

sponding quantities in the calcium 2-fluorobenzoate compound are 2.995 (2), 2.04 (2), 2.64 Å and 170°, respectively. Following Murray-Rust, Stallings, Monti, Preston & Glusker (1983) these parameters do not indicate significant C—F···H—O hydrogen bonding in the 2,6-difluorobenzoate salt in contrast to the 2-fluorobenzoate derivative. The degree of twist of the aromatic ring from the carboxylate ring plane also differs in the two salts. In the title compound, this dihedral angle is 48° compared to 41° in calcium 2-fluorobenzoate and 11° in 2-fluorobenzoic acid (Ferguson & Islam, 1975).

These differences in geometry in the two otherwise very similar structures probably result from the substitution of the second F atom for an H atom, which is the only difference in molecular formulation in the two salts. For example, in calcium 2,6-difluorobenzoate dihydrate, the shortest intermolecular non-bonded contact involving F(6) is a phenyl H atom, H(C5) ( $-x, -1-y, 1-z$ ), at 2.81 Å — whereas, for the corresponding 6 position in the aryl ring in calcium 2-fluorobenzoate dihydrate, the shortest contact to H(C6) is an O atom,  $OW^{ii}$ , from a water molecule at 2.67 Å. It is evident that some structural features in these compounds are influenced by the increase in van der Waals radius of F compared to H

atoms, as well as differences in the polarities of C—F and C—H bonds.

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## Structures of ( $\eta$ -Arene)( $\eta$ -cyclopentadienyl)iron(II) Salts. ( $\eta^6$ -Benzene)-( $\eta^5$ -cyclopentadienyl ethyl ketone)iron(II) Hexafluorophosphate

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**Abstract.**  $[\text{Fe}(\text{C}_6\text{H}_6)(\text{C}_5\text{H}_4\text{COCH}_2\text{CH}_3)][\text{PF}_6]$ ,  $M_r = 400.08$ , monoclinic,  $P2_1/c$ ,  $a = 7.096$  (3),  $b = 22.651$  (9),  $c = 9.305$  (4) Å,  $\beta = 95.09$  (2)°,  $V = 1490$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.78$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.710969$  Å,  $\mu = 12.17$  cm<sup>-1</sup>,  $F(000) = 808$ ,  $T = 208$  K,  $R = 0.0439$  ( $wR = 0.0424$ ) for 1938 unique reflections [ $R = 0.0346$ ,  $wR = 0.0359$  for 1604 reflections with  $I > 2.5\sigma(I)$ ]. The structure contains planar

aromatic rings with the carbonyl substituent group virtually in the plane of the cyclopentadienyl ring (3.4°). The iron–ring distances are 1.668 (2) and 1.547 (2) Å for cyclopentadienyl and benzene, respectively. A comparison with other ( $\eta$ -arene)( $\eta$ -cyclopentadienyl)iron(II) salt structures is also reported. For all the structures the Fe—C<sub>arene</sub> bond lengths are longer than the Fe—C<sub>cyclopentadienyl</sub> bond lengths despite the apparent closeness of the arene rings to the Fe atoms.

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**Introduction.** The sandwich structure, epitomized by ferrocene, has evoked great interest since its confirmation by X-ray crystallography in 1953 (Dunitz & Orgel, 1953). Since then there has been a large number of such studies on a wide variety of sandwich compounds, although iron complexes have continued to be the most abundantly investigated.

The chemical bonding in sandwich compounds has received great attention, with numerous attempts at rationalization (Jaffe, 1953; Dunitz & Orgel, 1955; Moffit, 1959; Clack & Warren, 1978). We have recently put forward a qualitative theory to explain the changes in bonding caused by substitution in the three major types of iron sandwich compound (Houlton, Miller, Roberts & Silver, 1990), *viz* ferrocenes, bis( $\eta$ -arene)iron(II) complexes and ( $\eta$ -arene)( $\eta$ -cyclopentadienyl)iron(II) salts. For the last type, charge redistribution effects were invoked to explain the seemingly anomalous data.

In an attempt to establish a structural basis for these effects we have solved the structure of ( $\eta$ -benzene)( $\eta$ -cyclopentadienyl ethyl ketone)iron(II) hexafluorophosphate (1), the first example of this type of complex containing a substituent on the cyclopentadienyl ring. Here we discuss the structure and make comparisons with the other ( $\eta$ -arene)( $\eta$ -cyclopentadienyl)iron(II) salts.

