

$[\eta^6\text{-1-Chloro-2-(pyrrolidin-1-yl)-benzene}](\eta^5\text{-cyclopentadienyl})\text{iron(II) hexafluoridophosphate}$ and $(\eta^5\text{-cyclopentadienyl})\{2\text{-}[\eta^6\text{-2-(pyrrolidin-1-yl)-phenyl]phenol\}\text{iron(II) hexafluoridophosphate}$

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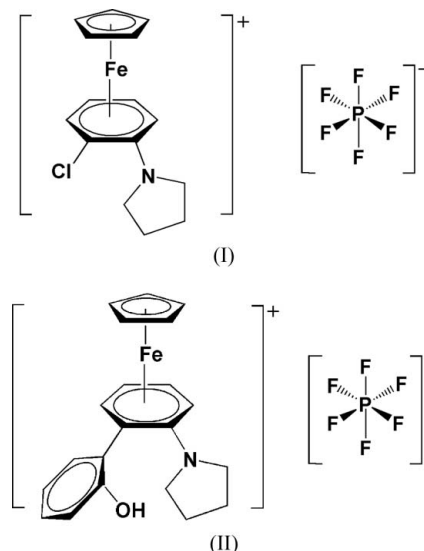
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In the complex salt $[\eta^6\text{-1-chloro-2-(pyrrolidin-1-yl)benzene}](\eta^5\text{-cyclopentadienyl})\text{iron(II) hexafluoridophosphate}$, $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_{10}\text{H}_{12}\text{ClN})]\text{PF}_6$, (I), the complexed cyclopentadienyl and benzene rings are almost parallel, with a dihedral angle between their planes of $2.3(3)^\circ$. In a related complex salt, $(\eta^5\text{-cyclopentadienyl})\{2\text{-}[\eta^6\text{-2-(pyrrolidin-1-yl)phenyl]phenol\}\text{iron(II) hexafluoridophosphate}$, $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_{16}\text{H}_{17}\text{NO})]\text{PF}_6$, (II), the analogous angle is $5.4(1)^\circ$. In both complexes, the aromatic C atom bound to the pyrrolidine N atom is located out of the plane defined by the remaining five ring C atoms. The dihedral angles between the plane of these five ring atoms and a plane defined by the N-bound aromatic C atom and two neighboring C atoms are $9.7(8)$ and $5.6(2)^\circ$ for (I) and (II), respectively.

Comment

$(\eta^6\text{-}o\text{-Chloro-}N\text{-pyrrolidinylbenzene})(\eta^5\text{-cyclopentadienyl})\text{iron(II) hexafluoridophosphate}$, along with similar *m*- and *p*-chloro-*N*-butylamino- and di-*N*-butylamino-, chloro-*N*-pyrrolidinyl- and di-*N*-pyrrolidinyl-, and some chlorocyanobenzene complexes with a cyclopentadienyliron(II) unit, were reported as part of a study of nucleophilic aromatic mono- and disubstitution reactions using *o*-, *m*- and *p*-dichlorobenzene-FeCp (Cp is cyclopentadienyl) complexes (Lee *et al.*, 1989) with amines and the cyanide anion. $(\eta^5\text{-Cyclopentadienyl})(\eta^6\text{-}o\text{-}N\text{-pyrrolidinyl-}o'\text{-hydroxybiphenyl})\text{iron(II) hexafluoridophosphate}$ was obtained in another nucleophilic substitution reaction, *viz.* a ring-opening reaction of a furan ring in dibenzofuran facilitated by η^6 -complexation with an FeCp moiety (Lee *et al.*, 1983). Having previously observed a distortion of the FeCp-complexed benzene ring, which resulted from the *o*-dipyrrolidinyl substitution of benzene

(Jenkins *et al.*, 2009), we resolved to take a closer look at FeCp complexes of related *o*-disubstituted benzenes in which one of the substituents is a pyrrolidinyl group, and the second may exert either steric hindrance or a significant electronic influence.



In the title complex salts, $[\eta^6\text{-1-chloro-2-(pyrrolidin-1-yl)benzene}](\eta^5\text{-cyclopentadienyl})\text{iron(II) hexafluoridophosphate}$, (I), and $(\eta^5\text{-cyclopentadienyl})\{2\text{-}[\eta^6\text{-2-(pyrrolidin-1-yl)phenyl]phenol\}\text{iron(II) hexafluoridophosphate}$, (II), the Fe ion is located at distances of 1.644 (4) and 1.663 (1) Å from the Cp plane, and at distances of 1.554 (4) and 1.557 (1) Å from the benzene ring plane, respectively. These values are close to those reported in the literature for similar complexes (see, for example, Piórko *et al.*, 1995; Fuentealba *et al.*, 2007; Manzur *et al.*, 2007, 2009; Hendsbee *et al.*, 2010, and references therein).

