Organometallics **1997,** *16,* 2343−2355

Fulvalenyl Mono- and Diiron Complexes: Photolytic and Electron-Transfer-Induced Substitution of the Benzene Ligands by Phosphines and CO in the Diiron Fulvalenyl Dibenzene Complexes $[Fe_2Fv(C_6H_6)_2]^{2+/0}$. Generation of the Average-Valence Species $[Fe_2FvL_6]^{3+}$ (L = Phosphine)†

Marc Lacoste, Marie-Hélène Delville-Desbois, Nicole Ardoin, and Didier Astruc*

Laboratoire de Chimie Organique et Organométallique, URA CNRS No. 35, Université Bordeaux I, 351, Cours de la Libération, 33405 Talence Cédex, France

Received December 17, 1996⊗

The bi-sandwich complex $[Fe_2Fv(C_6H_6)_2]^{2+}(PF_6^-)_2$ ($\mathbf{1}^{2+}$; Fv = μ_2-η^5:η^5-fulvalenyl, unless noted otherwise) synthesized from biferrocene, was photolyzed with visible light in acetonitrile in the presence of 1,2-bis(diphenylphosphino)ethane (dppe) or bis(diphenylphosphino)methane (dppm) at −15 °C to give $[Fe_2Fv(dppe)_2(NCMe)_2]^{2+}(PF_6^-)_2$ ($\mathbf{2a}^{2+}$) or $[Fe_2Fv(dppm)_2(NCMe)_2]^{2+}(PF_6^-)_2$ ($\mathbf{2b}^{2+}$). The complexes $\mathbf{2a}^{2+}$ and $\mathbf{2b}^{2+}$ reacted in refluxing 1,2-dichloroethane with CO to give $[Fe_2Fv(dppe)_2(CO)_2]^{2+}(PF_6^-)_2$ ($\mathbf{3a}^{2+}$) and $[Fe_2Fv(dppm)_2(CO)_2]^{2+}(PF_6^-)_2$ ($\mathbf{3b}^{2+}$), and $\mathbf{2a}^{2+}$ reacted similarly with PMe_3 to give $[Fe_2Fv(dppe)_2(PMe_3)]^{2+}(PF_6^-)_2$ ($\mathbf{4}^{2+}$). The direduced 38-electron (38e) complex **1** reacted at −15 °C with 1 atm of CO to give $[Fe_2(\mu_2\text{-}\eta^4\text{:}\eta^4\text{-Fv})(CO)_6]$ (**7**) and with PMe_3 to give $[Fe_2Fv(PMe_3)_4]$ (**9**). When $Na^+PF_6^-$ was present in stoichiometric amounts in THF, these reactions followed a different course and $Na^+PF_6^-$ induced electron transfer (disproportionation) by irreversibly dislocating ion pairs: the reaction of **1** with 1 atm of CO gave $[Fe(\eta^5\text{-Fv})(\eta^6\text{-}C_6H_6), Na^+PF_6^-]$ (**5**), and that with PMe_3 gave $[Fe_2Fv(PMe_3)_6]^{2+}(PF_6^-)_2$ ($\mathbf{8}^{2+}$) and the known complex $[Fe(PMe_3)_4]$ (**10**). The cyclic voltammograms (CV) of $\mathbf{2a}^{2+}$ and $\mathbf{2b}^{2+}$ contain irreversible oxidation and reduction waves, but the CVs of $\mathbf{3a}^{2+}$ and $\mathbf{3b}^{2+}$ showed two close reversible monoelectronic reduction waves (no oxidation wave). The CVs of the hexaphosphine complexes indicated partially or fully irreversible reduction waves, respectively, but two reversible waves at +0.71 and +0.95 V for $\mathbf{4}^{2+}$ and +0.70 and +1.08 V for $\mathbf{8}^{2+}$ (vs SCE, Pt, DMF, 0.1 M n-Bu_4NBF_4 −30 °C). The bielectronic reduction of $\mathbf{2a}^{2+}$ and the bielectronic oxidation of $\mathbf{4}^{2+}$ and $\mathbf{8}^{2+}$ using redox reagents led to decomposition, but the monoelectronic oxidation of $\mathbf{4}^{2+}$ and $\mathbf{8}^{2+}$ using $(p\text{-Br-}C_6H_4)_3N^+SbCl_6^-$ in CH_2Cl_2 gave the stable mixed-valence trications $\mathbf{4}^{3+}$ and $\mathbf{8}^{3+}$, for which the Mössbauer spectra showed delocalized average valency on the Mössbauer time scale. These studies have opened the route to a variety of mono- and diiron fulvalenyl organometallic compounds, confirming the great importance of the presence of $Na^+PF_6^-$. This salt can change reaction pathways and, in particular, induce electron-transfer reactions, underlining the extraordinary electronic flexibility of the fulvalenyl ligand and its ability to transfer the electron flow between two metal centers.

Introduction

Fulvalenyl complexes have attracted a great deal of attention over the last few decades, because the fulvalenyl bridge brings about considerable electronic delocalization between the two metal centers. The consequences have been the development of difulvalenylmetal sandwiches,[1,2] among the first mixed-valence complexes[1−6] useful in energy conversion devices,[2] and a versatile organotransition-metal chemistry.[7−22]

Although transition-metal fulvalenyl complexes have been synthesized with many metals, few general routes are known.[14] Vollhardt's group has developed a sys-

---

† This article is dedicated to Professor Gottfried Huttner on the occasion of his 60th birthday.

* To whom correspondence should be addressed. Telefax: Int. code + 5 56 84 66 46. E-mail: d.astruc@lcoo.u-bordeaux.fr.

⊗ Abstract published in *Advance ACS Abstracts*, May 1, 1997.

(1) First sandwich fulvalenyl complex (ferrocenylene): (a) Mueller-Westerhoff, U. T.; Eilbracht, P. *Tetrahedron Lett.* **1973**, 1855. (b) Mueller-Westerhoff, U. T.; Eilbracht, P. *J. Am. Chem. Soc.* **1972**, *94*, 9272. (c) Cowan, D. O.; LeVanda, C.; Collins, R. L.; Candela, G. A.; Mueller-Westerhoff, U. T.; Eilbracht, P. *J. Chem. Soc., Chem. Commun.* **1973**, 329. (d) Cowan, D. O.; Le Vanda, J.; Park, J.; Kaufman, F. *Acc. Chem. Res.* **1973**, *6*, 1.

(2) For a review, see: Mueller-Westerhoff, U. T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 702.

