Syntheses and X-ray Crystal Structures of Five- and Six-Coordinated Iron(I) and Iron(II) Complexes with the Same (η^5-C_5Me_5)Fe(dppe) Framework

Paul Hamon,[†] Loïc Toupet,[‡] Jean-René Hamon,[*,†] and Claude Lapinte[*,†]

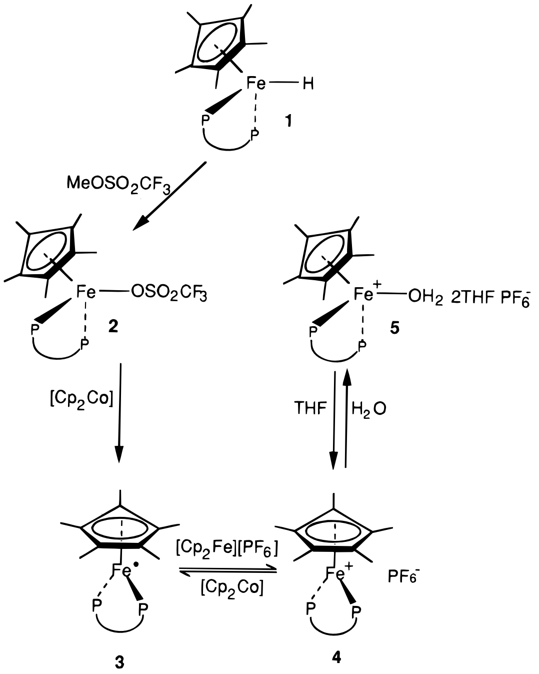
Laboratoire de Chimie des Complexes de Métaux de Transition et Synthèse Organique, URA CNRS 415, and Groupe Matière Condensée et Matériaux, URA CNRS 804, Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cedex, France

Received September 26, 1995[⊗]

*Summary: The one electron reduction of Cp*Fe(dppe)-(OSO_2CF_3) (**2**) with cobaltocene gave the d^7 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 d^6 iron(II) 16-electron complex [Cp*Fe(dppe)][PF_6] (**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 science[1] as well as in catalytic processes.[2] However, despite considerable efforts, no stable d^7 iron(I)[2,3] and d^6 iron(II)[4] compounds in the wide [(C_5R_5)FeL_2] 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)][PF_6] (**4**) complexes [Cp* = η^5-C_5Me_5, dppe = η^2-ethylenebis(diphenylphosphine)]. We also report on two related 18-electron iron derivatives, namely the triflate adduct [Cp*Fe(dppe)(OSO_2CF_3)] (**2**) and the organometallic iron aqua complex [Cp*Fe(dppe)($OH_2 \cdot 2THF$)][PF_6] (**5**), which both exist in solution as an equilibrium with the 16-electron cation [Cp*Fe(dppe)]$^+$ (**4**, Scheme 1).

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 quickly turned to an air- and moisture-sensitive green solid. Recrystallization from a THF/pentane mixture afforded the triflate complex Cp*Fe(dppe)(OSO_2CF_3) (**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)$_2$-(OSO_2CF_3), 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 crys-

---

[†] URA CNRS 415.

[‡] URA CNRS 804.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

(1) (a) Parshall, G. W. *Organometallics* **1987**, *6*, 687. (b) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385.

(2) (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978. (b) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217. (c) Trogler, W. C., Ed. *Organometallic Radical Processes*; Elsevier: New York, 1989. (d) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189.

(3) (a) Bianchini, C.; Laschi, F.; Masi, D.; Ottaviani, F. M.; Pastor, A.; Peruzzini, M.; Zanello, P.; Zanobini, F. *J. Am. Chem. Soc.* **1993**, *115*, 2723. (b) MacNeil, J. H.; Chiverton, A. C.; Fortier, S.; Baird, M. C.; Hynes, R. C.; Williams, A. J.; Preston, K. F.; Ziegler, T. *J. Am. Chem. Soc.* **1991**, *113*, 9834. (c) Fortier, S.; Baird, M. C.; Preston, K. F.; Morton, J. R.; Ziegler, T.; Jaeger, T. J.; Watkins, W. C.; MacNeil, J. H.; Watson, K. A.; Hensel, K.; Le Page, Y.; Charland, J.-P.; Williams, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 542.