In complex (I), the benzene and Cp rings are nearly parallel, with a dihedral angle of $2.3(3)^\circ$, while in complex (II), this angle is larger, reaching $5.4(1)^\circ$. This second value is among the largest reported from our work, along with the

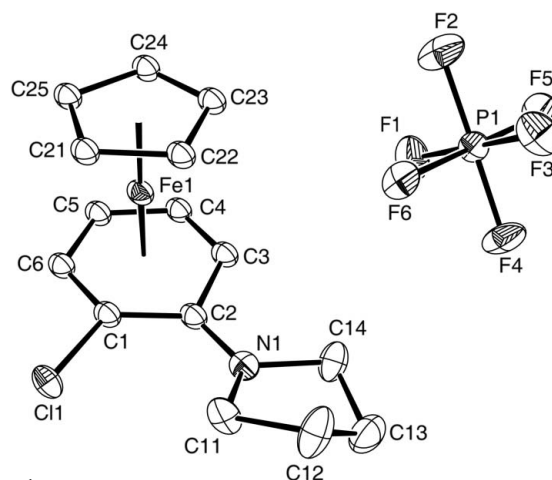


Figure 1
View of complex (I), showing the labeling of the non-H atoms and displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity.

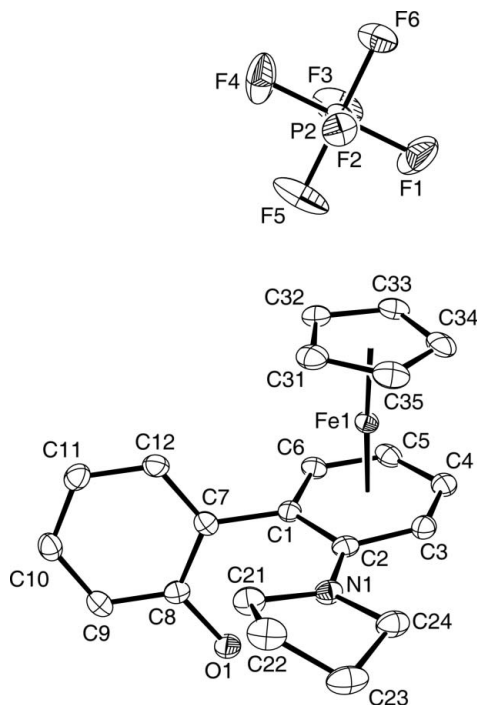


Figure 2

View of complex (II), showing the labeling of the non-H atoms and displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity.

value of $5.34(13)^\circ$ given previously by Jenkins *et al.* (2009). This is also similar to the value of 5.4° reported for the hexaethylbenzene–CpFe complex (Dubois *et al.*, 1989), although lower than the value of 7° reported for the 1,1'-trimethylenebenzene–CpFe cation (Nesmeyanov *et al.*, 1977). No standard uncertainties were provided by these authors in their reports.

For (I), the average Fe–C(benzene) distance is $2.098(10)$ Å, while the distances to the substituted atoms C1 and C2 are $2.085(10)$ and $2.237(8)$ Å, respectively. For (II), the corresponding values are $2.107(4)$ Å for the average, and $2.139(3)$ and $2.218(3)$ Å for the Fe1–C1 and Fe1–C2 distances, respectively. The distances from atom Fe1 to atom C2, which carries a pyrrolidin-1-yl substituent in both complexes, are among the largest reported for similar complexes, along with the value of $2.252(2)$ Å reported previously for one of the substituted ring C atoms of a dipyrrolidiny complex (Jenkins *et al.*, 2009). Other reports with similar Fe–C_{subst} distances include the structure of an Fe(Me₅Cp)phenoxide–water complex [C_{subst} bonded to O; $2.269(9)$ Å; Moulines *et al.*, 1995; Djakovitch *et al.*, 1996], a *p*-methylphenylhydrazine FeCp fragment in a tungsten complex [$2.24(1)$ Å; Ishii *et al.*, 1994] and an *N'*-isopropylidene hydrazone of *p*-methylphenylhydrazine [$2.201(5)$ Å; Manzur *et al.*, 2000]. Many of the Cp and pentamethyl-Cp complexes examined in a series of studies by Carrillo and coworkers (see, for example, Fuentealba *et al.*, 2007; Manzur *et al.*, 2000, 2007, 2009) have an Fe–C_{subst} (bonded to N) distance shorter than that found in our work.

The distance of the pyrrolidine N atom from the C1–C6 ring plane is $0.099(13)$ and $0.034(4)$ Å, respectively, in (I) and (II).