**Experimental.** The title compound was prepared by a standard procedure (Roberts & Wells, 1986) and recrystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  mixtures.  $^{13}\text{C}$  NMR spectra were run using a Bruker WP80 spectrometer. For  $[\text{Fe}(\eta\text{-C}_6\text{H}_6)(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$  in solvent acetone- $d_6$ ,  $^{13}\text{C}\{^1\text{H}\}$  resonances ( $\delta$  p.p.m. reference TMS,  $q$  = quaternary carbon) appeared at 89.22 ( $\text{C}_6\text{H}_6$ ) and 77.49 ( $\text{C}_5\text{H}_5$ ).  $[\text{Fe}(\eta\text{-C}_6\text{H}_6)(\eta\text{-C}_5\text{H}_4\text{COC}_2\text{H}_5)]\text{PF}_6$  gave peaks at 201.50  $q$  (CO), 90.27 ( $\text{C}_6\text{H}_6$ ), 86.24  $q$ , 79.70, 76.93 ( $\text{C}_5\text{H}_4$ ), 34.44, 7.62 ( $\text{C}_2\text{H}_5$ ).

Orange plate-like crystals were examined under a polarizing microscope for homogeneity. A well formed crystal,  $0.08 \times 0.42 \times 0.60$  mm, was selected and mounted on the tip of a glass fibre with use of epoxy cement. The density was not determined. Unit-cell parameters at 208 K were obtained from a least-squares fit of  $\chi$ ,  $\varphi$  and  $2\theta$  for 15 reflections in the range  $16.7 < 2\theta < 26.6^\circ$  recorded on a Nicolet P3 diffractometer with use of graphite-monochromated  $\text{Mo } K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$  at 295 K). The space group was determined from systematic absences ( $0k0$ ,  $k \neq 2n$ ,  $h0l$ ,  $l \neq 2n$ ). Intensity data were also recorded on a Nicolet P3 diffractometer at 208 K with use of  $\omega$ - $2\theta$  scans, for 2281 reflections ( $h, k \pm l$ ;  $-7 \leq h \leq 7$ ,  $0 \leq k \leq 24$ ,  $0 \leq l \leq 10$ ) with  $2\theta \leq 45^\circ$ . The methods of selection of scan rates and initial data treatment have been described (Lippert, Lock, Rosenberg & Zavagulis, 1977;

Hughes, Krishnamachari, Lock, Powell & Turner, 1977). Corrections for Lorentz-polarization effects but not absorption were applied to all reflections. Two standard reflections (135, e.s.d. 0.024% and 292, e.s.d. 0.021%), monitored every 48 reflections, showed no sign of crystal decomposition or instrument instability. Systematically absent reflections (74) were excluded and 269 symmetry-equivalent data were then averaged ( $R_{\text{int}} = 0.0144$ ) to give 1938 unique reflections.

The coordinates of the Fe and the P atoms were found from a three-dimensional Patterson synthesis with use of the program *SHELXS86* (Sheldrick, 1986). Full-matrix least-squares refinement of these coordinates followed by a three-dimensional electron-density synthesis revealed all the non-H atoms and confirmed the positional assignments for the heavy ones. After refinement the temperature factors of the non-H atoms, which were previously isotropic, were made anisotropic and further cycles of refinement revealed the positional parameters for all of the H atoms. These were included in subsequent cycles of refinement ( $U$  refined as a single variable for all H atoms). Further refinement using full-matrix least squares minimizing  $\sum w(|F_o| - |F_c|)^2$  was terminated when the maximum shift/e.s.d. reached 0.002 (254 variables). No correction for secondary extinction was necessary. Final  $R = 0.0439$ ,  $wR = 0.0424$  [ $w = (\sigma^2 F + 0.000225 F^2)^{-1}$ ],  $S = 1.6067$  for 1938 reflections. Maximum  $\Delta\rho = 0.35 \text{ e \AA}^{-3}$  at  $0.96 \text{ \AA}$  from H(21), minimum  $\Delta\rho = -0.41 \text{ e \AA}^{-3}$ . Scattering curves for the neutral atoms were taken from Cromer & Mann (1968) and anomalous-dispersion corrections (Cromer & Liberman, 1970) were applied to the curves for Fe and P atoms. Programs used: *XTAL2.6* (Hall & Stewart, 1989), data reduction and least-squares-planes calculation; *SHELXS86* (Sheldrick, 1986), structure solution; and *SHELX76* (Sheldrick, 1976), structure refinement. Figures were prepared with use of the program *SNOOPI* (Davies, 1983). All calculations were performed on a VAX 6420 computer. Final atomic positional parameters are given in Table 1, selected bond lengths and bond angles are given in Table 2.\*

The comparative crystal-structure data were obtained from the Cambridge Structural Database. Data thus derived do not include errors on the calculated distances. The  $R$  factors for the structures are quoted in Table 3.

