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# A spectroscopic study of bis($\eta^6$-arene)iron(II) salts

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## Abstract

A number of bis($\eta^6$-arene)iron(II) salts have been synthesised from the following ligands: benzene, toluene, ethylbenzene, *ortho, meta* and *para* xylenes, mesitylene, 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene, pentamethylbenzene, and hexamethylbenzene. The stabilities of these complexes in solution vary considerably both with solvent basicity and the degree of alkyl substitution. $^1$H and $^{13}$C NMR data are reported. The observed large upfield shifts of ligand $^{13}$C signals is discussed in terms of shielding by the $d_{z^2}$ electrons of the central iron atom. $^{13}$C shifts correlate reasonably well with the total charge density at the relevant carbon atom for a variety of sandwich complexes, including those discussed in this work. $^{57}$Fe Mössbauer data are presented; quadrupole splittings increase systematically with the number of methyl substituents on the ligands. These changes are explained in terms of imbalances in the electronic population of metal-based $e_2$ and ligand-based $e_1$ orbitals.

## Introduction

Bis-($\eta^6$-arene)iron(II) complexes ($Ar_2Fe^{2+}$) were first reported by Fischer and Böttcher [1], and the synthetic procedure has been modified [2] and improved [3] by Helling et al. The most convenient route involves the reaction of $AlCl_3/FeCl_3$ mixtures in an excess of the refluxing arene, and gives yields in excess of 60%. It is significant that only arenes bearing alkyl substituents have so far yielded bis($\eta^6$-arene)$Fe^{2+}$ complexes. There is a recent report [4] of the synthesis of bis($\eta$-chlorobenzene)iron(II) picrate and related complexes, though this has not yet been substantiated by analytical or spectroscopic data. An alternative synthetic route involves the $AlCl_3$-catalysed cleavage of acylferrocenes [5]. Heterocyclic ligands also give rise to such complexes; thus tetramethylthiophene and $FeCl_2$ in the presence of

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$AlCl_3$ in refluxing cyclohexane gives a 55% yield of bis(tetramethylthiophene)iron(II) hexafluorophosphate [6].

Structural studies are not common. Very recently the crystal structure of bis($\eta^6$-benzene)ruthenium(II) *p*-toluenesulphonate has been published [7]. Eclipsed benzene rings are present, with average C–C bond distances of 1.418 Å. The rings are exactly parallel, and are separated by 3.434 Å.

The Mössbauer spectra of $Ar_2Fe^{2+}$ species have not received systematic treatment. Parameters for the bis(hexamethylbenzene) and bis(benzene) derivatives have appeared [8] but have not been discussed in detail. Likewise very little work has been done on the $^{13}C$ NMR spectra of these complexes. As a part of our continuing programme devoted to structural studies of iron sandwich compounds, we have examined the $Ar_2Fe^{2+}$ complexes from the point of view of $^{57}Fe$ Mössbauer and $^{13}C$ NMR spectroscopy, and report our findings herein.

## Results and discussion

A series of alkyl (mainly methyl) substituted bis($\eta^6$-arene)iron(II) complexes were synthesised by Helling's improved method [3]. For the more heavily substituted derivatives there was evidence of dealkylation and isomerisation if high temperatures were used [9]. Thus the reaction of mesitylene with $FeCl_3/AlCl_3$ with the hydrocarbon as the solvent at 163° gave a mixture of tetramethylbenzene derivatives (77%) and the desired product (23%). When the reaction was conducted at a lower temperature in refluxing cyclohexane (80°) a 78% yield of bis($\eta^6$-mesitylene)iron(II) hexafluorophosphate was obtained. Table 1 lists the preparative details and the analyses of the compounds. Attempts to prepare complexes from the following arenes were unsuccessful: chlorobenzene, chlorotoluene, anisole, nonylbenzene, and 1,3,5-tri(2-propyl)benzene. Dehalogenation was found to occur for the chlorinated aromatics.

Table 1

Preparation of bis($\eta^6$-arene)iron(II) hexafluorophosphates

| Arene | Reaction time (h) [a] | Yield (%) | M.p. (°C) | Analysis (Found (calcd.) (%)) | |
|---|---|---|---|---|---|
| | | | | C | H |
| Mesitylene | 6 | 78 | 230–233 | 36.54<br>(36.88) | 4.23<br>(4.13) |
| 1,2,4,5-Tetramethylbenzene | 8 | 75 | 202–211 | 39.71<br>(39.11) | 4.97<br>(4.59) |
| 1,2,3,5-Tetramethylbenzene | 10 | 73 | 205–210 | 38.0<br>(39.11) | 4.5<br>(4.59) |
| 1,2,3,4-Tetramethylbenzene | 10 | 71 | 201–209 | 39.3<br>(39.11) | 4.8<br>(4.59) |
| Pentamethyl-benzene [b] | 10 | 82 | 201–204 | 43.4<br>(43.59) | 5.3<br>(5.32) |
| Hexamethylbenzene | 12 | 88 | 248–252 | 42.82<br>(43.00) | 5.70<br>(5.41) |
| Ethylbenzene | 6 | 58 | 161–166 | 33.8<br>(34.43) | 4.0<br>(3.61) |

[a] Refluxing cyclohexane. [b] Analysed as the iodide.

