Organometallics **1991**, *10*, 1045–1054 1045

Halo- and Alkyl(pentamethylcyclopentadienyl)(1,2-bis(diphenylphosphino)ethane)iron(III) 17-Electron Complexes: Synthesis, NMR and Magnetic Properties, and EHMO Calculations

Christophe Roger,[1a] Paul Hamon,[1a] Loic Toupet,[1b] Hassan Rabaâ,[1c] Jean-Yves Saillard,*[,1c]
Jean-René Hamon,*[,1a] and Claude Lapinte*[,1a]

Laboratoire de Chimie des Organométalliques, URA CNRS 415, Laboratoire de Chimie du Solide et Inorganique Moléculaire, URA CNRS 254, and Laboratoire de Physique Cristalline, URA CNRS 804, Université de Rennes I, 35042 Rennes, France

Received July 6, 1990

Reaction of Fe(dppe)Cl_2 (dppe = 1,2-bis(diphenylphosphino)ethane) with LiCp* (Cp* = η^5-pentamethylcylopentadienyl) in THF yields Fe(Cp*)(dppe)Cl (1). The X-ray crystal structure of 1 shows that it crystallizes in the triclinic space group *P*1 with unit cell parameters a = 10.410(7) Å, b = 10.987(3) Å, c = 16.872 (4) Å, α = 80.43 (2)°, β = 94.28 (5)°, γ = 70.92 (5)°, and Z = 2. The structure was solved and refined (5732 reflections) to the final residual values R = 0.37 and R_w = 0.36. Compound 1 reacts with LiI and $LiCH_3$ to afford respectively Fe(Cp*)(dppe)I (2) and Fe(Cp*)(dppe)CH_3 (4). The hydride Fe(Cp*)(dppe)H (3) can be obtained by reaction of 1 with $LiAlH_4$ or by direct preparation in 50% yield from Cp*H and Fe(dppe)Cl_2 reduced by a sonochemically (20 kHz) activated colloidal dispersion of potassium metal. The alkyl derivatives (Fe(Cp*)(dppe)R (R = CH_3 (4) and CH_2OCH_3 (5)) are synthesized from FeCp*$(CO)_2$R upon CO displacement by ultraviolet (UV) photolysis and trapping with dppe. Cyclic voltammetry (CV) reveals a reversible one-electron oxidation process for all these neutral iron(II) compounds including the hydride (3). Ferrocenium and trityl salts as well as molecular oxygen can be used to synthesize the halide and alkyl 17-electron [Fe(Cp*)(dppe)X]PF_6 complexes in 90–95% yield. ESR, Mössbauer, and NMR experiments indicate that the Cp* ring and the alkyl or halide ligands contribute significantly to the delocalization of the odd electron. EHMO calculations on the $[Fe(Cp)(PH_3)_2CH_2OH]^{\bullet+}$ model are fully consistent with this finding: the singly occupied HOMO, of predominantly $x^2 - y^2$ character, is found to be 52% localized on the metal, 28% on Cp, and 15% on CH_2OH. Magnetic susceptibility obeys the modified Curie–Weiss expression, and the important values of μ_B observed are attributed to an orbital contribution. The low and negative values observed for Θ characterize these complexes as having short-distance dominant antiferromagnetic interactions.

Introduction

Although organotransition-metal chemistry has been dominated by the 18-electron rule,[2] interest in 17-electron organometallic compounds has strongly increased in recent years.[3] Both interest in studying electron-transfer reaction[4,5] and interest in the physical properties of organometallic solids such as conductivity, magnetism, and optical effects[6–8] are the driving force behind the explosion of this new area of organometallic chemistry. In the Cp–iron series, 17-electron compounds $[FeCpL_2R]^{\bullet+}$ (L = tertiary phosphine; R = alkyl)[9] are formed on 1-electron oxidation of 18-electron iron(II) precursors. Oxidized species $[FeCp(CO)_2R]^{\bullet+}$ and $[FeCp(CO)(P)R]^{\bullet+}$[3,10] are believed to be intermediate in many oxidative metal–alkyl bond cleavage reactions of 18-electron alkyl analogues but are generally too unstable to be detected. The more electron-rich FeCp*(P_2)R series would be more appropriate for such mechanistic studies, but the number of works devoted to this class of compounds have been limited by their recent discovery and unusual synthetic pathway.[11] Starting from Cp*H and zerovalent iron atoms, Green et al. reported the first entry in this series, but their technique required an apparatus for the metal vapor synthesis.[12] Lehmkuhl et al. proposed an efficient entry to bis(monophosphine)iron complexes of the type Fe(Cp)L_2Cl (Cp = C_5H_5, C_5H_4Me, Cp*; L = $P(CH_3)_n(C_6H_5)_{3-n}$, n = 0–3),[13] and

---

[1] (a) Laboratoire de Chimie des Organométalliques. (b) Laboratoire de Physique Cristalline. (c) Laboratoire de Chimie du Solide et Inorganique Moléculaire.

[2] (a) Collman, J. P.; Hegedus, L. S. *Principles and Applications of organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. (b) For extensive references, see: *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: London, 1982; Chapters 19–43.

[3] (a) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217. (b) Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1984**, *23*, 1.

[4] (a) Chanon, M. *Bull. Soc. Chim. Fr.* **1982**. 197. (b) Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425. (c) Amatore, C.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1982**, *104*, 817. (d) Taube, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 329. (e) Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 643.

[5] Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978.

[6] Parshall, G. W. *Organometallics* **1987**, *6*, 687.

[7] Green, M. L. H.; Qin, J.; O'Hare, D. *J. Organomet. Chem.* **1988**, *358*, 375.

[8] Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201.

[9] Treichel, P. M.; Molzahn, D. C.; Wagner, K. P. *J. Organomet. Chem.* **1979**, *174*, 191.

[10] (a) Abrahamson, H. B.; Palazotto, M. C.; Reichel, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 4123. (b) Rogers, W. N.; Page, J. A.; Baird, M. C. *Inorg. Chem.* **1981**, *20*, 3521. (c) Healy, M. A.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1986**, 984. (d) Moore, B. D.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 1819. (e) Thomas, M. J.; Shackleton, T. A.; Wright, S. C.; Gillis, D. J.; Colpa, J. P.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1986**, 312. (f) Bly, R. S.; Bly, R. K.; Hossain, M. M.; Silverman, G. B.; Wallace, E. *Tetrahedron* **1986**, *42*, 1093.

[11] (a) Roger, C.; Marseille, P.; Salus, C.; Hamon, J.-R.; Lapinte, C. *J. Organomet. Chem.* **1987**, *336*, C13. (b) Morrow, J.; Catheline, D.; Desbois, M. H.; Manriquez, J. M.; Ruiz, J.; Astruc, D. *Organometallics* **1987**, *6*, 2605. (c) Desbois, M. H.; Nunn, C. M.; Cowley, A. H.; Astruc, D. *Organometallics* **1990**, *9*, 640.

[12] (a) Green, M. L. H.; Wong, L. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1442. (b) Green, M. L. H.; Wong, L. L. *J. Chem. Soc., Dalton Trans.* **1987**, 411.

[13] Lehmkuhl, H.; Mehler, G.; Benn, R.; Rufinska, A.; Schroth, G.; Krüger, C.; Raabe, E. *Chem. Ber.* **1987**, *120*, 1987.

0276-7333/91/2310-1045$02.50/0

Table I. Experimental Crystallographic Data for 1

formula	$C_{21}H_{23}ClFeCl$
fw	691
cryst system	triclinic
space group	*P*1
a, Å	10.410 (7)
b, Å	10.987 (3)
c, Å	16.872 (4)
α, deg	80.43 (2)
β, deg	94.28 (5)
γ, deg	70.92 (5)
V, Å^3	1722.4 (9)
Z	2
d_{calc}, Mg m^{-3}	1.27
cryst size, mm	0.10 × 0.22 × 0.30
$2\theta_{max}$, deg	50
hkl range	*h*, 0 to 10; *k*, −10 to 10; *l*, −17 to 17
diffractometer	CAD4 Enraf-Nonius
λ(Mo Kα radiatn), Å	0.71069
monochromator	graphite cryst
T, K	296
F(000)	698
abs coeff μ, cm^{-1}	6.3
scan type	$\omega/2\theta$
t_{max}, s	60
no. of reflcns read	5732
no. of unique reflecns	2886 [$I > 4\sigma(I)$]
R_{int}	0.012
R; R_w	0.037; 0.036
$\Delta\rho_{max}$, e Å^{-3}	0.34

more recently Astruc's[11] and Bercaw's[14] groups proposed an original route that used *t*-FeCp*(acac) previously reported by Manriquez.[15] This elegant route afforded the desired compounds in moderate yields.

In 1986 we reported that the complex FeCp*$(CO)_2CH_2OH$ reacts with the trityl cation via an electron-transfer mechanism and subsequent H atom abstraction via the 17-electron iron(III) intermediate [FeCp*$(CO)_2CH_2OH]^+$.[16] This led us to investigate the metal–alkyl C–H bond activation process in the case of the more electron-rich Fe(Cp*)(dppe)CH_2OCH_3 (5) complex, and more recently, we succeeded in the synthesis of the methoxycarbene [Fe(Cp*)(dppe)($CHOCH_3$)]PF_6 by a three-step α-hydride abstraction, via an ECE mechanism. The iron(III) 17-electron intermediate [Fe(Cp*)(dppe)CH_2OCH_3]PF_6 ($5PF_6$) was characterized by single-crystal X-ray diffraction.[17] The electron-rich ether complex Fe(Cp*)(dppe)CH_2OCH_3 has an interesting chemistry, allowing us to synthesize the single thermally stable methylene compound of the first-row transition metals.[18] Here, we wish to present (1) a convenient and direct access to the iron(II) precursor Fe(Cp*)(dppe)X (X = Cl (1), X = H (3)) from the easily available Fe(dppe)Cl_2 and Cp*H reagents including an X-ray structure of the chloro compound 1, the chloro ligand exchange to prepare the iodide derivative 2, and the synthesis of the alkyliron(II) compounds Fe(Cp*)(dppe)R (R = CH_3 (4), R = CH_2OCH_3 (5), (2) the cyclic voltammetry study of the redox system Fe(II)/Fe(III) and the one-electron oxidation of complexes 1–5 to synthesize the iron(III) species [Fe(Cp*)(dppe)X]PF_6, (3) the ESR, Mössbauer, and NMR spectroscopic data for these open-shell compounds, and (4) the magnetic properties of these half-sandwich iron solids, together with the $S = {}^1/_2$ cation-donor and $S = {}^1/_2$ anion-acceptor material [Fe(Cp*)(dppe)X]$^{\bullet+}$TCNQ$^{\bullet-}$ and a MO study of the electronic ground state of these d^5 iron(III) compounds. Part 1 has been partially communicated.[11a]