\* Lists of structure factors, anisotropic thermal parameters, least-squares-planes data, bond distances and angles involving H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54891 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^4$ ) for [Fe(C<sub>6</sub>H<sub>6</sub>)(C<sub>5</sub>H<sub>4</sub>COCH<sub>2</sub>CH<sub>3</sub>)]<sup>+</sup>.PF<sub>6</sub><sup>-</sup> with e.s.d.'s in parentheses

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)/3.$$

	x	y	z	$U_{\text{eq}}$
Fe(19)	2282.6 (8)	1345.3 (2)	3724.1 (6)	181
C(11)	545 (5)	632 (2)	3968 (4)	210
C(2)	2458 (6)	438 (2)	3877 (4)	231
C(3)	3587 (6)	707 (2)	5046 (5)	288
C(4)	2386 (6)	1061 (2)	5836 (4)	308
C(5)	529 (6)	1015 (2)	5177 (4)	287
O(1)	-2707 (4)	651 (1)	3288 (3)	363
C(1)	-1165 (6)	458 (2)	3022 (4)	220
C(2)	-937 (6)	46 (2)	1790 (5)	301
C(3)	-2799 (6)	-141 (2)	985 (5)	350
C(21)	1909 (6)	1610 (2)	1557 (5)	317
C(22)	809 (6)	1965 (2)	2396 (5)	330
C(23)	1615 (6)	2244 (2)	3633 (5)	357
C(24)	3569 (6)	2172 (2)	4059 (5)	340
C(25)	4649 (6)	1812 (2)	3224 (5)	329
C(26)	3849 (6)	1533 (2)	1986 (5)	300
P(1)	2717 (1)	8461 (1)	1566 (1)	221
F(1)	500 (3)	8498 (1)	1777 (3)	364
F(2)	4925 (3)	8428 (1)	1340 (3)	387
F(3)	2398 (3)	7828 (1)	829 (3)	453
F(4)	2315 (4)	8757 (1)	15 (3)	529
F(5)	3024 (4)	9096 (1)	2290 (3)	521
F(6)	3113 (4)	8162 (1)	3106 (3)	623

Table 2. Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) for [Fe(C<sub>6</sub>H<sub>6</sub>)(C<sub>5</sub>H<sub>4</sub>COCH<sub>2</sub>CH<sub>3</sub>)]<sup>+</sup>.PF<sub>6</sub><sup>-</sup> with e.s.d.'s in parentheses

Fe coordination			
Fe(1)—C(11)	2.058 (4)	Fe(1)—C(21)	2.098 (4)
Fe(1)—C(12)	2.063 (4)	Fe(1)—C(22)	2.088 (4)
Fe(1)—C(13)	2.064 (4)	Fe(1)—C(23)	2.091 (4)
Fe(1)—C(14)	2.063 (4)	Fe(1)—C(24)	2.094 (4)
Fe(1)—C(15)	2.058 (4)	Fe(1)—C(25)	2.072 (4)
Fe(1)—Ctd(1)	1.668 (2)	Fe(1)—C(26)	2.086 (4)
		Fe(1)—Ctd(2)	1.547 (2)
C(11)—Fe(1)—C(12)	40.8 (2)	C(21)—Fe(1)—C(22)	39.2 (2)
C(12)—Fe(1)—C(13)	40.5 (2)	C(22)—Fe(1)—C(23)	38.9 (2)
C(13)—Fe(1)—C(14)	40.3 (2)	C(23)—Fe(1)—C(24)	39.6 (2)
C(14)—Fe(1)—C(15)	39.9 (2)	C(24)—Fe(1)—C(25)	39.3 (2)
C(15)—Fe(1)—C(16)	40.4 (2)	C(25)—Fe(1)—C(26)	39.0 (2)
		C(26)—Fe(1)—C(21)	39.4 (2)
Ligand			
C(11)—C(12)	1.437 (5)	C(21)—C(22)	1.405 (6)
C(12)—C(13)	1.429 (6)	C(22)—C(23)	1.392 (6)
C(13)—C(14)	1.421 (6)	C(23)—C(24)	1.418 (7)
C(14)—C(15)	1.407 (6)	C(24)—C(25)	1.401 (7)
C(11)—C(15)	1.421 (6)	C(25)—C(26)	1.389 (6)
C(11)—C(1)	1.487 (5)	C(21)—C(26)	1.410 (6)
C(1)—O(1)	1.223 (5)	C(1)—C(2)	1.499 (6)
C(2)—C(3)	1.520 (6)		
C(11)—C(12)—C(13)	107.1 (4)	C(21)—C(22)—C(23)	120.8 (4)
C(12)—C(13)—C(14)	108.2 (4)	C(22)—C(23)—C(24)	119.9 (4)
C(13)—C(14)—C(15)	108.3 (4)	C(23)—C(24)—C(25)	118.8 (4)
C(14)—C(15)—C(11)	108.5 (4)	C(24)—C(25)—C(26)	121.4 (4)
C(15)—C(11)—C(12)	107.3 (4)	C(25)—C(26)—C(21)	119.8 (4)
C(1)—C(11)—C(12)	127.6 (4)	C(26)—C(21)—C(22)	119.3 (4)
C(1)—C(11)—C(15)	124.4 (4)	C(1)—C(1)—O(1)	119.0 (4)
C(11)—C(1)—C(2)	118.6 (4)	C(2)—C(1)—O(1)	122.4 (4)
C(1)—C(2)—C(3)	113.7 (4)		

