The aromaticity of ferrocene and some derivatives, ruthenocene and dibenzenechromium as determined *via* ring current assessment and ^{13}C anisotropic contributions to the ^{1}H NMR shielding

Leonidas Phillips,*[a] Frances Separovic[b] and Manuel J. Aroney[c]

[a] *AMBRI Ltd, 126 Greville St Chatswood, Sydney, NSW 2067, Australia*
[b] *School of Chemistry, University of Melbourne, Melbourne, VIC 3010, Australia*
[c] *School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia*

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The concept of aromaticity is examined in terms of a delocalised ring current contribution to the proton NMR shielding of ferrocene and related compounds. The source of the ring current is derived as a delocalised contribution to the experimentally determined chemical shift, where the local contribution is calculated from predictions based on the experimental ^{13}C shielding tensors. Examined are dibenzenechromium, ruthenocene, benzene, hexamethylbenzene and several derivatives of ferrocene with attention to: (i) the effects of complexation of the benzene ring, (ii) the protons in an aliphatic bridge on a ferrocene cyclopentadienyl ring, and (iii) the electric field effects of the permanent electric dipole moment in pentamethylferrocene.

Introduction

Following earlier work[1,2] on the magnetic structure of ferrocene, it was considered that an investigation based on the concept of aromaticity may provide a more intuitive understanding in terms of the ideas of delocalised ring currents and their contribution to the total magnetic chemical shift in this class of compounds. The entire concept of whether the classical notion of a delocalised ring current[3] is even applicable has received much debate. The accepted definition of aromaticity involves the idea of quantum mechanical resonance between several valence bond structures.[4] Attempts to empirically quantify aromaticity in this scheme involves the calculation of the resonance energy from thermodynamic data[5] with the partitioning of this energy to postulated structures[6] and the associated multiple bond character present. The latter can be related to delocalisation of electrons, or the presence of a 'ring-current', formulated semi-classically by Johnson and Bovey[7] then later, quantum mechanically by McWeeney.[8] In this approach a point dipole is introduced and its interaction with the current distribution, induced by the external magnetic field, is assessed *via* perturbation theory. It is this diamagnetic ring current of aromatic molecules that is addressed in this work. Elvidge and Jackman[9] and later Davies,[10] have suggested that if the contribution of the ring current to the shielding of ring protons or substituents can be determined it can be used as a measure of the aromaticity of the system.

A recent review by Lazzeretti[11] examines the development of the various ring current formalisms and their relation to the aromaticity of a molecule. Lazzeretti points out that although ring currents are not directly observable and their existence is not theoretically proven or denied, what we have addressed are the magnetic criteria for aromaticity. These range from enhanced diamagnetic properties such as magnetic exaltation, a topic already addressed by one of us[1] (LP), to enhanced magnetic anisotropy, $\Delta\chi$, a property we investigated[12] in 1983. It should be pointed out that strict agreement between ring current derived diamagnetism and the magnetic anisotropy will not occur due to the neglect of the significant contribution of Van Vleck paramagnetism to the anisotropy. Thus the measured anisotropy is the sum of oppositely signed contributions. The paramagnetic component is an excited state property, thereby making its experimental determination not accessible directly. However, a more negative value of $\Delta\chi$ than that calculated from a calculation based on group additivity for $\Delta\chi$ indicates ring delocalisation and a degree of aromaticity. Quantitation of aromaticity based on this criterion would be difficult. We note here the modelling introduced by Schleyer *et al.*,[13] called nucleus independent chemical shift (NICS), which uses magnetic shielding as a test dipole, calculated at the centre of a ring or positions above the ring. NICS uses *ab initio* calculations to predict the observed shielding arising from a ring current as a grid of absolute shielding values. This same scheme is used by Klod and Kleinpeter[14] to predict the shielding effect of magnetically anisotropic groups such as arene rings or multiple bonds. The presence of a substantially negative NICS value indicates the presence of a diatropic ring current and therefore aromaticity in the system. A NICS calculation has been applied to the organometallic compound benzenechromiumtricarbonyl and compared to that for free benzene,[15] with the finding that complexation does not reduce the aromaticity of benzene. This method appears to be a sensitive and elegant technique for predicting the aromaticity of compounds *via* calculations. Another application of *ab initio* calculations to investigate aromaticity and its relation to ^{1}H NMR shielding is that by Alkorta and Elguero,[16] which also calculates the predicted *total* shielding arising from a ring current.