The N atom in each complex is located on the opposite side of the plane defined by the complexed benzene ring with respect to the Fe atom attached to this ring. These values and the long Fe1–C2 distances prompted examination of additional selected angles and planes to discern possible deformations of a complexed aromatic ring. Examination of the Fe–C_{subst}–X angles (where X is the atom of a substituent bonded to the complexed benzene ring and C_{subst} is the atom in the complex ring to which substituent X is attached) revealed that for the two different substituents present in the studied complexes, the angles have quite different values. It was expected that a longer Fe–N (bonded to aromatic C) distance may be reflected in a smaller Fe1–C2–N1 angle. For (II), the values are $135.4(2)^\circ$ for Fe1–C1–C7 and $133.8(2)^\circ$ for Fe1–C2–N1, which is in agreement with the expected order. For (I), however, these values are $133.1(5)^\circ$ for Fe1–C1–C1 and $135.2(6)^\circ$ for Fe1–C2–N1, thus the expectations were not substantiated in the case of this complex. As the N atoms are found above the complexed benzene-ring plane, on the side opposite to Fe, in both complexes, the dihedral angles between the planes formed by each substituted C atom and its direct neighbors in a ring versus planes of other ring C atoms were also examined. For (I), a plane centered at C1 and defined by atoms C2/C1/C6 intersects the C2/C3/C4/C5/C6 plane at a dihedral angle of $6.4(5)^\circ$ and intersects the plane formed by the unsubstituted ring C atoms C3/C4/C5/C6 at a dihedral angle of $5.1(6)^\circ$, the angles being essentially the same. The C1/C2/C3 plane, centered upon C2, which is an N-bound C atom, intersects the C3/C4/C5/C6/C1 plane at an angle of $9.7(8)^\circ$ and intersects the plane defined by unsubstituted ring C atoms C3/C4/C5/C6 at an angle of $10.2(9)^\circ$. For (II), the values between planes are as follows: $2.8(2)^\circ$ between C2/C1/C6 and C2/C3/C4/C5/C6, $2.5(2)^\circ$ between C2/C1/C6 and C3/C4/C5/C6, $5.6(2)^\circ$ between C1/C2/C3 and C3/C4/C5/C6/C1, and $6.2(2)^\circ$ between C1/C2/C3 and C3/C4/C5/C6. These angles seem to suggest that a longer Fe1–C2 distance and a larger dihedral angle between the C1/C2/C3 planes and a plane defined by the ring C atoms excluding atom C2 observed for (I) may be a result of the electronic influence of the chlorine neighbor and, for (II), steric crowding exerted by the second, directly linked, benzene ring. Similar values, *viz.* $6.0(5)$ and $7.1(6)^\circ$, have been reported for phenylhydrazine complexes studied by Manzur *et al.* (2000). The pyrrolidine ring of (I) in the solid state adopts a twisted conformation with C12 and C13 located out of the plane defined by the remaining three atoms. In comparison with C12, atom C13 is further away from the *o*-chloro substituent and from the Fe atom. A similar situation is observed for (II), with C22 and C23 located out of the C21/N1/C24 plane. In comparison with C22, atom C23 is further away from the uncomplexed ring of the biphenyl skeleton and from the Fe atom. Bond lengths in the pyrrolidine rings of both complexes are similar and in line with literature values (Allen *et al.*, 1987). The N atoms in both complexes show similar bond lengths to ring atom C2 [$1.344(11)$ Å for (I) and $1.356(4)$ Å for (II)] and to the methylene C atoms of the pyrrolidine rings [range $1.476(4)$ – $1.484(12)$ Å]. The C2–N1 bond length in each complex,

which is in agreement with the $C_{ar}-Nsp^2$ bond length (Allen *et al.*, 1987), implies that depyramidalization of the N atom takes effect in both complexes. This suggestion is corroborated by the geometry around the N atom; the sum of angles is close to 360° in each complex [358.4 (9) and 357.1 (4) $^\circ$, respectively, in (I) and (II), and this may, as discussed by Manzur *et al.* (2000), result from a partial delocalization of the N1 lone pair of electrons toward the complexed benzene ring.

The average C—C bond length for the complexed benzene ring of (I) is 1.410 (14) Å. For (II), the average is 1.419 (4) Å and the bond between substituted atoms C1 and C2 [1.441 (4) Å] is slightly longer than the average. In (I), the C1—C1 bond length and the Fe1—C1 distance [1.728 (10) and 2.085 (10) Å, respectively] are similar to values reported for the same bonds in an *o*-dichlorobenzene—FeCp complex (Crane, 2003). The second benzene ring in (II) shows no unusual features, and the C1—C7 bond between the rings has a length of 1.491 (4) Å, which is in agreement with literature data (Allen *et al.*, 1987). The plane of this second ring is tilted at 74.9 (3) $^\circ$ with respect to the plane of the complexed ring.