All the hexafluorophosphate salts are soluble in common polar organic solvents such as acetone, acetonitrile, and nitromethane. Both solubility and stability in these solvents vary with the nature of the cation. Bis($\eta^6$-benzene)iron(II) hexafluorophosphate decomposes immediately in acetonitrile, but survives much longer in nitromethane. On the other hand, the bis($\eta^6$-hexamethylbenzene) complex is stable for several days in each of the above solvents. The stability of bis($\eta^6$-arene)iron(II) hexafluorophosphates increases with the number of methyl substituents on the ring. Such solvolytic stability can be attributed to either increasing metal ligand bond strength or steric-kinetic factors. For highly alkylated bis($\eta^6$arene)iron(II) hexafluorophosphates such as the hexamethylbenzene, pentamethylbenzene, and tetramethylbenzene complexes, it was possible to replace the $PF_6{}^-$ anion by other anions such as $Cl^-$, $Br^-$, $I^-$, $SO_4{}^{2-}$, $ClO_4{}^-$ and $ClSO_3^-$. However, bis(arene)iron(II) hexafluorophosphate salts with fewer than three methyl substituents decomposed immediately when the anion exchange reactions with the above nucleophiles were attempted. This reflects the stabilising influence of the methyl groups and their ability to provide steric hindrance to nucleophilic attack [10].

The most interesting feature of the infrared spectra is the low value of the carbon–carbon stretching modes in the ring; for the mesitylene complex these appear at 1550 $cm^{-1}$. This is a much lower frequency than that for mesitylene itself (1607 $cm^{-1}$) but higher than that for the $[(\eta^6\text{-mesitylene})FeCp]^+$ $PF_6{}^-$ complex (1542 $cm^{-1}$). This reflects the strong $d_\pi$–$p_\pi$ overlap in the ligand metal bond, which effectively reduces the bond order in the aromatic rings. The lower $\nu$(C=C) value for the $[ArFeCp]^+$ complex reflects the stronger bonding of the arene ligand, as predicted theoretically [11].

$^1H$ and $^{13}C$ chemical shifts are listed in Table 2 together with those of the corresponding $Ar_2Cr^0$, $[ArFeCp]^+$ and free arenes. The bis(benzene)iron(II) complex was too unstable in solvent acetone for recording of a spectrum, and was only slightly soluble in $MeNO_2$. Its $^{13}C$ shift, however, can be estimated from the additivity effects of simple substituents. Thus by comparing the shifts (in $MeNO_2$) for the *m*-xylene, *p*-xylene, and mesitylene complexes, values for the benzene complex can be calculated on the assumption of additivity of substituent effects, as well as the methyl substituent effects at each carbon (*ipso, ortho, meta, para*). These values appear in Table 3. The calculated $\delta$ value for the bis(benzene) complex is 94.9 ppm (cf. 93.4 for solvent acetone-$d_6$), 33.6 ppm upfield from that of benzene itself. It is instructive to compare this complexation shift with that for ferrocene. The cyclopentadienide ion has a shift of 102.1 ppm [17], compared with 68.1 ppm for ferrocene [18], giving a complexation shift of 34.0 ppm, identical within experimental error to that for the benzene ligand. This suggests that there is a common factor involved in producing the observed shielding. MO calculations show that the metal–ligand binding in ferrocene and bis(benzene) $Fe^{2+}$ is rather different [11].

It is unlikely that these changes in bonding would produce exactly the same shielding effects. An alternative explanation is that it is the $d_{z^2}$ electrons which cause the shielding. For both $(C_5H_5)_2Fe$ and $(C_6H_6)_2Fe^{2+}$ species, this filled orbital is not significantly involved in bonding, and the energy level is almost equally populated in each species [11]. Reduction in ring currents [19] would certainly not account for the magnitude of the observed changes in shift. Indeed, if the effect of charge on the shifts is eliminated, the real complexation shifts are much

