

25. Crystal Structure of Bis(η^6 -mesitylene)iron(II) Hexafluorophosphate

by T. Stanley Cameron*, Anthony Linden¹), and K. Craig Sturge²)

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada

and Michael J. Zaworotko*

Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia, B3H 3C3, Canada

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The crystal structure of $[\text{Fe}(\eta^6\text{-mesitylene})_2](\text{PF}_6)_2$ (**1**) is reported. The structure is intricately disordered with the Fe-atom occupying an $m\bar{3}m$ cubic site, but nonetheless the conformation and bonding is confirmed. The structure is discussed in the general context of Fe^{II} sandwich complexes.

1. Introduction. – A wide range of neutral and monocationic sandwich compounds has been characterized crystallographically [1] [2]. However, dicationic analogues have received comparatively little attention until recently, when it was realized that bis(arene)iron(II) dications, amongst other sandwich compounds, are capable of adopting stacked solid-state structures [3] [4]. Our interest in the chemistry of $[\text{Fe}(\eta^6\text{-arene})_2]^{2+}$ dications, and the structure and bonding in their derivatives [5–7] prompted us to examine the crystal structure of $[\text{Fe}(\eta^6\text{-mesitylene})_2](\text{PF}_6)_2$ (**1**).

2. X-Ray Crystallography. – Orange crystals of the title complex were sealed in thin walled capillaries. An *Enraf-Nonius CAD4* diffractometer (graphite monochromator, MoK_α radiation) was used to determine lattice parameters and for data collection. The lattice parameters were later confirmed by long-exposure rotation photographs and by upper-layer *Weissenberg* photographs. There was no evidence from these photographs to support a doubling (or greater factor) of the axial lengths. The photographs were also used to confirm that the systematic absences were consistent with an *F*-centred unit cell, and that none of the systematically absent reflections were even weakly observed. Data collection and refinement parameters are given in *Table 1*. Scattering factors for neutral atoms were taken from the *International Tables for X-Ray Crystallography* [8] and were corrected for the real part of the anomalous dispersion. The data were collected as for an *F*-centred orthorhombic cell. The intensities were reduced to a standard scale by routine procedures, [9] and *Lorentz*, polarisation, and absorption corrections (DIFABS [10]) were applied. The reflections were merged to a unique set [11]. Three reflections were found to have widely varying measurements, and these were excluded from the subsequent refinement. The structure was refined on *F* by full-matrix least-squares procedures,

¹) Present address: Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich.

²) Jointly associated with St. Mary's University.

Table 1. *Data Collection and Structure-Refinement Parameters*

Formula	$C_{18}H_{24}F_{12}FeP_2$
Formula weight	586.2
Crystal dimensions [mm]	$0.20 \times 0.24 \times 0.36$
Crystallised from	acetone
Data collection temperature	291 K
Crystal system	cubic
Space group	$Fm\bar{3}m$
No. of reflections used to determine lattice parameters ^b	25
2θ range for lattice parameters [°]	$30 < 2\theta < 36$
Unit cell dimensions a [Å]	13.433 (4)
Volume [Å ³]	2424 (1)
Z	4
X-Ray wavelength (MoK α) [Å]	0.70926
Calculated density [g·cm ⁻³]	1.606
Linear absorption coefficient [cm ⁻¹]	0.844
$F(000)$	1184
No. of standards	3
Crystal decomposition	none
Scan type	$\omega - 2\theta$
ω -Scan width [°]	$1.00 + 0.35 \tan\theta$
Scan speed [° min ⁻¹]	variable: 0.7–4.0
$2\theta_{max}$ [°]	50
Reflections measured	724 (488 with $I > 3\sigma(I)$)
Unique reflections	143
R_{int}	0.0209 (0.0228 for full data)
Reflections observed ($I > 3\sigma(I)$)	90 (3 omitted)
Parameters refined	27
Final Δ_{max}/σ	0.36
Data/parameter ratio	3.4 (5.3 for full data)
R	0.0224 (0.0393 for full data)
wR	0.0245 (0.0262 for full data)
$\Delta\rho$ (max) [e·Å ⁻³]	0.18 (at the Fe-site)