Table II. Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*,[a] Å^2
Fe	0.03464 (6)	0.13405 (5)	0.19571 (4)	2.75 (1)
Cl	−0.2038 (1)	0.1645 (1)	0.27376 (7)	3.90 (3)
P1	0.0853 (1)	0.0446 (1)	0.31270 (7)	2.95 (3)
P2	0.0187 (1)	0.3170 (1)	0.24162 (7)	2.94 (3)
C1	0.1836 (5)	−0.0117 (4)	0.1190 (3)	3.8 (1)
C2	0.2003 (5)	0.1096 (4)	0.0819 (3)	3.7 (1)
C3	0.0702 (5)	0.1837 (4)	0.0646 (3)	3.7 (1)
C4	−0.0249 (5)	0.1089 (4)	0.0911 (3)	3.8 (1)
C5	0.0432 (5)	−0.0106 (4)	0.1269 (3)	3.8 (1)
C6	0.2990 (6)	−0.1284 (5)	0.1342 (3)	5.3 (1)
C8	0.0473 (6)	0.3117 (5)	0.0131 (3)	5.2 (1)
C9	−0.1707 (5)	0.1464 (5)	0.0791 (3)	5.3 (1)
C10	−0.0223 (5)	−0.1188 (5)	0.1609 (3)	5.5 (1)
C11	−0.0174 (4)	0.1624 (4)	0.3933 (2)	3.2 (1)
C12	0.0010 (5)	0.2942 (4)	0.3562 (3)	4.0 (1)
C13	0.0381 (4)	−0.1026 (4)	0.3613 (3)	3.5 (1)
C14	−0.1043 (4)	−0.0967 (4)	0.4022 (3)	4.1 (1)
C15	−0.1405 (5)	−0.2101 (5)	0.4375 (3)	5.4 (1)
C16	−0.0409 (6)	−0.3263 (5)	0.4317 (3)	6.1 (1)
C17	0.1015 (6)	−0.3349 (5)	0.3904 (4)	6.3 (2)
C18	0.1417 (5)	−0.2222 (5)	0.3550 (3)	4.9 (1)
C19	0.2632 (4)	0.0102 (4)	0.3253 (3)	3.5 (1)
C20	0.2911 (5)	−0.0405 (5)	0.4008 (3)	4.8 (1)
C21	0.4193 (5)	−0.0482 (5)	0.4132 (3)	5.9 (2)
C22	0.5218 (5)	−0.0083 (5)	0.3501 (4)	5.9 (1)
C23	0.4989 (5)	0.0397 (5)	0.2746 (4)	5.8 (2)
C24	0.3682 (5)	0.0487 (4)	0.2617 (3)	4.4 (1)
C25	0.1648 (4)	0.3911 (4)	0.1981 (3)	3.4 (1)
C26	0.1626 (5)	0.4796 (4)	0.1285 (3)	4.4 (1)
C27	0.2766 (5)	0.5275 (5)	0.0883 (3)	5.7 (1)
C28	0.3951 (5)	0.4900 (5)	0.1166 (4)	6.5 (2)
C29	0.3988 (5)	0.4055 (5)	0.1863 (4)	6.0 (1)
C30	0.2830 (5)	0.3566 (4)	0.2275 (3)	4.5 (1)
C31	−0.1312 (4)	0.4620 (4)	0.2365 (3)	3.5 (1)
C32	−0.1465 (5)	0.5715 (4)	0.2737 (3)	4.6 (1)
C33	−0.2572 (5)	0.6839 (5)	0.2699 (4)	5.6 (2)
C34	−0.3524 (5)	0.6870 (5)	0.2290 (4)	6.4 (2)
C35	−0.3370 (5)	0.5812 (5)	0.1908 (4)	6.5 (2)
C36	−0.2280 (5)	0.4663 (5)	0.1953 (3)	4.7 (1)
C40	0.447	0.364	0.418	8.1*
C41	0.498	0.421	0.447	10.0*
C42	0.500	0.500	0.500	10.0*

[a] Values marked with an asterisk denote atoms refined isotropically.

Table III. Selected Bond Distances (Å) for Fe(Cp*)(dppe)Cl (1)

Fe–C(1)	2.101 (4)	Fe–C(5)	2.082 (4)
Fe–C(2)	2.114 (4)	Fe–Cl	2.346 (1)
Fe–C(3)	2.128 (4)	Fe–P(1)	2.197 (1)
Fe–C(4)	2.134 (4)	Fe–P(2)	2.210 (1)

Table IV. Selected Bond Angles (deg) for Fe(Cp*)(dppe)Cl (1)

P(1)–Fe–P(2)	84.98 (5)	Cl–Fe–P(1)	86.03 (4)
C(13)–P–C(19)	101.9 (2)	Cl–Fe–P(2)	87.23 (5)
C(25)–P–C(31)	98.7 (2)		

Results and Discussion

1. Synthesis of Fe(Cp*)(dppe)Cl (1) and Fe(Cp*)(dppe)I (2). Treatment of Fe(dppe)Cl_2[19] with Cp*Li gave Fe(Cp*)(dppe)Cl (1) after 1 h in refluxing THF. The chloroiron complex was easily isolated as dark green mi-

---

(14) (a) Bray, R. G.; Bercaw, J. E.; Gray, H. B.; Hopkins, M. D.; Paciello, R. A. *Organometallics* **1987**, *6*, 922. (b) Paciello, R. A.; Manriquez, J. M.; Bercaw, J. E. *Organometallics* **1990**, *9*, 260.

(15) Bunuel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* **1985**, *4*, 1680.

(16) Guerchais, V.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1986**, 663.

(17) Roger, C.; Toupet, L.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1988**, 713.

(18) Roger, C.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1598.

(19) Mays, M. J.; Sears, P. L. *J. Chem. Soc., Dalton Trans.* **1973**, 1873.

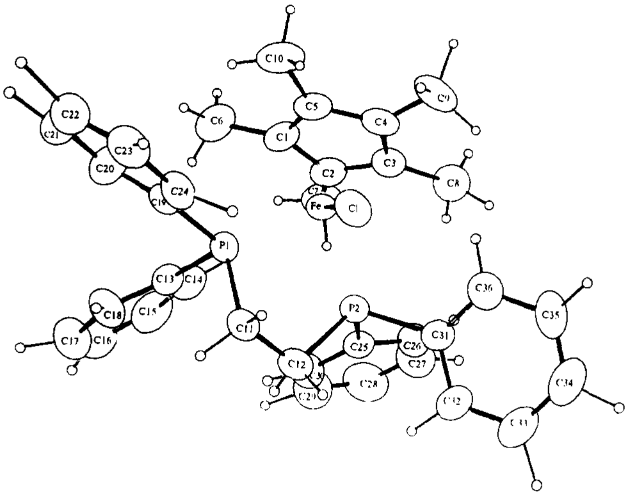


Figure 1. ORTEP view of the X-ray structure of complex Fe(Cp*)(dppe)Cl (1). The solvate has been omitted for clarity.

crocrystals in 85% yield after extraction with diethyl ether (eq 1). This high-yield reaction is identical with the route

$$\mathrm{Fe(dppe)Cl_2 + Cp^*Li \rightarrow \underset{1\ (85\%)}{Fe(Cp^*)(dppe)Cl} + LiCl} \qquad (1)$$

recently reported by Lehmkuhl[13] and constitutes, up to now, the best entry into the $\mathrm{Fe(Cp^*)(L_2)X}$ analogues. The metal–chlorine bond was evidenced in the ^{35}Cl NMR by a broad resonance at −116 ppm. Crystals of $1\cdot0.5\mathrm{C_5H_{12}}$ were grown by slow diffusion of pentane into the ether solution, and a single-crystal X-ray structure was determined. The unit cell contained two molecules of 1 and one molecules of pentane. The X-ray data were collected as outlined in Table I, and the refinement gave the structure shown in Figure 1. Atomic coordinates and selected bond lengths and angles are listed in Tables II–IV.

The Fe–Cl bond length [2.346 (1) Å] is rather similar to the distances determined for inorganic iron(II) compounds.[20] The molecule adopts a pseudooctahedral geometry usually observed for piano-stool complexes, with the Cp* ring occupying three coordination sites and the chlorine and phosphorous atoms occupying the other three sites. The Fe–P(1) and Fe–P(2) bond lengths compare well with Fe–P bond lengths determined in the Cp and Cp* series for cationic compounds.[21] The angle P(1)–Fe–P(2) is slightly smaller than that in the Cp series and possibly adopted in order to diminish the nonbonding interactions between the chelate-ring phenyl groups and the methyl substituents of the cyclopentadienyl ligand.

The reactivity of 1 reflected the labile character of the Fe–Cl bond. Hence, the chlorine atom was deplaced by acetonitrile in less than 1 min, and after metathesis with $\mathrm{NH_4PF_6}$, the known $\mathrm{[Fe(Cp^*)(dppe)NCMe]PF_6}$ complex[22] was recovered in 83% yield (eq 2). From a synthetic point

$$\mathrm{\underset{(1)}{Fe(Cp^*)(dppe)Cl} + CH_3CN \xrightarrow{NH_4PF_6} \underset{83\%}{[Fe(Cp^*)(dppe)CH_3CN]PF_6}} \qquad (2)$$

of view, this route to $\mathrm{[Fe(Cp^*)(dppe)CH_3CN]PF_6}$ is shorter and more efficient than the known procdure starting from $\mathrm{[Fe(C_2Me_5)(CO)_2]_2}$.[22] The new complex Fe(Cp*)(dppe)I (2) is readily prepared by substitution of chlorine by iodine with the potassium or the lithium salt (eq 3). The complex Fe(Cp*)(dppe)I (2) can be isolated as brown crystals in 95% yield, and its NMR data are very similar to those of 1.

$$\mathrm{\underset{1}{Fe(Cp^*)(dppe)Cl} + MI \rightarrow \underset{2\ (95\%)}{Fe(Cp^*)(dppe)I} + MCl} \qquad (3)$$

$$\mathrm{M = Li, K}$$

Complex 1 afforded the hydride 3 or the deuterated analogue Fe(Cp*)(dppe)D (**3*d***$_1$) by reduction with $\mathrm{LiAlH_4}$ or $\mathrm{LiAlD_4}$, as already observed for similar compound (eq 4).[12,13]

$$\mathrm{\underset{1}{Fe(Cp^*)(dppe)Cl} + LiAlH_4 \rightarrow \underset{3}{Fe(Cp^*)(dppe)H}} \qquad (4)$$

The reaction of 1 with Grignard reagent followed the same behavior as previously described. Whereas methylmagnesium afforded the alkyl compound $\mathrm{Fe(Cp^*)(dppe)CH_3}$ (4), ethylmagnesium gave the hydride 3 via, presumably, the ethyl derivative Fe(Cp*)(dppe)Et and subsequent β-H abstraction.[12,13]