Table 2

$^{13}$C chemical shifts [a] for benzene ring carbons in bis($\eta^6$-arene)iron(II) hexafluorophosphates; bis($\eta^6$-arene)chromium complexes [b]; ($\eta^6$-arene)($\eta^6$-cyclopentadienyl)iron(II) hexafluorophosphates [c] and free arenes [d] together with $^1$H NMR data [e]

| Arene species | | $^1$C NMR data | | | | | $^1$H NMR data | |
|---|---|---|---|---|---|---|---|---|
| | | C(1) | (C(2) | C(3) | C(4) | C(5) | δ(ArH) | δ(Me) |
| Benzene | $Ar_2Fe^{2+}$ [f] | 94.9 [g] | – | – | – | – | 6.80 | – |
| | $ArFe^{2+}$ [h] | 93.4 [g] | – | – | – | – | – | – |
| | $Ar_2Cr^0$ | 74.6 | – | – | – | – | 4.12 | – |
| | $ArFe^+$ Cp | 87.3 | – | – | – | – | 6.49 | – |
| | Free arene | 128.7 | – | – | – | – | 7.27 | – |
| Toluene | $Ar_2Fe^{2+}$ [h] | [113.4] | 93.3 | 93.6 | 90.0 | – | 6.54 | 2.16 |
| | $Ar_2Cr^0$ | [88.2] | 77.9 | 75.0 | 75.0 | – | 4.16 | 1.98 |
| | $ArFe^+$ Cp | [103.1] | 87.7 | 86.6 | 85.4 | – | 6.40 | 2.55 |
| | Free arene | [137.8] | 129.3 | 128.5 | 125.6 | – | 7.20 | 2.35 |
| *o*-Xylene | $Ar_2Fe^{2+}$ [h] | [110.4] | – | 93.3 | 92.3 | – | – | – |
| | $Ar_2Cr^0$ | [88.6] | – | 79.3 | 76.1 | – | 4.06 | 2.02 |
| | $ArFe^+$ Cp | [101.9] | – | 87.9 | 85.2 | – | – | – |
| | Free arene | [136.4] | – | 129.9 | 126.1 | – | – | – |
| *m*-Xylene | $Ar_2Fe^{2+}$ [f] | [114.0] | 93.6 | – | 92.3 | 94.2 | 6.40 | 2.24 |
| | $Ar_2Fe^{2+}$ [g] | [111.9] | 92.1 | – | 90.8 | 92.8 | – | – |
| | $Ar_2Cr^0$ | [87.9] | 80.5 | – | 77.8 | 75.8 | 4.06 | 2.02 |
| | $ArFe^+$ Cp | [102.4] | 85.8 | – | 85.8 | 88.6 | 6.33 | 2.53 |
| | Free arene | [137.5] | 130.1 | – | 126.4 | 128.3 | 6.95 | 2.30 |
| *p*-Xylene | $Ar_2Fe^{2+}$ [f] | [112.2] | 93.5 | – | – | – | – | – |
| | $Ar_2Fe^{2+}$ [h] | [110.2] | 92.2 | – | – | – | – | – |
| | $Ar_2Cr^0$ | [88.3] | 75.0 | – | – | – | 4.12 | 2.01 |
| | $ArFe^+$ Cp | [101.4] | 87.1 | – | – | – | – | – |
| | Free arene | [134.5] | 129.1 | – | – | – | – | – |
| Mesitylene | $Ar_2Fe^{2+}$ [f] | [113.4] | 91.5 | – | – | – | 6.18 | 2.08 |
| | $Ar_2Fe^{2+}$ [g] | [111.6] | 90.2 | – | – | – | – | – |
| | $Ar_2Cr^0$ | [88.0] | 80.1 | – | – | – | 3.94 | 2.04 |
| | $ArFe^+$ Cp | [101.8] | 86.7 | – | – | – | 6.30 | 2.52 |
| | Free arene | [137.6] | 127.4 | – | – | – | 6.70 | 2.25 |
| Durene | $Ar_2Fe^{2+}$ [g] | [107.1] | – | 93.9 | – | – | 6.16 | 2.20 |
| | Free arene | [133.8] | – | 131.2 | – | – | 6.90 | 2.20 |
| Hexa-methyl-benzene | $Ar_2Fe^{2+}$ [h] | [103.4] | – | – | – | – | – | 2.30 |
| | $Ar_2Cr^0$ [i] | [83.5] | – | – | – | – | – | – |
| | $ArFe^+$ Cp | [98.1] | – | – | – | – | – | 2.58 |
| | Free arene | [132.3] | – | – | – | – | – | 2.20 |

[a] ppm from TMS; quaternary (*ipso*) carbons in parentheses; dashes refer to repeated values. [b] Data from ref. 12, solvent benzene. [c] Data from ref. 13, solvent $CD_3NO_2$. [d] Data from ref. 14 converted using δ($C_6H_6$) 128.7 ppm. [e] Data for $Ar_2Cr^0$ from ref. 15. [f] This work, solvent $CH_3NO_2$. [g] This work, calculated value. [h] This work, solvent $CD_3COCD_3$. [i] Datum from ref. 16, solvent $C_6D_6$.

higher (e.g. 54.2 ppm for ferrocene) [20]. Further evidence of different shielding mechanisms for complexed arenes comes from a comparison of the $^1$H and $^{13}$C chemical shifts of the arene-metal complexes (Table 2) which run roughly parallel. The free arene data do not show this effect.