Table 2. *Fractional Atomic Positional Parameters and Isotropic Temperature Factors [Å²] with E.s.d.'s in Parentheses*

Atom	x/a	y/b	z/c	$U_{eq}/U(iso)^a$
Fe	0.0	0.0	0.0	0.0580 (4)
P	0.25	0.25	0.25	0.0875 (7)
F	0.2595 (9)	0.2595 (9)	0.1332 (2)	0.125 (3)
C(1)	-0.0255 (3)	-0.0255 (3)	-0.1549 (4)	0.074 (4)
C(2)	0.0200 (5)	0.0200 (5)	-0.2468 (4)	0.088 (4)
C(3)	0.0151 (8)	-0.1105 (3)	-0.1105 (3)	0.077 (3)
H(3)	0.074 (4)	-0.140 (6)	-0.138 (6)	0.075 (7)
H(21)	-0.008 (3)	0.091 (2)	-0.266 (3)	0.140 (8)
H(22)	0.011 (3)	-0.022 (2)	-0.313 (1)	0.150 (8)
H(23)	0.098 (1)	0.031 (3)	-0.243 (3)	0.137 (8)

^a) Equivalent isotropic temperature factor, U_{eq} , for non-H-atoms, defined as one third of the trace of the orthogonalised U_{ij} tensors.

initially using SHELX76 [12], and subsequently with CRYSTALS [11]. Refinements minimised the function $\sum w(|F_o| - |F_c|)^2$, where $w = 0.18/[\sigma^2(F) + 0.000935F^2]$. Details of the refinement strategy are given after the discussion of the structure itself. The refinement converged with $R = 0.0224$ for 90 reflections with $I > 3\sigma(I)$ ($R = 0.0293$ for 140 reflections of the full data, $R = 0.0306$ for 143 reflections). The final difference map was essentially featureless ($+0.18$ to -0.20 e \AA^{-3}). Fractional atomic coordinates are given in Table 2, and interatomic distances and interbond angles are listed in Table 3. A view of the complex is shown in Fig. 1.

Table 3. Interatomic Distances [\AA] and Interbond Angles [$^\circ$] for **1** with E.s.d.'s in Parentheses

Distances		Angles ^{a)}	
Fe–C(1)	2.136 (5)	C(3)–C(1)–C(3')	117.1 (5)
Fe–C(3)	2.109 (6)	C(1)–C(3)–C(1')	122.9 (5)
C(1)–C(2)	1.507 (8)	C(2)–C(1)–C(3)	121.4 (5)
C(1)–C(3)	1.399 (8)	C(2)–C(1)–C(3')	121.4 (5)
Fe–(ring plane)	1.599 (4)		

^{a)} Primed atoms are in the following symmetry related positions: ' : z, x, y; '' : y, z, x.

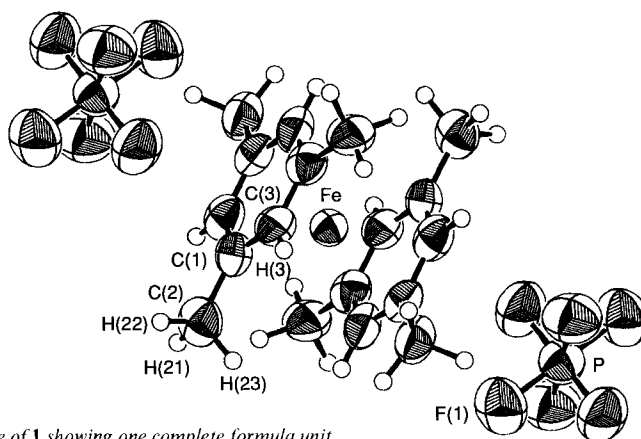


Fig. 1. The structure of **1** showing one complete formula unit and the atom numbering