(3) For a recent review on various kinds of dimetal fulvalenyl complexes see ref. 4, Chapter 2.

(4) Astruc, D. *Electron-Transfer and Radical Processes in Transition Metal Chemistry;* VCH: New York, 1995.

(5) For dimetal fulvalenyl complexes with various metals see the following. (a) Iron: LeVanda, C.; Bechgaard, K.; Cowan, D. O.; Mueller-Westerhoff, U. T.; Eilbracht, P.; Candela, G. A.; Collins, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 3181. (b) Cobalt: Davison, A.; Smart, J. C. *J. Organomet. Chem.* **1973**, *49*, C43. (c) Vanadium: Smart, J. C.; Pinsky, B. L.; Fredrich; M. F.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 4371. (d) Nickel: Smart, J. C.; Pinsky, B. L. *J. Am. Chem. Soc.* **1977**, *99*, 956.

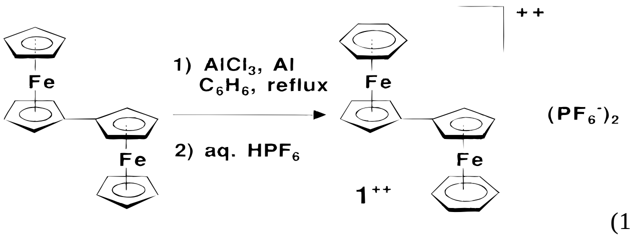
(6) For more recent work on mixed-valence biferrocenenium derivatives see: (a) Hendrickson, D. N.; Oh, S. M.; Dong, T.-Y.; Kambara, T.; Cohn, M. J.; Moore, M. F. *Comments Inorg. Chem.* **1985**, *4*, 329. (b) Webb, R. J.; Geib, S. J.; Staley, D. L.; Rheingold, A. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1990**, *112*, 5031.

(7) Obendorf, D.; Schottenberger, H.; Rieke, C. *Organometallics* **1991**, *10*, 1293.

(8) For a recent comprehensive report on organometallic fulvalenyl chemistry, see: Tilset, M.; Vollhardt, K. P. C.; Boese, R. *Organometallics* **1994**, *13*, 3146.

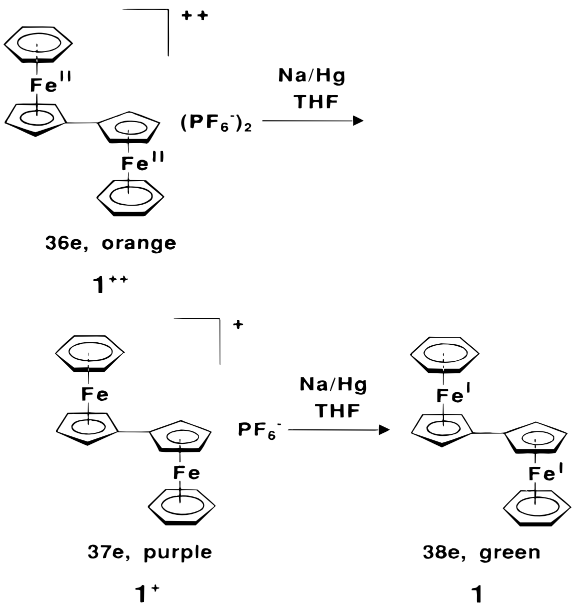
S0276-7333(96)01060-6 CCC: $14.00

tematic and practical synthesis of transition-metal carbonyl fulvalenyl complexes by heating dihydrofulvalene with metal carbonyls.[24−29] This quite general method does not apply to iron, however. We have synthesized and examined the electronic structure of diiron fulvalenyl bis(arene) complexes.[30−32] The dicationic complexes **1**$^{2+}$ are directly accessible from biferrocene by the classical ligand substitution reaction using aluminum chloride and the arene (eq 1).



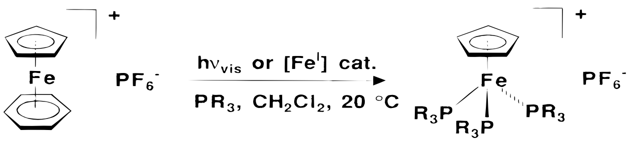
(1)

Given our interest in electron-transfer processes,[4] we have synthesized and studied the mono- and direduced forms **1**$^{+}$ and **1**, respectively (eq 2).



(2)

The substitution lability of 19-electron complexes is well-known,[30,33−39] and we thought that this property could apply to **1** and might lead to the possibility of replacing the arene ligands by others under mild conditions.[38] This would indeed provide a facile route to organometallic fulvalenyl diiron complexes with various ligands. Meanwhile, it was essential to compare this possibility to the direct reactivity of the 18-electron dication using thermal and photochemical means. These considerations simply parallel those which led us to the investigation of the mononuclear chemistry[40] (eq 3).



(3)

In mononuclear chemistry, the reactivity of 19-electron [Fe^{I}Cp(arene)], generated by stoichiometric electron transfer to the 18e cation, was shown to be

---

(9) For the pioneering work by Rausch on organometallic fulvalenyl complexes see: (a) Rausch, M. D. *J. Am. Chem. Soc.* **1960**, *82*, 2080. (b) Rausch, M. D. *J. Org. Chem.* **1961**, *26*, 1802. (c) Rausch, M. D.; Kovar, R. F.; Kraihemzel, C. S. *J. Am. Chem. Soc.* **1972**, *94*, 1271. For more recent work, see: Bitterwolf, T. E.; Spink, W. C.; Rausch, M. D. *J. Organomet. Chem.* **1989**, *363*, 189.

(10) (a) Köhler, F. H.; Doll, K. H.; Prössdorf, W.; Muller, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 151. (b) Hudeczek, P.; Köhler, F. H. *Organometallics* **1992**, *11*, 1457.

(11) (a) Herrmann, W. A.; Andrejewski, D.; Herdtweck, E. *J. Organomet. Chem.* **1987**, *319*, 183. (b) Ashworth, T. V.; Cuenca, A.; Herdtweck, E.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 289.

(12) (a) Gambarotta, S.; Chiang, M. Y. N. *Organometallics* **1987**, *6*, 897. (b) Wielstra, Y.; Meetsma, A.; Gambarotta, S.; Khan, S. *Organometallics* **1990**, *9*, 876. (c) Alvaro, L.; Cuenca, T.; Flores, J. C.; Royo, P.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1992**, *11*, 3301.

(13) Lemenovskii, D. A.; Fedin, V. P.; Slovohotov, Y. L.; Struchkov, Y. T. *J. Organomet. Chem.* **1982**, *228*, 153.