The *ipso* substituent factors (*Δi*) listed in Table 3 are also worthy of note. These

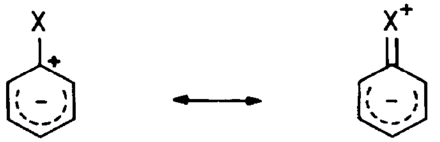
Table 3

Additivity factors $\Delta_n$, ppm [a] for $[Ar_2Fe^{2+}]$, $[Ar_2Cr]$, $[ArFe^+Cp]$ and free arene

| Compound | $B$ [b] | $\Delta_i$ | $\Delta_o$ | $\Delta_m$ | $\Delta_p$ |
|---|---|---|---|---|---|
| $[Ar_2Fe^{2+}]$ [c] | 94.9 | 19.7 | −0.8 | −0.6 | −1.8 |
| $[Ar_2Fe^{2+}]$ [d] | 93.4 | 18.8 | −0.7 | −0.3 | −1.8 |
| $[Ar_2Cr^0]$ [e] | 74.1 | 13.6 | 3.3 | 0.4 | 0.4 |
| $[ArFe^+Cp)$ [c] | 87.3 | 15.8 | 0.4 | −0.7 | −1.9 |
| Free arene | 128.5 | 9.1 | 0.7 | −0.1 | −3.0 |

[a] $\Delta_n$ is the shift relative to the value for the unsubstituted compound. $n = i$ (*ipso*), $o$ (*ortho*), $m$ (*meta*), $p$ (*para*). Negative values upfield from reference. [b] $^{13}C$ shift of unsubstituted derivatives. [c] Solvent nitromethane. [d] Solvent $CD_3COCD_3$. [e] Data from Ref. 13, solvent benzene.

parameters are thought to depend on the contributions of the following canonical forms of the ligated arene [13]:



The greater the charge on the metal, the greater the polarisation of the ligand and hence the greater the positive charge on the *ipso* carbon. The results obtained clearly support this simple postulate. For the $Ar_2Fe^{2+}$ species, there is relatively little difference in the *o*-, *m*-, and *p*-substituent factors, which would be in keeping with the above formulations. The importance of the effect of charge on the metal is nicely illustrated by the data for the neutral chromium species [12], where the values of $\Delta_i$ are significantly lower than the corresponding values for $Ar_2Fe^{2+}$ or $ArFe^+Cp$ species. Transmission of electronic effects to the *para* position is also much reduced in the $Ar_2Cr^0$ complexes. For the $Ar_2Fe^{2+}$ complexes $\Delta\delta_p$ [$= \delta(C(4)) - \delta$(unsubstituted derivative)] for Ar = toluene, *m*-xylene and mesitylene are −1.8, −2.6, and −3.4 ppm, respectively, whereas those for the $Ar_2Cr^0$ species show the reverse trend (+0.4, +3.2, +5.5, respectively). The absence of a normal response to substituents for the chromium analogues indicates a strong quenching of mesomeric substituent effects by metal coordination. This is reflected in the relatively small contribution (42%) of resonance effects in the chromium series compared with that in the free ligand (89%) [12].

There is little difference in the bond orders of the $Ar_2M^0$ and $Ar_2M^{2+}$. Thus the average C–C bond distance in $(C_6H_6)_2Cr^0$ is 1.417(3) Å [21], compared with a value of 1.414(2) Å in $[(C_6H_6)_2Ru]^{2+}(OTs^-)_2$ [17], and thus the argument that complexation shifts are due to changes in hybridisation does not hold. There is a shift difference of 20.8 ppm between $(C_6H_6)_2Fe^{2+}$ and $(C_6H_6)_2Cr^0$, which is very close to that calculated by Ogorodnikova [20] for the effect of charge alone on the complexation shifts (19.2 ppm).

The effect of formal charge on $^{13}C$ shifts of sandwich complexes can be seen in Table 4. Increase in the positive charge on the central metal atom leads to an increase in the $\delta$ value in an approximately linear fashion. For the mixed species, $[ArMCp]^{n+}$, there are average downfield shifts of 20 ± 2 ppm per unit positive charge, but for the more limited data of the symmetrical species the effect is markedly smaller (~10 ppm).

