2)_{w_2=0}$ / m <sup>5</sup> A <sup>-2</sup> mol <sup>-1</sup>	$10^{29} \Delta\chi$ / J T <sup>-2</sup> molecule <sup>-1</sup>
Fe( $\eta^5\text{-C}_5\text{Me}_5$ ) <sub>2</sub>	2.25 ± 0.09	−12.9 ± 0.5	33.4 ± 1.4	77.6 ± 3.6
Fe( $\eta^5\text{-C}_5\text{H}_5$ )( $\eta^5\text{-C}_5\text{Me}_5$ )	−2.52 ± 0.21	14.5 ± 1.2	−32.1 ± 2.8	−101 ± 11
Fe( $\eta^5\text{-C}_5\text{H}_5$ ) <sub>2</sub> <sup>c</sup>	−4.33 ± 0.24	24.9 ± 1.4	−39.3 ± 2.1	−92.2 ± 0.6
Fe( $\eta^5\text{-C}_5\text{H}_5$ )( $\eta^5\text{-C}_5\text{Cl}_5$ )	−1.07 ± 0.26	6.2 ± 1.5	−19.5 ± 5.2	−140 ± 40
Ru( $\eta^5\text{-C}_5\text{H}_5$ ) <sub>2</sub> <sup>c</sup>	−2.06 ± 0.22	11.8 ± 1.3	−23.5 ± 2.4	−53.3 ± 6.0

<sup>a</sup> Reliable measurements could not be made for decachloroferrocene due to solubility limitations. <sup>b</sup>  $w_2$  refers to the solute weight fraction. <sup>c</sup> Data from ref. 6.

**Table 2**  $^1\text{H}$  and  $^{13}\text{C}$  NMR solution-state chemical shifts,  $\delta$ , of the metallocenes studied<sup>a</sup>

Molecule	Nucleus	$^{13}\text{C}$ shift/ppm <sup>b</sup>	$^1\text{H}$ shift/ppm
$\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2$	$^*\text{C}_5\text{Me}_5$	78.73	—
	Me	9.84	1.64
$\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)$	$^*\text{C}_5\text{Me}_5$	80.29	—
	$\text{C}_5\text{H}_5$	71.53	3.55
	Me	11.66	1.87
$\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$	$\text{C}_5\text{H}_5$	68.28	4.04
$\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Cl}_5)$	$\text{C}_5\text{Cl}_5$	88.18	—
	$\text{C}_5\text{H}_5$	79.64	4.26
$\text{Fe}(\eta^5\text{-C}_5\text{Cl}_5)_2$ <sup>c</sup>	$\text{C}_5\text{Cl}_5$	90.56	—
$\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$	$\text{C}_6\text{H}_6$	74.90	4.26
$\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$ <sup>c</sup>	$\text{C}_6\text{H}_6$	74.93	4.213 ( $T = 323\text{ K}$ )
			4.223 ( $T = 298\text{ K}$ )
			4.227 ( $T = 278\text{ K}$ )
$\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2$	$\text{C}_5\text{H}_5$	70.42	4.43
$\text{C}_6\text{H}_6$	$\text{C}_6\text{H}_6$	128.79	7.16
$\text{C}_6\text{Me}_6$	$^*\text{C}_6\text{Me}_6$	131.78	—
	Me	16.68	2.14
$\text{C}_6\text{Cl}_6$	$\text{C}_6\text{Cl}_6$	133.15	—

<sup>a</sup> In  $\text{C}_6\text{D}_{12}$  solvent except as noted otherwise. <sup>b</sup> The  $^{13}\text{C}$  shifts, apart from those of  $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2$  and  $\text{C}_6\text{Me}_6$ , are from ref. 9. <sup>c</sup> In  $\text{C}_6\text{D}_6$  solvent.

tensor  $\Delta\eta$ , describing the temperature-independent contribution to the Cotton–Mouton constant, has been shown to be negligible for such highly anisometric systems.<sup>12–14</sup>

