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Syntheses and X-ray Crystal Structures of Five- and Six-Coordinated Iron(I) and Iron(II) Complexes with the Same (η^5 -C₅Me₅)Fe(dppe) Framework

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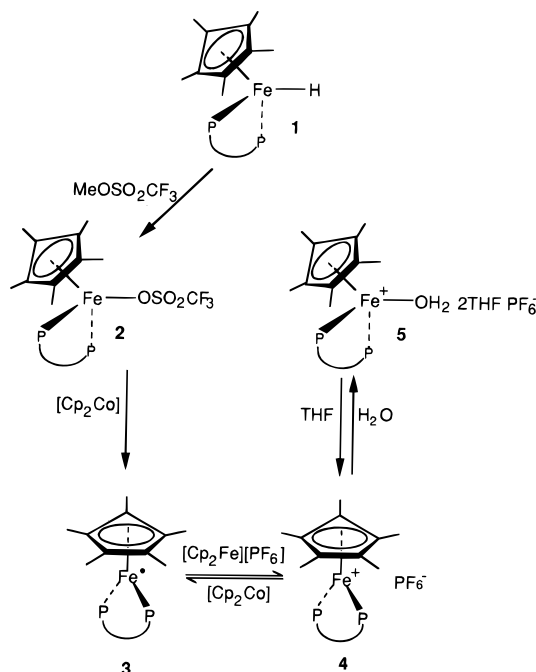
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Summary: The one electron reduction of Cp*Fe(dppe)-(OSO₂CF₃) (**2**) with cobaltocene gave the d⁷ iron(I) Cp*Fe(dppe) (**3**, 90%) as thermally stable orange crystals, whereas the one-electron oxidation of **3** with ferrocenium hexafluorophosphate afforded the new d⁶ iron(II) 16-electron complex [Cp*Fe(dppe)][PF₆] (**4**, 98%) isolated as an stable orange powder. The X-ray crystal structures of **3** and **4** show that their major structural difference concerns the "pyramidalization" of the metal center.

Organometallic radicals and coordinatively unsaturated transition metal complexes are recognized to play an important role in material science¹ as well as in catalytic processes.² However, despite considerable efforts, no stable d⁷ iron(I)^{2,3} and d⁶ iron(II)⁴ compounds in the wide [(C₅R₅)FeL₂] series (R = H, alkyl, aryl; L = two-electron ligand) have ever been isolated and X-ray characterized.⁵ In this communication, we report the synthesis, the isolation, the X-ray characterization, and the electrochemical behavior of the neutral 17-electron iron(I) [Cp*Fe(dppe)] (**3**) and the 16-electron iron(II) [Cp*Fe(dppe)][PF₆] (**4**) complexes [Cp* = η^5 -C₅Me₅, dppe = η^2 -ethylenebis(diphenylphosphine)]. We also report on two related 18-electron iron derivatives, namely the triflate adduct [Cp*Fe(dppe)(OSO₂CF₃)] (**2**) and the organometallic iron aqua complex [Cp*Fe(dppe)(OH₂·2THF)][PF₆] (**5**), which both exist in solution as an equilibrium with the 16-electron cation [Cp*Fe(dppe)]⁺ (**4**, Scheme 1).

Treatment of a diethyl ether solution of the iron hydride Cp*Fe(dppe)H (**1**)⁶ with an excess of methyl triflate caused the formation of a yellow suspension that

Scheme 1



quickly turned to an air- and moisture-sensitive green solid. Recrystallization from a THF/pentane mixture afforded the triflate complex Cp*Fe(dppe)(OSO₂CF₃) (**2**) in 85% yield as dark green crystals.⁷ The triflate was demonstrated to be covalently bound to the metal center in the solid state by X-ray crystallographic analysis.⁸ As expected, the Fe–O bond distance of 2.128(4) Å is longer than the Fe–O bond length measured in a previously reported iron triflate compound [Cp*Fe(CO)₂-(OSO₂CF₃), 2.007(3) Å]⁹ and rather long in comparison with the data available in the literature.¹⁰

Treatment of **2** with 0.9 equiv of cobaltocene in THF at –80 °C, followed by removal of the solvent under vacuum at –20 °C and crystallization from pentane, gave Cp*Fe(dppe) (**3**) as thermally stable orange crystals.

