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Key indicators

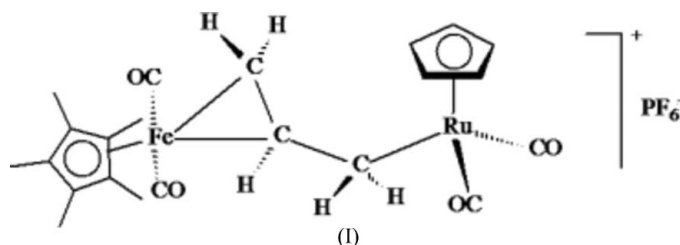
Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.030
 wR factor = 0.078
Data-to-parameter ratio = 21.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>. $[\mu\text{-}1\kappa\text{C}^1:2(\text{C}^2, \text{C}^3\text{-}\eta)\text{-Allyl}]\text{tetracarbonyl-}1\kappa^2\text{C}, 2\kappa^2\text{C-(}1\eta^5\text{-cyclopentadienyl)(}2\eta^5\text{-penta-}1\text{-methylcyclopentadienyl)rutheniumiron hexafluorophosphate}$

In the molecule of the title compound, $[\text{FeRu}(\text{C}_3\text{H}_5)(\text{C}_5\text{H}_5)(\text{C}_{10}\text{H}_{15})(\text{CO})_4]\text{PF}_6$, two metal centers are bridged by an allyl chain, resulting in a chiral heterobimetallic molecular ion, with hexafluorophosphate as counter-ion. Both enantiomers are present in the crystal structure, forming a racemate.

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Comment

The structure determination of the title compound, (I), was undertaken as part of our ongoing study of the reactions of mixed-ligand, homo- and heterobimetallic compounds (Friedrich *et al.*, 1990). In (I), a σ, π -allyl chain bridges two metal centers, forming a chiral, heterodinuclear molecular cation. The Fe and Ru atoms are coordinated in pseudo-octahedral fashions by η^5 -pentamethylcyclopentadienyl and η^5 -cyclopentadienyl ligands, respectively, and also by two carbonyl ligands and by the bridging allyl chain. The molecular geometry is illustrated in Fig. 1, where C12 is a chiral atom.



On the Fe side of the molecular ion, the metal is coordinated by the allyl chain *via* two σ -bonds (this coordination could also be viewed as being *via* a π bond), while the Ru atom is coordinated *via* a single σ -bond. It is thought that this coordination occurs because the side containing the pentamethylcyclopentadienyl ligand can better stabilize the charge on the molecular ion around the Fe atom due to its enhanced electron-donating capability compared to the cyclopentadienyl ligand. It should be emphasized that, even though the H atoms were positioned geometrically, they could be observed in the Fourier map, which confirmed the allyl coordination in the molecular cation.

Both enantiomers are present in the crystal structure, resulting in a racemic mixture. The asymmetric unit consists of one molecular cation and one anion, with four asymmetric units in the unit cell. In the pentamethylcyclopentadienyl ligand and in the cyclopentadienyl ligand, atoms C1–C7 and C16–C20 are coplanar, with maximum deviations of 0.034 (3) and 0.009 (4) Å for atoms C2 and C19, respectively, from their least-squares planes; the dihedral angle between the two planes is 59.3 (1)°.

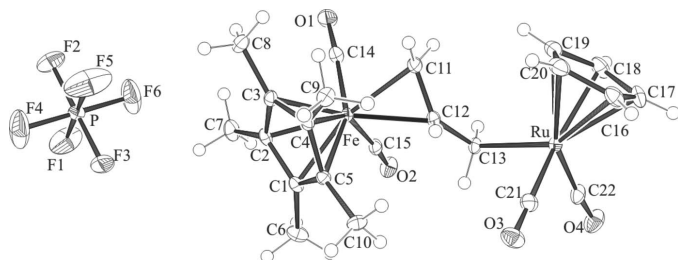


Figure 1
The asymmetric unit of the title compound with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

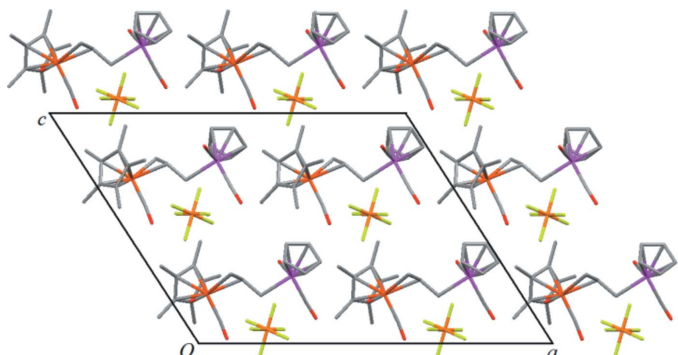


Figure 2
Packing diagram for (I), viewed down the *b* axis.