To obtain the magnetizability anisotropy from  ${}_m\text{C}_2$ , the sign of the polarizability anisotropy must be known with reference to molecular orthogonal axes. Earlier analysis of the polarizabilities of methylated ferrocenes<sup>9</sup> enabled the sign of  $\Delta\alpha$  to be specified for decamethylferrocene,  $\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2$ . For ferrocene and ruthenocene, the sign of  $\Delta\chi$  had earlier been established from crystal state studies.<sup>6</sup>

In order to develop a physical model that would provide insight into the relationship between experimentally determined  $\Delta\chi$  values and NMR shifts, the following argument was adopted. The chemical shift is often deconvoluted into contributions arising from purely empirical components, *e.g.* local atomic properties or neighbouring environment factors. Of the latter, those originating from the presence of delocalized electrons or due to the presence of a magnetically anisotropic group are the most relevant. We define the term  $\sigma_{\Delta\chi}$  to represent the contribution to the shielding arising from the magnetic anisotropy of a group or bond. This includes the magnetic field arising from electrons not centred on the atom in question or its bonding electrons. McConnell<sup>15</sup> and Pople<sup>16</sup> were the first to quantify this factor. For an axially symmetric group or bond, G, the magnetic point dipole induced at the origin by the randomly oriented magnetic field will produce a secondary field at some nucleus, N, remote from it. Choosing a coordinate system with the major axis along the bond direction, McConnell has advanced the following expression (in SI units)

$$\sigma_{\Delta\chi} = \frac{\Delta\chi}{3R^3} (1 - 3 \cos^2 \theta) \frac{\mu_0}{4\pi} \quad (3)$$

where  $\Delta\chi$  is the magnetic anisotropy of the group or bond G;  $R$  is the distance between the resonant nucleus and the centre of the induced magnetic dipole of G;  $\theta$  is the angle between  $R$  and the symmetry axis of G. Note that for a dipolar field to be an accurate approximation, the distance  $R$  must be large in relation to the orbital radius of G, typically  $R > 0.3\text{ nm}$ .

A more rigorous approach has been advanced by Stiles and co-workers.<sup>17–19</sup> However, for a description of  $\sigma_{\Delta\chi}$  that is suitably tractable in relation to the available data, the treatment of ApSimon and co-workers.<sup>20–23</sup> was preferred. According to this scheme, the dipole is no longer considered a point, but rather is assigned a length  $S$ , which is taken to be 75% of half the bond length. This empirical choice of  $S$  was adopted for

C–C and C–H together with the directional bond magnetic susceptibilities of Davies.<sup>24</sup> The non-point dipole equation in SI units is

$$\sigma_{\Delta\chi} = \frac{\mu_0}{4\pi} \left\{ \left[ \frac{\Delta\chi}{3} \left( \frac{1 - 3 \cos^2 \theta}{R^3} \right) \right] + \frac{S^2}{R^5} \right. \\ \times \left[ \frac{-(\chi_{\parallel} + 2\chi_{\perp})}{2} + 5(\chi_{\parallel} \cos^2 \theta + \chi_{\perp} \sin^2 \theta) \right. \\ \left. \left. - \frac{35}{6}(\chi_{\parallel} \cos^4 \theta + \chi_{\perp} \sin^4 \theta) \right] \right\} \quad (4)$$

where  $\chi_{\parallel}$  is the magnetic susceptibility of the bond along the bond axis,  $\chi_{\perp}$  is the magnetic susceptibility in a direction perpendicular to the bond axis and  $\Delta\chi$  is the magnetic anisotropy, in units of  $\text{J T}^{-2} \text{ molecule}^{-1}$ . The distances  $R$  and  $S$  are in metres,  $\theta$  is the inclination of the vector  $R$  to the axially symmetric bond axis to which  $\chi_{\parallel}$ ,  $\chi_{\perp}$  and  $\Delta\chi$  refer. The point of origin of the induced dipole, of length  $S$ , is chosen to be the centre of the bond. This same origin determines the distance  $R$  to the nucleus being investigated. For the metallocenes the delocalized bonding between the cyclopentadienyl rings and the metal commends the metal–ring distance as the appropriate measure of the bond length. The cyclopentadienyl–metal bond, which contains the magnetically anisotropic C–C linkages as well as bonding to the electron-rich metal, would dominate the molecular anisotropy.

