# metal-organic papers

# [$\mu$-1$\kappa C^1$:2($C^2$,$C^3$-$\eta$)-Allyl]tetracarbonyl-1$\kappa^2 C$,2$\kappa^2 C$-(1$\eta^5$-cyclopentadienyl)(2$\eta^5$-pentamethylcyclopentadienyl)diiron(II) hexafluorophosphate

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In the title molecule, [Fe$_2$(C$_3$H$_5$)(C$_5$H$_5$)(C$_{10}$H$_{15}$)(CO)$_4$]PF$_6$, an allyl chain bridges two Fe metal centres, forming a chiral positively charged molecular ion, with hexafluorophosphate as the counterion. In the crystal structure, both enantiomers are present.

## Comment

This structure determination was undertaken as part of our ongoing study of the reactions of mixed-ligand homo- and heterobimetallic compounds (Friedrich, Howie *et al.*, 2004). The crystal structure of the title compound, (I), is isostructural with the related heterobimetallic compound [Cp*(CO)$_2$Fe-CH$_2$CH$^+$CH$_2$RuCp(CO)$_2$]PF$_6^-$, (II) (Friedrich *et al.*, 2006).



(I)
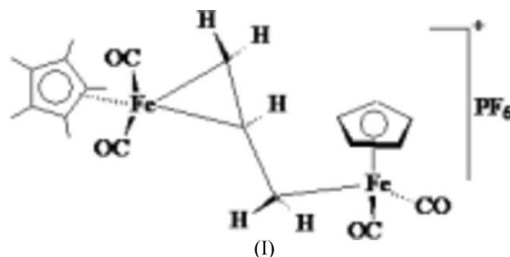
The molecular geometry and labelling scheme employed for (I) are illustrated in Fig. 1. In the molecule, two Fe metal centres are bridged by a $\sigma$,$\pi$-allyl chain, to form a molecular cation. Both Fe atoms are coordinated in a pseudo-octahedral fashion, with atom Fe1 coordinated by an $\eta^5$-pentamethyl-cyclopentadienyl ligand, two carbonyl ligands and the bridging allyl chain. Atom Fe2 is coordinated by an $\eta^5$-cyclopentadienyl ligand, two carbonyl groups and the bridging allyl chain. The two Fe metal centres differ in their type of coordination by the allyl chain. Atom Fe1 is coordinated by the allyl chain *via* two $\sigma$ bonds, which can also be considered as a $\pi$ bond. The second metal atom, atom Fe2, is coordinated by the allyl chain *via* a single $\sigma$ bond. This coordination by the allyl chain was confirmed by the fact that the H atoms were observed in difference Fourier maps, even though they were eventually included in calculated positions.

The same type of coordination was observed for (II), where the double bond of the allyl chain occurs on the side of the molecule containing the pentamethylcyclopentadienyl ligand. As previously suggested (Friedrich *et al.*, 2006), in (I), the pentamethylcyclopentadienyl ligand can better stabilize the charge on the molecular ion around atom Fe1, due to its enhanced electron-donating capability compared with the cyclopentadienyl ligand.

The ion pair of (I) crystallizes in the non-centrosymmetric space group *Cc* but both enantiomers are present in the
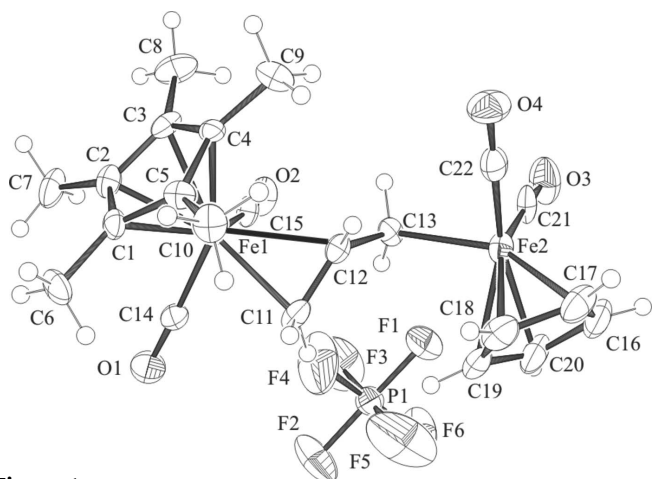
**Figure 1**
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres.
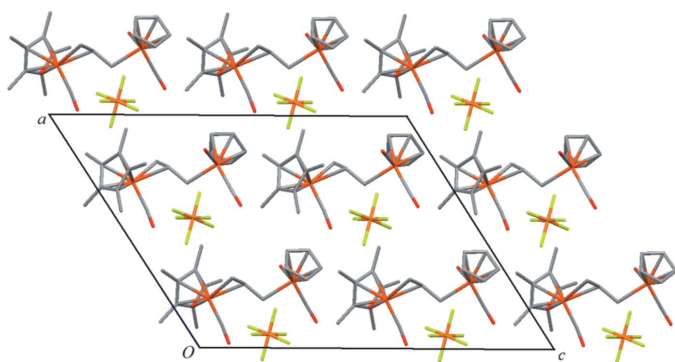


**Figure 2**
A packing diagram for (I), showing a rod representation for bonds and viewed along the *b* axis. H atoms have been omitted.

structure, by virtue of the *c*-glide symmetry. The allyl C11—C12 bond length of 1.389 (8) Å is slightly longer than a C—C double bond (expected length 1.34 Å; Brown & LeMay, 1981) and shorter than a C—C single bond (typical value 1.54 Å), and compares favourably with the corresponding bond length of 1.394 (3) Å observed for (II). This suggests that this bond displays character intermediate between single- and double-bond. The C12—C13 bond, with a bond length of 1.462 (8) Å, is slightly shorter than a C—C single bond, and is similar to the value of 1.476 (4) Å reported for the corresponding bond length in (II).