While the computation of NICS by *ab initio* theory would be an interesting complement and extension to our work (since it represents a different approach to the study of aromaticity), this would entail a large scale theoretical computational investigation that is beyond the scope of this project. Rather, what we have set out to do is report experimental data and use these as input to provide information on the contribution of local effects upon the ^{1}H shielding constant. Hence by comparing this local contribution to the experimentally determined chemical shift, the variation attributed to

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delocalisation effects could be gauged. While *ab initio* theory has the capacity to yield accurate chemical shifts, it is not applicable in the context of this work, since the current computational implementations of the theory evaluate only the total chemical shifts and do not partition them into local and non-local contributions.[17]

We propose to use a scheme whereby the degree of delocalisation is derived semi-empirically once the corrections, arising from local anisotropic contributions due to carbon, are removed from the measured ^{1}H chemical shifts. It is relevant to stress here that this is a partitioning of the measured chemical shift into contributions arising from a delocalised effect, the ring current, and a purely localised property. This treatment is not aimed at predicting the observed shielding of the atoms in the examined molecules as these quantities are accessible experimentally and are given in Table 1 below. The local contribution is calculated from an electron loop treatment, using as experimental input the ^{13}C shielding tensor elements and the molecular structure.

Experimental

The synthesis of the substituted ferrocenes is given elsewhere,[18] while the determination of the solid state NMR spectra was carried out using Bruker CXP 100 and Bruker CXP 300 (Bruker, Rheinstetten, Germany) NMR spectrometers. NMR spectra were acquired using a cross polarization (CP) sequence[19] with the lower frequency instrument used for magic angle spinning[20] (MAS) and the higher field for static powder spectra. The following parameters were used for both instruments: ^{1}H frequency of 90 or 300 MHz, ^{13}C frequency of 22.5 or 75.4 MHz, ^{1}H $\pi/2$ pulse 6.5 μs, contact time 5 ms, recycle time 2 s, typically 400 scans and sweep width 62.5 kHz, with 50 Hz line broadening for static spectra obtained at 268 and 293 K and 12.5 kHz sweep width and 20 Hz line broadening for MAS spectra spun at 4 kHz at room temperature (293 K).

Theory

The ring-current hypothesis was proposed by Pauling[3] to account for the diamagnetic anisotropy of benzene, then later used by Pople[21] to explain the anomalous ^{1}H NMR shift of aromatic compounds. Pople developed the use of a molecular orbital (MO) theory of diamagnetism to describe induced currents on a localised atomic basis, which he extended to conjugated aromatic hydrocarbons.[3] Based on this work he apportioned 30–40% of the diamagnetic anisotropy to local effects, similarly assigning 0.7 ppm of the 1.5 ppm ’aromatic’ shift in benzene to local effects. Sergeev and Grimberg[3] achieved better experimental agreement by introducing a current distribution function into the ring-current hypothesis.

McCollor,[3] using electron donor-acceptor complexes, carried out an experimental investigation of ring current effects in metallocenes. This was manifested in the ^{1}H NMR shift between free and complexed acceptor, indicating ferrocene to have ≈60% and ruthenocene ≈40% of the corresponding benzene shift. These findings are consistent with the presence of ring currents in the cyclopentadienyl rings compatible to the metal ring charges postulated[12] earlier for these compounds.