The Ru—C13 [2.182 (3) Å] bond length is similar to those reported for Ru—C σ -bonds [2.164 (7), 2.180 (9) and 2.189 (3) Å (Finch *et al.*, 1989; Gafoor *et al.*, 1996)]. In (I), the Fe—C(allyl) [2.173 (2) and 2.291 (3) Å] bond lengths are significantly different from one another, indicating an unsymmetrical coordination to the Fe atom. These bonds are longer than expected for an Fe—C [2.069 (10) and 2.057 (3) Å (Hill *et al.*, 1999; Friedrich *et al.*, 2004)] single bond. However, a single Fe—C (2.338 Å) bond was reported for an Fe atom coordinated by a η -4,1,3-butadienyl ligand (Casey *et al.*, 1988).

The allyl C11—C12 [1.394 (3) Å] bond is slightly longer than a C=C double bond (typical value of 1.33 Å), and shorter than a C—C single bond (expected length 1.54 Å). It is suggested that this bond displays both single- and double-bond character. The C12—C13 [1.476 (4) Å] bond is slightly shorter than a C—C single bond. In the crystal structure of the related ionic compound (CpFe(CO)₂CH₂CH⁺CH₂Fe—Cp(CO)₂PF₆[−], (II) (Laing *et al.*, 1977), (where Cp is η^5 -C₅H₅), a more symmetrical cation was described. The authors reported only one metal—C σ -bond per metal center and, in addition, the presence of a weak Fe...CH interaction for both metals. Fe—C σ -bond lengths were given as 2.13 and 2.12 Å, and the weak Fe...CH interaction distances were given as 2.59 and 2.72 Å. The C—C bonds to the β -carbon were given as 1.41 and 1.43 Å. In (I), the longer Fe—C12(allyl) [2.291 (3) Å] bond is significantly shorter than the weak Fe...CH interactions reported in (II), and the long Ru...C12 [2.975 (3) Å] distance clearly indicates that the type of coordination is different from that observed in (II). Thus, in going from the more symmetrical compound (II) to the title compound (I) by

substituting an Fe metal atom with an Ru atom, as well as replacing the Cp ligand coordinated to the Fe atom with a Cp* ligand, [where Cp* is η^5 -C₅(CH₃)₅], a different type of coordination is observed.

The coordination observed in (I) is similar to that adopted by the monometallic compound dicarbonyl(η -2-3,3-dimethylbutene)(η^5 -pentamethylcyclopentadienyl)iron tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, (III) (Coombs *et al.*, 2004), where Fe—C(allyl) bond lengths are 2.096 (6) and 2.233 (7) Å, and the C—C allyl bond lengths are 1.393 (9) and 1.551 (9) Å. The packing of ions, as viewed down 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)₂Fe-(C₃H₆)Ru(CO)₂Cp (0.50 g, 0.98 mmol) (Friedrich *et al.*, 1990) with Ph₃CPF₆ (0.38 g, 0.98 mmol) following a procedure related to reported methods (King & Bisnette, 1967; Friedrich & Moss, 1993) and crystals were grown by slow diffusion, over several days, of a fivefold excess of diethyl ether into a concentrated solution of compound (I) in acetone held at 278 K (yield 0.57 g, 88.6%, m.p. 392–393 K).

Crystal data

[FeRu(C₃H₅)(C₅H₅)(C₁₀H₁₅)-
(CO)₄]PF₆
M_r = 655.31
Monoclinic, *Cc*
a = 21.246 (2) Å
b = 8.3301 (18) Å
c = 16.459 (2) Å
 β = 123.109 (6)°
V = 2440.0 (7) Å³
Z = 4

D_x = 1.784 Mg m^{−3}
Mo *K* α radiation
Cell parameters from 1090
reflections
 θ = 2–32°
 μ = 1.35 mm^{−1}
T = 100 (2) K
Block, yellow
0.40 × 0.20 × 0.20 mm

Data collection

Oxford Excalibur2 diffractometer
 ω -2 θ scans
Absorption correction: multi-scan
(Blessing, 1995)
*T*_{min} = 0.608, *T*_{max} = 0.766
11813 measured reflections
7095 independent reflections

6827 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.021
 θ _{max} = 31.9°
h = −30 → 31
k = −12 → 9
l = −23 → 23

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.030
wR(*F*²) = 0.078
S = 1.05
7095 reflections
336 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.055P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = 0.024
 $\Delta\rho$ _{max} = 0.80 e Å^{−3}
 $\Delta\rho$ _{min} = −0.79 e Å^{−3}
Absolute structure: Flack (1983);
3030 Friedel Pairs
Flack parameter: 0.007 (14)

H atoms were positioned geometrically [C—H = 0.93 and 0.98 (CH), 0.97 (CH₂) and 0.96 Å (CH₃)] and constrained to ride on their parent atoms, with *U*_{iso}(H) = 1.2 (1.5 for methyl) times *U*_{eq}(C).

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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