Table 4

$^{13}C$ chemical shifts [a] as a function of formal charge for first row transition metal sandwich complexes with 18 electron configurations

| Ligand 1 | Ligand 2 | Metal | Formal charge | $\delta_1$ | $\delta_2$ | Reference |
|---|---|---|---|---|---|---|
| $C_5Me_5$ | $C_5Me_5$ | Mn | $-1$ | 72.4 | 72.4 | 22 |
| $C_5H_5$ | $C_5H_5$ | Fe | 0 | 67.9 | 67.9 | 23 |
| $C_5Me_5$ | $C_5Me_5$ | Fe | 0 | 79.0 | 79.0 | 18 |
| $C_6H_6$ | $C_6H_6$ | Cr | 0 | 74.6 | 74.6 | 24 |
| $C_6Me_6$ | $C_6Me_6$ | Cr | 0 | 83.5 | 83.5 | 16 |
| $C_6H_6$ | $C_5H_5$ | Fe | $+1$ | 87.3 | 75.6 | 13 |
| $C_6H_6$ | $C_5Me_5$ | Fe | $+1$ | 92.3 | 90.4 | 25 |
| $C_6Me_6$ | $C_5H_5$ | Fe | $+1$ | 98.1 | 77.3 | 13 |
| $C_6Me_6$ | $C_5Me_5$ | Fe | $+1$ | 98.4 | 87.0 | 25 |
| $C_5H_5$ | $C_5H_5$ | Co | $+1$ | 85.0 | 85.0 | 26 |
| $C_6H_6$ | $C_5H_5$ | Co | $+2$ | 107.6 | 97.4 | 27 |
| $C_6H_6$ | $C_5Me_5$ | Co | $+2$ | 107.6 | 112.8 | 27 |
| $C_6Me_6$ | $C_5H_5$ | Co | $+2$ | 119.2 | 96.8 | 27 |
| $C_6H_6$ | $C_6H_6$ | Fe | $+2$ | 94.9 | 94.9 | this work |
| $C_6Me_6$ | $C_6Me_6$ | Fe | $+2$ | 103.4 | 103.4 | this work |

[a] ppm from TMS.

To date no charge density calculations have appeared for the $Ar_2Fe^{2+}$ species. Clack has, however, reported INDO molecular orbital calculations on the $ArFe^+Cp$ derivatives [28], and also $Fe(C_5H_5)_2$ and $Cr(C_6H_6)_2$ [11], in which the total positive charge ($q_t$), $\pi$-electron density and $\sigma$-electron density for both complexed and uncomplexed arenes are assessed. We have found that, if data for Cl, for toluene and methyl benzoate, which are anomalous, are excluded there is a reasonably good correlation ($r = 0.983$, 11 points) between $q_t$ and the $^{13}C$ chemical shifts ($\delta$) of the free arenes (Ar), yielding the relationship $\delta = 152\ q_t + 123.7$.

Such correlations have been noted before for monosubstituted benzenes with slopes of 176 [29] and 164 [30] ppm per electronic charge.

A similar relationship is found for the complexed ligands when data for the following compounds are used: $C_6H_5Fe^+Cp$, $C_6H_6Co^{2+}Cp$ [31], $(C_6H_6)_2Fe^{2+}$ [32], $(C_6H_6)_2Cr$ [11] and $FeCp_2$ [11], it yields the equation $\delta = 188\ q_t + 60.9$ ($r = 0.950$ 15 points). The slopes of such plots are therefore not appreciably changed when the arene or Cp ligand is complexed to a metal.

Plots of $\delta$ vs. $\pi$-electron density ($\pi_D$) are much more scattered, but if only *para* carbons were used the linearity is dramatically improved ($r = 0.995$, 0.997 for Ar and $ArFe^+Cp$, respectively). The slopes of these plots are $-184$ and $-203$ ppm/e respectively, which compare with the slope of $-167.8$ ppm/e [33,34] for plots of $\delta$ vs. $\pi_D$ for a series of charged and uncharged aromatics based on $\pi_D$ data from Hückel MO theory. [For a discussion of the validity of such correlations see Ref. 19]. The total charge density therefore appears to be a better parameter for such correlations than the $\pi$ charge density alone for these types of complex.