2. Sonochemically Assisted Synthesis of Fe(Cp*)(dppe)H (3). Ultrasound irradiation (20 kHz) of clean potassium metal in THF with an immersion titanium horn to focus the ultrasonic energy into the liquid afforded an activated gray-blue colloidal dispersion of potassium metal, which has proven to be a very efficient reducing reagent for organometallic compounds.[11a,23] To this solution warmed to 50 °C was added half-equivalent amounts of $\mathrm{Fe(dppe)Cl_2}$ and Cp*H, and the sonication was continued for 10 min (eq 5). After workup, the iron hydride

$$\mathrm{Fe(dppe)Cl_2 + Cp^*H \xrightarrow{2K,\ 20\ kHz} \underset{3\ (50\%)}{Fe(Cp^*)(dppe)H}} \qquad (5)$$

Fe(Cp*)(dppe)H (3) was isolated as orange microcrystals in 50% yield. The chloro complex Fe(Cp*)(dppe)Cl is not an intermediate in this reaction, since 1 was quantitatively recovered after 10 min of 20-kHz irradiation in a THF colloidal dispersion of potassium at 50 °C, and no traces of the hydride 3 were found. This reaction could proceed via the formation of a transient "Fe(dppe)" intermediate followed by oxidative addition of Cp*H. This assumption is supported by the preparation of transition-metal carbonyl complexes from carbon monoxide and metal halide reduced by sodium under ultrasound conditions similar to those previously reported by Suslick.[24,25] On the other hand, Green and co-workers have succeeded in the preparation of the related compound $\mathrm{Fe(Cp^*)(PMe_3)_2H}$ from oxidative addition of Cp*H to $\mathrm{Fe(C_6H_6)(PMe_3)_2}$.[12] Moreover, when the synthesis of 3 was carried out with Cp*D, incorporation of deuterium was observed (see Experimental Section). Finally, this reaction is a quick and convenient one-pot synthesis of the metal hydride Fe(Cp*)(dppe)H (3) directly from the metal halide. Surprisingly, 3 did not yield 1 by reaction with $\mathrm{CH_2Cl_2}$ even after refluxing for 48 h. The stability of the hydride 3 in $\mathrm{CH_2Cl_2}$ contrasts with the data previously reported for the analogous $\mathrm{Fe(Cp^*)(PMe_3)_2H}$.[12]

3. Synthesis of Fe(Cp*)(dppe)R (R = $\mathrm{CH_3}$ (4), R = $\mathrm{CH_2OCH_3}$ (5)) by Photolysis. It has been claimed that this well-known route to carbonyl-free complexes extensively used in Cp series is not successful in making diphos

---

(20) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 3, Table 4.1.

(21) (a) Rieley, P. E.; Capshew, C. E.; Pettit, R.; Davis, R. E. *Inorg. Chem.* **1978**, *17*, 408. (b) Lacoste, M.; Varret, F.; Toupet, L.; Astruc, D. *J. Am. Chem. Soc.* **1987**, *109*, 6504. (c) Hamon, J.-R.; Saillard, J.-Y.; Toupet, L.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1662.

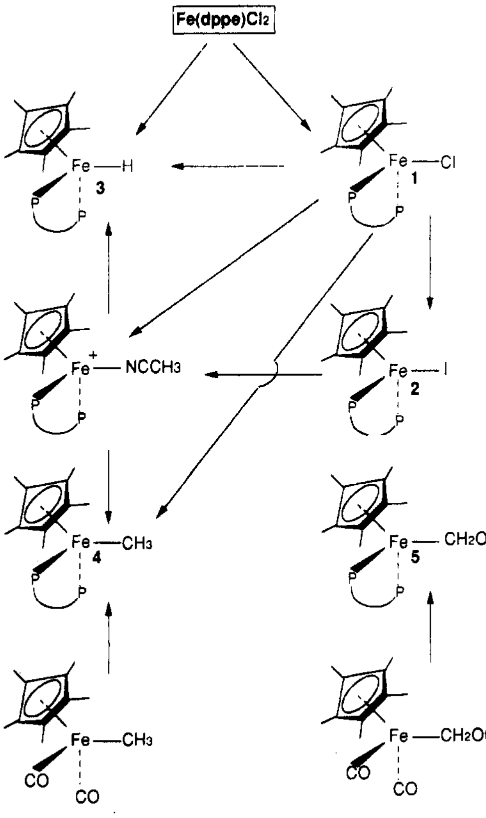
(22) Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094.

(23) Roger, C.; Tudoret, M.-J.; Guerchais, V.; Lapinte, C. *J. Organomet. Chem.* **1989**, *365*, 347.

(24) Suslick, K. S.; Johnson, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 6856.

(25) The formation of **3**d_1 observed by mass spectroscopy, when the synthesis of **3** is carried out with Cp*D, supports oxidative addition of Cp*H.

Scheme I. Access to the Iron(II) Fe(Cp*)(dppe)X Complexes



compounds in the Cp* series from their Fp*R (Fp* = Fe(Cp*)(CO)$_2$) parent.[11b,c] UV photolysis of a yellow toluene solution of the dicarbonyl Fp*R and dppe gave the thermally stable red complex Fe(Cp*)(dppe)R (eq 6).

$$\mathrm{Fe(Cp^*)(CO)_2R} + \mathrm{dppe} \xrightarrow{h\nu} \underset{\mathbf{4,\,5}}{\mathrm{Fe(Cp^*)(dppe)R}} \qquad (6)$$

$$\mathbf{4},\ \mathrm{R} = \mathrm{CH_3},\ 95\%;\ \mathbf{5},\ \mathrm{R} = \mathrm{CH_2OCH_3},\ 95\%$$

To summarize, two convenient one-pot entries in the iron(II) Fe(Cp*)(dppe)X series have been found and the synthesis of the alkyl compound Fe(Cp*)(dppe)CH$_3$ has been achieved in three steps from the easily available Cp*H and Fe(dppe)Cl$_2$, in 79% overall yield. Moreover, UV photolysis of the Fp* alkyl and alkoxyalkyl derivatives and dppe affords the Fe(Cp*)(dppe)R homologues (Scheme I).

4. Cyclic Voltammograms of Fe(Cp*)(dppe)X Complexes. The initial scans in the cyclic voltammograms of complexes **1**–**5** from +1 to −1 V (vs SCE) are all characterized by reversible one-electron processes in dichloromethane, acetonitrile, or THF with the (i_p^a/i_p^c) current ratio of unity (eq 7). The anodic and cathodic peak

$$\mathrm{Fe(Cp^*)(dppe)R} \rightleftarrows [\mathrm{Fe(Cp^*)(dppe)R}]^+ + e^- \qquad (7)$$

separation ($E_p^c - E_p^a$) is 60 mV in acetonitrile and approaches 60 mV in dichloromethane with a 100 mV s^{-1} scan rate. A plot of i_p^a against the square root of the scan speed was linear for all complexes across a range 20–500 mV s^{-1} (correlation coefficient > 0.99), as expected for a diffusion-controlled electrode process.[26] The data for peak potentials and current peak ratio are compiled in Table V. The ferrocene–ferrocenium couple was used as an internal calibrant for the potential measurements.

Table V. Reversible CV Parameters of Fe(Cp*)(dppe)X Complexes[a]

compd	X	solvent	E_p^a,[b] V	(E_p^1 + E_p^c)/2, V
3	H	CH$_2$Cl$_2$	−0.430	−0.395
3	H	THF	−0.240	−0.190
3	H	CH$_3$CN	−0.420	−0.370
2	Cl	CH$_2$Cl$_2$	−0.280	−0.235
2	Cl	THF	−0.140	−0.070
3	I	CH$_2$Cl$_2$	−0.220	−0.150
3	I	THF	0.050	+0.005
4	CH$_3$	CH$_2$Cl$_2$	−0.580	−0.535
5	CH$_3$CH$_2$O	CH$_2$Cl$_2$	−0.550	−0.505

[a] Solutions were 10^{-4} M in the complex with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte at a platinum electrode with a scan rate of 100 mV s^{-1}. [b] Vs SCE.

The magnitude of the reversible oxidation potential E_0 listed in Table V is a function of the electron-withdrawing abilities of the R ligands. The negative values of the oxidation potentials show these half-sandwich complexes to be electron-rich compounds. The permethylation of the C$_5$ ring causes a shift of the E_0 values of about 0.3 V, as already observed for other series.[9,27,28]

5. Chemical Oxidations: Synthesis of the 17-Electron Iron(III) [Fe(Cp*)(dppe)Cl]PF$_6$ and [Fe(Cp*)(dppe)R]PF$_6$ Complexes. The addition of 1 equiv of [FeCp$_2$]PF$_6$ to a solution of **1**, **4**, or **5** in CH$_2$Cl$_2$ resulted in a rapid color change from green to brown for **1** and from red to yellow-brown for **4** and **5**. After precipitation by diethyl ether, the Fe(III) complexes [Fe(Cp*)(dppe)Cl]PF$_6$ (**1**PF$_6$) and [Fe(Cp*)(dppe)R]PF$_6$ (R = CH$_3$ (**4**PF$_6$), X = CH$_2$OCH$_3$ (**5**PF$_6$)) were isolated as brown microcrystals in 86–92% yield. They are thermally and air-stable compounds with CV waves identical with those of their parent Fe(II) complexes. Their structure was confirmed by elemental analysis and an X-ray crystal structure for **5**PF$_6$.[17]

The ESR spectra of fine powdered sample of compounds **4**PF$_6$ and **5**PF$_6$ suspended in a THF matrix frozen at 140 K exhibited two broad signals (**4**PF$_6$, g = 2.48, 2.03; **5**PF$_6$, g = 2.44, 2.08) typical of low-spin iron(III) complexes. The hyperfine coupling Fe–P was not detected at this temperature. Three **g**-tensor components are expected for these 17-electron iron(III) species in an octahedral symmetry, as previously observed for the transient 17-electron intermediates [Fe(Cp*)(CO)$_2$R]$^{\bullet+}$ [16] and for the stable species [Fe(Cp*)(pentadienyl)]$^{\bullet+}$.[29] However, two components have also been observed for certain carbonylcyclopentadienylmetal complexes. Since these species are axially symmetric, two **g**-tensor components are observed ($g_\perp \gg g_\parallel \approx 2.0023$), as expected for species having a $(d_{z^2})^1$ configuration, when the z axis is defined as the projection of the metal–X vector in a plane parallel to the Cp* ligand.[29b] It means that, in the more classical coordinate system corresponding to a permutation of the x and z axis, the singly occupied HOMO is of predominant $d_{x^2-y^2}$ character. This is in full agreement with our MO calculations (vide infra).