Hence, by using the experimentally determined molecular magnetic anisotropy and mean magnetizability to represent the delocalized metal–ring bond, a reasonable estimate of the chemical shift arising from the magnetically anisotropic metal–ring bond can be ascertained. As was applied to the electric polarizability studies<sup>9</sup> of these axially symmetric molecules (*i.e.*,  $\alpha_{xx} = \alpha_{yy}$  or  $\chi_{xx} = \chi_{yy}$ ), the parallel and perpendicular magnetizability components of the metal–ring bond are derived from the following molecular relations:

$$\chi_{\parallel} = \chi_{zz} = \chi + \frac{2}{3} \Delta\chi \quad (5)$$

$$\chi_{\perp} = \chi_{xx} = \chi - \frac{1}{3} \Delta\chi \quad (6)$$

where  $\chi = (\chi_{zz} + 2\chi_{xx})/3$  and  $\Delta\chi = (\chi_{zz} - \chi_{xx})$  for the axial symmetry present in these molecules.

## Results and discussion

The NMR chemical shift has a dependence upon both the local electric field due to neighbouring dipolar bonds and to the

magnetic anisotropy of the metal–ring bond.<sup>25–28</sup> Contributions arising from higher orders of the electric field are expected to be small for the metallocenes of this study.<sup>29</sup> The geometry of ferrocene is such that the protons and iron atom are on a surface at which the interaction of their atomic charges with the molecular electronic quadrupole moment<sup>30</sup> is nullified, *i.e.* the cone about the iron atom for which  $\theta = \cos^{-1}(1/\sqrt{3}) = 54.7^\circ$ . Due to the structural similarities, this simplification is also expected to apply reasonably well to the persubstituted ferrocenes. The carbon Cp atoms lie very close<sup>31</sup> to this surface (within  $18^\circ$ ). This configuration also means that there will be negligible screening due to a magnetic point dipole centred on the iron atom. The overall result is to make the ring carbons, protons and/or substituents, sensitive probes of the magnetic environment associated with the delocalized metal–ring bond.

The purely electronic contribution to the  $^{13}\text{C}$  NMR shielding would be determined by the charge and associated bond polarization, while effects due to the magnetic anisotropy of bonds can play a significant role for hydrogen atoms.<sup>32,33</sup> For carbon nuclei the effect on the chemical shift due to the contri-

bution arising from  $\sigma_{\Delta\chi}$  (being independent of the nature of the atom) will be a much smaller perturbation, amounting to between 2–10% of the observed chemical shift. The results are compiled in Table 3 for both the proton and carbon nuclei of these molecules.

The difference between the magnetic anisotropies of free and complexed rings can be probed by examining changes in  $\sigma_{\Delta\chi}$  between similarly substituted ferrocene and benzene molecules. The latter represents a close, if imperfect, approximation to the free uncoordinated  $\text{C}_5\text{H}_5$  ligand. For the benzene molecules the magnetic origin is taken to be the centre of the ring, while the induced dipole length is taken as 75% of half the ring radius. These results are presented in Table 4. In absolute magnitude, the largest calculated differences occur in the cyclopentadienyl framework carbon atoms, with a calculated shielding shift of from 1.8 ppm for ferrocene to 12.4 ppm for the methylated carbons of pentamethylferrocene,  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)$ , relative to the carbons of the free benzene ring. Since the ferrocenyl carbons are directly bonded to the iron, it is expected that they would be most affected by the magnetic anisotropy of the metal–ring bond.