(4) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley and Sons: New York, 1988; p 716. (b) Kazlauskas, R. J.; Wrighton, M. S. *Organometallics* **1982**, *1*, 602.

(5) During the reviewing process of this paper, a d^6 iron(II) complex was published: Leal, A. D.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *Organometallics* **1995**, *14*, 3839.

(6) (a) Roger, C.; Marseille, P.; Salus, C.; Hamon, J.-R.; Lapinte, C. *J. Organomet. Chem.* **1987**, *336*, C13. (b) Roger, C.; Hamon, P.; Toupet, L.; Rabaâ, H.; Saillard, J.-Y.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1991**, *10*, 1045.

(7) Analytical data for **2**−**5** are as follows. Anal. Calcd for $C_{37}H_{39}F_3FeO_3P_2S$ (**2**): C, 60.17; H, 5.32. Found: C, 59.82; H, 5.33. Calcd for $C_{36}H_{39}FeP_2$ (**3**): C, 73.35; H, 6.67. Found: C, 73.76; H, 6.82. Calcd for $C_{36}H_{39}F_6FeP_3$ (**4**): C, 58.87; H, 5.35. Found: C, 58.55; H, 5.63. Calcd for $C_{44}H_{57}F_6FeO_3P_3$ (**5**): C, 58.94; H, 6.41. Found: C, 58.97; H, 6.49.

(8) Hamon, P.; Toupet, L.; Hamon, J.-R.; Lapinte, C. Work in progress.

(9) Humphrey, M. B.; Lamanna, W. M.; Brookhart, M.; Husk, G. R. *Inorg. Chem.* **1983**, *22*, 3355.

(10) (a) Hamon, P.; Toupet, L.; Hamon, J.-R.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1994**, 931. (b) Churchill, M. R.; Wormald, J. *Inorg. Chem.* **1983**, *22*, 3355. (c) Darensbourg, D. J.; Day, C. S.; Fisher, M. B. *Inorg. Chem.* **1981**, *20*, 3577.