The Mössbauer spectra of crystallized samples of **4**PF$_6$ and **5**PF$_6$ recorded at zero field are characteristic of pure iron(III) complexes. The nonequivalence of the intensities of the two lines of the Mössbauer spectra can be explained

---

[26] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

[27] Asdar, A.; Tudoret, M.-J.; Lapinte, C. *J. Organomet. Chem.* **1988**, *349*, 353. See ref 13.

[28] Kadish, K. M.; Lacombe, D. A.; Anderson, J. E. *Inorg. Chem.* **1986**, *25*, 2246.

[29] (a) Elschenbroich, C.; Bilger, E.; Ernst, R. D.; Wilson, D. R.; Kralic, M. S. *Organometallics* **1985**, *4*, 2068 and references therein. (b) Symons, M. C. R.; Bratt, S. W.; Wyatt, J. L. *J. Chem. Soc., Dalton Trans* **1983**, 1377.

Table VI. Mössbauer Parameters of $\mathrm{Fe(C_5Me_5)(dppe)X}$ and $\mathrm{[Fe(Cp^*)(dppe)X]PF_6}$ Complexes

compd	X	DI, $\mathrm{mm^{-1}}$	SQ, $\mathrm{mm^{-1}}$
3	H	0.20	2.08
4	CH_3	0.15	1.95
5	CH_2OCH_3	0.13	1.97
$4PF_6$	CH_3	0.35	0.76
$5PF_6$	CH_2OCH_3	0.25	0.95

by magnetic relaxation phenomenon.[30] As previously observed for the ferrocenium ion,[31] the single quadrupole doublet is temperature independent between 77 and 300 K and the parameters (see Table VI) are well differentiated from those the iron(II) parent compounds. The isomeric shifts are weaker for the iron(II) than for the iron(III) complexes whereas the quadrupole splitting are much smaller in these latter compounds. The purities of the iron(II) and iron(III) samples may be verified by the observation of single Mössbauer quadrupole doublet in the spectra.

The oxidation of the iron(II) precursors 4 and 5 was also carried out with trityl cation.[11b] Competitive α-hydride abstraction is not observed,[32] nor does α-hydrogen atom abstraction occur after the electron-transfer (ET) step. The iron(III) compounds $4PF_6$ and $5PF_6$ were isolated with yields identical with those obtained when the oxidation is performed with ferrocenium salt. In contrast to the H atom abstraction previously observed for the tungsten,[33] rhenium,[34] and iron[16,17,35] alkyl complexes (which are known to transfer H^- to Ph_3C^+ according to an ET mechanism), $Ph_3C^\bullet$ is unable to abstract $H^\bullet$ from $4PF_6$ or $5PF_6$. Similar data has already been mentioned,[11b] and the explanation of this feature can be found by examining the structural data.[17] The bulky trityl radical cannot approach either the oxygen atom or the hydrogen atoms of the α-carbon atom. The methyl groups of the Cp* ring together with the phenyl substituants of the dppe ligand prevent an interaction at a distance shorter than 2.65 Å between the C atom of the trityl radical and the oxygen atom of the organoiron species (the distance to the hydrogen atom being still longer), as calculated from the crystal data. A faster reaction of the trityl radical with the solvent occurs to afford Ph_3CCl.[35] More surprisingly, $Ph_3COO^\bullet$, which is known to be a more efficient H atom abstracting reagent,[34b] does not produce any compounds other than $4PF_6$ and $5PF_6$.

Methylene chloride solutions of the organoiron(II) complexes Fe(Cp*)(dppe)R reacted with dioxygen, but decomposition took place and no identifiable compounds were isolated. The oxidation reaction has been monitored by low-temperature ESR experiments. Into a quartz ESR tube containing a CH_2Cl_2 solution of $\mathrm{Fe(Cp^*)(dppe)CH_3}$ cooled to −80 °C was injected 1 mL of oxygen. The reaction was immediately quenched by freezing at 77 K and the ESR spectrum recorded at 140 K. Besides the two signals corresponding to $4PF_6$ (g = 2.03, 2.48) two **g**-tensor components were observed at g = 2.01 and 2.48 (this latter signal being partly obscured by the organometallic compounds) and attributed to the superoxide radical anion by comparison with literature data.[36] These two sets of signals irreversibly and simultaneously disappeared at 210 K and corresponded to the decomposition of the organoiron species by the superoxide radical anion. In contrast, after addition of a stoichiometric amount of KPF_6, the ESR spectrum produced the same pattern at 140 K, but warming up resulted in the disappearance of the set of signals of $O_2^{\bullet-}$, while those of 4^+ remained unchanged. A synthetic procedure to produce the Fe(III) complexes $\mathrm{[Fe(Cp^*)(dppe)R]PF_6}$ from their iron(II) precursors and molecular oxygen was achievd with a 80% yield (eq 8). In

$$\mathrm{Fe(Cp^*)(dppe)R + O_2 \xrightarrow{KPF_6} [Fe(Cp^*)(dppe)R]PF_6} \quad (8)$$

the absence of added salt, the cage formed by the cationic iron(III) species and $O_2^{\bullet-}$ in the solvent is expected to be very reactive and resulted in the decomposition of the organoiron species. In contrast, in the presence of added salt, the formation of $\mathrm{[Fe(Cp^*)(dppe)R]PF_6}$ and KO_2 occurs and this exchange is known to be very fast[37] and to prevent any further reaction between the organoiron(III) species and $O^{2\bullet-}$; this interesting behavior is well-known in organic chemistry[38] and has been fully studied for the $\mathrm{CpFe^I}$(arene) complexes.[39]

6. Synthesis of the 17-Electron Iron(III) [Fe(Cp*)(dppe)X]TCNQ Complexes. The reaction of TCNQ with sandwich metallocenes can result in a variety of 1:1 products with different structural motifs.[40] The half-sandwich transition-metal complexes, although of different symmetry, are also electron rich and can be readily oxidized by this organic cyano acceptor. Reaction of complexes 4 and 5 with a stoichiometric amount of TCNQ in methylene chloride resulted in spontaneous electron transfer to give a solution containing $\mathrm{[Fe(Cp^*)(dppe)R]^{\bullet+}TCNQ^{\bullet-}}$ (X = CH_3 (4TCNQ), X = CH_2OCH_3 (5TCNQ)). Slow crystallization by slow pentane diffusion afforded pure microcrystalline samples of $S = {}^1/_2$ cation-donor and $S = {}^1/_2$ anion-acceptor material. The halide compound Fe(Cp*)(dppe)Cl was also oxidized by addition of 1 equiv of TCNQ, affording the biradical salt $\mathrm{[Fe(Cp^*)(dppe)Cl]^{\bullet+}TCNQ^{\bullet-}}$ in a quantitative yield. The specificity of this reaction shows that the electron-transfer process is much faster than the chlorine–nitrile ligand-exchange reaction in contrast with the fast formation of $\mathrm{[Fe(Cp^*)(dppe)NCMe]PF_6}$ described in eq 2.

7. NMR Study of the $\mathrm{[Fe(Cp^*)(dppe)X]PF_6}$ Complexes. In the solution of the 300-MHz ^1H NMR spectra of $\mathrm{[Fe(Cp^*)(dppe)X]PF_6}$ (X = Cl ($1PF_6$), X = CH_3 ($4PF_6$), X = CH_2OCH_3 ($5PF_6$)), care was taken to ensure that only the Fe(III) species was present in solution, since the neutral iron(II) complex impurities lead to electron exchange, giving shifted peaks. Five ($1PF_6$), six ($4PF_6$), or seven ($5PF_6$) broad resonances were observed (see Experimental Section and Figure 2) between +9 and −28 ppm. Typical line widths (20 °C) were 600 Hz for methyl ring protons and 350 Hz for a methyl or methylene proton bounded to

---

(30) Varret, F. Personal communication.

(31) Collins, R. L. *J. Chem. Phys.* **1965**, *42*, 1072.

(32) (a) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. (b) Cutler, A. R. *Ibid.* **1979**, *101*, 604. (c) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C13. (d) Constable, A. G.; Gladysz, J. A. *Ibid.* **1980**, *202*, C12. (e) Kagley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760. (f) Knors, C.; Kuo, C.-H.; Lauher, J. W.; Eigenbrot, C.; Helquist, P. *Organometallics* **1987**, *6*, 1988. (g) Seeman, J. I.; Davies, S. G. *J. Am. Chem. Soc.* **1985**, *107*, 6522. (h) Guerchais, V.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1986**, 894. (i) Guerchais, V.; Lapinte, C.; Thépot, J.-Y.; Toupet, L. *Organometallics* **1988**, *7*, 604.

(33) (a) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570. (b) Jernakoff, Cooper, N. J. *Ibid.* **1984**, *106*, 3026.

(34) (a) Asaro, M. F.; Bodner, G. S.; Gladysz, J. A.; Cooper, N. J. *Organometallics* **1985**, *4*, 1020. (b) Bodner, G. S.; Gladysz, J. A.; Nielsen, M. F.; Parker, V. D. *J. Am. Chem. Soc.* **1987**, *109*, 1757.

(35) Bridger, R. F.; Russel, G. A. *J. Am. Chem. Soc.* **1963**, *85*, 3765.

(36) Fee, J. A.; Valentine, J. S. *Superoxide and Superoxide Dismutase*; Academic Press: New York, 1977; pp 19–60.

(37) Simon, J. D.; Peters, K. S. *Acc. Chem. Res.* **1984**, *17*, 277.

(38) Loupy, A.; Tchoubar, B. *Effets de sels en chimie organique et organométallique*; Dunod Université: Paris, 1988.

(39) Hamon, J.-R.; Astruc, D. *Organometallics* **1988**, *7*, 1036.

(40) (a) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. (b) Miller, J. S.; O'Hare, D. M.; Chakraborty, A.; Epstein, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 7853. (c) Ward, M. D.; Fagan, P. J.; Calabrese, J. C.; Johnson, D. C. *J. Am. Chem. Soc.* **1989**, *111*, 1719.

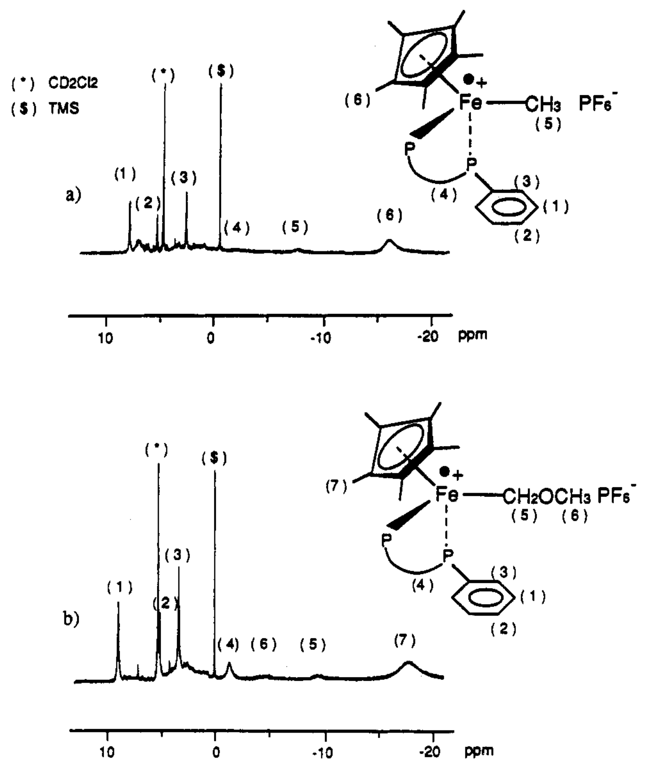


Figure 2. ^{1}H NMR spectra (293 K) of [Fe(Cp*)(dppe)X]PF$_6$: (a, top) X = CH$_3$ (4); (b, bottom) X = CH$_2$OCH$_3$ (5).