We propose to use a scheme based on the carbon shielding tensor being used to predict the *localised contribution* to the shielding of a neighbouring proton. The NMR shielding parameter is a second rank tensor, with the trace of the tensor being given by the isotropic solution value. The solution values have been given for the proton and carbon nuclei in an earlier publication.[2] Much more information is contained in the

Table 1 Calculated local anisotropic proton chemical shifts and experimental values

Molecule	σ_{LA}[a]	$\delta^{\mathrm{H}}_{\mathrm{expt}}$[b]	$\delta^{\mathrm{C}}_{\mathrm{expt}}$[b]
$\mathrm{Fe}(\eta^5\text{–}\mathrm{C_5Me_5})_2$[c]	−1.916	1.64	9.843 (Me) 78.734 (*C$_5$Me$_5$)
$\mathrm{Fe}(\eta^5\text{–}\mathrm{C_5H_5})(\eta^5\text{–}\mathrm{C_5Me_5})$[d]	−2.083 (Me)	1.874	11.661
	−8.796 (Cp)	3.546	71.527 (*C$_5$H$_5$) 80.29 (*C$_5$Me$_5$)
$\mathrm{Fe}(\eta^5\text{–}\mathrm{C_5H_5})_2$[e]	−5.492	4.04	68.28
$\mathrm{Fe}(\eta^5\text{–}\mathrm{C_5H_5})_2$[f]	−7.383	4.04	68.28
$\mathrm{Ru}(\eta^5\text{–}\mathrm{C_5H_5})_2$[g]	−4.814	4.43	70.42
$\mathrm{Ru}(\eta^5\text{–}\mathrm{C_5H_5})_2$[h]	−5.377	4.43	70.42
$\mathrm{Cr}(\eta^6\text{–}\mathrm{C_6H_6})_2$[i]	−6.934	4.26	74.903
$\mathrm{Fe}(\eta^5\text{–}\mathrm{C_5H_5})(\eta^5\text{–}\mathrm{C_5H_4CH_2CMe_2CH_2})$[j]	−5.492 (Cp)	4.04	Not Available
	−3.501 (CH$_2^{\mathrm{Endo}}$)	2.55	
	−2.940 (CH$_2^{\mathrm{Exo}}$)	2.18	
	−1.349 (Me$^{\mathrm{Endo}}$)	1.40	
	−1.476 (Me$^{\mathrm{Exo}}$)	1.06	
$\mathrm{C_6Me_6}$ (*C$_6$Me$_6$)[k]	−0.596	2.14	131.78 (*C$_6$Me$_6$) 16.85 (C$_6$*Me$_6$)
$\mathrm{C_6H_6}$[l]	−4.163	7.16	128.79

[a] σ_{LA} is calculated from eqn. (6). Unless otherwise quoted the solid state NMR data is taken from ref. 34. [b] The solvent used for these solution NMR measurements is d$_{12}$-cyclohexane.[2] The experimental chemical shift δ is given relative to TMS = 0 for protons, $\delta^{\mathrm{H}}_{\mathrm{expt}}$, and relative to d$_{12}$-cyclohexane = 26.4 ppm for carbon atoms, $\delta^{\mathrm{C}}_{\mathrm{expt}}$. The relevant carbon atom is asterisked. [c] The X-ray diffraction crystal structure of $\mathrm{Fe}(\eta^5\text{–}\mathrm{C_5Me_5})_2$ is used from ref. 38. [d] The X-ray diffraction crystal structure of $\mathrm{Fe}(\eta^5\text{–}\mathrm{C_5H_5})(\eta^5\text{–}\mathrm{C_5Me_5})$ is used from ref. 18. [e] The electron diffraction gas phase structure of $\mathrm{Fe}(\eta^5\text{–}\mathrm{C_5H_5})_2$ is used,[39] where the molecular Cp rings are assumed to occupy an eclipsed configuration. [f] The neutron diffraction crystal structure of $\mathrm{Fe}(\eta^5\text{–}\mathrm{C_5H_5})_2$ is used,[40] where the molecular Cp rings are assumed to occupy a staggered configuration. [g] The electron diffraction gas phase structure of $\mathrm{Ru}(\eta^5\text{–}\mathrm{C_5H_5})_2$ is used,[41] where the molecular Cp rings are assumed to occupy an eclipsed configuration. [h] The X-ray diffraction crystal structure of $\mathrm{Ru}(\eta^5\text{–}\mathrm{C_5H_5})_2$ is used,[42] where the molecular Cp rings are assumed to occupy an eclipsed configuration. [i] The electron diffraction gas phase structure of $\mathrm{Cr}(\eta^6\text{–}\mathrm{C_6H_6})_2$ is used,[43] where the molecular benzene rings are assumed to occupy an eclipsed configuration. [j] The structural parameters for $\mathrm{Fe}(\eta^5\text{–}\mathrm{C_5H_5})(\eta^5\text{–}\mathrm{C_5H_4CH_2CMe_2CH_2})$ were derived by positioning a hypothetical methylene bridge onto the derived coordinate map of ferrocene. The experimental NMR chemical shifts are quoted[44] for the methylene bridge of the 2,2-dimethyl(1,2)-ferrocenophane molecule, while the Cp resonance is as recorded for $\mathrm{Fe}(\eta^5\text{–}\mathrm{C_5H_5})_2$ in the above Table. [k] The electron diffraction gas phase[45] and the crystal structure[46] of $\mathrm{C_6Me_6}$ are used. The solid state NMR data is taken from ref. 33. [l] The structural data is taken from ref. 47.