(7) Analytical data for **2–5** are as follows. Anal. Calcd for C₃₇H₃₉F₃FeO₃P₂S (**2**): C, 60.17; H, 5.32. Found: C, 59.82; H, 5.33. Calcd for C₃₆H₃₉FeP₂ (**3**): C, 73.35; H, 6.67. Found: C, 73.76; H, 6.82. Calcd for C₃₆H₃₉F₆FeO₃P₃ (**4**): C, 58.87; H, 5.35. Found: C, 58.55; H, 5.63. Calcd for C₄₄H₅₇F₆FeO₃P₃ (**5**): C, 58.94; H, 6.41. Found: C, 58.97; H, 6.49.

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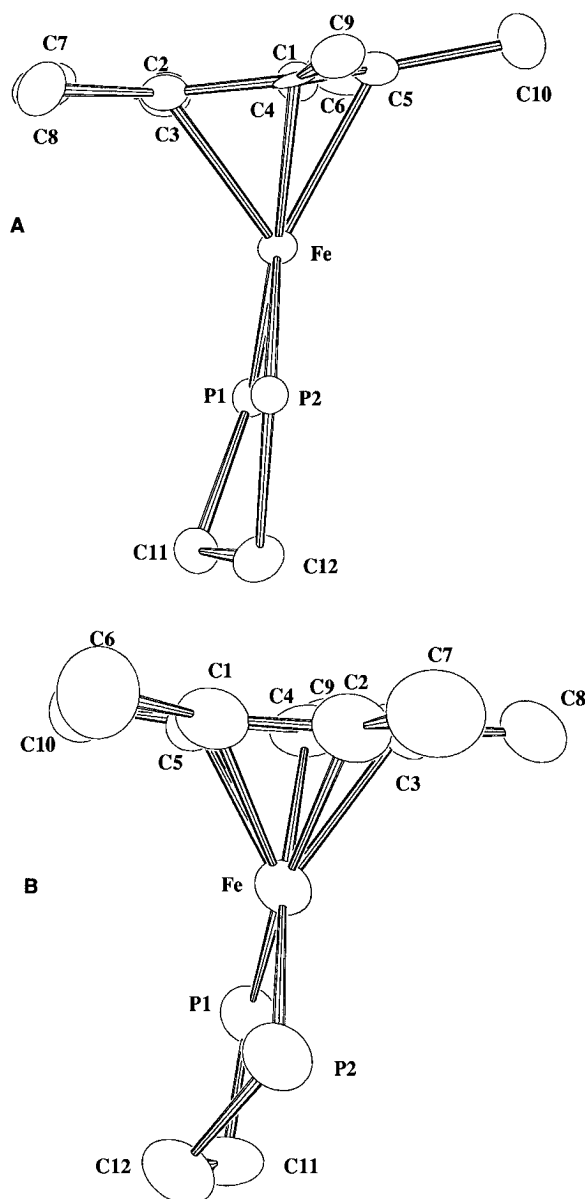


Figure 1. Solid-state molecular structures of **3** (A) and **4** (B), with 50% probability thermal ellipsoids. The phenyl rings of the dppe ligand are omitted for clarity. Selected interatomic distances (Å) and angles (deg): **3**, Fe–P(1) = 2.126(3), Fe–P(2) = 2.148(3), Fe–Cp*_{centroid} = 1.722(4), P(1)–Fe–P(2) = 86.87(8); **4**, Fe–P(1) = 2.259(4), Fe–P(2) = 2.231(4), Fe–Cp*_{centroid} = 1.777(4), P(1)–Fe–P(2) = 86.5(2).

tals in 90% yield ($\mu_{\text{eff}} = 1.5 \mu_{\text{B}}$). The molecular structure of **3** determined by a single-crystal X-ray diffraction analysis consists of discrete monomeric 17-electron d⁷ Fe(I) complex.^{7,11,12} The geometry of **3** is roughly intermediate between a C_{2v} pyramidal structure with a vacant site and a distorted C_{2v} planar polyhedron, assuming that the pentamethylcyclopentadienyl group occupies three ligand sites and the dppe the two others (Figure 1A). The presence of the seventeenth electron

causes a lowering of the symmetry as it can be pointed out by comparison with the structure of **4** (see below). The complex **3** constitutes the first neutral half-sandwich 17-electron iron-centered radical to be isolated and structurally characterized.^{3,13}