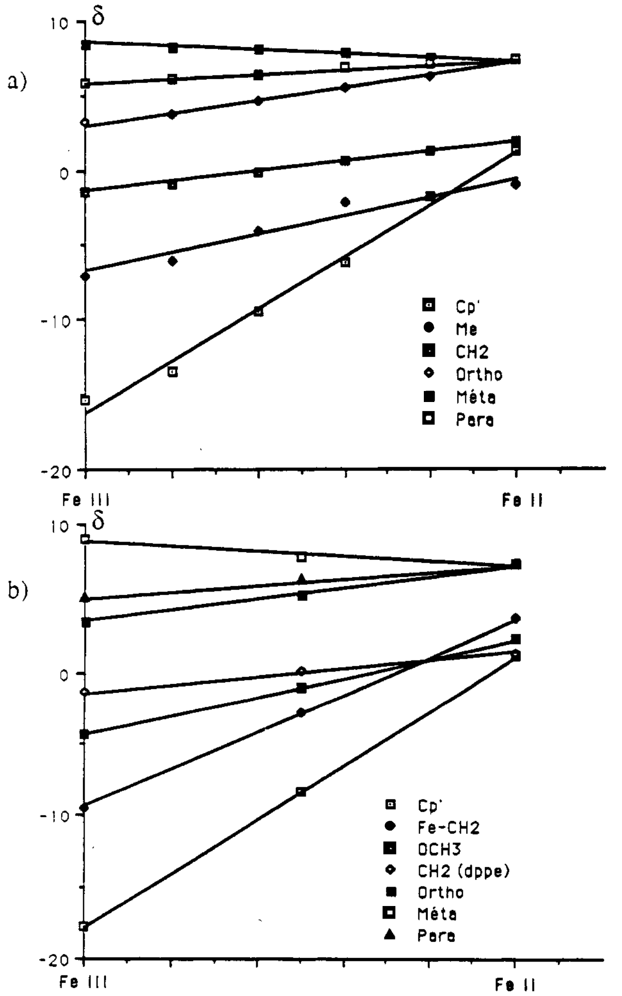


Figure 3. ^{1}H NMR chemical shift vs the Fe(II)/Fe(III) ratio for Fe(Cp*)(dppe)X/[Fe(Cp*)(dppe)X]PF$_6$ for (a) X = CH$_3$ (4) and (b) X = CH$_2$OCH$_3$ (5).

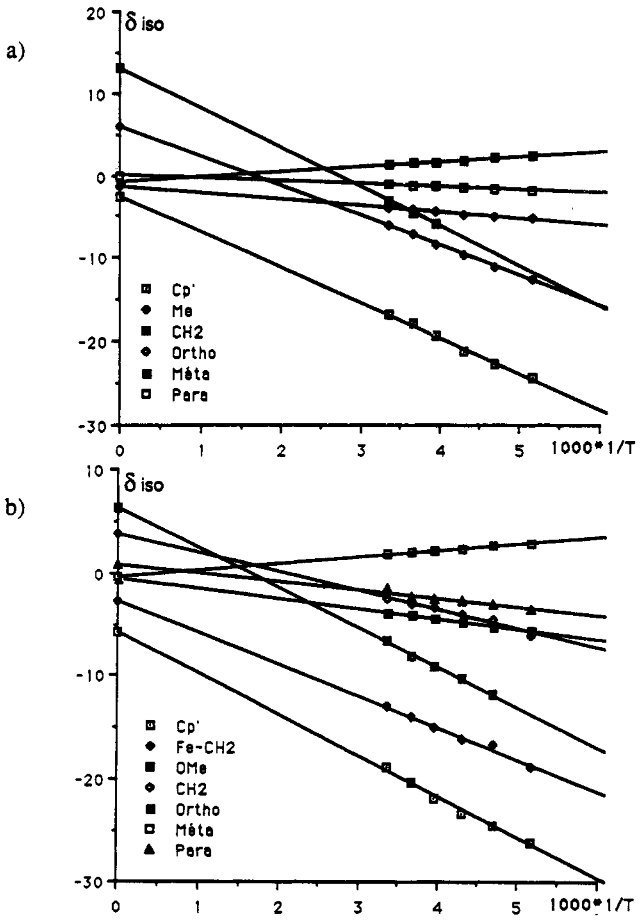


Figure 4. ^{1}H NMR isotopic chemical shift vs 1/*T* for (a) [Fe(Cp*)(dppe)CH$_3$]PF$_6$ (4PF$_6$) and (b) [Fe(Cp*)(dppe)CH$_2$OCH$_3$]PF$_6$ (5PF$_6$).

the α-carbon atom for compounds 4PF$_6$ and 5PF$_6$, whereas lines were broader (2400 Hz for the Cp* methyl group) in the ^{1}H NMR spectrum of the halide 1PF$_6$. The range of the chemical shifts is in agreement with a low-spin Fe(III) compound and rather different from the data observed for a high-spin Fe(II) derivative.[41]

Complete assignment was probed by recording the spectra of different samples of Fe(III) complexes containing various molar ratios of its corresponding Fe(II) analogue. For each mixture a single set of peaks was observed as expected for a fast electron exchange in the NMR time scale. The linear relationship observed for the chemical shift (δ ppm) vs the molar ratio of the diamagnetic and paramagnetic species (Figure 3) allowed correlation between the chemical shifts of these two species and definitely established the assignment shown in Figure 4. Variable-temperature ^{1}H NMR spectroscopy showed that the isotropic chemical shifts (δ_{iso}) of all the peaks exhibited a linear shielding vs 1/*T* over the range 193–298 K (except for the H meta peak for which a weak deshielding is observed) (Figure 4), as expected for a paramagnetic compound.[42]

The upfield shift is more pronounced for the methyl proton of the C$_5$ ring and the alkyl ligands than for the diphos protons. The line widths of the resonances increased with decreasing temperatures. This appears to be due to decreasing electronic relaxation times at lower

---

[41] Hill, D. H.; Sen, A. *J. Am. Chem. Soc.* **1988**, *110*, 1650.

[42] (a) La Mar, G. N.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 1782. (b) La Mar, G. N.; Walker, F. A.; Delphin, D. *Nuclear Magnetic Resonance of Paramagnetic Metalloporphyrins*; Academic Press: New York, 1979; Vol. 4.

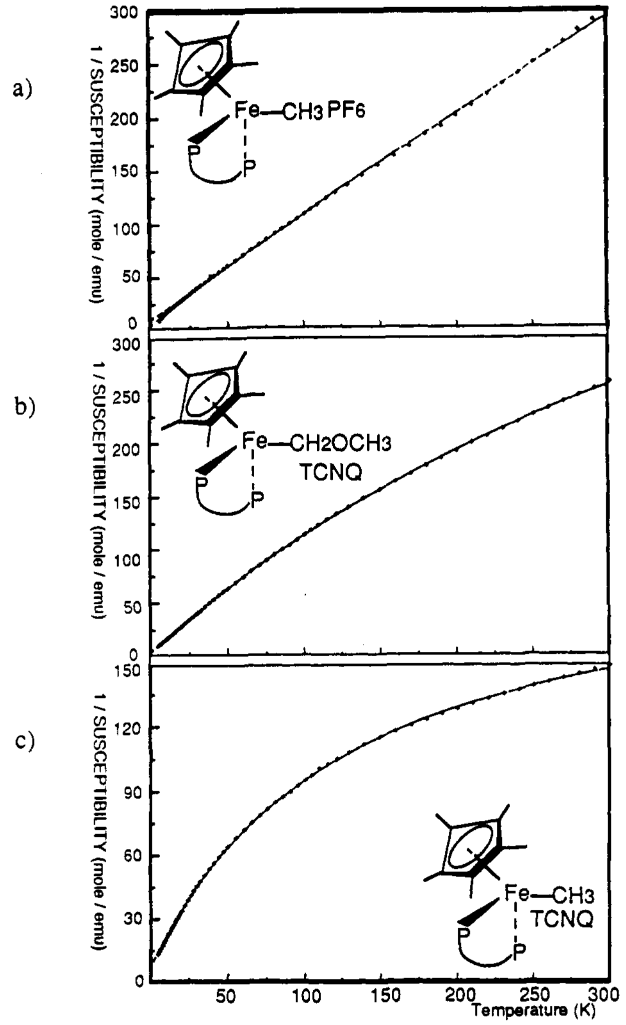


Figure 5. Inverse molar susceptibility as a function of the temperature for (a) $4PF_6$, (b) 5TCNQ, and (c) 4TCNQ.

temperatures. It may be expected that the half-sandwich Fe(III) complexes, like other paramagnetic sandwich compounds, have a metal–ligand spin delocalization mechanism dominated by the Fermi contact interaction rather than a dipolar interaction.[43] Anderson and Drago have estimated the dipolar contribution to the contact shifts of cyclopentadienyl and arene sandwichs and found it to be small.[44] In view of the similar pseudooctahedral geometry and the rather small deviation of g values from g_e, the free electron value, in these d^5 Fe(III) cations, it can be assumed that the chemical shifts will reflect primarily the spin densities on the ligands.[43b] We can therefore deduce from the NMR data that the ligand contribution to the delocalization of the unpaired electron is predominantly on the Cp* ring and on the alkyl ligand. This conclusion agrees well with the MO calculations reported below.