3. Description of the Structure. – From the dimensions of the unit cell, it was clear that it contained only four cations and eight anions. This would require the Fe-atom to be located at either 0,0,0 or $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Both of these sites have crystallographic $m\bar{3}m$ symmetry, and either position can be chosen arbitrarily. Based on the peak positions of the C-atoms in a Fourier map phased on the Fe-atom at 0,0,0, the mesitylene ring exhibits 3 symmetry (and, as discussed below, disorder completes the full $m\bar{3}m$ crystallographic symmetry of the cationic sites). The locations of all the C-atoms of the cation are, therefore, defined by the positions of only three C-atoms in mesitylene (= 1,3,5-trimethylbenzene). These three atoms are the C-atom of one Me group, and C(1) and C(2) of the ring.

If all C–C bond lengths are assumed to be equal, a mesitylene group can be drawn within an equilateral triangle with the C-atoms of the Me groups at the apices of the triangle, and C(2), C(4), and C(6) of the ring at the centres of the sides of the triangle (see

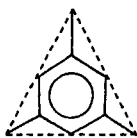


Fig. 2. An idealised mesitylene group showing the Me groups forming an equilateral triangle

Fig. 2). A bis-mesitylene sandwich is formed by two staggered mesitylene groups (see Fig. 1) with the result that the Me groups form a regular octahedron about the central Fe-atom (see Fig. 3a). These six Me groups define the 'envelope' of the dication. As a consequence of the $m\bar{3}m$ site symmetry of the Fe-atom, the mesitylene groups are extensively disordered, and can occupy any of the four pairs of opposite faces of the octahedron. However, no matter which pair of opposite faces is chosen, the six Me groups will always be in the same place, and for any two different choices of opposite faces, there will be two common ring C-atoms (see Fig. 3).

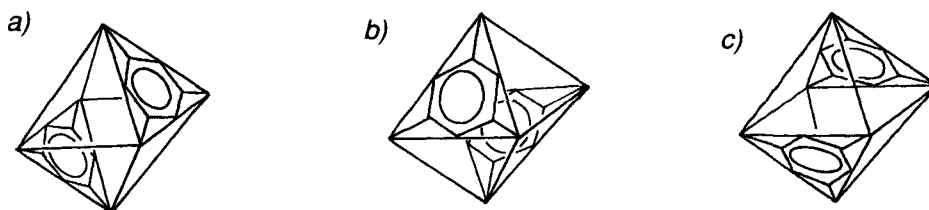


Fig. 3. Three of the four pairs of faces occupied by the disordered mesitylene groups

In reality, a mesitylene group does not fit exactly into the equilateral triangle described above, since the ring C–C and the C–Me bond lengths are not equal. The Me group thus protrudes somewhat beyond the apex of the triangle (C(2) in Table 2 should be at site (e) $[0,0,x]$ for the true apex) and the positions of the Me groups then differ slightly (0.63 \AA) from one arrangement of the mesitylene groups to another (see Fig. 4). Similarly,