## $^{57}$Fe Mössbauer spectroscopy

The Mössbauer spectroscopic data are presented in Table 5. The quadrupole splittings ($\Delta$) are in the range 1.90–2.10 mm $s^{-1}$, and the isomer shifts (IS) are in

Table 5

$^{57}$Fe Mössbauer data [a] for bis($\eta^6$-arene)iron(II) complexes [b] at 80 K

| Compound | Arene substituent | IS | $\Delta$ | $\tau$ |
|---|---|---|---|---|
| **1** | H | 0.53(1) | 1.90(1) | 0.18 |
| **2** | Me | 0.53(1) | 1.93(1) | 0.12 |
| **3** | 1,2-$Me_2$ | 0.56(1) | 2.00(1) | 0.17 |
| **4** | 1,3-$Me_2$ | 0.56(1) | 2.00(1) | 0.15 |
| **5** | 1,4-$Me_2$ | 0.56(1) | 2.02(1) | 0.18 |
| **6** | 1,3,5-$Me_3$ | 0.56(1) | 2.01(1) | 0.14 |
| **7** | 1,2,3,4-$Me_4$ | 0.57(3) | 2.03(4) | 0.11 |
| **8** | 1,2,3,5-$Me_4$ | 0.56(1) | 2.00(1) | 0.11 |
| **9** | 1,2,4,5-$Me_4$ | 0.56(1) | 2.00(1) | 0.11 |
| **10** | $Me_5$ | 0.60(1) | 2.07(1) | 0.11 |
| **11** | $Me_6$ | 0.64(1) | 2.10(1) | 0.13 |
| **12** | Et | 0.56(1) | 2.00(1) | 0.15 |
| **13** | 1,3,5-$Me_3$ [c] | 0.55(1) | 1.96(1) | 0.13 |
| **14** | 1,3,5-$Me_3$ [d] | 0.56(1) | 2.00(1) | 0.14 |
| **15** | 1,3,5-$Me_3$ [e] | 0.56(1) | 2.00(1) | 0.14 |
| **16** | 1,3,5-$Me_3$ [f] | 0.57(1) | 2.00(1) | 0.13 |

[a] IS, $\Delta$, $\tau$ are isomer shifts, quadrupole splittings and width at half-peak height all in mms$^{-1}$. [b] All hexafluorophosphate salts unless otherwise stated. [c] $BF_4^-$ salt. [d] $I^-$ salt. [e] $BPh_4^-$ salt. [f] Reineckate salt.

the range 0.53–0.64 mm s$^{-1}$. Change of anion had no appreciable effect on the parameters.

All the values of $\Delta$ are smaller than that for ferrocene, and reflect the different nature of the ligand to metal binding. Recent MO calculations on iron sandwich compounds [11] such as $Ar_2Fe^0$ and ferrocene $Cp_2Fe$ show that there are substantial differences between these derivatives in the ligand bonding. For the arene complexes the major contribution to the ligand-iron bonding arises from donation of metal $d_{x^2-y^2}$ and $d_{xy}$ electrons to the $\pi^*$ orbitals of the arene, whereas metal–ligand $\pi$-bonds dominate in ferrocene [35,36].

Evidence in support of this has been found in the electronic absorption spectra of a series of compounds that include $Cp_2Fe^0$, $ArFe^+Cp$ and $(C_6Me_6)_2Fe^{2+}$ [37]. Ligand field parameters were derived. These were consistent with an increased bonding interaction between the $e_{2g}$ metal orbitals and benzene ring orbitals of the appropriate symmetry for the $(C_6Me_6)_2Fe^{2+}$ complex in comparison to $Cp_2Fe$. Moreover, the $ArFeCp^+$ complexes showed intermediate behaviour [37].

This analysis is consistent with the reduction in $\Delta$ in going from $Cp_2Fe$ to the $Ar_2Fe^{2+}$ complex (2.4 mm s$^{-1}$ to 1.9 mm s$^{-1}$). Gol'danski et al. [38] attributed the reduction in $\Delta$ in going from $Cp_2Fe^0$ to (mesitylene)$_2Fe^{2+}$ to a greater interaction of the $e_{2g}$ $d$ orbitals with the ring orbitals in the latter case. The result is to reduce the electron density in the $e_{2g}$ orbitals, and thereby the positive contribution to the field gradient $V_{zz}$ (remembering that $V_{zz}(a_{1g}) = -4/7\langle r^{-3}\rangle$, $V_{zz}(e_{2g}) = +4/7\langle r^{-3}\rangle$ and $V_{zz}(e_{1g}) = -2/7\langle r^{-3}\rangle$).