(14) A very interesting route to dirhodium compounds is that initiated by oxidative coupling of mononuclear complexes (for discussions, see ref 3): (a) McKinney, R. J. *J. Chem. Soc., Chem. Commun.* **1980**, 603. (b) McKinney, R. J. *Inorg. Chem.* **1982**, *21*, 2051. (c) Freeman, M. J.; Orpen, A. G.; Connelly, N. G.; Manners, I.; Raven, S. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2283. (d) Connelly, N. G.; Lucy, A. R.; Payne, J. D.; Galas, A. M. R.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1983**, 1879. (e) Chin, T. T.; Geiger, W. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 5002.

(15) For more recent works on organometallic fulvalenyl complexes, see refs 16−23.

(16) Dong, T.-Y.; Lee, S.-H.; Chang, C. K.; Lin, K.-J. *J. Chem. Soc., Chem. Commun.* **1995**, 2456.

(17) Manriquez, J.; Ward, M. D.; Reiff, W. M.; Calabrese, J. C.; Jones, N. L.; Carroll, P. J.; Bunel, E. E.; Miller, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 6182.

(18) (a) Kovács, I.; Baird, M. C. *Organometallics* **1995**, *14*, 4074, 4084, 5469; **1996**, *15*, 3588.

(19) Kerber, R. C.; Waldbaum, B. *Organometallics* **1995**, *14*, 4742.

(20) Chin, T. T.; Geiger, W. E. *Organometallics* **1995**, *14*, 1316.

(21) Scott, P.; Hitchcock, P. B. *J. Organomet. Chem.* **1995**, *497*, C1.

(22) Cano, A.; Cuenca, T.; Galakhov, M.; Rodriguez, G. M., Royo, P.; Cardin, C. J.; Convery, M. A. *J. Organomet. Chem.* **1995**, *493*, 17.

(23) Ward, M. D. *Chem. Soc. Rev.* **1995**, 121.

(24) The fulvalenyl dianion route is general and has been systematically developed by Vollhardt's group.[25−29] For a review, see: McGovern, P. A.; Vollhardt, K. P. C. *Synlett* **1990**, 493.

(25) Vollhardt, K. P. C.; Weidman, T. W. *Organometallics* **1984**, *3*, 82.

(26) Huffman, M. A.; Newman, D. A.; Tilset, M.; Tolman, W. B.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 1926.

(27) Kahn, A. P.; Newman, D. A.; Vollhardt, K. P. C. *Synlett* **1990**, 141.

(28) (a) Tilset, M.; Vollhardt, K. P. C. *Organometallics* **1985**, *4*, 2230. (b) Tolman, W. B.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 582.

(29) Moulton, R.; Weidman, T. W.; Vollhardt, K. P. C.; Bard, A. J. *Inorg. Chem.* **1986**, *25*, 1846.

(30) Reference 4, Chapter 5.

(31) (a) Desbois, M.-H.; Astruc, D.; Guillin, J.; Mariot, J.-P.; Varret, F. *J. Am. Chem. Soc.* **1985**, *107*, 52. (b) Desbois, M.-H.; Astruc, D.; Guillin, J.; Varret, F.; Trautwein, A. X.; Villeneuve, G. *J. Am. Chem. Soc.* **1989**, *111*, 5800. (c) Delville, M.-H.; Rittinger, S.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1992**, 519. (d) See also ref 32.

(32) For fulvalenyldiiron monoarene complexes, see: Desbois, M.-H.; Astruc, D.; Guillin, J.; Varret, F. *Organometallics* **1989**, *8*, 1841.

(33) Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139.

(34) (a) Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 643. (b) *Chem. Rev.* **1988**, *88*, 1189. (c) *Comments Inorg. Chem.* **1987**, *6*, 61.

(35) Kotz, J. C. In *Paramagnetic Organometallic Species in Activation, Selectivity, Catalysis*; Chanon, M., Julliard, M., Poite, J. C., Eds.; NATO ASI Series C, No. 257; Kluwer: Dordrecht, The Netherlands, 1989; p 171.

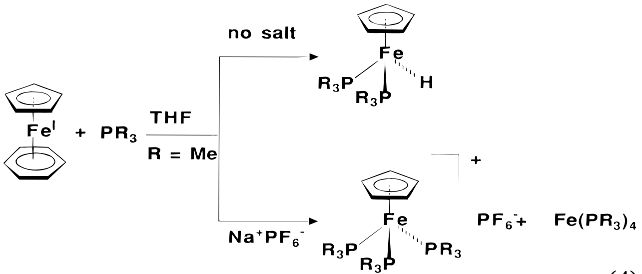
(36) (a) Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217. (b) *Comments Inorg. Chem.* **1986**, *5*, 215. (c) *Prog. Inorg. Chem.* **1988**, *36*, 125.

(37) Astruc, D. In *Mechanisms and Processes in Molecular Chemistry*; Astruc, D., Ed.; New J. Chem. 16; Gauthiers-Villars: Paris, 1992; p 305.

(38) (a) Moinet, C.; Román, E.; Astruc, D. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *121*, 241. (b) Ruiz, J.; Lacoste, M.; Astruc, D. *J. Am. Chem. Soc.* **1990**, *112*, 5471. (c) Boudeville, Ph.; Burgot, J.-L.; Darchen, A. *New J. Chem.* **1995**, *19*, 179.

(39) (a) Shi, Q. Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 71; **1982**, *104*, 4032. (b) Brown, T. L. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; J. Organomet. Chem. Libr. 22; Elsevier: New York, 1990; p 27.

dramatically dependent on the presence of a salt such as $Na^+PF_6^-$.[38b,41−43] Simple ligand substitution followed by H atom abstraction from the medium was observed in various solvents in the absence of a salt, whereas the presence of $Na^+PF_6^-$ provoked disproportionation of Fe^I by driving the electron transfer through ion-pair exchange (eq 4).