8. Magnetic Properties of the 17-Electron Iron(III) [Fe(Cp*)(dppe)X]Y Complexes (Y = PF_6, TCNQ). The 4–300 K Faraday balance susceptibility showed that $4PF_6$ and $5PF_6$ can be fit to the modified Curie–Weiss law, $\chi_M = \chi_0 + C/(T - \Theta)$ (Figure 5).[40,45] The magnetic susceptibilities of [Fe(Cp*)(dppe)CH_3]PF_6 (2.79 μ_B, $\Theta = -9.5$ K, $\chi_0 = 2.6093 \times 10^{-4}$ emu/mol), [Fe(Cp*)(dppe)-CH_2OCH_3]PF_6 (2.29 μ_B, $\Theta = -5.1$ K, $\chi_0 = 1.9558 \times 10^{-4}$ emu/mol), and [Fe(Cp*)(dppe)(CH_3]TCNQ (2.16 μ_B, $\Theta = -4.1$ K, $\chi_0 = 4.8922 \times 10^{-4}$ emu/mol) have been measured. In the last complex, where each cation and anion has a spin, the magnetic moment is in rather good agreement with the value expected for two independent doublets, i.e., 2.83 μ_B, but for the first two complexes a single spin is located on the low-spin iron(III) cation and the magnetic moments are greater than the calculated value, i.e., 1.73 μ_B. The determination of the magnetic moment for [Fe(Cp*)(dppe)CH_3]PF_6 in solution by the Evans method[46] (2.39 μ_B) probes the determination in the solid state and indicates that this important value should be attributed to an orbital contribution rather than dominant orientational effects in the solid state.[45c,47] The low and negative values observed for Θ thereby characterize these complexes as having short-distance dominant antiferromagnetic interactions. As shown by the crystal structures of **2** and $5PF_6$,[17] these complexes do not possess linear chains necessary for cooperative magnetic properties. Structural modifications should be introduced to favor such orientations of these iron(III) species in the crystal structure.

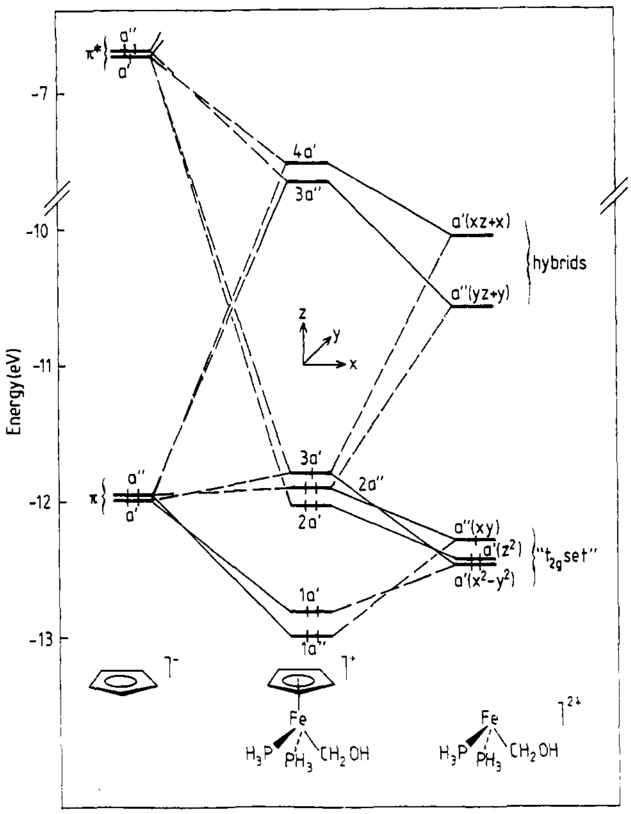


Figure 6. MO interaction diagram of $[Fe(Cp)(PH_3)_2(CH_2OH)]^{\cdot+}$.

MO Calculations. In order to shed some light on the nature of the singly occupied orbital of the 17-electron [Fe(Cp*)(dppe)R]$^+$ complexes, we have undertaken extended Hückel (EH) calculations[48] on this type of compound, using the weighed H_{ij} formula.[49] Although the

---

[43] (a) Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1984**, *103*, 758. (b) Koelle, U.; Fuss, B.; Rajasekharan, M. V.; Ramakrishna, B. L.; Ammeter, J. H.; Böhm, M. C. *Ibid.* **1984**, *106*, 4152. (c) Merkert, J.; Nielson, R. M.; Weaver, M. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 7084.

[44] Anderson, S. E., Jr.; Drago, R. S. *J. Am. Chem. Soc.* **1970**, *92*, 4244.

[45] (a) Bernier, J. C.; Poix, P. *Actual. Chim.* **1978**, (2), 7. (b) Pauthenet, R. *Tech. Ing.* **1983**, (3), D175. (c) Miller, J. S.; Calabrese, J. C.; Rommelmann, M.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *103*, 679 and references therein.

[46] Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

[47] (a) Englman, R. *The Jahn-Teller Effect in Molecules and Crystals*; Wiley: New York, 1972. (b) Sturge, M. D. *Solid State Phys.* **1968**, *20*, 91.

[48] (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomp, W. N. *Ibid.* **1962**, *36*, 2179. (c) *Ibid.* **1962**, *37*, 2872.

Table VII. Percent Localization of the Three Highest Occupied MO's in $[Fe(Cp)(PH_3)_2(CH_2OH)]^{\bullet +}$

	Fe	Cp	CH_2OH	$(PH_3)_2$
3a′	52	28	15	5
2a″	71	17	6	6
2a″	92	1	1	6

results obtained by this method of calculation have to be taken with caution, especially when dealing with radicals, we think that our theoretical and experimental results are complementary and that, taken as a whole, they contribute significantly to the understanding of the electronic structure of these compounds.

Calculations on the $[Fe(Cp)(PH_3)_2CH_2OH]^{\bullet +}$ model[50] were undertaken by assuming a C_s symmetry based on the averaged structure of $5PF_6$[17] and assuming the following other bond distances (Å): C–H = 1.09; O–H = 0.97; P–H = 1.41. The EH atomic parameters are taken from the literature.[52] The MO diagram of this complex is shown on Figure 6 on the basis of the interaction of the $[Fe(PH_3)_2(CH_2OH)]^{2+}$ fragment with the cyclopentadienyl anion. The metallic fragment exhibits a classical frontier orbital pattern, of the pyramidal ML_3 type:[53] three nonbonding d-type orbitals (the "t_{2g}" set) lying below two weakly antibonding hybrids. The three orbitals of the t_{2g} have very small ligand character (less than 6%); one of them, antisymmetric with respect to the *xz* plane, is of *xy* dominant character, while the two others are symmetric and consist primarily of $x^2 - y^2$ and z^2 major character. The two hybrids are significantly separated in energy caused by the good donor ability of the CH_2OH^- ligand, the frontier orbital of which renders the metallic hybrid, which lies in the symmetry plane, to be more antibonding. The MO diagram of $[Fe(Cp)(PH_3)_2(CH_2OH)]^{\bullet +}$ is now easy to understand; the major bonding interaction occurs between the two metallic hybrids and the occupied π orbitals of the Cp ligand, while the nature of the singly occupied MO depends on the way the t_{2g} set interacts. These latter interactions are not very strong, since the t_{2g} orbitals have their lobes pointing in directions that are unfavorable for a good overlap with the Cp orbitals. The in-plane $x^2 - y^2$ and *xy* frontier orbitals of the metallic fragment interact principally with the occupied π orbitals of the cyclopentadienyl ligand, which are close in energy (Figure 6). As a result, they are somewhat destabilized. A second-order mixing with the metallic hybrids restrains this destabilization. This second-order stabilizing effect is stronger for the *xy* orbital, because of the lower energy of the a″ metallic hybrid. As a result, the a′ MO of $x^2 - y^2$ dominant character lies 0.07 eV above the a″ MO of dominant *xy* character. As usually observed in sandwich and half-sandwich complexes, the z^2 metallic orbital does not overlap the π ligand orbital but a low-lying σ_{CC} MO. The result is a very small destabilization for this level, which lies below the two other components of the t_{2g} set in the complex. In addition, second-order mixing between the $x^2 - y^2$ and z^2 fragment orbitals contributes to the 0.23-eV separation between 2a′ and 3a′ in the complex. This level ordering of the t_{2g} levels in the complex does not vary when reasonable changes of the molecular structure or the atomic parameters are made. Calculations on the $[Fe(Cp)(P(H)_2(CH_2)_2P(H)_2)(CH_2OH)]^{\bullet +}$ model, assuming a C_s symmetry, leads to results that are very similar in terms of MO ordering and localization. Table VII gives the localization of the three highest occupied levels of $[Fe(Cp)(PH_3)_2(CH_2OH)]^{\bullet +}$.

One can see that, among the t_{2g} levels, the presumed singly occupied MO, 3a′, is the one that is the more delocalized on the ligands; it is delocalized on the Cp ligand because of its mixing with the π(Cp) and π^*(Cp) levels and on CH_2OH because of the second-order mixing with the a′ metallic hybrid. This result is in full agreement with our experimental findings. As a consequence, the molecular structure of the parent 18-electron species should exhibit some differences in its Fe–ligand bond distances.[54]

Experimental Section

General Data. Reagent grade tetrahydrofuran (THF), diethyl ether, and pentane were predried and distilled over sodium benzophenone ketyl prior to use. Acetonitrile was refluxed over P_2O_5 and distilled over Na_2CO_3. Pentamethylcyclopentadiene, anhydrous $FeCl_2$, and its bis(diphenylphosphino)ethane (dppe) adduct were prepared according to published procedures.[19,55] Other chemicals were used as received. Photolyses were performed with a Hanovia lamp (450 W, 250 nm) equipped with a quartz jacket, at room temperature under a stream of argon. All the manipulations were carried out under argon atmosphere with Schlenk techniques or in a Jacomex 532 drybox filled with nitrogen. Routine NMR spectra were recorded by using a Brucker AW 80-MHz instrument. High-field NMR spectra experiments were performed on a multinuclear Brucker instrument. Chemical shifts are given in parts per million relative to tetramethylsilane (TMS) for ^1H and ^{13}C NMR spectra, H_3PO_4 for ^{31}P NMR spectra, and NH_4Cl for ^{35}Cl NMR spectra. Cyclic voltammograms were recorded by using a PAR 362 instrument. Mass spectra were recorded with a Varian MAT 311 spectrometer. Magnetic susceptibility measurements were performed with a SQUID (susceptometer quantum interference device) instrument. The interatomic distance have been measured with the molecular modeling system Chem3D from Cambridge Scientific Computing. Elemental analyses were performed at the Center for Microanalyses of the CNRS at Lyon-Villeurbanne, France.

1. **Synthesis of $Fe(C_5Me_5)(dppe)Cl$ (1).** To a slurry of 1.42 g (10 mmol) of C_5Me_5Li in 10 mL of THF was added 5.25 g (10 mmol) of $Fe(dppe)Cl_2$, and the mixture was refluxed for 1 h or stirred overnight at room temperature. The solution gradually turned red-green. At 20 °C the solvent was removed under vacuum and the dark residue extracted with 300 mL of diethyl ether. Removal of the solvent followed by recrystallization from CH_2Cl_2/pentane provided 5.30 g (85%) of $Fe(C_5Me_5)(dppe)Cl$ as dark green crystals.