In ferrocene derivatives the changes in $\Delta$ arise from the imbalance in electronic population between the $e_2$ (predominantly metal-based $3d_{xy}$, $3d_{x^2-y^2}$) orbitals and the $e_1$ orbitals (predominantly ligand based). Electron-releasing groups would increase the ligand contribution to the $e_1$ orbital lessening the demand for metal

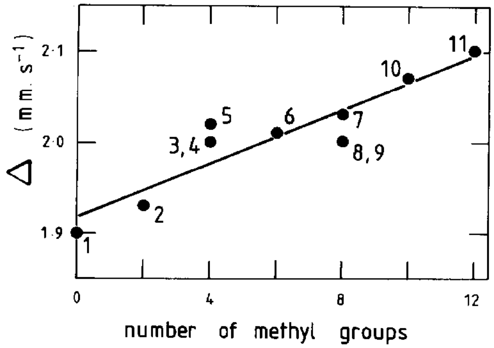


Fig. 1. Plot of quadrupole splittings (Δ) versus number of methyl groups for $Ar_2Fe^{2+}(PF_6^-)_2$, numbering as in Table 5.

contribution. This results in an increase in $\Delta$ (as less metal electron density is needed), the converse being true for electron withdrawing groups [39].

The bonding in $Ar_2Fe^{2+}$ species is similar to that in ferrocene, but the lower $\Delta$ value (1.90 mm $s^{-1}$) observed can be interpreted as reflecting a more even distribution of metal *d* electron density between the $e_2$ and $e_1$ molecular orbitals (after Gol'danskii). The degree of metal bonding from the $e_2$ orbitals to the benzene rings will be influenced by the total electron density on the ring, which, as for ferrocene, will be substituent-dependent. Hence electron donating groups will reduce electron requirements from the metal $e_2$ orbitals and change the overall bonding picture to one more like that for ferrocene. This can be viewed as the electron-rich benzene ring becoming electronically more like a $Cp^-$ ring.

In accord with this explanation the $\Delta$'s observed in Table 5 increase from 1.90 mm $s^{-1}$ for $(C_6H_6)_2Fe^{2+}$ to 2.10 mm $s^{-1}$ for $(C_6Me_6)_2Fe^{2+}$. Fig. 1 shows a plot of $\Delta$ against a number of methyl groups and reveals a reasonably linear increase in $\Delta$

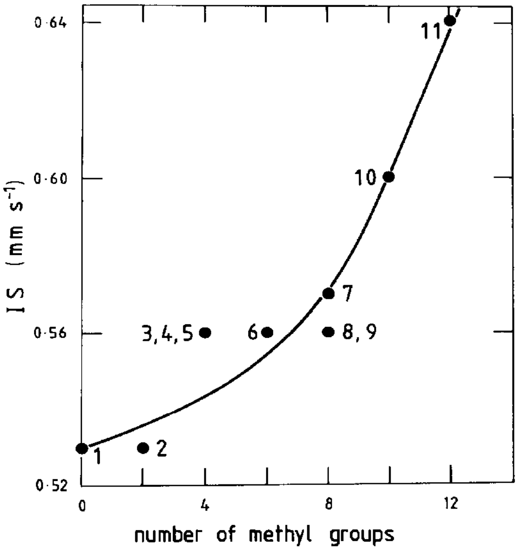


Fig. 2. Plot of isomer shift (IS) versus number of methyl groups for $Ar_2Fe^{2+}(PF_6^-)_2$, numbering as shown in Table 5.

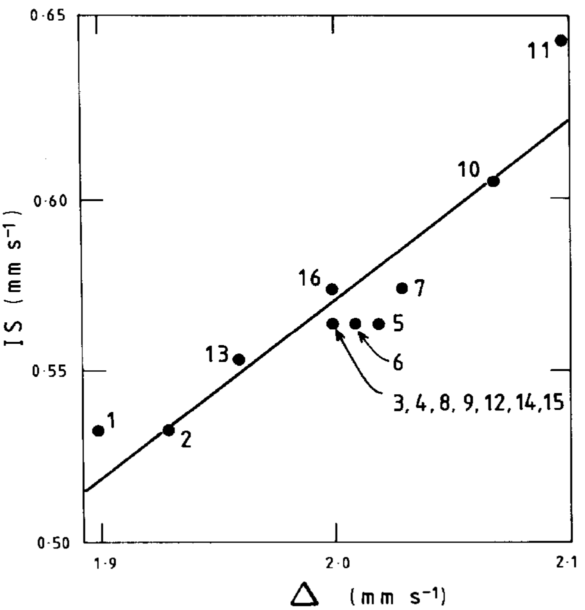


Fig. 3. Plot of quadrupole splittings (Δ) versus isomer shifts (IS) for $Ar_2Fe^{2+}$ salts, numbering as shown in Table 5.

with increasing number of methyl substituents. There is also a correlation between IS and number of methyl substitutents (Fig. 2). An increase in IS for $^{57}Fe$ is due either to a decrease of *s* electron density at the nucleus or an increase in *p* and/or *d* electron shielding. Methyl substituents on the arene rings donating electron density would reduce the need for the latter to remove '*s*' electron density from the iron. The modified benzene rings in these complexes will change the demands made on the iron in participating in the bonding needing less overall iron *p* and/or *d* electron density. Therefore as the benzene ring becomes more electron-rich (with increased methlyation), the contribution of iron electron density to the bonding is reduced, and hence the shielding of the nucleus increases. This is shown as an increase in the isomer shift (cf. $(C_6H_6)_2Fe^{2+}$ $\delta = 0.53$; $(C_6Me_6)_2Fe^{2+}$ $\delta = 0.64$).