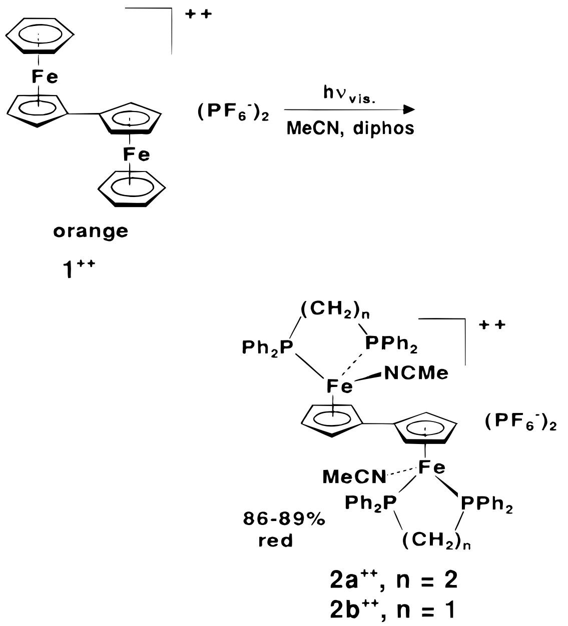
(4)

Obviously, similarities and differences were forecasted; in particular, the electronic delocalization through the fulvalenyl bridge between the two metal centers renders the bimetallic systems considerably richer and more versatile than the mononuclear ones. As a consequence, electron-transfer reactions have been extremely useful in fulvalenyldimetal chemistry, especially with first-row transition metals.[41−46] Stoichiometric electron transfer has provided redox recognition in heteronuclear chemistry,[41,42] and catalytic electron transfer (electron-transfer chain)[33−36,46,47,50,51] has been responsible for spectacular reactivity.[43,44] In the present work, however, chain reactions are not efficient, and we are now comparing stoichiometric electron transfer with photolysis.[29,48,49]

Results

1. Reactions Starting from the 36e Complex $[Fe_2Fv(C_6H_6)_2]^{2+}(PF_6^-)_2$ (1^{2+}). The orange 36e complex $[Fe_2Fv(C_6H_6)_2]^{2+}(PF_6^-)_2$ (1^{2+}), accessible in 40% yield by double ligand exchange from biferrocene (eq 1),[53a,b] has been used throughout this work as the starting material. We show here two kinds of reactions, those starting from 1^{2+} and those using the green 38e complex **1**, obtained from 1^{2+} by Na/Hg reduction in THF at −20 °C (eq 2).

Photolysis of 1^{2+} using visible light at −15 °C (in acetonitrile) in the presence of a diphosphine ligand P_2 such as 1,2-bis(diphenylphosphino)ethane (dppe) or bis(diphenylphosphino)methane (dppm) leads to the formation in high yield of a deep red air-sensitive complex of the type $[Fe_2FvP_4(NCMe)_2]^{2+}(PF_6^-)_2$ (2^{2+}), in which each benzene ligand has been replaced by one diphosphine and one acetonitrile (eq 5).



(5)

We attempted this reaction using excess PMe_3 instead of the diphosphine but could not get the reaction to work.

The complexes 2^{2+} can serve to bring another ligand into the coordination sphere of iron. They react in dichloroethane at reflux to give the substitution of the acetonitrile ligand by CO and, at 20 °C, by PMe_3. The red solution progressively turns yellow, and the CO and PMe_3 yellow complexes (respectively 3^{2+} and 4^{2+}) could be isolated in high yields (eq 6, Figure 1). In both examples, the acetonitrile ligand, which has no π-acceptor properties, is replaced by π-acceptors which form strong bonds with the metal.

2. Reactions Starting from the 38e Complex $[Fe_2Fv(C_6H_6)_2]$ 1. The green biradical 38e complex $[Fe_2Fv(C_6H_6)_2]$ (**1**) is very air-sensitive; it is thermally stable up to −15 °C. Thus, a convenient way to use it is to generate it at −20 °C by Na/Hg reduction of 1^{2+} in THF and to handle this THF solution (**1** is soluble in THF). However, such THF solutions contain $Na^+PF_6^-$ ($Na^+PF_6^-$ is also soluble in THF). Since we know from the mononuclear chemistry that the reactions of the 19e $[Fe^ICp(arene)]$ complexes are very dependent on the presence of $Na^+PF_6^-$, it is essential to also purify **1** from $Na^+PF_6^-$. Thus, two kinds of reactions have been

---

(40) Arene substitution is easily achieved by photolysis in mononuclear $[FeCp(arene)]^+$ complexes; see: (a) Mann, K. R.; Gill, T. P. *Inorg. Chem.* **1980**, *19*, 3007. (b) Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758. (c) Catheline, D.; Astruc, D. *J. Organomet. Chem.* **1984**, *272*, 417.

(41) Ruiz, J.; Lacoste, M.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1989**, 813.

(42) Astruc, D. *Acc. Chem. Res.* **1991**, *24*, 36.

(43) Astruc, D.; Delville-Desbois, M.-H.; Lacoste, M.; Ruiz, J.; Moulines, F.; Hamon, J.-R. Recent Advances in the Chemistry of the Main-Group Elements. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1994**, *87*, 11−22.

(44) Delville, M.-H.; Brown, D. S.; Vollhardt, K. P. C.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1991**, 1355.

(45) Brown, D. S.; Delville, M.-H.; Vollhardt, K. P. C.; Astruc, D. *New J. Chem.* **1992**, *16*, 899.

(46) Brown, D.; Delville-Desbois, M.-H.; Vollhardt, K. P. C.; Astruc, D. *Angew. Chem.* **1994**, *106*, 715; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 661.

(47) Brown, D. S.; Delville, M.-H.; Vollhardt, K. P. C.; Astruc, D. *Organometallics* **1996**, *15*, 2360.

(48) Preliminary communication: Delville, M.-H.; Lacoste, M.; Astruc, D. *J. Am. Chem. Soc.* **1992**, *114*, 8310.

(49) Moulton, R.; Bard, A. J. *Organometallics* **1988**, *7*, 351.

(50) Reference 4, Chapter 6.

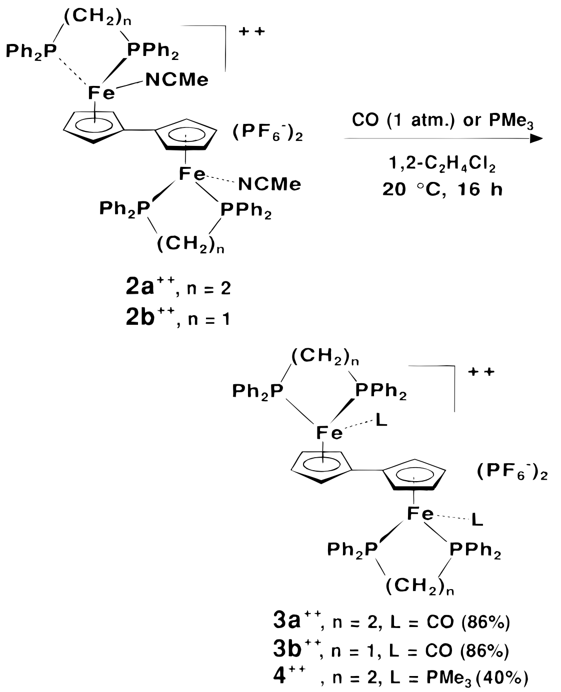
(51) (a) Chanon, M.; Tobe, M. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 1. (b) Chanon, M. *Bull. Soc. Chem. Fr.* **1982**, 197; **1985**, 209. (c) Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425. (d) Chanon, M. *Acc. Chem. Res.* **1987**, *20*, 214. (e) Chanon, M.; Eberson, L. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988.