In (I), the Fe1—C(allyl) bond lengths of 2.167 (5) and 2.300 (6) Å differ significantly from one another, indicating an unsymmetrical coordination to the Fe atom. The corresponding Fe—C(allyl) bond lengths in (II) were reported as 2.173 (2) and 2.291 (3) Å. In the literature, shorter values than those observed for (I) and (II) have been reported for Cp*Fe—C σ bonds [2.069 (10) and 2.057 (3) Å; Hill *et al.*, 1999; Friedrich, Onani *et al.*, 2004]. However, a single Fe—C bond length of 2.338 Å has been reported for an Fe atom coordinated by an η-4,1,3-butadienyl ligand (Casey *et al.*, 1988).

In view of the foregoing, we conclude that atom Fe1 is coordinated by the carbenium ion in a fashion similar to what would be expected of bonding between a metal centre and an olefin. This is attributed to the electron-rich pentamethyl-cyclopentadienyl (Cp*) ligand and the increased acceptor ability of the carbenium ion. The Cp* ligand causes the metal centre to be electron-rich, thus increasing the metal-*d* to olefin-π backbonding component of the bond. This increased backbonding component is thought to be responsible for increased pyramidalization at the bound C atoms, resulting in a more metallacyclopropane structure than that seen in the related but more symmetrical compound [CpFe-$(CO)_2CH_2CHCH_2FeCp(CO)_2]PF_6$ (Laing *et al.*, 1977). Similar bonding has been reported in metal complexes of strong acceptor ligands such as tetrafluoroethylene (Curnow *et al.*, 1992).

The larger than normal anisotropic displacement ellipsoids for the F atoms of the $PF_6{}^-$ anion may indicate some disorder for these atoms, but no attempt was made to model the anion as disordered. The packing of the ions, as viewed along the *b* axis, is illustrated in Fig. 2. Enantiomers alternate along the *c* axis.

## Experimental

Compound (I) was prepared by the reaction of $[Cp*(CO)_2$-$Fe(C_3H_6)Fe(CO)_2Cp]$ (0.27 g, 0.58 mmol; Friedrich *et al.*, 1990) with $Ph_3CPF_6$ (0.22 g, 0.58 mmol), following a procedure related to reported methods (King & Bisnette, 1967; Friedrich & Moss, 1993), and crystals were grown by slow diffusion over several weeks of a twofold excess of hexane into a concentrated solution of (I) in acetone held at 278 K (yield = 0.29 g, 82.4%; m.p. = 403–405 K) .

*Crystal data*

| | |
|---|---|
| $[Fe_2(C_3H_5)(C_5H_5)(C_{10}H_{15})$-$(CO)_4]PF_6$ | $D_x = 1.647$ Mg m$^{-3}$ |
| $M_r = 610.09$ | Mo $K\alpha$ radiation |
| Monoclinic, $Cc$ | Cell parameters from 343 |
| $a = 21.198$ (7) Å | reflections |
| $b = 8.360$ (3) Å | $\theta = 2$–$32°$ |
| $c = 16.611$ (7) Å | $\mu = 1.32$ mm$^{-1}$ |
| $\beta = 123.43$ (3)° | $T = 200$ (2) K |
| $V = 2456.7$ (18) Å$^3$ | Thin plate, yellow |
| $Z = 4$ | $0.20 \times 0.20 \times 0.05$ mm |

*Data collection*

| | |
|---|---|
| Oxford Excalibur2 diffractometer | 3684 reflections with $I > 2\sigma(I)$ |
| $\omega$–$2\theta$ scans | $R_{int} = 0.062$ |
| Absorption correction: multi-scan | $\theta_{max} = 31.9°$ |
| (*SORTAV*; Blessing, 1995) | $h = -27 \rightarrow 31$ |
| $T_{min} = 0.778$, $T_{max} = 0.937$ | $k = -12 \rightarrow 11$ |
| 11364 measured reflections | $l = -23 \rightarrow 23$ |
| 6555 independent reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o{}^2) + (0.0563P)^2]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.061$ | where $P = (F_o{}^2 + 2F_c{}^2)/3$ |
| $wR(F^2) = 0.134$ | $(\Delta/\sigma)_{max} = 0.001$ |
| $S = 0.86$ | $\Delta\rho_{max} = 0.67$ e Å$^{-3}$ |
| 6555 reflections | $\Delta\rho_{min} = -0.41$ e Å$^{-3}$ |
| 317 parameters | Absolute structure: Flack (1983), |
| H-atom parameters constrained | with 2621 Friedel pairs |
| | Flack parameter: 0.35 (2) |

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All H atoms were observed in a difference Fourier map but were placed in calculated positions, with aromatic C—H distances of 0.93 Å, methyl C—H distances of 0.96 Å, methylene C—H distances of 0.97 Å and methine C—H distances of 0.98 Å, and were refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}(C)$ for methyl H. The Flack parameter (Flack, 1983) indicates that the crystal is an inversion twin, with the ratio of components 0.35 (2):0.65 (2).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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