0276-7333/96/2315-0010$12.00/0

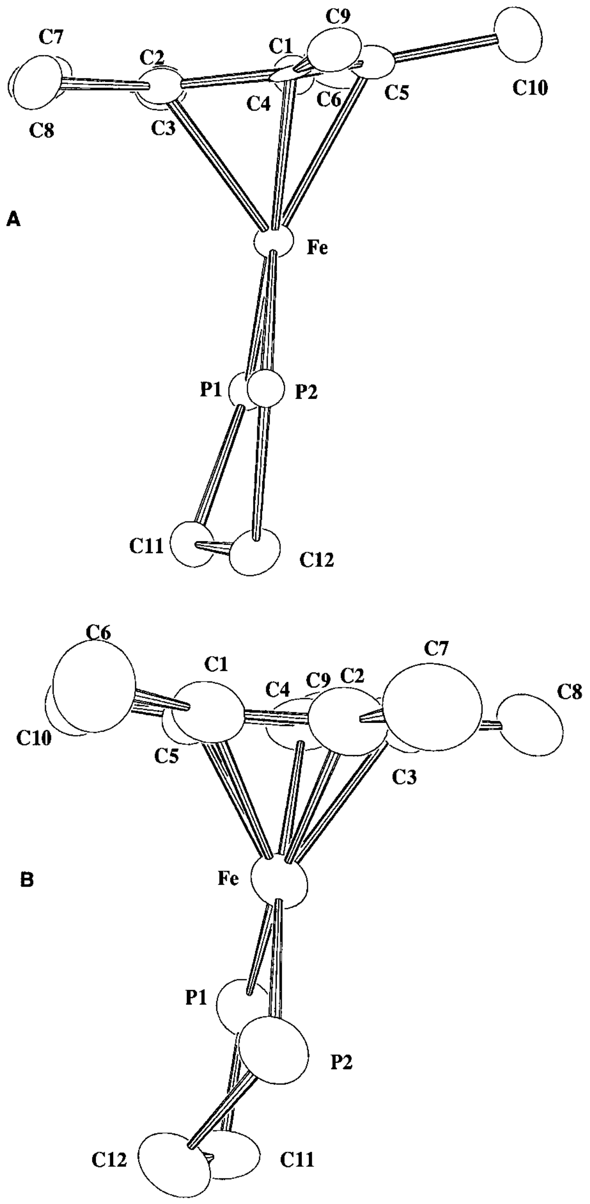


Figure 1. Solid-state molecular structures of **3** (A) and **4** (B), with 50% probability thermal ellipsoids. The phenyl rings of the dppe ligand are omited for clarity. Selected interatomic distances (Å) and angles (deg): **3**, Fe$-$P(1) = 2.126(3), Fe$-$P(2) = 2.148(3), Fe$-$Cp*$_{\mathrm{centroid}}$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

tals in 90% yield ($\mu_{\mathrm{eff}} = 1.5\,\mu_{\mathrm{B}}$). The molecular structure of **3** determined by a single-crystal X-ray diffraction analysis consists of discrete monomeric 17-electron d^7 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)][PF$_6$] (**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 dsp^3). 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 $\mu_{\mathrm{eff}} = 3.3\,\mu_{\mathrm{B}}$ (310 K, Evans' method)[17] corresponding to two unpaired electrons. The planar structure of **4**, usually observed for d^8 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 d^6 complexes of the [CpML$_2$] type having only 16-electron valence should be pyramidal compounds,[19] in agreement with experimental data.[20]

---

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

(12) Crystal data for Cp*Fe(dppe) (**3**): C$_{36}$H$_{39}$FeP$_2$, monoclinic, $P2_1/n$, a = 10.522(2) Å, b = 15.772(4) Å, c = 24.107(5) Å, β = 91.95(2)°, V = 3998(2) Å^3, Z = 4, D_{calc} = 1.337 g cm^{-3}, $R(F)$ = 6.2% for 2217 independent reflections ($2\theta_{\max}$ = 50°, 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.

(13) For rare examples of *in situ* ESR-characterized CpFe(L)$_2$ radicals see: (a) Ruiz, J.; Lacoste, M.; Astruc, D. *J. Am. Chem. Soc.* **1990**, *112*, 5471. (b) Jonas, K.; Klusmann, P.; Goddard, R. *Z. Naturforsch.* **1995**, *50b*, 394.

(14) Crystal data for [Cp*Fe(dppe)][PF$_6$] (**4**): C$_{36}$H$_{39}$FeF$_6$P$_3$, monoclinic, Cc, a = 19.612(10) Å, b = 8.422(6) Å, c = 20.513(9) Å, β = 113,-88(5)°, V = 3098(2) Å^3, Z = 4, D_{calc} = 1.264 g cm^{-3}, $R(F)$ = 5.7% for 2162 independent reflections ($2\theta_{\max}$ = 50°, 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]

(17) Isostructural diamagnetic complexes of Ru were characterized *in situ* by NMR: (a) Kirchner, K.; Mauthner, K.; Mereiter, K.; Schmid, R. *J. Chem. Soc., Chem. Commun.* **1993**, 892. (b) Joslin, F. L.; Pontier Johnson, M.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 2781.

(18) Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 277.

(19) Hoffmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536.

The coordinatively unsaturated complex **4** could be regarded as a strong Lewis acid. It exhibits a rich chemistry with many solvents and small molecules. To illustrate this ability a THF solution of complex **4** was treated with 5 equiv of H_2O. Slow diffusion of pentane into the solution provided a diamagnetic green crystalline material which was recovered in 90% yield and identified as $[Cp^*Fe(dppe)(H_2O{\cdot}THF)][PF_6]$ (**5**) by an X-ray crystal structure determination.[7,8,21,22] Organoiron aquo compounds were previously suggested to be putative reaction intermediates, and only the complex $[Cp^*Fe(CO)_2(H_2O)][OSO_2CF_3]$ was spectroscopically identified.[23] Crystallization of complexes **4** and **5** from a THF solution strongly indicates that the formation of the THF derivative $[Cp^*Fe(dppe)(THF)][PF_6]$ is unlikely.