**Table 3** The chemical shift arising from the magnetic anisotropy,  $\sigma_{\Delta\chi}$ , of the metal–ring bond and the aromatic benzenoid bond for hydrogen and carbon nuclei

Molecule	$10^{29} \Delta\chi$ /J T <sup>-2</sup> molecule <sup>-1</sup>	$10^{29} \chi_{xx}$ /J T <sup>-2</sup> molecule <sup>-1</sup> <sup>a</sup>	$10^{29} \chi_{zz}$ /J T <sup>-2</sup> molecule <sup>-1</sup> <sup>a</sup>	$S/10^{-10}$ m <sup>b</sup>	$R_H/10^{-10}$ m (°/deg.) <sup>c</sup>	$\sigma_{\Delta\chi}$ ( <sup>1</sup> H)/ppm <sup>c</sup>	$R_H/10^{-10}$ m (°/deg.) <sup>c</sup>	$\sigma_{\Delta\chi}$ ( <sup>13</sup> C)/ppm <sup>c</sup>
$\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2$	$77.6 \pm 3.6$	$-392 \pm 8$	$-314 \pm 9$	0.6233	3.410 (74.2)	Me: $1.00 \pm 0.04$	1.479 (55.8) 2.866 (71.3)	* $\text{C}_5\text{Me}_5$ : $-1.46 \pm 0.19$ Me: $1.74 \pm 0.06$
$\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)$	$-101 \pm 11$	$-253 \pm 12$	$-354 \pm 14$	0.6236 0.6154 0.6154	2.249 (68.9) 3.169 (74.2)	Cp: $-0.10 \pm 0.28$ Me: $-0.34 \pm 0.11$	1.452 (55.1) 1.451 (55.6) 2.839 (72.5)	$\text{C}_5\text{H}_5$ : $-6.91 \pm 0.43$ * $\text{C}_5\text{Me}_5$ : $-6.47 \pm 0.43$ Me: $-0.34 \pm 0.15$
$\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$	$-92.2 \pm 0.6$	$-179 \pm 5$	$-271 \pm 5$	0.6229	2.309 (69.7)	Cp: $-0.44 \pm 0.16$	1.452 (55.6)	$\text{C}_5\text{H}_5$ : $-5.39 \pm 0.26$
$\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Cl}_5)$	$-140 \pm 40$	$-350 \pm 18$	$-490 \pm 29$	0.6229 <sup>d</sup> 0.6236 <sup>e</sup> 0.6154 <sup>e</sup>		Cp: $-0.16 \pm 0.86$ Cp: $-0.15 \pm 0.90$		$\text{C}_5\text{H}_5$ , $\text{C}_5\text{Cl}_5$ : $-9.2 \pm 1.4$ $\text{C}_5\text{H}_5$ : $-9.6 \pm 1.3$ $\text{C}_5\text{Cl}_5$ : $-9.0 \pm 1.3$
$\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2$	$-53.3 \pm 6$	$-280 \pm 6$	$-334 \pm 7$	0.6837	2.524 (68.8)	Cp: $0.60 \pm 0.11$	1.526 (53.3)	$\text{C}_5\text{H}_5$ : $-5.82 \pm 0.21$
$\text{C}_6\text{H}_6$	$-106 \pm 4^f$	$-55.5 \pm 1.7^g$	$-161.5 \pm 2.8$	0.5239	2.481 (90)	$\text{C}_6\text{H}_6$ : $-1.78 \pm 0.09$	1.397 (90)	$\text{C}_6\text{H}_6$ : $-3.55 \pm 0.67$
$\text{C}_6\text{Me}_6$	$-136 \pm 7^f$	$-157 \pm 10^h$	$-294 \pm 11$	0.5213	3.084 (90)	Me: $-1.12 \pm 0.11$	1.39 (90) 2.93 (90)	* $\text{C}_6\text{Me}_6$ : $5.95 \pm 2.2$ Me: $-1.25 \pm 0.13$
$\text{C}_6\text{Cl}_6$	$-144 \pm 10^f$	$-194 \pm 12^i$	$-338 \pm 14$	0.5224			1.393 (90)	$\text{C}_6\text{Cl}_6$ : $9.5 \pm 2.8$