(52) Lacoste, M.; Astruc, D.; Garland, M.-J.; Varret, F. *Organometallics* **1988**, *7*, 2253.

(53) (a) Lee, C. C.; Demchuk, K.; Sutherland, R. G. *Synth. React. Inorg. Met.-Org. Chem.* **1978**, *8*, 36. (b) See ref 31c for an improved procedure.

(54) Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272. (b) Karsh, H.-H.; Klein, H.-F.; Schmidbauer, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 637.

(55) See ref 4, Chapter 2, and: Bard A. J.; Faulkner, L. P. *Electrochemical Methods*; Wiley: New York, 1980; Chapter 6.



(6)

carried out: those using THF solutions generated by Na/Hg reduction of $\mathbf{1}^{2+}$ and which contain stoichiometric amounts of $Na^+PF_6^-$ and those for which $Na^+PF_6^-$ has been removed. In order to remove $Na^+PF_6^-$, it is necessary to evaporate THF *in vacuo* at or below −20 °C, extract the residue with pentane or toluene−pentane (1:5), and filter.

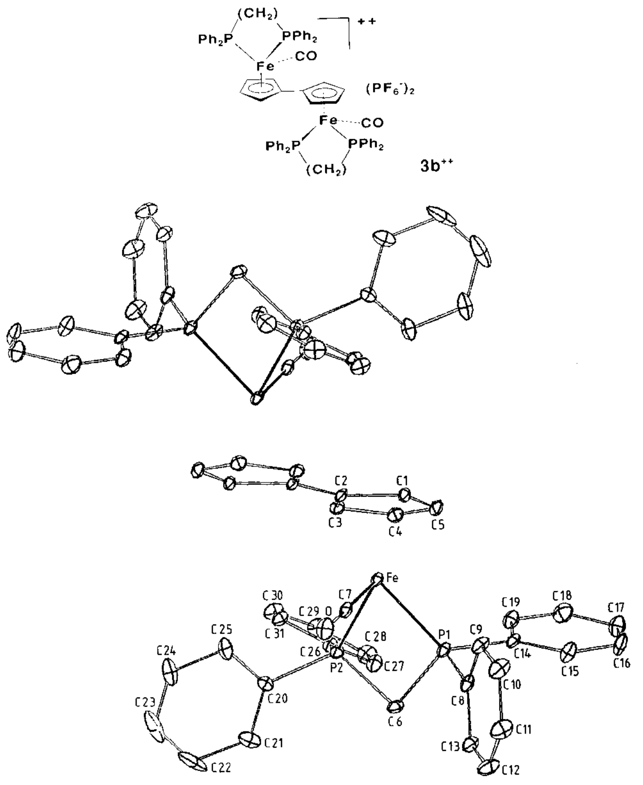
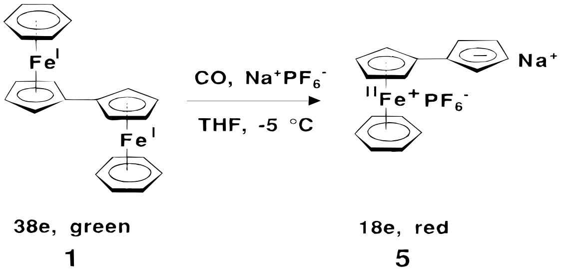


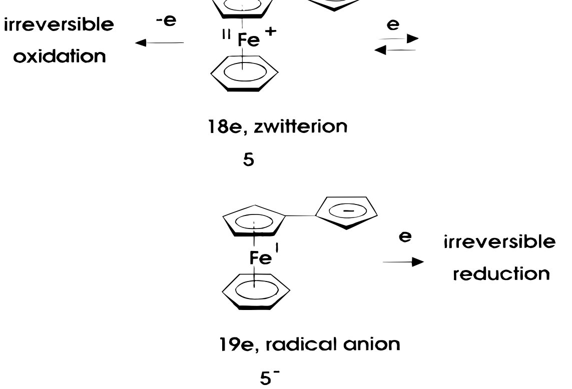
Figure 1. ORTEP view of the X-ray crystal structure of $[Fe_2Fv(dppm)_2(CO)_2]^{2+}(PF_6^-)_2$ ($\mathbf{3b}^{2+}$). Bond distances and angles: mean Fe−Cp (centroid), 1.720 Å; Cp−Cp link, 1.459(12) Å; mean P−C, 1.806(7) Å; mean Fe−P, 2.199(2) Å; Fe−CO, 1.762(8) Å; FeCO angle, 178.7(6)°; PFeP angle, 74.88(7)°; PCP angle, 93.2(3)°. Reproduced with permission from ref 52.

(a) Reaction of 1 with CO in THF in the Presence of $Na^+PF_6^-$. Let us start by the example which, from the experimental standpoint, is the simplest one: the direct use of **1** in THF solution containing $Na^+PF_6^-$, generated by Na/Hg reduction of $\mathbf{1}^{2+}$ at −20 °C. When the green solution is allowed to react between −40 and −5 °C with CO at atmospheric pressure, the color changes to red around −5 °C and, after the temperature is raised to 20 °C, the red complex can be obtained in 42% yield. Much to our surprise, this complex did not show any carbonyl band in the infrared spectrum. This red compound turned out, from its NMR data and elemental analysis, to be the monoiron fulvalenyl complex $[FeFv(C_6H_6),Na^+PF_6^-]$ (**5**), resulting from the loss of $Fe(C_6H_6)$ from **1** (eq 7).