The 17-electron complex **13** reacts with ferrocenium hexafluorophosphate to afford the new half-sandwich iron(II) 16-electron complex [Cp*Fe(dppe)][PF₆] (**4**) isolated as an orange powder in 98% yield. X-ray-quality crystals of **4** were grown by slow diffusion of pentane into a THF solution of **4**. The 16-electron structure of the organometallic cation **4** was established by an X-ray crystal structure (Figure 1B).^{7,14} The molecule is close to the C_{2v} symmetry. Examination of the structural data reveals that the one-electron oxidation of **3** to **4** significantly affects the bonding pattern of the Cp*Fe(dppe) framework. In particular, an increase of the average Fe–P bond distance by 0.11 Å and a slight increase of the Fe–Cp* centroid of 0.04 Å are observed.¹⁵ Whereas the P–Fe–P bond angles are the same in **3** and **4** (~86.5°), the major structural difference between these two five-coordinated iron complexes concerns the “pyramidalization” of the metal center. Indeed, the angle defined by the ring centroid, the Fe atom, and the middle of the P(1)–P(2) vector is close to 180° in **4** (175.2°), indicating that the coordination around the metal atom is pseudo-trigonal bipyramidal (hybridization dsp³). In the 17-electron neutral complex **3** a distortion of the trigonal bipyramidal environment toward an octahedral one is observed. The corresponding angle of 167.8° is intermediate between those expected for a trigonal bipyramid (180°) and an ideal octahedral geometry (144.7°).¹⁶ Moreover, it is noteworthy that the shortest distance between the iron center and the ortho carbon atoms of the phenyl groups of the dppe is 3.50 Å, definitely excluding an agostic interaction between the electron-deficient metal center and a C–H bond. In THF solution, the complex **4** exhibits a magnetic moment $\mu_{\text{eff}} = 3.3 \mu_{\text{B}}$ (310 K, Evans' method)¹⁷ corresponding to two unpaired electrons. The planar structure of **4**, usually observed for d⁸ 18-electron systems such as CpCo(CO)₂,¹⁸ is a consequence of its high-spin electronic configuration. In contrast, it was predicted on the basis of MO calculations that the diamagnetic d⁶ complexes of the [CpML₂] type having only 16-electron valence should be pyramidal compounds,¹⁹ in agreement with experimental data.²⁰

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(14) Crystal data for [Cp*Fe(dppe)][PF₆] (**4**): C₃₆H₃₉FeF₆P₃, monoclinic, C_c , $a = 19.612(10)$ Å, $b = 8.422(6)$ Å, $c = 20.513(9)$ Å, $\beta = 113.88(5)^\circ$, $V = 3098(2)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.264$ g cm⁻³, $R(F) = 5.7\%$ for 2162 independent reflections ($2\theta_{\text{max}} = 50^\circ$, scan $\omega/2\theta = 1$). All non-hydrogen atoms were found by direct methods with the SHELX-86 program. Hydrogen atoms were idealized, and the whole structure was refined.

(15) Fe–P bond distance variation upon one-electron oxidation could be interpreted in terms of a π -back-bonding contribution: Orpen, A. G.; Connelly, N. G. *Organometallics* **1990**, *9*, 1206.

(16) Note that in the pseudo-octahedral complexes **2** and **5** the corresponding values are both equal to 153.2°.⁸

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(11) Details of the structure determinations are provided as Supporting Information.

(12) Crystal data for Cp*Fe(dppe) (**3**): C₃₆H₃₉FeP₂, monoclinic, $P2_1/n$, $a = 10.522(2)$ Å, $b = 15.772(4)$ Å, $c = 24.107(5)$ Å, $\beta = 91.95(2)^\circ$, $V = 3998(2)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.337$ g cm⁻³, $R(F) = 6.2\%$ for 2217 independent reflections ($2\theta_{\text{max}} = 50^\circ$, scan $\omega/2\theta = 1$). All non-hydrogen atoms were found by direct methods with the SHELX-86 program. Hydrogen atoms were idealized, and the whole structure was refined.