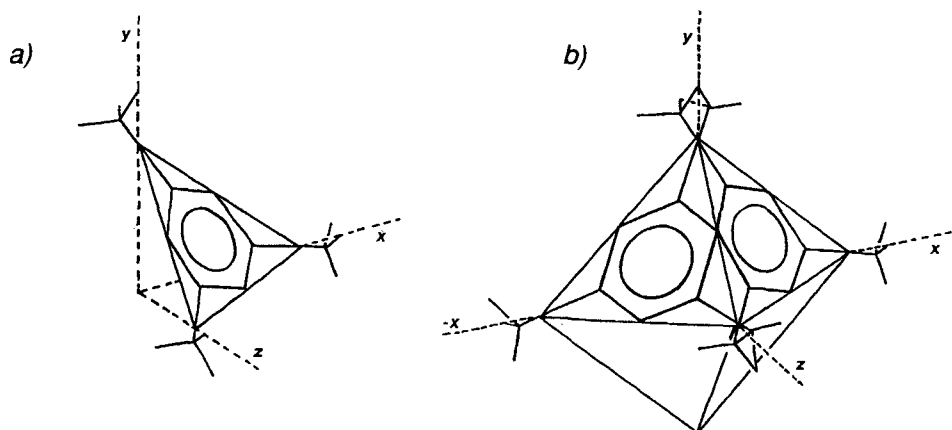


Fig. 4. Using the true positions for the Me groups, the arrangement of the H-atoms is shown: a) H(22) lies on the z-axis; b) two adjacent faces indicate how the H-atom positions are shared by the different orientations of the mesitylene rings

C(3) is not sitting right on the edge of the triangle, which is at site (*h*) $[0,y,y]$, but protrudes outside the edge of the triangle by 0.20 Å. The proximity to site (*h*) is reflected in the correlation coefficient between the *x* coordinate and U_{11} for atom C(3) of -0.918 .

The H-atoms of the Me group were located on the difference map. Given the disorder in the mesitylene groups the final refined positions (see below) of these H-atoms must be treated with *great* caution. The atoms are apparently in general positions so that the conformation shown in *Fig. 1* is only one of two possible arrangements with the other given by a reflection through a mirror perpendicular to the plane of the mesitylene ring and along the C(1)–C(2) bond. However, H(22) is close to the special position (*e*) $[0,0,x]$. If H(22) is placed on this special position, H(21) and H(23) then become related by the special position (*j*) $[0,y,z$ and $y,0,z]$ (see *Fig. 4a*). In this situation, H(22) is common³) to the four Me groups that are generated by the disorder (see *Fig. 4b*) at each apex of the octahedron. The remaining two Me H-atoms in the four Me groups then combine to form a torus around the cell axis with the H-atoms from adjacent faces becoming coincident (see *y*- or *z*-axis in *Fig. 4b*), since there are only four possible permutations of $0, \pm y, z$ and $\pm y, 0, z$. Thus, for H-atoms in these special positions, all four disordered arrangements have one H-atom in common, and any two adjacent arrangements have two other common H-atoms (see *Fig. 4b*). The refined general positions for the H-atoms are a modification of the special arrangement which keeps the formerly coincident atoms *ca.* 0.45 Å apart and spreads them more evenly over the surface of a hemisphere above each apex.

The P-atom is at the eight-fold multiplicity site (*c*) $[\frac{1}{4}, \frac{1}{4}, \frac{1}{4}]$, and, therefore, the PF_6^- is also disordered with two distinct octahedra of F-atoms about it. Both F octahedra are defined by the same single F-atom at site (*k*) $[x,x,z]$. The PF_6^- ions are on the three-fold axis of the $[\text{Fe}(\text{mes})_2]^{2+}$ ion with the F-atoms nestling between the Me groups of the adjacent ring, as seen in *Fig. 1*. The site symmetry of the Fe-atom dictates that there are eight equivalent PF_6^- ions surrounding each cation in a fluorite packing arrangement.

4. Structure Solution and Refinement. – Discussion of the refinement strategy has been deferred, until the structure has been described, since this strategy was imposed by the limitations of the structure. It was previously noted that space-group considerations indicated that the Fe-atom would be at the unit cell origin. A *Fourier* map phased on this position revealed the positions of the P-, F-, and C-atoms. Routine least-squares refinements with isotropic thermal parameters on all non-H-atoms converged at about $R \approx 0.07$, the actual value varying according to small differences in the starting values of the atomic parameters. A difference map calculated at this stage revealed the positions of the H-atoms. Routine least-squares refinements of the complete structure with anisotropic thermal parameters on just the C- and F-atoms (Fe and P are isotropic by symmetry) converged over the range of $R = 0.039\text{--}0.054$, again depending on small variations in the starting parameters. In the structure, the mesitylene group is defined by three atoms, C(1) and C(3) in the ring and C(2), the Me C-atom attached to C(1). However, as a result of the disorder there is a second C-atom close to C(3), there are three other C-atoms close to C(2) and even C(1), which is near the apex of the octahedron (see