<sup>a</sup> The components  $\chi_{xx}$  and  $\chi_{zz}$  are calculated using eqns. (5) and (6). Values of the mean magnetizability are given in ref. 1. <sup>b</sup> The induced dipole length  $S$  is calculated from 75% of half the metal–cyclopentadienyl ring bond length for the metallocenes with the origin located at the midpoint of this bond. For the benzene compounds,  $S$  is taken as the same ratio of the ring radius (equal to the C–C bond length). The electron diffraction-derived values are used for  $\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2$ ,<sup>37</sup>  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ <sup>31,37</sup> and  $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2$ <sup>31</sup> since they would better reflect the solution-state structure. For  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)$  the crystallographic values derived earlier<sup>2</sup> were employed. <sup>c</sup> The chemical shifts are calculated using eqn. (4) and published geometries<sup>2,31,37–39</sup> where available, or assumed values as outlined in the following table notes *d* and *e*. The quoted uncertainties are based on the errors in  $\Delta\chi$  and  $\chi$ . The symbols Me and Cp refer to the methyl and cyclopentadienyl ring protons respectively, while the asterisked carbon refers to the resonant nucleus. <sup>d</sup> The ferrocene geometry is assumed in  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Cl}_5)$ . <sup>e</sup> In this model the geometry of the  $\text{C}_5\text{H}_5\text{-Fe}$  system is taken to be the same as that of  $\text{C}_5\text{H}_5\text{-Fe}$  of pentamethylferrocene, while that of  $\text{C}_5\text{-Fe}$  in  $\text{C}_5\text{Cl}_5\text{-Fe}$  is analogous to that of  $\text{C}_5\text{Me}_5\text{-Fe}$  in pentamethylferrocene. <sup>f</sup> Ref. 40. <sup>g</sup> Ref. 41. <sup>h</sup> Ref. 42. <sup>i</sup> Ref. 43.

**Table 4** Differences,  $\Delta$ , in the predicted shielding shift,  $\sigma_{\Delta\chi}$ , and the experimental chemical shifts,  $\delta$ , between the ferrocenes and the analogous benzene, hexamethylbenzene or hexachlorobenzene molecules

Metallocene	Benzene	Differences <sup>a</sup> /ppm	H in Me	$\text{C}_n\text{H}_n$ * <sup>b</sup>	C in Me	$\text{C}_n^*\text{Me}_n$	$\text{C}_n^*\text{H}_n$	$\text{C}_n^*\text{Cl}_n$
$\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2$	$\text{C}_6\text{Me}_6$	$\Delta\sigma_{\Delta\chi}$	$2.12 \pm 0.12$	—	$2.99 \pm 0.14$	$-7.41 \pm 2.2$	—	—
		$\Delta\delta$	$-0.50$	—	$-6.84$	$-53.05$	—	—
$\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)$	$\text{C}_6\text{H}_6$ , $\text{C}_6\text{Me}_6$	$\Delta\sigma_{\Delta\chi}$	$0.78 \pm 0.14$	$1.68 \pm 0.29$	$0.91 \pm 0.20$	$-12.4 \pm 2.2$	$-3.36 \pm 0.8$	—
		$\Delta\delta$	$-0.27$	$-3.61$	$-5.02$	$-51.49$	$-57.26$	—
$\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$	$\text{C}_6\text{H}_6$	$\Delta\sigma_{\Delta\chi}$	—	$1.34 \pm 0.18$	—	—	$-1.84 \pm 0.72$	—
		$\Delta\delta$	—	$-3.12$	—	—	$-60.51$	—
$\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Cl}_5)$	$\text{C}_6\text{H}_6$ , $\text{C}_6\text{Cl}_6$	$\Delta\sigma_{\Delta\chi}$	—	$1.63 \pm 0.90$	—	—	$-6.05 \pm 1.46$	$-18.5 \pm 3.1$
		$\Delta\delta$	—	$-2.90$	—	—	$-49.15$	$-44.97$
$\text{Fe}(\eta^5\text{-C}_5\text{Cl}_5)_2$	$\text{C}_6\text{Cl}_6$	$\Delta\sigma_{\Delta\chi}$	—	—	—	—	<sup>d</sup>	—
		$\Delta\delta$	—	—	—	—	—	$-42.59$