Thus both the explanation for the observed isomer shifts and Δ's are consistent with a decreasing amount of $e_2$ metal electron density in the bonding as the number of methyl substituents on the ring increases. This is confirmed by the correlation between $\delta$ and $\Delta$ for the $Ar_2Fe^{2+}$ complexes (Fig. 3).

## Conclusions

$^{57}Fe$ Mössbauer spectroscopy provides a quantitative measure of the metal-ligand donation via the IS value, which can be used to detect the increased interaction of the $e_2$ metal orbitals with the $e_2$ ring orbitals compared with that in ferrocene. The higher the IS value the lower is the metal donation to the ring orbitals, and vice versa (cf. $(C_6Me_6)_2Fe^{2+}$ and $(C_6H_6)_2Fe^{2+}$). The QS is, however, generally the more useful parameter in the discussion of sandwich complexes, and provides a qualitative measure of the iron electron density distribution.

## Experimental

All solvents were rigorously dried with activated molecular sieve (Grade 4A) prior to use. The bis($\eta^6$-arene)iron(II) hexafluorophosphates were prepared by the method developed by Helling [3] involving use of an excess of arene and a 1/2 ratio of $FeCl_3/AlCl_3$. The conditions used, yields, and analyses appear in Table 1. The products were characterised by $^1H$ NMR spectrocopy (Table 2). The products were precipitated from aqueous solution by addition of either saturated aqueous $NH_4PF_6$ or 70% aqueous $HPF_6$ and were purified by recrystallisation from $MeNO_2/Et_2O$ mixtures to give amorphous powders. Bis($\eta^6$-mesitylene)iron(II) hexafluorophosphate was prepared by ligand exchange from diacetylferrocene [5]. Exchange of the $PF_6^-$ anion for other anions ($X^-$) was effected by dropwise addition of an acetone solution of either HX or LiX to a solution of bis($\eta^6$-hexamethylbenzene)iron(II) hexafluorophosphate in acetone. The precipitated complex was filtered off, washed with acetone and dried under vacuum. No reaction was observed for $X^- = NO_3^-$, $CF_3CO_2^-$. Addition of HX or LiX to nitromethane solutions of the less alkylated complexes (benzene, toluene) resulted in complete decomposition. The results of the anion exchange reactions appear in Table 6. In addition to these derivatives, the perchlorate and chlorosulphonate salts were also prepared, together with the iodides and bromides of the pentamethylbenzene and durene complexes. Reineckates were prepared by shaking a slurry of two equivalents of Reinecke salts in a solution of one equivalent of $Ar_2Fe^{2+}(PF_6^-)_2$. After 5 min the purple colour of the Reinecke salt changed to a deep orange. The mixture was filtered and washed well with water to give high yields (> 80%) of the corresponding Reineckate. This method was successful even for the benzene and toluene complexes. The $BPh_4^-$, $BF_4^-$, and $I^-$ salts were also formed by treating the product aqueous solutions of $Ar_2Fe^{2+}(AlCl_4^-)_2$ obtained at the end of the preparative procedure with the appropriate salt.

$^1H$ NMR and $^{13}C$ NMR spectra were recorded on Varian EM 360 and Bruker WP80 spectrometers, respectively. Mössbauer spectra were determined and fitted as previously described [40].

Table 6

Yields and analytical data for bis($\eta^6$-hexamethylbenzene)iron(II) salts obtained by metathetical exchange from the corresponding hexafluorophosphate

| Reagent | Yield (%) | M.p. (°C) | Analysis (Found (calcd.) (%)) | |
|---|---|---|---|---|
| | | | C | H |
| HCl | 96 | 183–187 | 64.0<br>(63.9) | 8.2<br>(8.0) |
| LiCl | 92 | 183–187 | – | |
| LiBr | 96 | 243–246 | 53.9<br>(53.4) | 7.0<br>(6.7) |
| HI | 95 | 248–251 | 46.0<br>(45.5) | 6.0<br>(5.7) |
| LiI | 89 | 249–251 | | |
| $H_2SO_4$ | 96 | 176–180 | 60.9<br>(60.5) | 8.0<br>(7.6) |

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