^1H NMR (C_6D_6): 8.05–7.00 (m, Ph, 20 H), 2.00–1.50 (m, CH_2, 4 H); 1.40 (s, CH_3, 15 H), ^{13}C NMR (CD_2Cl_2): 140.2–131.3 (m, Ph), 83.6 (s, C_5 ring), 30.2 (tt, CH_2, $^1J_{CH}$ = 127 Hz, $^2J_{CP}$ = 21 Hz), 10.3 (q, Me, $1J_{CH}$ = 126 Hz). ^{31}P NMR (C_6D_6): 91.6. ^{35}Cl NMR (C_6D_6): -116. Anal. Calcd for $C_{36}H_{39}ClFeP_2 \cdot Et_2O$: C, 68.73; H, 7.07; Cl, 5.05. Found: C, 69.12; H, 6.89; Cl, 4.85.

X-ray data (Table I) were collected on a dark green crystal of 1 mounted on a glass fiber. The cell parameters were obtained by fitting a set of 25 high-θ reflections. During the data collection, intensity controls showed no appreciable decay (less than 0.4%). After Lorentz and polarization corrections (no absorption corrections) the iron and chloride atoms were located by Patterson synthesis. The remaining non-hydrogen atoms of the complex were found after a scale factor refinement and a difference Fourier calculation. After isotropic refinement (R = 0.10), the pentane molecule (crystallization solvent) appears. This molecule is situated on a symmetry center and is not disordered. After an anisotropic refinement (R = 0.06) of all the non-hydrogen and nonsolvent atoms, the hydrogen atoms were located by a difference

---

(49) Ammeter, J. H.; Burgi, G. H.; Thibault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

(50) More recent calculations on the methyl cation $[Fe(Cp)(PH_3)_2CH_3]^{\bullet +}$ have also been performed. They lead to similar results in terms of level ordering and MO localization.[51]

(51) Rabaâ, H.; Saillard, J. Y. Work in progress.

(52) Lacoste, M.; Rabaâ, H.; Astruc, D.; Le Beuze, A.; Saillard, J. Y.; Précigoux, G.; Courseille, C.; Ardouin, N.; Bowyer, W. *Organometallics* **1989**, *8*, 2233.

(53) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, 711.

(54) This point will be discussed in a forthcoming publication of the X-ray structure of $1PF_6$.

(55) Kohl, F. X.; Jutzi, P. *J. Organomet. Chem.* **1983**, *243*, 119.

Fourier map between 0.57 and 0.26 e Å^{-3}. The whole structure was refined by full-matrix least-squares techniques (use of F magnitude; x, y, z, and β_{ij} for Fe, Cl, C, and P; x, y, and z fixed for H; solvent molecule isotropic). Atomic scattering factors are from ref 56. All the calculations were performed on a Digital PDP 11/60 computer with the SDP package.[57]

2. Reaction of Fe(C_5Me_5)(dppe)Cl (1). With CH_3CN. To a green solution of 0.625 g (1 mmol) of 1 in a mixture of CH_2Cl_2/diethyl ether (80/20) containing 1 mmol of NH_4PF_6 at 20 °C was added 63 μL (1.2 mmol) of CH_3CN. The color turned red. After the solutions were stirred overnight, the solvents were removed under vacuum and the residue was extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2/pentane afforded 0.643 g (83%) of red microcrystals identified as [Fe(C_5Me_5)(dppe)-NCMe]PF_6 by comparison of its ^{1}H and ^{13}C NMR parameters with those of the literature data.[22]

With KI or LiI: Preparation of Fe(C_5Me_5)(dppe)I (2). A green solution of 0.625 g (1 mmol) of 1 in CH_2Cl_2 containing 0.200 g (1.2 mmol) of KI was stirred for 6 h at 20 °C. The color changed from green to red-brown. The solution was filtered, and the slow diffusion of pentane gave 0.680 g (95%) of dark brown crystals of Fe(C5Me5)(dppe)I. Anal. Calcd for $C_{36}H_{39}FeIP_2$: C, 60.36; H, 5.49; I, 17.71; P, 8.65. Found: C, 59.94; H, 5.60; I, 17.43; P, 8.52. Mass spectrum: calcd for $C_{36}H_{39}FeIP_2$, m/e 716.0920; found, m/e 716.0920. ^{1}H NMR (C_6D_6): 7.30–6.90 (m, Ph, 20 H); 2.09 (m, CH_2, 4 H), 1.61 (s, CH_3, 15 H), {^{1}H}^{13}C NMR (C_6D_6): 141.8 (d, Ph, C_{para}), 139.0 (dd, Ph, C_{ipso}), 135.5 (d, Ph, C_{ortho}), 134.5 (d, Ph, C_{meta}), 83.6 (C_5 ring), 32.2 (CH_2), 11.5 (Me). ^{31}P NMR (C_6D_6): 95.08.

With $LiAlH_4$. To a -80 °C THF solution of 1 mmol (620 mg) of 1 was slowly added 2 mmol (76 mg) of $LiAlH_4$. The temperature was increased to room temperature over a period of 3 h, and the color of the solution turned dark orange. The solvent was removed under vacuum until the appearance of a gummy residue. The residue was extracted with pentane. Recrystallization from pentane afforded 0.560 g (95%) of 3.

With $LiAlD_4$. Following the procedure described above, $3d_1$ was prepared in 70% yield.

With CH_3MgI. To a solution of 1 mmol of CH_3MgI in diethyl ether at room temperature was added dropwise a diethyl ether solution of 0.510 g (0.8 mmol) of 1. The stirring was maintained 1 h. The solvent was removed under vacuum and the dark residue extracted with pentane. Recrystallization from pentane at -20 °C provided 0.300 g (50%) of orange microcrystals identified as 4 by comparison of its ^{1}H and ^{31}P NMR parameters with those of the literature.[11b,53]

With CH_3CH_2MgI. In a procedure identical with that described above, a solution of 0.510 g (0.8 mmol) of 2 in diethyl ether was added to a solution of CH_3CH_2MgI, in diethyl ether at 20 °C. After workup, 0.42 g (90%) of 3 was recovered and identified by comparison with an authentic sample.

With Potassium. To a gray-blue THF solution of irradiated potassium (1.2 mmol, 48 mg) was added 0.625 g (1 mmol) of 1. The color immediately turned black, and the 20-kHz irradiation was continued for an additional 20 min. Extraction with pentane, followed by recrystallization from CH_2Cl_2/pentane afforded 0.620 g (100%) of the starting material.

3. Synthesis of Fe(C_5Me_5)(dppe)H (3). Method A. To a 6-mmol gray-blue colloidal (0.234 g) potassium dispersion in THF prepared by a 5-min irradiation of 20-kHz ultrasound were added successively 3 mmol (1.575 g) of $FeCl_2$(dppe) and 3 mmol (0.408 g) of C_5Me_5H. Irradiation was maintained for 30 min before removal of the solvent under vacuum and extraction with pentane (3 × 25 mL). By concentration of the dark yellow solution, 1.5 mmol (0.890 g) of 1 was isolated as orange microcrystals.

Method B. Following the procedure described above, 3 is prepared from C_5Me_5D. The complexes 3 and $3d_1$ are recovered in 50% yield. The ratio $3/3d_1$ (90/10) was established by high-resolution mass spectroscopy.

Analytical data for 3 are as follows. IR (Nujol mull): ν_{Fe-H}, 1869.0 cm^{-1}. ^{1}H NMR (C_6D_6): 7.45 (m, 20 H, Ph), 2.00–1.72 (m, 4 H, CH_2), 1.62 (s, 15 H, C_5Me_5), -16.77 (t, 1 H, $^2J_{PH}$ = 67 Hz). {^{1}H}^{13}C NMR (C_6D_6): 142.6–133.4 (m, Ph), 85.2 (s, C_5 ring), 33.3 (t, CH_2, J_{PC} = 23.5 hz), 11.5 (s, Me). ^{31}P NMR (C_6D_6): 107.95.

Synthesis of Fe(C_5Me_5)(dppe)D ($3d_1$). To a THF suspension of 0.5 mmol (0.42 g) of [Fe(C_5Me_5)(dppe)$NCCH_3$]PF_6[22] cooled to -80 °C was added 2 mmol (0.08 g) of $LiAlD_4$. The temperature was allowed to increase to 20 °C, and the mixture was kept 1 h at this temperature. The solvent was removed under vacuum until a gummy residue appeared. Extraction with pentane followed by evaporation of the solvent to dryness provided 0.26 g (63%) of $3d_1$ as an orange powder.

IR (Nujol mull): ν_{Fe-D}, 1331.2 cm^{-1}. ^{1}H NMR (CD_2Cl_2): -17.06 (t, $^2J_{PD}$ = 10.2 Hz).

4. Synthesis of Fe(C_5Me_5)(dppe)CH_3 (4). Method A. To a 20 °C THF solution of 1 mmol (0.620 g) of 2 was added 20 mmol of CH_3Li in THF. The solution was stirred for 2 h, and the solvent was removed under vacuum. The residue was dissolved in 10 mL of toluene and the mixture hydrolyzed with 10 mL of aqueous Na_2CO_3. The biphasic mixture was frozen and the orange toluene solution filtered. Removal of the solvent under vacuum followed by washing with 3 × 10 mL of pentane and drying gave 1.00 g (83%) of an orange powder identified as Fe(C_5Me_5)(dppe)CH_3. Comparison of its ^{1}H NMR parameters with those of the literature[11b,58] are slightly different. ^{1}H NMR (C_6D_6): 7.45 (m, 20 H, Ph), 1.7 (m, 4 H, CH_2), 1.47 (s, 15 H, C_5Me_5), -0.83 (t, 3 H, Fe–CH_3). {^{1}H}^{13}C NMR (C_6D_6): 136.4 (m, Ph), 85.5 (s, C_5 ring), 28.7 (t, CH_2, J_{CP} = 21 Hz), 10.5 (s, Me). ^{31}P NMR (C_6D_6): 106.44.

Method B. To a toluene solution (210 mL) of 5 mmol (1.31 g) of Fe(C_5Me_5)$(CO)_2CH_3$[22] was added 5 mmol (1.99 g) of dppe. This solution was irradiated for 16 h at 250 nm. After trap to trap removal of the solvent the solid residue was dissolved in CH_2Cl_2 (3 mL) and slow diffusion of pentane affords 2.87 g of 4 (94%).

