X-Ray Crystallographic Determination of the Structure of $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_8H_8)^+][SbF_6^-]$, a Heptafulvene Derivative of Iron(II)

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Summary A single-crystal *X*-ray diffraction study of $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_8H_8)^+][SbF_6^-]$ shows the heptafulvene moiety to be bonded to the iron atom *via* an iron–carbon σ-bond, the cationic charge thus residing within the conjugated seven-membered ring of the heptafulvene system.

HEPTAFULVENE (I) is a conjugated, non-benzenoid hydrocarbon which is stable only in dilute solution at −170°, and which cannot be isolated.[1] Kerber and his co-workers[2] have shown that $[Ph_3C^+][PF_6^-]$ will abstract a β-hydrogen from $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}CH_2CH_2Ph)$ (II), yielding the styrene complex, (III). $[Ph_3C^+][SbF_6^-]$ also abstracts a

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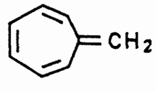
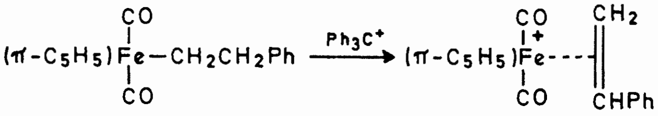
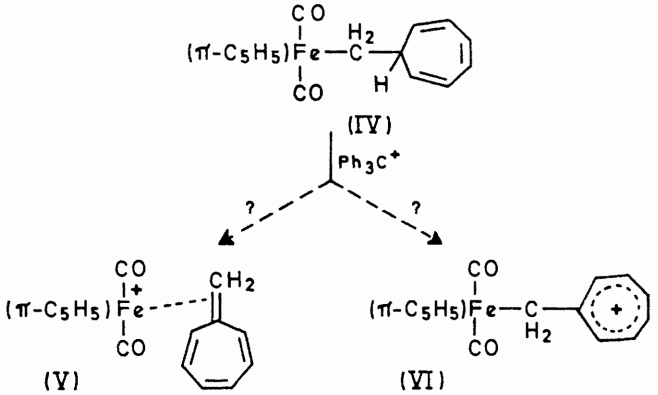
β-hydrogen from (π-C_5H_5)Fe(CO)$_2$(σ-C_8H_9) (IV), yielding the first-reported stable transition-metal complex of hept fulvene, [(π-C_5H_5)Fe(CO)$_2$(C_8H_8)$^+$][SbF_6^-]. Unfortunately, ^{1}H nuclear magnetic resonance studies on this product fail to provide unambiguous information as to whether the heptafulvene ligand is π-bonded (V) or σ-bonded (VI) to the central iron atom.[2] We have now undertaken a single-crystal X-ray diffraction study of [(π-C_5H_5)Fe(CO)$_2$(C_8H_8)$^+$][SbF_6^-].



(I)



(II) (III)



(IV) (V) (VI)

Crystals were obtained as thin red-brown needles from CH_2Cl_2–Et_2O under N_2. *Crystal data*: $C_{15}H_{13}SbO_2F_6Fe$, M 516.85, monoclinic, a = 7·075, b = 13·952, c = 36·747 Å, β = 91·76°, U = 3626 Å^3, D_m = 1·78 ± 0·06, D_c = 1·89 g cm^{-3}, Z = 8, space group $P2_1/c$ (C^5_{2h}; No. 14).

Reflections to $\sin\theta$ = 0·75 (Cu-K_α radiation, $\bar{\lambda}$ = 1·5418 Å) were collected with a 0·01°-incrementing Supper Pace "Buerger Automated Diffractometer" using equi-inclination Weissenberg geometry and a 'stationary-background, ω-scan, stationary-background' counting sequence.[3] All data were corrected for absorption (μ = 181 cm^{-1}).

The asymmetric unit of the crystal contains two [(π-C_5H_5)-Fe(CO)$_2$(C_8H_8)$^+$] cations and two [SbF_6^-] anions; the analysis thus requires the location of 50 non-hydrogen atoms. Iron positions (0·514, 0·467, 0·207; 0·524, 0·690, 0·427) and antimony positions (0·012, 0·310, 0·454; 0·017, 0·095, 0·188) were obtained from a Patterson map; the remaining 46 non-hydrogen atoms were located from a Fourier synthesis. Full-matrix least-squares refinement of positional and isotropic thermal parameters has led to convergence at R = 12·3%. Estimated standard deviations on bond lengths [*e.g.*, σ(Fe–C) = 0·05, σ(C–C) = 0·07 Å] are larger than normal due to two factors: (i) crystals decompose fairly rapidly (*ca.* 25% in 24 h) in the X-ray beam, and (ii) diffraction data are weak—of the 3797 measured reflections only 1521 are significantly (3σ) above background.

The [SbF_6^-] ions each have the expected O_h symmetry, the mean Sb–F bond distance being 1·82 Å (*cf.*, 1·78 Å in $Na^+SbF_6^-$).[4] The two independent [(π-C_5H_5)Fe(CO)$_2$(C_8H_8)$^+$] ions have essentially the same geometry, the heptafulvene ligand of each being bonded to the iron(II) centre *via* a σ-bond, the ion thus corresponding to structure (VI) [see Figure]. The positive charge of the cation presumably resides within the seven-membered ring of the heptafulvene ligand.

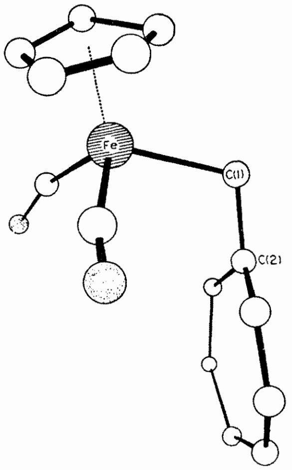


FIGURE. *The stereochemistry of a* [(π-C_5H_5)Fe(CO)$_2$(C_8H_8)$^+$] *ion.*

(The following values are the mean of those from the two crystallographically-independent cations.) The Fe–C(1) distance of 2·16 ± 0·05 Å is in agreement with the more-accurately-measured Fe–C σ-bond lengths of 2·11 ± 0·02 Å in (π-C_5H_5)Fe(CO)$_2$(σ-C_5H_5)[5] and 2·06 ± 0·02 Å in (π-C_5H_5)Fe(CO)$_2$(CH_2CO_2H).[6] There is no significant interaction between the iron atom and the β-carbon atom [Fe · · · C(2) = 3·00 Å]. The eight carbon atoms of the heptafulvene ligand form a plane (root-mean-square deviation 0·04 Å) in which the C(1)–C(2) bond length is 1·47 Å and the mean carbon–carbon distance within the seven-membered ring is 1·44 Å. Average Fe–(CO) and C–O distances are 1·84 and 1·17 Å, respectively, with angles between the monodentate ligands being (OC)–Fe–(CO) = 99 and (OC)–Fe–C(1) = 98°. The iron atom lies 1·78 Å below the planar (π-C_5H_5) ring, with individual iron-carbon distances averaging 2·10 Å. The mean carbon–carbon distance within the π-cyclopentadienyl system is 1·42 Å.

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