³) This can be visualised as follows. The mesitylene ring is in the $\{x,x,x\}$ plane with the C–Me bond passing through and ‘beyond’ the *x*-axis. The C–H bond is then arranged so that the H-atom falls back on the *x*-axis. This point will now be common for any of the four planes generated by $\{x, \pm x, \pm x\}$.

Fig. 4), has three other C-atoms close to it. The consequences of disorder on the location of adjacent (disordered) H-atoms has been outlined.

On refinement, because the C- and H-atoms were under the competing influence of adjacent sites, some method had to be devised to restrain them to one chemical unit. Ultimately, the structure was refined under restraints [13] where the tolerances were adjusted to be just enough to dissuade the atoms from wandering to adjacent chemical units. Atomic positions of the nine C-atoms of the mesitylene group, with appropriate equivalences of all the parameters and appropriate adjustments of the occupation factors were used at this stage of the refinement. The C(1)–C(3) distance⁴⁾ was restrained to the aromatic C–C distance of 1.40(3) Å, and the C(1)–C(2) length to 1.52(3) Å. The ring was kept planar by restraining the Fe–C(1), Fe–C(1'), and Fe–C(1'') and Fe–C(3), Fe–C(3') and Fe–C(3'') distances to be equal and *ca.* 2.13(4) Å (the actual value was allowed to refine), and the Fe–C(2), Fe–C(2'), and Fe–C(2'') distance was restrained at 1.57 times the value of the Fe–C(ring) distance and was given a tolerance of ± 0.05 Å. The locations of the H-atoms were established (see above) at a late stage in the refinement, when the positions of the heavy atoms had all been refined to convergence. At this stage, the positions of the H-atoms were refined with the positions of the heavy atoms fixed; the C–H distances were restrained at 1.08(2) Å, and in the Me group the H–H distances and the C(1)–H distances were restrained, with a tolerance of ± 0.03 Å, to suitable lengths to ensure tetrahedral geometry. The final cycles of refinement had the H-atoms riding on the atom to which they were attached. C(1), C(2), and C(3) were restricted to special position (*k*). This refinement converged at $R = 0.0224$. When the Me H-atoms were restricted to special positions (*e*) and (*j*) (see above) the number of refined parameters was reduced from 41 to 36 and the refinement converged at $R = 0.0297$. Thus, the drop in the R value for the structure with H-atoms in general positions remains significant [14] to a probability level $\alpha = 0.005$.

The positions of the F-atoms also present some difficulty. The estimated standard deviations of the F-atom parameters show large values for x , y , U_{11} , U_{22} , and U_{12} . This reflects strong correlations between these parameters and a tendency for the F-atom to move from $x = y = 0.2595$ to $x = y = \frac{1}{4}$. The correlation coefficients with absolute value greater than 0.5 for the F-atom are: $\rho(x, U_{11}) = \rho(y, U_{22}) = -0.985$; $\rho(x, U_{12}) = \rho(y, U_{12}) = -0.986$; $\rho(U_{11}, U_{12}) = \rho(U_{22}, U_{12}) = 0.970$. When, however, the F-atom is placed at $\frac{1}{4}, \frac{1}{4}, z$ (*m*), the values of U_{11} and U_{22} rise, and the R factor converges at $R = 0.0246$. While the change in R factor is significant at the 0.5% probability level [14], the distinction between the two structures is, at best, a fine one.