unaveraged principal components of the shielding tensor. By carrying out NMR spectroscopy on solid powders a broader signal is obtained, whose envelope shape and position contains information about the chemical shielding tensor components of the nucleus being observed, the local site symmetry, rotational motion, *etc*. Alternate methods employ liquid crystals or nematic solvents for carbon[22] and proton[23] work, or the use of multiple pulse techniques in the solid state for the determination of the proton tensor components for ferrocene.[24]

It is noteworthy that for the protons of ferrocene the least shielded direction is along the metal–ring axis, while for the carbon components, this is assigned as the axis of greatest shielding. The shielding on carbon observed upon complexation, such as when an aromatic benzene ring is bonded to a chromium tricarbonyl complex,[25] is accounted for by the large change in the shielding components within the plane of the ring. This could be interpreted as an increased electron circulation about the radial direction and would rationalise the observed shielding of the protons.

The charge on a proton is determined principally by the charge on the carbon to which it is bonded. Analogously the *anisotropy* in the shielding about a carbon atom will have a strong effect on the shielding of a bound proton. Evaluation of the ^{13}C shielding anisotropy requires the determination of the principal components of the ^{13}C shielding tensor. Experimentally the method of proton-enhanced nuclear induction spectroscopy, or the cross polarization (CP) method, developed by Pines, Gibby and Waugh,[19] is used. A summary of the theory, results and applications of this method is given by Speiss.[26]

To model the effect the large anisotropy associated with aromatic carbon nuclei would have on proton shielding, a free electron loop scheme is used.[27] This localised contribution to the components of the proton shielding are given by the general formula:[28,29]

$$\sigma_{ii}^{\mathrm{H}} = \frac{a}{\pi}\frac{1}{[(a+p)^2+z^2]^{1/2}}\cdot\left[K+\frac{a^2-p^2-z^2}{(a-p)^2+z^2}\cdot E\right]\cdot\sigma_{ii}^{\mathrm{C}} \qquad (1)$$

where σ_{ii}^{H} and σ_{ii}^{C} are the diagonal components of the proton and carbon shielding tensor, respectively. *K* and *E* are complete elliptical integrals of the first and second kind, with argument:

$$k^2 = \frac{4ap}{(a+p)^2+z^2} \qquad (2)$$

To evaluate the elliptical integrals *K* and *E*, either a power series expansion[30] or the application of Gaussian quadrature[31] to approximate the integrals can be employed, thus:

$$\int_a^b \mathrm{f}(x)\mathrm{d}x = \sum_{i=1}^{n} c_i\,\mathrm{f}(x_i) \qquad (3)$$

