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

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In the complex salt \([\eta^6-1\text{-chloro-2-(pyrrolidin-1-yl)-benzene}(\eta^5\text{-cyclopentadienyl})\text{iron(II)} \text{hexafluoridophosphate} \times \text{PF}_6\), (I), the complexed cyclopentadienyl and benzene rings are almost parallel, with a dihedral angle between their planes of 2.3 (3)°. In a related complex salt, \((\eta^5\text{-cyclopentadienyl})[2-\eta^6-2\text{-2-(pyrrolidin-1-yl)- phenyl]phenol} \text{iron(II)} \text{hexafluoridophosphate} \times \text{PF}_6\), (II), the analogous angle is 5.4 (1)°. 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)° for (I) and (II), respectively.

Comment

\((\eta^6\text{-Chloro-N-pyrrolidinylbenzene})(\eta^5\text{-cyclopentadienyl})\text{iron(II)} \text{hexafluoridophosphate} \times \text{PF}_6\), 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. \((\eta^5\text{-Cyclopentadienyl})(\eta^6\text{-N-pyrrolidinyl-o'-hydroxybiphenyl})\text{iron(II)} \text{hexafluoridophosphate} \times \text{PF}_6\) obtained in another nucleophilic substitution reaction, viz. a ring-opening reaction of a furan ring in dibenzofuran facilitated by \(\eta^6\)-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.
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–Csubst–X angles (where X is the atom of a substituent bonded to the complexed benzene ring and Csubst 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)° for Fe1–C1–C7 and 133.8 (2)° for Fe1–C2–N1, which is in agreement with the expected order. For (I), however, these values are 133.1 (5)° for Fe1–C1–C7 and 135.2 (6)° 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)° and intersects the plane formed by the unsubstituted ring C atoms C3/C4/C5/C6 at a dihedral angle of 5.1 (6)°, 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)° and intersects the plane defined by unsubstituted ring C atoms C3/C4/C5/C6 at an angle of 10.2 (9)°. For (II), the values between planes are as follows: 2.8 (2)° between C2/C1/C6 and C2/C3/C4/C5/C6, 2.5 (2)° between C2/C1/C6 and C3/C4/C5/C6, 5.6 (2)° between C1/C2/C3 and C3/C4/C5/C6/C1, and 6.2 (2)° between C1/C2/C3 and C3/C4/C5/C6. These angles 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)°, 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,

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 value of 5.34 (13)° 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 Fe—C subst distances, including the structure of an dipyrrolidinyl complex (Jenkins et al., 2009) for one of the substituted ring C atoms of a trimethylenebenzene–C14 complex, along with the value of 2.252 (2) Å reported for Fe1–C2 distances prompted examination of additional selected angles and planes to discern possible deformations of a complexed aromatic ring. Examination of the Fe—Csubst—X angles (where X is the atom of a substituent bonded to the complexed benzene ring and Csubst 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 values 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)° for Fe1—C1—C7 and 133.8 (2)° for Fe1—C2—N1, which is in agreement with the expected order. For (I), however, these values are 133.1 (5)° for Fe1—C1—C7 and 135.2 (6)° 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)° and intersects the plane formed by the unsubstituted ring C atoms C3/C4/C5/C6 at a dihedral angle of 5.1 (6)°, 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)° and intersects the plane defined by unsubstituted ring C atoms C3/C4/C5/C6 at an angle of 10.2 (9)°. For (II), the values between planes are as follows: 2.8 (2)° between C2/C1/C6 and C2/C3/C4/C5/C6, 2.5 (2)° between C2/C1/C6 and C3/C4/C5/C6, 5.6 (2)° between C1/C2/C3 and C3/C4/C5/C6/C1, and 6.2 (2)° between C1/C2/C3 and C3/C4/C5/C6. These angles 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)°, 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=C—Nsp² bond length (Allen et al., 1987), implies that deprotonalization 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)°, respectively, in (I) and (II), and this may, as discussed by Manzur et al. (2000), result from a partial delocalization of the N 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 in the literature (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)° with respect to the plane of the complexed ring.

### Experimental
Complex (I) was prepared from (o-dichlorobenzene)FeCpPF₆ 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)FeCpPF₆ 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>V (Å³)</th>
<th>Z</th>
<th>(\mu) (mm⁻¹)</th>
<th>T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(C₅H₅)(C₁₀H₁₂ClN)]PF₆</td>
<td>822.6 (4)</td>
<td>2</td>
<td>1.25</td>
<td>100</td>
</tr>
<tr>
<td>[Fe(C₅H₅)(C₁₀H₁₂ClNO)]PF₆</td>
<td>2004.8 (4)</td>
<td>4</td>
<td>0.90</td>
<td>100</td>
</tr>
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</table>

#### Data collection

<table>
<thead>
<tr>
<th>Bruker APEXII CCD diffractometer</th>
<th>7536 measured reflections</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption correction: multi-scan (SADABS; Bruker, 2008)</td>
<td>2553 reflections with (I &gt; 2\sigma(I))</td>
</tr>
<tr>
<td>(R_{int} = 0.058)</td>
<td></td>
</tr>
</tbody>
</table>

#### Refinement

\[R(F^2 > 2\sigma(F^2)) = 0.081\]

\[wR(F^2) = 0.206\]

\[S = 1.09\]

2880 reflections

227 parameters

507 restraints

H-atoms parameters constrained

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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.

References