<sup>a</sup>  $\Delta$  refers to the difference given by the ferrocene shift minus the corresponding benzene shift; *e.g.* from Table 3, for Me(H) in  $\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2$  relative to  $\text{C}_6\text{Me}_6$ ,  $\Delta\sigma_{\Delta\chi} = 1.00 - (-1.12) \text{ ppm} = 2.12 \text{ ppm}$ .  $\Delta\delta$  is obtained in an analogous manner from the  $\delta$  values in Table 2. The error in  $\Delta\delta$  for protons is  $\pm 0.01 \text{ ppm}$ , while for carbon it is  $\pm 0.05 \text{ ppm}$ ; \* refers to the resonant nucleus. <sup>b</sup>  $n = 5$  refers to the cyclopentadienyl ring while  $n = 6$  refers to the benzene ring. <sup>c</sup> The geometry based on the pentamethylferrocene molecule is used for these calculations. <sup>d</sup> For this molecule the Cotton–Mouton constant could not be determined due to solubility limitations.

**Table 5** Differences,  $\Delta'$ , in the predicted shielding shift,  $\sigma_{\Delta\chi}$ , and the experimental chemical shifts,  $\delta$ , between the pentasubstituted ferrocenes and the analogous persubstituted or unsubstituted ferrocene.

Ferrocene 1	Ferrocene 2	Differences <sup>a</sup> /ppm	H in Me	C <sub>5</sub> H <sub>5</sub> <sup>*</sup>	C in Me	C <sub>5</sub> *Me <sub>5</sub>	C <sub>5</sub> *H <sub>5</sub>	C <sub>5</sub> *Cl <sub>5</sub>
Fe( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )	Fe( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> , Fe( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	$\Delta'\sigma_{\Delta\chi}$ $\Delta'\delta$	$-1.34 \pm 0.12$ 0.23	$0.34 \pm 0.32$ -0.49	$-2.08 \pm 0.16$ 1.82	$-5.01 \pm 0.47$ 1.56	$-1.52 \pm 0.50$ 3.24	—
Fe( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )( $\eta^5$ -C <sub>5</sub> Cl <sub>5</sub> )	Fe( $\eta^5$ -C <sub>5</sub> Cl <sub>5</sub> ) <sub>2</sub> , Fe( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	$\Delta'\sigma_{\Delta\chi}$ $\Delta'\delta$	— —	$0.3 \pm 0.9$ 0.22	— —	— —	$-4.2 \pm 1.3$ 11.35	— -2.38

<sup>a</sup>  $\Delta'$  refers to the difference given by the Ferrocene 1 shift minus the corresponding Ferrocene 2 shift (both from Table 3). The error in  $\Delta'\delta$  for protons is  $\pm 0.01$  ppm, while for carbon it is  $\pm 0.05$  ppm.

Examining the calculated chemical shift differences  $\Delta\sigma_{\Delta\chi}$ , given in Table 4, we observe a relatively large variation upon complexation.

When the  $\Delta\sigma_{\Delta\chi}$  differences are compared to the experimental differences ( $\Delta\delta$ ) for the <sup>13</sup>C resonances in Cp, which range from *ca.* 49 to 60 ppm, it is apparent that some other factor, apart from any magnetic anisotropy dependent shift, causes the major part of the shielding in the complexed species.