The computational time using the quadrature is dramatically reduced, with no apparent deviation until much higher series expansions ($n \approx 60$) are employed. The electron current loop has a radius, a, of circulation about each carbon atom, chosen[29] as 0.47 Å, while p and z are cylindrical coordinates.[27]

The second rank shielding tensor of the carbon atom has the three principal directions determined experimentally, thereby allowing the components of the proton tensor to be calculated. Note that this calculation refers only to the *local*-contribution to the proton shielding, which we define as σ_{LA}. Thus, the delocalised contribution, arising from any delocalised electron flow, needs to be determined. Although eqn. (1) can derive all tensor components of the local contribution to the proton tensor, the opinion of the authors in ref. 28 was heeded and only the isotropic value ofσ_{LA} was determined. The isotropic proton shielding is given by averaging the components as follows:

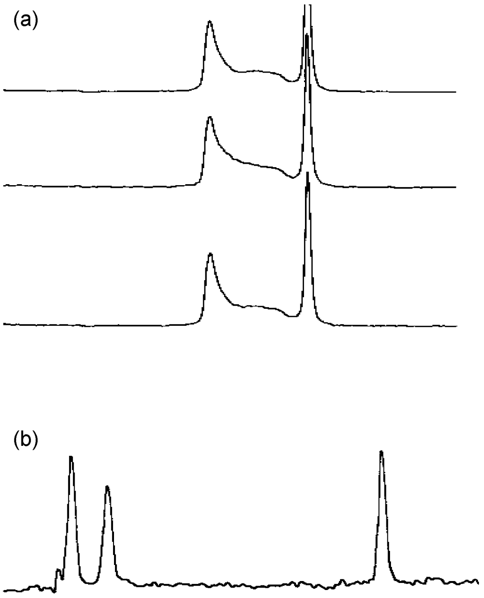

Fig. 1 (a) Solid state static ^{13}C CP NMR spectra of Fe(η^5–C$_5$H$_5$)(η^5–C$_5$Me$_5$) with contact times of 1 (top), 5 and 10 (bottom) ms at room temperature. The horizontal scale is 400 ppm wide. (b) ^{13}C magic angle spinning CP NMR spectrum of Fe(η^5–C$_5$H$_5$)(η^5–C$_5$Me$_5$) at room temperature. The horizontal scale is 100 ppm wide with the peaks on the left from the Cp ring carbons and the one on the right from the methyl carbons.

$$\langle\sigma_{\mathrm{LA}}\rangle = \frac{1}{3}[\sigma_{11}^{\mathrm{H}}+\sigma_{22}^{\mathrm{H}}+\sigma_{33}^{\mathrm{H}}] \qquad (4)$$

This averaging must be taken over three equally probable orientations of the aromatic carbon, that is with the external field perpendicular to the C–H bond, but either perpendicular or parallel to the plane of the ring, respectively, or with the field directed along the C–H bond.

Applying the simplification of axial symmetry to the carbon shielding components, that is $\sigma_{11}^{\mathrm{C}} = \sigma_{22}^{\mathrm{C}}$ (a valid assumption as seen from the ^{13}C powder spectrum in Fig. 1), with the 3 direction being along the highest symmetry axis, reduces eqns. (1) and (4) to:[28]

$$\langle\sigma_{\mathrm{LA}}\rangle = \frac{1}{3}\left\{\frac{a^3\sigma_{11}^{\mathrm{C}}}{[a^2+r_{\mathrm{CH}}^2]^{3/2}} + \frac{a(\sigma_{33}^{\mathrm{C}}+\sigma_{11}^{\mathrm{C}})}{\pi(a+r_{\mathrm{CH}})}\cdot\left[K+\frac{a+r_{\mathrm{CH}}}{a-r_{\mathrm{CH}}}\cdot E\right]\right\} \qquad (5)$$

where r_{CH} is the radial distance from the carbon atom to the proton. In eqn. (5) the absolute values for the ^{13}C shielding components are required. For example, values for organic compounds,[32] alkyl benzenes,[33] metallocenes,[34] or arene chromium tricarbonyl complexes[35] are given relative to liquid benzene. The correction factor used to convert to an absolute scale is the addition of 74 ppm to the quoted value relative to benzene. This factor derives from the difference between an *ab initio* calculation for methane[36] (204.8 ppm) and the isotropic value relative to benzene[37] (130.9 ppm). The value for methane is close to a more recent report[16] that quotes the isolated chemical shift as 195.1 ppm, so the factor of 74 ppm is retained.