The initial scan in the cyclic voltammograms of the four complexes **2**−**5**, from −1.5 to +0.5 V, are identical and display two reversible oxidation waves in THF (0.1 M $nBu_4N^+PF_6^-$, 20 °C, 0.1 V/s) with the E_0 potential at -0.73 ± 0.01 V and $+0.24 \pm 0.01$ V (vs SCE). The chemical reversibility at the platinum electrode is established for each redox system by the ratio of the anodic to cathodic peak current $i_{pa}/i_{pc} = 1$. As a consequence of the same E_0 values observed for the compounds **2**−**5**, it must be concluded that (i) the same redox systems described by eq 1 are involved in the four cases and (ii) in THF the oxygen-containing ligands of the complexes **2** and **5** are dissociated (eq 2). Indeed, much more negative reduction potentials are expected for the one-electron reduction of an isostructural 18-electron cation into a 19-electron entity than for a 16-electron cation into a 17-electron compound.[24] On the other hand, as for **2**, the one-electron reduction of **5** with 0.9 equiv of cobaltocene in THF at −80 °C gave **3** (90%). In THF solution, the complexes **2** and **5** are paramagnetic and their magnetic moments determined by NMR are 1.9 and 2.9 μ_B, respectively. These values clearly support a strong dissociation of the triflato and aquo adducts **2** and **5** in solution.

$$\underset{\mathbf{3}}{[\mathrm{Cp^*Fe(dppe)}]^{\bullet}} \overset{-\theta}{\rightleftharpoons} \underset{\mathbf{4}}{[\mathrm{Cp^*Fe(dppe)}]^{+}} \overset{-\theta}{\rightleftharpoons} \underset{\mathbf{4^+}}{[\mathrm{Cp^*Fe(dppe)}]^{\bullet 2+}} \tag{1}$$

$$[\mathrm{Cp^*Fe(dppe)(L)}]^{+} \overset{-\theta}{\rightleftharpoons} [\mathrm{Cp^*Fe(dppe)}]^{+} + \mathrm{L}$$

$$\mathrm{L} = \mathrm{OSO_2CF_3},\ \mathrm{H_2O} \tag{2}$$

In summary, we have prepared by electron transfer reactions and X-ray characterized two new and rare complexes displaying unusual electronic and structural flexibility at a metal center with the same Cp*Fe(dppe) backbone, which constitute a unique family of 18-, 17-, and 16-electron compounds. Efforts are currently underway to explore the chemistry of these complexes.

Acknowledgment. We thank Prof. J.-Y. Saillard (Rennes, France) for perceptive discussions.

Supporting Information Available: For **3** and **4**, text describing X-ray procedures, complete tables of atomic coordinates and *B* values and their estimated standard deviations, bond lengths and angles, and anisotropic temperature factors, and ORTEP diagrams (31 pages). Ordering information is given on any current masthead page.

OM950766L

---

(20) (a) Winter, C. H.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7560. (b) Brookhart, M.; Lincoln, D. M.; Volpe, A. F., Jr.; Schmidt, G. F. *Organometallics* **1989**, *8*, 1212. (c) Kölle, U.; Kossakowski, J.; Raabe, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 773.

(21) The role of hydrogen bonding is important in stabilizing the solid-state structure of aquo transition metal complexes: (a) Stang, P. J.; Cao, D. H.; Poulter, G. T.; Arif, A. M. *Organometallics* **1995**, *14*, 1110. (b) Braga, D.; Grepioni, F. *Acc. Chem. Res.* **1994**, *27*, 51.

(22) For a review on organometallics aqua complexes of transition metal see: Koelle, U. *Coord. Chem. Rev.* **1993**, *135/136*, 623.

(23) Tahiri, A.; Guerchais, V.; Toupet, L.; Lapinte, C. *J. Organomet. Chem.* **1990**, *381*, C47.

(24) The irreversible reduction of $[Cp^*Fe(dppe)(CO)][PF_6]$ occurs at −1.65 V vs SCE. Hamon, J.-R.; Lapinte, C. Unpublished results.