It is known, however, that eqns. (3) and (4) are valid within a series of homologous compounds.<sup>34</sup> To examine the validity of our approach, differences between the chemical shifts within the ferrocene derivatives themselves were also obtained and are presented in Table 5. In this Table the differences between calculated and experimental shifts are much smaller and they are of comparable magnitude. For the pentasubstituted molecules, the presence of internal metal–ligand dipole moments of opposite orientation with regard to the protonated cyclopentadienyl ring may generate chemical shifts arising from an electric field contribution that have not been quantified in this treatment.

An independent check is required to test the validity of the model presented. In assessing the contribution of an electric field arising from intramolecular charge separation to the chemical shift of a ring carbon atom, we must consider the factors affecting the observed resonance. As has been indicated by the significant differences between  $\Delta\sigma_{\Delta\chi}$  and  $\Delta\delta$  in Table 4, large shielding contributions arise from bonding to the metal. These factors will be dependant on: (i) the metal orbitals with which the ring carbon interacts, (ii) the nature of the atom bonded to the ring carbon, *i.e.* proton, carbon or chlorine, (iii) the contribution from the magnetic field of the metal–ring bond and (iv) any interannular charge displacement.

A comparison is made of intramolecular charge distributions from experimental dipole moments with those obtained by deconvoluting the <sup>13</sup>C chemical shifts ( $\delta$ ) into component contributions according to eqn. (7):

$$\delta = \sigma_{\Delta\chi} + \sigma_{\text{Electronic}} + \sigma_{\text{Framework}} \quad (7)$$

where  $\delta$  is the experimentally determined NMR chemical shift,  $\sigma_{\Delta\chi}$ , is given in Table 3 and equates to point (iii),  $\sigma_{\text{Electronic}}$  is the screening effect of molecular electronic charges as covered

in point (iv), and  $\sigma_{\text{Framework}}$  covers the screening of the ring carbon arising from bonding to both the iron atom and the ring substituent. The  $\sigma_{\text{Framework}}$  term pertains to the electronic backbone of the molecule and encompasses both points (i) and (ii) above. For example, it can be accounted for in pentamethylferrocene by comparing the <sup>13</sup>C resonances of this molecule with those of ferrocene and decamethylferrocene.

Due to the symmetry and planarity of the Cp ring and the ring substituents of ferrocene, pentamethylferrocene and decamethylferrocene, the experimental dipole moment<sup>3</sup> can be taken to directly reflect the charge difference between the protonated and methylated rings of pentamethylferrocene. A similar approach could not be applied to the chlorinated series since the structures could not be determined<sup>†</sup>; the unavailability of the Cotton–Mouton constant for decachloroferrocene, Fe( $\eta^5$ -C<sub>5</sub>Cl<sub>5</sub>)<sub>2</sub>, also prevented the determination of  $\sigma_{\Delta\chi}$  for this molecule. The following argument is restricted to ferrocene and the methylated ferrocenes.

We define a corrected chemical shift,  $\delta'$ , as the difference between the experimental NMR shift,  $\delta$ , and the magnetic anisotropy contribution,  $\sigma_{\Delta\chi}$ . The difference  $\Delta\delta'$  is that between  $\delta'$  of corresponding C<sub>5</sub>H<sub>5</sub> or C<sub>5</sub>Me<sub>5</sub> rings of pentamethylferrocene, decamethylferrocene and ferrocene resonances. The quantity  $\Delta\delta'$  should then represent the electric field effect  $\sigma_{\text{Electronic}}$  upon the chemical shift for each type of ring. The final difference between the  $\Delta\delta'$  of the protonated and methylated rings will directly report on the charge difference arising from any interannular charge donation. Using the proportionality constant of  $-160$  ppm electron<sup>-1</sup>,<sup>32,35</sup> the  $\Delta\delta'$  in Table 6 will translate to an equivalent electric charge of  $0.011 \pm 0.004$  electrons per carbon atom.