The final extension to eqn. (5) is to include the effect of all aromatic carbon atoms upon any given proton. In the metallocene case the expression is taken as the sum over all the ring carbons of both cyclopentadienyl ligands, where r_{CH} is replaced by r_i, the distance from the respective aromatic carbon to the proton in question, with *K* and *E* evaluated accordingly.[28]

$$\langle\sigma_{\mathrm{LA}}\rangle = \frac{1}{3}\sum_{i}\left\{\frac{a^{3}\sigma_{11}^{\mathrm{C}}}{[a^{2}+r_{i}^{2}]^{3/2}} + \frac{a(\sigma_{33}^{\mathrm{C}}+\sigma_{11}^{\mathrm{C}})}{\pi(a+r_{i})}\cdot\left[K+\frac{a+r_{i}}{a-r_{i}}\cdot E\right]\right\} \qquad (6)$$

The ^{13}C components were derived from solid state measurements so, strictly, the possibility of state effects should be considered. Although the proton anisotropy determinations for benzene in the solid and liquid crystal phases[23] differ due to neighbouring intermolecular contributions, this effect is not expected to be as pronounced for carbon nuclei, that is the trace of the ^{13}C shielding components from the solid state shows little variation when compared to the isotropic solution values.[34]

Results and discussion

The results of our solid state measurements reproduce the findings of Pines *et al.*[34] for the molecules ferrocene, ruthenocene and decamethylferrocene although only the room temperature values were determined, hence the departure from axial symmetry, reported for the shielding tensor in decamethylferrocene at low temperature, could not be verified. The spectrum for pentamethylferrocene, again at room temperature and 268 K, showed the same axially symmetric pattern for both the methyl and ring carbon atoms (see Fig. 1). Indeed, the values of the tensor components were barely different from those for the free ferrocene and permethylated derivative, thus the shielding tensors reported for these latter molecules were used in the calculations when referring to the protonated and methylated rings of the pentamethylferrocene molecule. Magic angle spinning experiments were performed on the pentamethylferrocene sample to confirm that the signals were arising from equivalent carbon resonances.

Geometries for ferrocene and ruthenocene were taken from the solid state (X-ray and neutron diffraction) and the gaseous state (electron diffraction), while those for penta- and decamethylferrocene were taken from the solid state. See Table 1 for references. The results of calculations based on eqn. (6) are given in Table 1. The important result emerges from the calculation that by far the largest contribution to the proton screening arises from the directly bonded carbon atom; for benzene and ferrocene it contributes 79% and 48%, respectively.

Dibenzenechromium and benzene

The effect of benzene complexation to a metal is examined by comparing dibenzenechromium and the free ligand ring benzene. If we define a quantity Δ to represent the difference between the complexed and uncomplexed ring in the entries in Table 1, then the following equalities hold:

$$\Delta\sigma_{\mathrm{LA}} = -2.77 \pm 0.12\ \mathrm{ppm} \quad \text{and} \quad \Delta\delta^{\mathrm{H}}{}_{\mathrm{expt}} = -2.90 \pm 0.01\ \mathrm{ppm} \qquad (7)$$

The two difference values are indistinguishable within the cumulative errors, where the error in $\Delta\sigma_{\mathrm{LA}}$ arises from variations in σ_{LA} from geometrically equivalent sites. This close agreement between these difference values indicates that a substantial part of the observed proton shielding variation between the complexed and free benzene ring, long a source of speculation, can be attributed to purely local effects. Thus, there is no need to argue that quenching of the proposed ring current in benzene has occurred upon complexation, nor indeed that it has changed substantially. This finding is in accord with the NICS calculation for benzene in benzenechromiumtricarbonyl.[15] The difference of 0.13 ppm between the expectation values for the two Δ terms would most likely be assignable to a shielding change associated with the chromium atom bonding. Unfortunately, the same comparison can not be made for the metallocene molecules, since the $C_5H_5^-$ or $C_5Me_5^-$ species as aromatic entities do not exist independent of complexation to a counter ion.