The vibration ellipsoids of C(3) in the mesitylene group give some indication that the whole group might be precessing about the molecular three-fold axis. However, there is no support for this suggestion, when the displacement parameters of the C-atoms of the group are included in a *tls* analysis [15] of the rigid-body librations.

5. Comparison with Related Structures. – $[\text{Fe}(\eta^6\text{-mesitylene})_2]\text{X}_2$ systems have a long structural history. The *Mössbauer* studies of the diperchlorate were reported in 1965 [16]. The X-ray crystal structures of the dichloride and dibromide were examined photograph-

⁴⁾ There is no need to restrain any other length in the ring. C(1) is at x_1, x_1, z_1 and C(3) is at z_3, x_3, x_3 . The distance [Å] between them is given by $13.433\{(x_1 - z_3)^2 + (x_1 - x_3)^2 + (z_1 - x_3)^2\}^{1/2}$. C(3') is at x_3, z_3, x_3 which clearly is at the same distance as C(3) from C(1).

ically in 1970 [17] and were found [18] to be so seriously disordered as to preclude further study with the (then) scarce diffractometer time. (The diiodide has been examined recently, and it too is disordered [19].) The preparation of $[\text{Fe}(\text{mes})_2][\text{PF}_6]_2$ ($\text{mes} = \eta^6\text{-mesitylene}$) has been reported many times [20]. In some cases, the hexafluorophosphate was an intermediate in the preparation of a related salt for which there was a structure determination. *Green* and *Prout* [17] briefly examined the hexafluorophosphate crystals in 1970, and it is probable that other groups also examined this structure. However, there appears to be no previously published report of the solution to the structure.

The simple binary salts of the di-arene systems, where the arene molecule has at least C_3 symmetry seem to be notorious for the disorder of their structures. Apart from the $[\text{Fe}(\text{mes})_2]$ dichloride, dibromide, and diiodide mentioned above, the $[\text{Ru}_2(\text{mes})_2(\text{OH})_3]$ salt is disordered [21] as is the neutral tri-decker $[\text{Cr}_2(\text{mes})_3]$ [22]. The anionic species $\text{K}[\text{V}(\text{mes})_2]$ presents a structure with an ambiguous space group ($P2_12_12_1$ or $P2_1$) and a poorly diffracting crystal so that no definitive resolution of the fine details of the structure is possible [23]. $[\text{Co}(\text{C}_6(\text{CH}_3)_6)_2]\text{PF}_6$ is not reported as disordered [24], but the diagram of the vibration ellipsoids for the hexamethylbenzene show, for the Me C-atoms, some very large major axes of the ellipses which are all in the plane of the ring. At the very least, there is some substantial librational disorder in the cation and a disordered staggered/eclipsed conformation cannot be ruled out. $[\text{Cr}(\text{C}_6\text{H}_6)_2]\text{I}$ is disordered [25] and, although the corresponding bromide is not disordered, its low-temperature phase resembles that of the iodide [26]. It is, therefore, no surprise to discover that $[\text{Fe}(\text{mes})_2][\text{PF}_6]_2$ is also disordered. It is probable that these metal/bis-arene ions present a large and fairly regular shape which allow a number of alternative packing modes of similar energy, whereas more irregularly shaped ions are more restricted in their packing opportunities.

An interesting counter-example is given by the $[\text{M}(\text{mes})_2][\text{C}_6(\text{CN})_6]$ ($\text{M} = \text{Fe}, \text{Ru}$) salts which are not disordered [3]. In this case, however, the cation and anion form a 'super-ionic' donor-acceptor (DA) complex and, since there are usually strict orientational requirements to allow the DA interaction [27], these interactions will strongly discourage structural disorder.