**Discussion.** The molecular structure is shown in Figs. 1 and 2.

The two aromatic rings are planar ( $\pm 0.001 \text{\AA}$  for the C<sub>5</sub> ring;  $\pm 0.004 \text{\AA}$  for the C<sub>6</sub> ring) and are tilted with respect to one another by  $3.4 (2)^\circ$ . The iron–ring distances are  $1.668 (2)$  and  $1.547 (2) \text{\AA}$  for the cyclo-

pentadienyl and benzene respectively. These distances lie within the previously established ranges for such complexes (see Table 3). The carbonyl substituent group lies virtually in the plane of the cyclopentadienyl ring being only  $3.1 (2)^\circ$  out of the plane. While the Fe—( $\eta$ -C<sub>5</sub>H<sub>4</sub>) distance is within the known range, the average Fe—C distance [ $2.061 (4) \text{\AA}$ ] lies outside the range found for the other derivatives (Table 4). These, however, all contain an unsubstituted cyclopentadienyl ring. This seeming paradox is a consequence of the increase in ring size owing to the electron-withdrawing nature of the COCH<sub>2</sub>CH<sub>3</sub> moiety. For the C<sub>5</sub> ring in (1) C—C<sub>av</sub> =  $1.423 (6) \text{\AA}$ , this compares with  $\sim 1.40 \text{\AA}$  for compounds (2)–(11) (see Table 4).\*

Ring expansion can also be seen in the arene rings, on complexation. A comparison of the average C—C bond lengths for benzene uncomplexed and in (1)

\* Such C—C distances are, however, not unusual for carbonyl cyclopentadienyl derivatives and the same distances in *Fc*COCH<sub>3</sub>, *Fc*CHO and *Fc*CO*Fc* are  $1.422 (4)$  and  $1.414 (4) \text{\AA}$ ,  $1.402 (14)$  and  $1.435 (25) \text{\AA}$ , respectively (where *Fc* = C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>5</sub>) (Roberts, Silver, Yamin, Drew & Eberhardt, 1988). *Fc*COCH<sub>3</sub> has two molecules per unit cell.

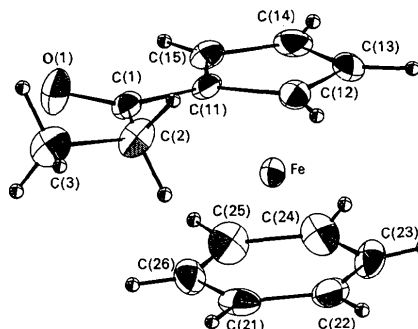


Fig. 1. Molecular structure of (1) including numbering scheme.

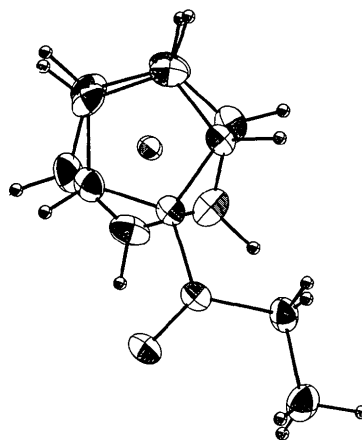




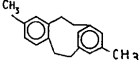




Fig. 2. Molecular structure of (1) showing the relative orientation of the arenes.