2,2-Dimethyl(1,2)ferrocenophane

A more exacting test of the model under investigation would be to monitor the effect upon bonded protons independent of the aromatic framework, yet still within the field of influence of the ferrocenyl nucleus. A suitable choice is the ferrocenophane class of compounds, specifically one where the substituents did *not* involve a bridge between both of the ferrocene rings due to the observed tilt of the rings imposed by the bridge,[48] which would presumably invalidate the use of the proposed carbon tensor values. To this end the 2,2-dimethyl(1,2)ferrocenophane molecule[44] was chosen, where a 3-carbon bridge traverses two adjacent ring carbons on the one ring with the midpoint bridge carbon being permethylated (see Fig. 2). This permits the use of the endo and exo positions of both the CH_2 and methyl group protons, as well as the Cp ring protons, as a probe of the magnetic environment surrounding the complexed cyclopentadienyl rings.

Since there are no solid state ^{13}C NMR data available for this molecule, we assumed that the shielding of the ferrocenyl core is essentially unchanged from that of free ferrocene. Thus, the carbon tensor data for ferrocene were used for 2,2-dimethyl(1,2)ferrocenophane. A plot of the calculated σ_{LA} *versus* the experimental $\delta^{\mathrm{H}}{}_{\mathrm{expt}}$ for the bridge protons is given in Fig. 3. In this graph the calculated values are negative in sign when generated using eqn. (6) while the experimental chemical shifts are positive in sign. Hence the plot of the two will have a negative slope as is seen from Fig. 3. Here the Cp ring proton $\delta^{\mathrm{H}}{}_{\mathrm{expt}}$ chemical shift is represented by the ferrocene value in d_{12}-cyclohexane. Although the plot has a good correlation coefficient ($R^2 = 0.9806$), if the endo methyl group is ignored a significantly better correlation is obtained ($R^2 = 0.9997$) and will be discussed below. The point to note about this plot is that the model of a free electron loop about the aromatic carbon effectively predicts the observed NMR shifts. This implies that any contribution from a delocalised ring current, not already incorporated in the carbon shielding tensor, is substantially invariant. This is in harmony with the result derived from the dibenzenechromium analysis.

In regard to the predicted shielding of the endo methyl group protons—their proximity to the iron atom would enhance shielding due to overlap with metal orbitals of appropriate symmetry. To quantitatively determine the degree of this interaction we take the linear relation described in Fig. 3 (omitting the endo methyl protons), that is:

$$\delta^{\mathrm{H}}{}_{\mathrm{expt}} = -0.7401\ \sigma_{\mathrm{LA}} - 0.02347 \qquad (8)$$

to derive a predicted endo methyl proton shift of 0.975 ppm. From this is subtracted the actual measured value of 1.40 ppm to give a metal shielding contribution of −0.425 ppm.

To further explore the nature of this interaction recourse to a theoretical model is necessary. The model of Buckingham and Stevens[49] describing the NMR spectra of transition metal

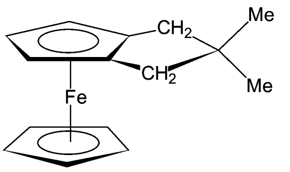

Fig. 2 2,2-Dimethyl(1,2)ferrocenophane.