(7)

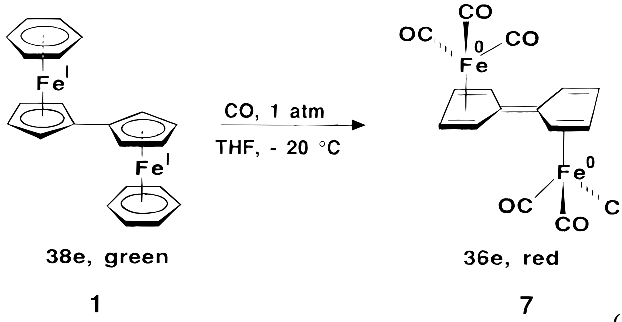
The structure of **5** is, in particular, shown by the usual location of the signal of the benzene ligand in the $[FeCp(C_6H_6)]^+$ cation at 6.10 ppm (CD_3COCD_3) in the ^1H NMR spectrum, the Mössbauer parameters (isomer shift, IS = 0.52 mm s^{-1} vs Fe; quadrupole splitting, QS = 1.60 mm s^{-1}) that are also the usual ones for a $[Fe^{II}Cp(arene)]^+$ cation, and elemental analysis showing the presence of 1 equiv of $Na^+PF_6^-$ after recrystallization. The first reduction potential is found by cyclic voltammetry at $E° = -1.32$ V vs SCE (DMF, 0.1 M n-Bu_4NBF_4, Pt, 20 °C). The irreversible oxidation of the cyclopentadienyl anion is consistently found at $E_{p_a} = +0.81$ V vs SCE, and an irreversible second reduction wave corresponding to the reduction of the 19e anion is found at $E_{p_c} = -2.23$ V vs SCE (eq 8).



(8)

A much less soluble product is extracted from the above reaction of **1** with CO in THF + $Na^+PF_6^-$: it is formed in only 10% yield, and its structure, deduced from ^1H NMR and infrared data, was found to be $[(C_6H_6)Fe^+FvFe^+(CO)_2]_2(PF_6^-)_2$ (**6**).

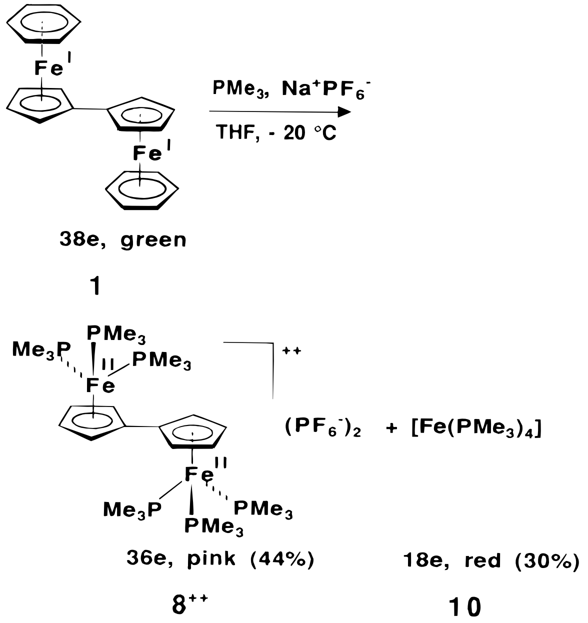
(b) Reaction of 1 with CO in the Absence of $Na^+PF_6^-$. When the reaction of **1** with CO is carried out in the absence of $Na^+PF_6^-$ in toluene, the new red complex $[Fe_2Fv(CO)_6]$ (**7**) results from the replacement of the two benzene ligands by six carbonyls (eq 9). The complex **7** is found to be diamagnetic; *i.e.*, intramolecular coupling has occurred in the fulvalenyl ligand.



(9)

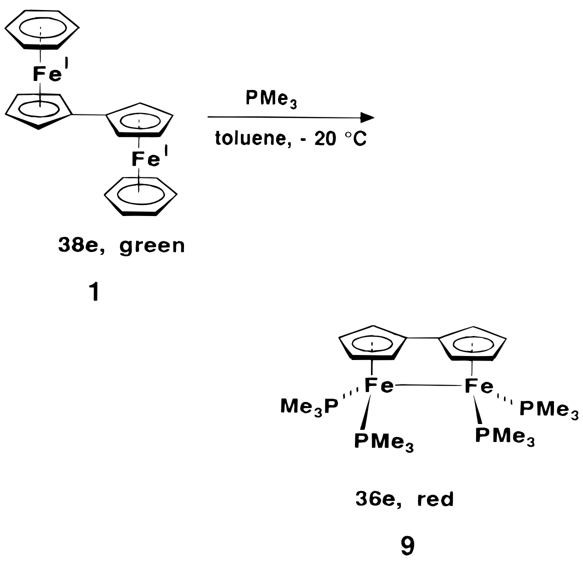
Although **7** is slightly thermally unstable, it can be characterized by ^{1}H and ^{13}C NMR and infrared spectra. The ^{1}H spectrum showed two triplets each representing 4 H's for the fulvalene ligand whereas three peaks at 88.6, 88.5, and 76.0 are found in the fulvalene region in $^{13}C\{^1H\}$ NMR. The CO ligands are found at 218.6 ppm, and the infrared spectrum (CH_2Cl_2) shows bands at 1940 and 2000 cm^{-1} indicating terminal carbonyls.

(c) Reaction of 1 with PMe$_3$ in THF in the Presence of Na$^+$PF$_6^-$. The reaction of **1** with PMe$_3$ in THF at −20 °C in the presence of $Na^+PF_6^-$ gives the orange THF-insoluble dication $[Fe_2Fv(PMe_3)_6]^{2+}(PF_6^-)_2$ (**8**$^{2+}$) in 50% yield, and the known THF-soluble red complex $[Fe(PMe_3)_4]$ (**10**) in 30% yield (eq 10). The complex **8**$^{2+}$ is characterized by the signal at 22.4 ppm in the ^{31}P NMR spectrum and other diagnostic peaks in the ^{1}H and ^{13}C NMR spectra. The Mössbauer spectrum shows parameters (IS = 0.320 mm s^{-1} vs Fe, QS = 1.762 mm s^{-1} at 20 °C) close to those found for **8**$^{2+}$, confirming the symmetrical bis-piano-stool dicationic Fe^{II} structure supported by elemental analysis.



(10)

(d) Reaction of 1 with PMe$_3$ in the Absence of Na$^+$PF$_6^-$. The reaction of **1** with PMe$_3$ in toluene in the absence of $Na^+PF_6^-$ at −20 °C gives the air-sensitive, thermally unstable red complex $[Fe_2Fv(PMe_3)_4]$ (**9**) (eq 11). The diamagnetic complex **9** is characterized by the two triplets representing four protons each at 3.65 and 3.34 ppm in the ^{1}H NMR spectrum, the signal at 26.7 ppm in ^{31}P NMR, and the peaks at $(M - PMe_3)^+$, $(M - 4PMe_3)^+$, $(PMe_3)^+$, and $(FeFv)_n{}^+$, ($n = 2, 3$; biferrocenylene and triferrocenylene, respectively) in the mass spectrum.