Table 3. Iron–ring distances (Å) for ( $\eta$ -arene)( $\eta$ -cyclopentadienyl)iron(II) salts\*

$\eta$ -Arene	Arene—Fe (D1)	Cp—Fe (D2)	D1 + D2	R factor	Reference
(1) $C_6H_6$	1.547 (2)	1.668 (2)	3.215 (2)	0.0424	This work
(2) $C_6(CH_2CH_3)_6$	1.551	1.684	3.235	0.045	Hamon, Saillard, Le Beuze, McGlinchey & Astruc (1982)
(3) 	1.545	1.672	3.217	0.046	Lynch, Thomas, Simonsen, Piórko & Sutherland (1986)
(4) 	1.540	1.671	3.211	0.070	Liqing, Kezhen, Lun & Peizhi (1984)
(5) 	1.522	1.661	3.183	0.08	Liqing, Kezhen, Lun & Peizhi (1984)
(6)† $C_6(CH_3)_6$	1.547	1.666	3.213	0.045	Lequan, Lequan, Jaouen, Ouahab, Batail, Padiou & Sutherland (1985)
(7) $C_6H_5B(C_6H_5)_3$	1.537	1.662	3.199	0.036	Rogers & Hrcir (1984)
(8) 	1.582	1.653	3.235	0.045	Johnson & Treichel (1977)
(9) 	1.570	1.659	3.229	0.069	Koray, Zahn & Ziegler (1985)
(10) 	1.544 1.552	1.664 1.664	3.208 3.216	0.045	Lynch, Thomas, Simonsen, Piórko & Sutherland (1986)
(11)‡ 	1.56–1.57	1.63–1.63		0.094	Lacoste, Rabaa, Astruc, Le Beuze, Saillard Précigoux, Coureille, Ardoin & Bowyer (1989)
Range (e.s.d.)	1.522–1.582 (0.06)	1.653–1.684 (0.031)	3.183–3.235 (0.052)		

\* All with  $PF_6^-$  anion unless otherwise stated.

† Anion =  $(TCNQ)_2^-$  (TCNQ = tetracyanoquinodimethane).

‡ This structure is included in the table but not in the analysis owing to the poor resolution. Data from the original reference.

Table 4. Selected bond lengths (Å) for ( $\eta$ -arene)( $\eta$ -cyclopentadienyl)iron(II) salts\*

$\eta$ -Arene	$C_{arene}$ —Fe	$C_{Cp}$ —Fe	C— $C_{Cp}$	Reference
(1)	2.109 (4)	2.061 (4)	1.423 (6)	This work
(2)	2.108	2.054	1.384 (10)	Hamon, Saillard, Le Beuze, McGlinchey & Astruc (1982)
(3)	2.092	2.054	1.404 (7)	Lynch, Thomas, Simonsen, Piórko & Sutherland (1986)
(4)	2.073	2.032	—	Liqing, Kezhen, Lun & Peizhi (1984)
(5)	2.080	2.027	1.382	Liqing, Kezhen, Lun & Peizhi (1984)
(6)†	2.092	2.043	—	Lequan, Lequan, Jaouen, Ouahab, Batail, Padiou & Sutherland (1985)
(7)	2.087	2.048	1.41 (1)	Rogers & Hrcir (1984)
(8)	2.122	2.038	1.402	Johnson & Treichel (1977)
(9)	2.106	2.036	1.39 (3)	Koray, Zahn & Ziegler (1985)
(10)	2.088	2.053	1.413 (6)	Lynch, Thomas, Simonsen, Piórko & Sutherland (1986)
(11)‡	2.094	2.049	1.406 (6)	Lacoste, Rabaa, Astruc, Le Beuze, Saillard Précigoux, Coureille, Ardoin & Bowyer (1989)
	2.12 (3)	2.04 (4)	1.44 (4)	
	2.11 (3)	2.03 (4)	1.42 (4)	

\* Structures as in Table 4. All with  $PF_6^-$  anion unless otherwise stated.

† Anion =  $(TCNQ)_2^-$  (TCNQ = tetracyanoquinodimethane).

‡ Two molecules per unit cell.

reveals an increase from 1.390 (Roberts & Caserio, 1977) to 1.403 (7) Å. This is slightly larger than the corresponding change for [(3,8- $\eta$ )-5,13-dimethyl-[2,2]metacyclophane( $\eta$ -cyclopentadienyl)iron] hexafluorophosphate of 1.392 (7) to 1.41 (2) Å on complexation (Johnson & Treichel, 1977). This increase in ring size is in keeping with the donation of metal electron density (from  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals) into antibonding orbitals on the arene ring.