In the cation, the conformation of the rings with the Ph C-atoms eclipsed with respect to each other and the Me groups staggered, is that expected from both steric and

Table 4. Comparison of the Fe–Arene Bonding and Contact Distances [Å] within a Series of Fe–Sandwich Complexes

Complex	Type ^{a)}	Fe–C ^{b)}	Fe–(Plane)	C–C ^{c)}	Ref.
1	A	2.123 (6)	1.599 (4)	1.399 (8)	This work
$[\text{Fe}(\text{C}_6\text{H}_3\text{Me}_3)_2][\text{C}_6(\text{CN})_6]$	A	2.11 (1)	1.58	1.406 (5)	[3]
$[\text{Fe}(\text{C}_6\text{Me}_6)_2][\text{iso}-\text{C}_4(\text{CN})_6]$	A	2.162 (8)	1.63	1.42 (1)	[4]
$[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_6\text{Et}_6)]\text{PF}_6$	B	2.11 (2)	1.55	1.43 (1)	[28]
$[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_6\text{Et}_6)]\text{BPh}_4$	B	2.10 (1)	1.54	1.42 (1)	[29]
$[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_6(\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)_6)]\text{PF}_6$	B	2.11 (3)	1.54	1.44 (4)	[30]
$[\text{Fe}(\text{Et}-\text{C}_6\text{H}_3\text{Me}_3)(\text{C}_6\text{H}_3\text{Me}_3)]\text{PF}_6$	C	2.11 (2)	1.57	1.41 (1)	[5]
$[\text{Fe}(\text{CH}_2\text{Cl}-\text{C}_6\text{Me}_6)(\text{C}_6\text{Me}_6)]\text{PF}_6$	C	2.11 (2)	1.55	1.40 (1)	[6]
$[\text{Fe}(\text{C}_6\text{Me}_6)_2]\text{PF}_6$	D	2.178 (8)	1.68	1.39 (2)	[4]
$[\text{Fe}(\text{C}_6\text{Me}_6)(\text{C}_5\text{H}_5)]$	D	2.100 (7)	1.58	–	[31]

^{a)} A = $[\text{Fe}(\text{arene})_2]^{2+}$, B = $[\text{Fe}(\text{arene})(\text{C}_5\text{H}_5)]^+$, C = $[\text{Fe}(\text{arene})(\text{cyclohexadienyl})]^+$, D = 19-electron complex.

^{b)} Average Fe–C(ring) distances involving the arene ring.

^{c)} Average C(ring)–C(ring) distances involving the arene ring.

electronic considerations [1]. *Table 4* summaries Fe–C(ring), Fe–(ring plane), and C(ring)–C(ring) distances for the arene rings of a number of Fe^{II} arene complexes. While the disorder in the present structure precludes any close comparison between the cation and the examples given in the table, it is clear that the cation has Fe–C, Fe–(plane), and C–C distances which are not significantly different from any of the mono- or dications listed in *Table 4*, with the exception of the bis(hexamethylbenzene), where the Fe–C lengths are significantly longer.

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Experimental. – *Bis*(η^6 -mesitylene)iron(II) hexafluorophosphate (**1**) was prepared *via* slight modification of the procedure originally described by Helling and Braitsch [32]. Anh. FeCl₃ (5.0 g, 0.0308 mol) was stirred with 100 ml of mesitylene and 12.33 g (0.0925 mol) of anh. AlCl₃ at 20° for 20 h. The mixture was hydrolysed with 150 ml of H₂O at 0°, and the orange aq. phase was separated and precipitated with sat. aq. NH₄PF₆ soln. Following washing with H₂O and Et₂O and drying under vacuum, 9.58 g (53%) of the orange solid **1** was obtained. The identity and purity of **1** was confirmed *via* ¹H- and ¹³C-NMR. ¹H-NMR ((CD₃)₂CO): 6.50 (s, 3 H); 2.64 (s, 9 H). ¹³C-NMR ((CD₃)₂CO): 113.3 (s); 92.0 (d); 19.7 (q). Crystals of **1** suitable for X-ray crystallography were obtained by slow evaporation of an acetone solution at –15°.

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