(11)

3. Electron-Transfer Chemistry of the Piano-Stool Diiron Fulvalenyl Complexes [Fe$_2$FvP$_4$L$_2$]$^{2+}$. Three types of complexes have been examined: L = CH_3CN (**2**$^{2+}$), CO (**3**$^{2+}$), and PMe$_3$ (**4**$^{2+}$ and **8**$^{2+}$). The electrochemistry very much depends on the nature of L. The complexes have been analyzed by cyclic voltammetry (CV) in DMF at −30 °C on Pt. The waves are diffusion-controlled, which has been verified by checking that $i_pv^{1/2}$ is constant. As two close waves are sometimes found by CV, diffusion control has been verified using chronoamperometry, as well as electrochemical reversibility. Ferrocene is used as an internal standard. The acetonitrile complexes **2a**$^{2+}$ and **2b**$^{2+}$ show an almost irreversible wave ($i_c/i_a = 0.2$) at 0.77 V vs SCE (**2a**$^{2+}$) or 0.70 V vs SCE (**2b**$^{2+}$) and a second almost irreversible wave ($i_c/i_a = 0.1$) at +1.12 V vs SCE for **2a**$^{2+}$ (not well-defined for **2b**$^{2+}$ in this region). On the reduction side, an irreversible wave is found at −1.48 V vs SCE in the CV of **2a**$^{2+}$.

On the other hand, all the waves are shifted to more positive or less negative values for the carbonyl complexes **3**$^{2+}$, as expected. On the anodic side, the shift is so large that the oxidation to Fe^{III} cannot be observed up to the limit of +1.5 V vs SCE in DMF. On the cathodic side, two reversible one-electron waves are observed at −1.20 and −1.32 V vs SCE on Hg even at 20 °C, as shown by CV and chronoamperometry. The difference between the cathodic and anodic peak potentials is 60 mV for the first wave, and these E_p values do not vary with the scan rate, confirming that a one-electron electrochemically reversible wave is involved (Figure 2). The comproportionation constant at 300 K is $K = 104$; thus, the mixed-valence complex should be isolable.

$$[Fe^{II}Fe^{II}]^{2+} + [Fe^{I}Fe^{I}] \rightleftarrows 2[Fe^{II}Fe^{I}]^{+}$$

Two more irreversible reduction waves are observed at −1.90 and −2.00 V vs SCE.

The behavior of the complexes **4**$^{2+}$ and **8**$^{2+}$, bearing six phosphine ligands on the two iron atoms, is almost

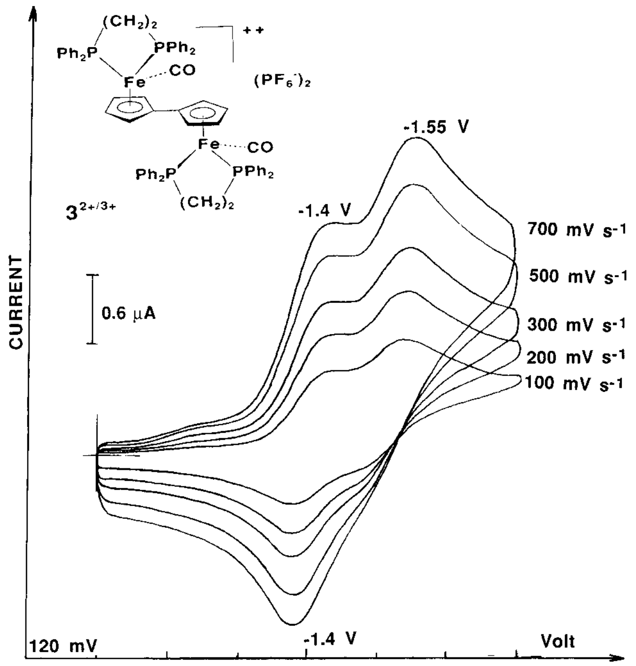


Figure 2. Cyclic voltammetry of $\mathbf{3}^{2+}$ (DMF, 0.1 M *n*-Bu_4N^+-BF_4^-, working electrode Pt, reference electrode Ag, internal reference Cp_2Fe, $T = -38$ °C). The scan rates are shown to the right of the CV waves.

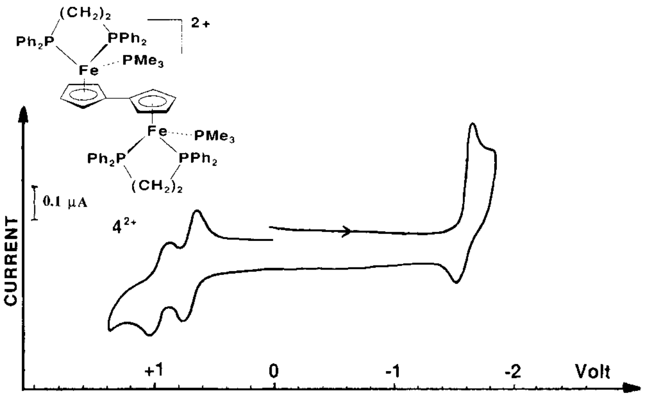


Figure 3. Cyclic voltammetry of $\mathbf{4}^{2+}$ (DMF, 0.1 M *n*-Bu_4N^+-BF_4^-, working electrode Pt, reference electrode Ag, internal reference Cp_2Fe, −30 °C, scan rate 400 mV s^{-1}.

identical. The complex $\mathbf{4}^{2+}$ shows a chemically and electrochemically reversible first one-electron-oxidation wave at +0.71 V vs SCE, whereas $\mathbf{8}^{2+}$ shows the same reversible wave at +0.70 V vs SCE. The first oxidation wave is characterized by $E_{p_a} - E_{p_c}$ values of 0.06 V without shift of these E_p values upon changing scan rate. The second oxidation wave is almost chemically reversible for $\mathbf{4}^{2+}$ at +0.95 V vs SCE ($i_c/i_a = 0.9$) but much less so for $\mathbf{8}^{2+}$ at +1.08 V vs SCE ($i_c/i_a = 0.5$) (see Figure 3). On the reduction side, a partially reversible wave is observed at −1.58 V vs SCE ($i_c/i_a = 0.3$), whereas the hexakis-PMe_3 complex $\mathbf{8}^{2+}$ shows irreversible reduction waves near −2 V vs SCE. The potentially reversible wave of **4** appears to involve two electrons (by comparison with the height of the other waves), *i.e.* reduction to the neutral 18-electron fulvalene complex **4**, whose stability seems weak.