Experimental

Complex (I) was prepared from (*o*-dichlorobenzene)FeCp·PF₆ and pyrrolidine according to the method of Lee *et al.* (1989). Complex (II) was prepared by ring opening of dibenzofuran in a reaction of (dibenzofuran)FeCp·PF₆ with pyrrolidine as described by Lee *et al.* (1983). In each case, the crystals used for data collection were grown by cooling of a solution in a mixture of acetone, diethyl ether and dichloromethane at 280 K for an extended period of time. It should be noted that, despite our numerous crystallization attempts under different conditions, the quality of the crystals of complex (I) was not as good as the quality of those of complex (II), and this affected both our results and their analysis.

Compound (I)

Crystal data

[Fe(C ₅ H ₅)(C ₁₀ H ₁₂ ClN)]PF ₆	$V = 822.6$ (4) Å ³
$M_r = 447.57$	$Z = 2$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 7.000$ (2) Å	$\mu = 1.23$ mm ⁻¹
$b = 13.401$ (4) Å	$T = 100$ K
$c = 8.805$ (3) Å	$0.24 \times 0.20 \times 0.15$ mm
$\beta = 95.183$ (4) $^\circ$	

Data collection

Bruker APEXII CCD diffractometer	7536 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2008)	2880 independent reflections
$T_{min} = 0.522$, $T_{max} = 0.746$	2553 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.058$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.081$	$\Delta\rho_{max} = 1.89$ e Å ⁻³
$wR(F^2) = 0.206$	$\Delta\rho_{min} = -1.12$ e Å ⁻³
$S = 1.09$	Absolute structure: Flack (1983),
2880 reflections	1374 Friedel pairs
227 parameters	Flack parameter: 0.36 (5)
507 restraints	
H-atom parameters constrained	

Compound (II)

Crystal data

[Fe(C ₅ H ₅)(C ₁₆ H ₁₇ NO)]PF ₆	$V = 2004.8$ (4) Å ³
$M_r = 505.22$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 10.9764$ (11) Å	$\mu = 0.90$ mm ⁻¹
$b = 9.4221$ (10) Å	$T = 100$ K
$c = 19.393$ (2) Å	$0.33 \times 0.30 \times 0.28$ mm
$\beta = 91.608$ (1) $^\circ$	

Data collection

Bruker APEXII CCD diffractometer	9910 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2008)	3451 independent reflections
$T_{min} = 0.691$, $T_{max} = 0.745$	2720 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	281 parameters
$wR(F^2) = 0.122$	H-atom parameters constrained
$S = 0.85$	$\Delta\rho_{max} = 0.60$ e Å ⁻³
3451 reflections	$\Delta\rho_{min} = -0.36$ e Å ⁻³

For (I) and (II), the H atoms were placed in geometrically idealized positions, with C—H distances of 1.0 Å for all complexed, uncomplexed aromatic and Cp H atoms, 0.99 Å for aliphatic H atoms, and 0.84 Å for the hydroxy H atoms. H atoms were constrained to ride on the parent C atom, with $U_{iso}(H) = 1.2U_{eq}(C)$ for the aromatic, Cp and aliphatic H atoms, and $U_{iso}(H) = 1.5U_{eq}(O)$ for the hydroxy H atoms. The structure of (I) contains two molecules of a single enantiomer in the unit cell, and the structure itself was refined as an enantiomeric mixture. The major twin domain refined to 0.64 (5). A warning was generated by PLATON (Spek, 2009); ADDSYM indicated $P2_1/m$ pseudosymmetry. The pseudo-inversion symmetry indicated is not present as crystallographic symmetry, as a complete overlap of the two molecules is not formed upon application of the proposed inversion symmetry element (only 88% of the atoms are related by the additional symmetry element). Additionally, an extensive search for the cell of apparently higher symmetry was attempted using CELL_NOW (Bruker, 2008), with a total of 4399 reflections indexed and a minimum $I/\sigma(I)$ value of 1.75 for the spots harvested. The search for a larger cell was unsuccessful and therefore the pseudo-symmetry warning was ignored and the refinement was completed in the space group $P2_1$. Three outlying reflections with h, k, l values (4,0,0), (4,1,1) and (4,0,2) were omitted from the refinement. This complex contains a Cp ring which is π -bonded to an Fe atom, and the thermal motion of this Cp ring resulted in unsatisfactory anisotropic displacement parameters for atoms C1—C6 (coordinated aromatic ring) and atoms C21—C25 (complexed Cp ring). This was resolved through the use of restraints applied to the refinement of these atoms: the U^{ij} components of these atoms were restrained to be equal to within 0.001 Å² and their anisotropic displacement parameters were restrained to be equal to within 0.02 Å².

For both compounds, data collection: APEX2 (Bruker, 2010); cell refinement: SAINT (Bruker, 2010); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3089). Services for accessing these data are described at the back of the journal.

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