This means that the ring carbon atoms are experiencing a chemical shift arising from a charge of  $0.0112 \pm 0.0043$  electrons. Now turning to the dipole moment data<sup>3</sup> and the crystal structure<sup>2</sup> it is found that the assigned charges, required to reproduce the measured dipole moment of  $(3.00 \pm 0.07) \times 10^{-30}$  C m, are not sensitive to the charge locations within the rings of the molecule. Thus, by fixing a single point charge in the ring or partitioning the charge

<sup>†</sup> Several unsuccessful attempts were made to determine X-ray crystal and electron diffraction structures in our own and other laboratories.

**Table 6** Interannular charge separation and the resultant shielding of the ring carbon atoms of Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>, Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub> and Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)

Metallocene	Ring	$\delta^a$ /ppm	$\sigma_{\Delta\chi}^b$ /ppm	$\delta'^c$ /ppm	$\Delta\delta'^d$ /ppm	$\Delta\delta'(\text{C}_5\text{H}_5) - \Delta\delta'(\text{C}_5\text{Me}_5)^e$
Fe( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	C <sub>5</sub> H <sub>5</sub>	68.28	− 5.39	73.67	4.77 ± 0.50 (C <sub>5</sub> H <sub>5</sub> )	− 1.80 ± 0.69 ppm = 0.011 ± 0.004 electrons
Fe( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )	C <sub>5</sub> H <sub>5</sub>	71.53	− 6.91	78.44		
Fe( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )	C <sub>5</sub> Me <sub>5</sub>	80.29	− 6.47	86.76	6.57 ± 0.47 (C <sub>5</sub> Me <sub>5</sub> )	
Fe( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub>	C <sub>5</sub> Me <sub>5</sub>	78.73	− 1.46	80.19		

<sup>a</sup>  $\delta$  refers to the experimental chemical shift given in Table 2. <sup>b</sup>  $\sigma_{\Delta\chi}$  is given in Table 3. <sup>c</sup>  $\delta'$  is defined to equal  $\delta - \sigma_{\Delta\chi}$  for either the C<sub>5</sub>H<sub>5</sub> or C<sub>5</sub>Me<sub>5</sub> ring systems. <sup>d</sup>  $\Delta\delta'$  is the difference between the pentamethylferrocene ring  $\delta'$  and the corresponding homoannular ferrocene  $\delta'$  value. <sup>e</sup> A proportionality constant of  $-160$  ppm per electron was used to convert the magnetic resonance shift to a corresponding electric charge.

between the ring carbon atoms, we determine a total charge of  $0.056 \pm 0.001$  electrons per ring. Assigning this charge to the ring carbons results in an average ring carbon charge of  $0.0112 \pm 0.0003$  electrons per ring carbon atom, in excellent accord with the value determined from the corrected  $^{13}\text{C}$  resonance differences.

The outcome of this analysis is that the model presented for the  $\sigma_{\Delta\chi}$  determinations is self-consistent and reproduces the magnetic shielding fairly accurately for distances of the order of several bond lengths. Furthermore, the sense of the dipole moment is determined from the chemical shift analysis, such that the negative end is located in the  $\text{C}_5\text{H}_5$  ring of pentamethylferrocene and the positive end lies in the  $\text{C}_5\text{Me}_5$  ring. This is in accord with the hyperconjugative character of alkyl groups,<sup>36</sup> feeding electronic charge into the conjugated aromatic system across to the  $\text{C}_5\text{H}_5$  ring.

## Acknowledgements

Helpful discussions with Associate Professors F. Separovic and M. K. Cooper on the general trend of the NMR parameters and the syntheses, respectively, are gratefully acknowledged. Thanks must go to Professor N. J. Hush for discussing the electric field dependence, to Professor G. L. D. Ritchie for allowing the use of the Cotton–Mouton effect apparatus, and especially to Dr B. Cornell for support and the use of computing facilities.

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Paper a908438j