5. Synthesis of Fe(C_5Me_5)(dppe)CH_2OCH_3 (5). To a toluene solution (210 mL) of 5 mmol (1.46 g) of Fe(C_5Me_5)-$(CO)_2CH_2OCH_3$[22] was added 5 mmol (1.99 g) of dppe. This solution was irradiated for 16 h at 250 nm. After trap to trap removal of the solvent, the solid residue was dissolved in CH_2Cl_2 (3 mL) and slow diffusion of pentane affords 3.08 g of 4 (95 %). ^{1}H NMR (C_6D_6): 7.4 (m, 20 H, Ph), 3.82 (t, 2 H, CH_2O–, $^3J_{PH}$ = 4.3 Hz), 2.49 (s, 3 H, OCH_3), 1.48 (m, 4 H, CH_2), 1.38 (s, 15 H, Me). {^{1}H}^{13}C NMR (C_6D_6): 137 (m, Ph), 85.9 (s, C_5 ring), 79.4 (t, CH_2O, $^2J_{PC}$ = 25.3 Hz), 62.9 (s, OCH_3), 31.6 (t, CH_2, J_{CP} = 21 Hz), 10.2 (s, Me). ^{31}P NMR (C_6D_6): 112.2. Anal. Calcd for $C_{38}H_{44}FeOP_2$: C, 71.93; H, 6.99. Found: C, 71.56; H, 6.82.

6. Synthesis of [Fe(C_5Me_5)(dppe)R]PF_6 (R = Cl ($1PF_6$), R = CH_3 ($4PF_6$), R = CH_2OCH_3 ($5PF_6$)). Method A. To a 20-mL CH_2Cl_2 solution of 3 mmol of 1 (1.87 g), 4 (1.81 g), or 5 (1.90 g) at 20 °C was added 3 mmol (0.990 g) of [Cp_2Fe]PF_6. The solution was stirred for 10 min and the solvent removed under vacuum. The solid residue was washed with diethyl ether before being crystallized in CH_2Cl_2/Et_2O mixture. Red brown crystals were recovered in 86–95% yield ($1PF_6$, 1.99 g; $4PF_6$, 2.07 g; $5PF_6$, 2.15 g).

Method B. Following the procedure described above, $4PF_6$ and $5PF_6$ were synthesized in 90–95% yield by using Ph_3CPF_6.

Method C. In a Schlenck tube under a dry oxygen atmosphere were introduced 1 mmol of $4PF_6$ (0.604 g) or 1 mmol of $5PF_6$ (0.634 g), 1 mmol (0.185 g) of KPF_6, and 15 mL of CH_2Cl_2. The solution was stirred for 2 h at room temperature and gradually turned dark red-brown. The solution was filtered, and the solvent was removed under vacuum. The solid residue was washed with diethyl ether. Recrystallization from CH_2Cl_2/ether provided 0.606 g of $4PF_6$ (81%) of 0.630 mg of $5PF_6$ (81%).

$1PF_6$. ^{1}H NMR (CH_2Cl_2, 298 K): 7.87 (m-H, Ph), 6.72 (p-H, Ph), 3.88 (o-Ph), -3.87 (P–CH_2–), -28.08 (C_5Me_5). Anal. Calcd for $C_{36}H_{39}ClF_6FeP_3$: C, 56.16; H, 5.16; Cl, 4.6; P, 12.07. Found: C, 56.07; H, 5.27; Cl, 4.31; P, 12.57.

$4PF_6$. ^{1}H NMR (CH_2Cl_2, 298 K): 5.90 (p-H, Ph), 8.44 (m-H, Ph), 3.20 (o-H, Ph), -1.41 (P–CH_2–), -7.06 (CH_3), -15.41 (C_5Me_5). ESR (THF, 133 K): g = 2.44, 2.04. Mössbauer (77 K, Fe): SQ

---

(56) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(57) Frenz, B. A. Enraf-Nonius Structure Determination Package, SDP Users Guide, College Station, TX, 1985.

(58) The data reported in ref 11b are slightly different from our own measurements. This observation seems to be due to traces of iron(III) impurities eventually produced by contamination with oxygen in the sample of the reported compound.

= 0.76 mm s^{-1}, DI = 0.35 mm s^{-1}. Anal. Calcd for $C_{37}H_{42}F_6FeP_3$: C, 59.29; H, 5.65. Found: C, 59.07; H, 5.77.

5PF$_6$. ^{1}H NMR (CH_2Cl_2, 298 K): 5.16 (*p*-H, Ph), 8.97 (*m*-H, Ph), 3.42 (*o*-H, Ph), −1.33 (P–CH_2–), −4.34 (OCH_3), −9.40 (CH_2O), −17.73 (C_5Me_5). ESR (THF, 133 K): *g* = 2.48, 2.03. Mössbauer (77 K, Fe): SQ = 0.95 mm s^{-1}, DI = 0.35 mm s^{-1}. Anal. Calcd for $C_{38}H_{44}F_6FeP_3$: C, 58.55; H, 5.69. Found: C, 58.23; H, 5.73.

7. Synthesis of [Fe(C_5Me_5)(dppe)R]TCNQ (R = CH_3 (4TCNQ), R = CH_2OCH_3 (5TCNQ)). To a 10-mL CH_2Cl_2 solution of 3 mmol of 4 (1.81 g) or 5 (1.90 g) at 20 °C was added 3 mmol (0.612 g) of TCNQ. The red solution immediately turned green, and after the mixture was stirred for 1 h, 100 mL of ether was added. A dark green salt was precipitated and then washed with ether. Green microcrystals were recovered in 75% (4TCNQ, 1.81 g) or 70% yield (5TCNQ, 1.88 g). 4TCNQ, Anal. Calcd for $C_{49}H_{46}FeN_4P_2$ (4TCNQ): C, 72.77; H, 5.73; N, 6.93. Found: C, 72.49; H, 5.88; N, 6.71. Calcd for $C_{50}H_{48}N_4FeOP_2$ (5TCNQ): C, 71.6; H, 5.77; N, 6.68. Found: C, 71.31; H, 5.63; N, 6.97.

Acknowledgment. We are grateful to J. E. Guerchais (Brest, France), F. Varret (Paris), and H. Noël for the ESR, Mössbauer, and magnetic measurement facilities. S. Sinbandhit (CRMPO, Rennes, France) is gratefully acknowledged for NMR assistance. We are also indebted to the Laboratoires Standa (Caen, France) for financial support to C.R.

Supplementary Material Available: For 1, complete tables of atomic coordinates and their estimated standard deviations, bond lengths and angles, and general temperature factor expressions (5 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

A Ferracarborane Analogue to [Fp]$^-$. Synthesis and Reactions of [*closo*-3,3-$(CO)_2$-3,1,2-$FeC_2B_9H_{11}$]$^{2-}$

Sharon S. Lee, Carolyn B. Knobler, and M. Frederick Hawthorne*

Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90024

Received July 6, 1990

Reduction of [*closo*-3,3,3-$(CO)_3$-3,1,2-$FeC_2B_9H_{11}$] (1) with 2 equiv of sodium naphthalide affords the high-yield synthesis of a formal iron(0) ferracarborane dianion [*closo*-3,3-$(CO)_2$-3,1,2-$FeC_2B_9H_{11}$]$^{2-}$ (**3**), as monitored by ^{11}B NMR spectroscopy. Complex **3** serves as a nucleophile in a variety of alkylation, acylation, and metalation reactions to yield ferracarborane anions of the type [*closo*-3,3-$(CO)_2$-3-L-3,1,2-$FeC_2B_9H_{11}$]$^-$ (**4**, L = CH_3; **5**, L = $CH_2C_6H_5$; **6**, L = $COCH_3$; **7**, L = SnC_6H_5). The molecular structure of [N$(C_2H_5)_4$][**7**] has been determined by X-ray diffraction techniques. Compound **7** crystallized in the triclinic space group $P\bar{1}$ with a = 11.209 (1) Å, b = 13.026 (1) Å, c = 13.595 (1) Å, α = 79.959 (3)°, β = 84.143 (3)°, γ = 66.060 (2)°, V = 1785 Å^3, and Z = 2. In situ reactions of **3** with allyl and methylallyl chloride followed by subsequent loss of CO induced by ultraviolet radiation, resulted in the isolation of the corresponding η^3-allyl derivatives, [*closo*-3-CO-3-(η^3-CH_2CRCH_2)-3,1,2-$FeC_2B_9H_{11}$]$^-$ (**8**, R = H; **9**, R = CH_3). The structure of **8** as the PPN$^+$ salt was also elucidated by single-crystal X-ray diffraction and found to crystallize in the monoclinic space group $P2_1/m$ with a = 9.1250 (7) Å, b = 25.011 (2) Å, c = 18.517 (2) Å, β = 91.328 (3)°, V = 4225 Å^3, and Z = 4 (two crystallographically different half-anions and one cation in the asymmetric unit). Migratory insertion of alkyls was demonstrated in the preparation of [*closo*-3-CO-3-$COCH_3$-3-P$(CH_3)_3$-3,1,2-$FeC_2B_9H_{11}$]$^-$ (**10**) by heating **4** and excess P$(CH_3)_3$ in THF for 7 days at the reflux temperature. A single-crystal X-ray diffraction study of [PPN][**10**] is reported. Complex **10** crystallized in the triclinic space group $P\bar{1}$ with a = 10.086 (4) Å, b = 15.390 (6) Å, c = 17.027 (7) Å, α = 112.636 (8)°, β = 96.647 (8)°, γ = 100.206 (9)°, V = 2351 Å^3, and Z = 2. The closo 12-vertex icosahedral geometry composed of a polyhedral FeC_2B_9-d_6 framework and pseudooctahedral coordination exhibited by the iron atom are common structural features displayed by all three of the ferracarboranes that were characterized crystallographically.

Introduction

The derivative chemistry of the ubiquitous [(η^5-C_5H_5)Fe$(CO)_2$] moiety, also known as Fp, is extensively documented in the literature.[1] In view of the close structural and electronic similarities of the dicarbollide and the cyclopentadienyl ligands,[2] we have continued our ongoing investigation of ferracarborane chemistry by developing a route to the metallacarborane counterparts of these Fp derivatives.

Recently, we reported the synthesis and structural characterization of mononuclear iron(II) ferracarboranes[3] and also that of [*closo*-(η^6-(C_6H_6)-3,1,2-$FeC_2B_9H_{11}$].[4] As an effort to expand the relatively unexplored family of metallacarboranes containing iron, we have synthesized a ferracarborane analogue of [Fp]$^-$, the very nucleophilic [*closo*-3,3-$(CO)_2$-3,1,2-$FeC_2B_9H_{11}$]$^{2-}$ (**3**). In addition, we have prepared a series of novel ferracarborane anions via the reaction of a variety of electrophiles with **3**. We also report here the detailed accounts of the synthesis and the full spectroscopic and structural characterization of three

---

(1) Gmelin Handbook of Inorganic Chemistry, Organoiron Compounds, Series B, Vols. 14, 1989, 85–122.

(2) (a) Hawthorne, M. F.; Young, D. C.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 1818. (b) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F., Jr.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879. (c) Hawthorne, M. F. *Acc. Chem. Res.* **1968**, *1*, 28.

(3) Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *Organometallics*, in press.

(4) Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *J. Organomet. Chem.* **1990**, *394*, 29.

0276-7333/91/2310-1054$02.50/0