Previously, we have analyzed a large number of substituted ferrocenyl structures (Roberts, Silver, Yamin, Drew & Eberhardt, 1988). For electron-withdrawing groups, three structural types were found on the basis of C—C bonds within the substituted  $\eta$ - $C_5H_4$  and C—C distances exocyclic to the

$\eta$ - $C_5H_4$ . Structure (1) does not fit any of these categories.

Tables 3 and 4 contain bond lengths and selected molecular dimensions for the existing crystal structure data for ( $\eta$ -arene)( $\eta$ -cyclopentadienyl)iron(II) salts, derived from the Cambridge Structural Database. The iron–ring and intramolecular ring–ring distances are contained in Table 3. Most interesting is the seeming closeness of the arene ring in comparison to the cyclopentadienyl ring. The average iron–ring distance of 1.549 Å for arenes compares with 1.666 Å for the cyclopentadienyl rings, this giving an average intra ring–ring distance of 3.215 Å. This is intermediate between the values of 3.32 Å for ferrocene (Dunitz, Orgel & Rich, 1956)

and 3.16 (7) Å for bis(mesitylene)iron(II) [C<sub>6</sub>(CN)<sub>6</sub>] (Ward, 1987), as would be expected.

Evidence for the enhanced donor ability of the cyclopentadienyl ligands over the arene type is clearly demonstrated from the crystallographic data. The range of substituents on the arene rings is extensive. Substitution on an aromatic ring would be expected to influence the iron–ring distance slightly. Indeed, the range for these distances is large (1.522–1.582; e.s.d. 0.06 Å) in comparison to that of iron–cyclopentadienyl (1.653–1.684; e.s.d. 0.03 Å). However, the extended range of bonding distances for the arenes, we suggest, reflects the weaker bonding to iron for this type of ligand in comparison to the cyclopentadienyl type. The small range of iron–cyclopentadienyl ring distances is indicative of stronger bonding. Although only one example of a substituted cyclopentadienyl ring is known, that of (1), its iron–ring distance lies very close to the mean value for such distances in the unsubstituted cases, and is not at the larger extreme of the range as might have been expected.

Table 4 contains Fe–C distances for both ring types. It can be seen that, despite the apparently short iron–arene ring distances, the Fe–C(C<sub>6</sub>) distances are all longer than those for the Fe–C(C<sub>5</sub>). This is due to the greater radius of the C<sub>6</sub> rings compared to C<sub>5</sub> (1.414 Å for benzene, 1.216 Å for C<sub>5</sub>H<sub>5</sub>) (Beck, Hummel, Burgi & Ludi, 1987).

It is interesting to compare the difference between Fe–C distances for the C<sub>5</sub>H<sub>5</sub> cases and for (1). The difference, (Fe–C<sub>6</sub>) – (Fe–C<sub>5</sub>), is much smaller (0.027 Å) in the latter case than in the former (range found 0.035–0.084 Å), demonstrating again the C<sub>5</sub>H<sub>4</sub>COCH<sub>2</sub>CH<sub>3</sub> ring expansion.

The fact that all the structural investigations of (η-arene)(η-cyclopentadienyl)iron(II) salt structures have been isolated studies has made it difficult to rationalize differences in terms of the substituent groups. A more systematic structural study, using simple substituents whose electronic effects are well characterized, would establish if charge redistribution effects are manifest in the structures of these salts or are too small to be discerned.

However, consideration of these structures illustrates the usefulness of weak ligands. Arene ligands are weaker than their cyclopentadienyl counterparts, the greater range of bonding distances highlighted in this work, is testament to this. <sup>57</sup>Fe Mössbauer spectroscopy of the bis(arene)Fe<sup>2+</sup> salts shows changes in both isomer shift and quadrupole splitting, whereas comparable ferrocenyl derivatives only show changes in quadrupole splitting. This not only confirms the weaker nature of the arene binding but also demonstrates that a wider range of iron electronic environments can be created in this case. The implications of this are that the strong donor ability of cyclopentadienyl ligands makes essentially little demand on the iron electron density. For the weaker arene ligand, the iron must participate more in the bonding, thus delocalizing its electron density to a greater extent. This fact then offers a greater potential for influencing or even controlling the metal electron density by judicious choice of the weak ligand. This has obvious implications for the design of electron-transfer systems.

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