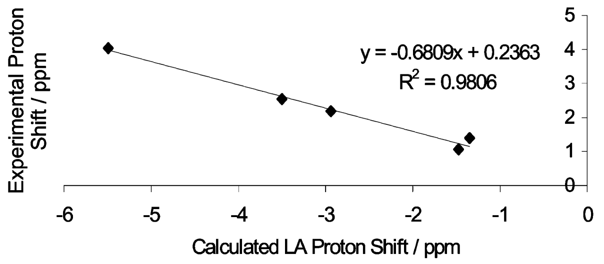

Fig. 3 Plot of σ_{LA} *versus* $\delta^{H}{}_{expt}$ for 2,2-dimethyl(1,2)ferrocenophane.

hydrides is adopted. Although this paper deals with octahedral symmetry, the approximation to the ferrocene geometry is adequate. By converting to the atomic units used in Buckingham's work and for a choice of a d orbital exponent $k = 2.8 \pm 0.2$, a predicted diamagnetic shielding of $\sigma^{d} = 0.043 \pm 0.012$ ppm is obtained. If this diamagnetic contribution is subtracted from the derived metal shielding then a paramagnetic contribution of -0.468 ppm remains. Sources of this paramagnetic shift would be expected from interactions of the proton with suitable 3d metal orbitals and possible metal donation into empty $2p_{\pi}$ orbitals of the attached methyl carbon.

1,2,3,4,5-Pentamethylferrocene

The final extension is to use this model to account for any electronic perturbation arising from the presence of a molecular electric dipole moment. Vector analysis of the moment of pentamethylferrocene has previously been reported in ref. 2. It was found that the observed dipole of $(3.00 \pm 0.07) \times 10^{-30}$ C m can be resolved into a total charge of 0.056 ± 0.001 electrons per ring. Furthermore, this is accurately reproduced by the difference in the chemical shifts of the aromatic ring carbons for each ring, thus:

$$\begin{aligned}\delta^{C}{}_{expt}(C_5H_5) - \delta^{C}{}_{expt}(C_5Me_5) &= 71.527 - 80.290 \text{ ppm} \\ &= -8.763 \text{ ppm} \\ &\equiv 0.055 \text{ electrons}\end{aligned}$$

using a proportionality constant of -160 ppm electron^{-1}.[37,50]

With regard to the proton chemical shifts, the quantity that will also need to be examined is the difference between each type of ring. Once more the difference between the experimental chemical shift and the calculated local anisotropic contribution will reveal any changes arising from any electric field or any changes in the nature of the ring current. However, since the permethylated ring contains only methyl protons, these cannot be directly compared to the ring protons of the C_5H_5 ring. In this case it is necessary to examine the difference between the pentamethylferrocene ring protons and those of ferrocene, while for the methyl protons those of pentamethylferrocene and decamethylferrocene need to be investigated. We define Δ', in Table 2, to refer to the pentamethylferrocene parameters minus those of ferrocene or decamethylferrocene as appropriate.

Table 2 Δ' values for pentamethylferrocene relative to ferrocene or decamethylferrocene

	C_5H_5	C_5Me_5
$\Delta'\delta^{H}$	-0.494	0.234
$\Delta'\sigma_{LA}$	-1.412	-0.167
$\Delta'\delta^{H} - \Delta'\sigma_{LA}$	0.918	0.401
Electron equivalent[a]	0.0962	0.0420
Electron difference	0.054	

[a] The proportionality constant of 9.54 ppm electron^{-1} is used.[51]

From the entries in Table 2 it is apparent that the model employed here produces very satisfactory agreement for the charge separation as determined experimentally by both dipole moment and ^{13}C linear electric field effects. A further corollary that can be drawn from the results in Table 2 is that there appears to be no significant change in any ring current as detected by the chemical shift of the protons.

Conclusion

The most pertinent result to be drawn from the three examples cited is that, within the confines of the model used, there is no discernable change in any contribution to the proton chemical shift that is of a delocalised or ring current nature. If we assume this to be a measure of the aromaticity of the organic frameworks involved, then it can be concluded that, at least for the molecules studied, complexation does not perturb the aromaticity of these ligands within the limitations of the model used.

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