Despite the very positive value of the oxidation potential of the diiron hexaphosphine fulvalenyl dications, we attempted monoelectronic oxidation reactions using a strong one-electron oxidant which does not have coordinating properties, $(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$ ($E° = 1.06$ V vs SCE in DMF). Given that its redox potential is more positive than the second oxidation potential of $\mathbf{4}^{2+}$, this oxidant might, in principle, oxidize the dication $\mathbf{4}^{2+}$ up to the tetracation $\mathbf{4}^{4+}$.[56a,57] Although $\mathbf{4}^{2+}$ is insoluble in common polar solvents, the oxidation reactions were attempted using a suspension of $\mathbf{4}^{2+}$ in dichloromethane. Two reactions were performed, one using 1 equiv of oxidant to obtain a stoichiometric monoelectronic oxidation, the other using 2 equiv of oxidant to obtain a stoichiometric bielectronic oxidation. Each reaction was carried out for 12 h at 20 °C. The reaction mixtures were filtered, washed to remove the neutral triarylamine, and the insoluble residues, as well as the diamagnetic precursors, were submitted to Mössbauer spectroscopy. We also synthesized the complexes $[FeCp(PMe_3)_3]^{n+}$ ($n = 2, 3$)[56b] in order to use the 17e Fe^{III} complexes as references for Fe^{III} in the same geometrical environment. The mono- and dinuclear Fe^{II} complexes have rather similar parameters, and the QS values close to 2 mm s^{-1} are also similar to those of the $[FeCp(arene)]^+$ cations;[58−60] *i.e.*, the replacement of the arene by three phosphines has no influence on the QS value. Although the removal of one electron has no influence on the IS, it considerably influences the QS value, which decreases from 1.87 to 0.63 mm s^{-1}. Thus, the measurement of the QS is a powerful way to examine the electronic properties of this family of complexes. The QS values of the fulvalenyl precursors $\mathbf{4}^{2+}$ and $\mathbf{8}^{2+}$ are only slightly lower than that of $[Fe^{II}Cp(PMe_3)_3]^+PF_6^-$, so that this latter series $[FeCp(PMe_3)_3]^{n+}$ can be used for comparison. The Mössbauer spectra of the monoelectronic oxidation reaction products shows only one new quadrupole doublet together with the doublet, of some unreacted precursor. The value of QS for the new doublet is intermediate between those of Fe^{II} and Fe^{III} (see Table 1), indicating that the $Fe^{II}Fe^{III}$ species is an average-valence system (delocalized, class III) on the Mössbauer time scale (10^{-7} s)[61−65] (eq 12).

---

(56) (a) Steckhan, E. *Top. Curr. Chem.* **1987**, *142*, 1. (b) Treichel, P. M.; Komar, D. A. *J. Organomet. Chem.* **1981**, *206*, 77.

(57) This rule of thumb based on the redox potentials only neglected the electrostatic factor, which in the present case is not nil but is small, given the large size of ions involved in the redox reaction. For a precise discussion and counter examples, see ref. 4, Chapter 1.

(58) (a) Stukan, R. A.; Vol'kenau, N. A.; Nesmeyanov, A. N.; Gol'danskii, I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, *8*, 1473. (b) Fitzsimmons, B. W. *J. Phys. C* **1980**, *1*, 33.

(59) Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758.

(60) For Mössbauer data of organoiron complexes, see also: Greewood, N. N.; Gibb, T. C. *Mössbauer Spectroscopy*; Chapman and Hall: London, 1971; p 234.

(61) (a) For Mössbauer studies of average-valence diiron complexes, see refs 6, 31, and 61b,c. (b) Lacoste, M.; Rabaa, H.; Astruc, D.; Ardoin, N.; Varret, F.; Saillard, J.-Y.; Le Beuze, A. *J. Am. Chem. Soc.* **1990**, *112*, 9548. (c) Lacoste, M.; Varret, F.; Toupet, L.; Astruc, D. *J. Am. Chem. Soc.* **1987**, *109*, 6504.

(62) For the first mixed-valence bimetallic complex and its characterization, see: (a) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988. (b) Taube, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 329.

(63) (a) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247. (b) Allen, G. C.; Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 357, 391.

(64) For recent reviews, see ref 4, Chapter 1, and ref 65.

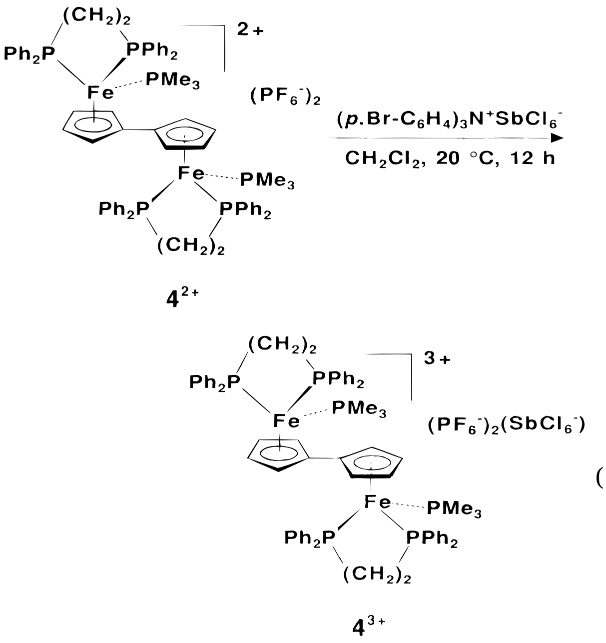
(65) *Mixed Valency Systems: Applications in Chemistry, Physics and Biology* Prassides, K., Ed.; NATO ASI Series C, No. 343; Kluwer: Dordrecht, The Netherlands, 1991.

(66) (a) Bütenschön has isolated $[Fe_2Fv(CO)_4]$, which has an Fe−Fe bond: Bister, H. J.; Bütenschön, H. *Synlett* **1992**, 22. (b) Recently, Vollhardt has reported $[Cr_2Fv(CO)_4]$, which has a weak Cr−Cr bond: McGovern, P. A.; Vollhardt, K. P. C. *J. Chem. Soc., Chem. Commun.* **1996**, 1593 and references cited therein.

Table 1. Cyclic Voltammetry Data for the Piano-Stool Diiron Fulvalenyl Dications[a]

	$E°$(ox)	i_c/i_a	$E°$(ox)	i_c/i_a	$E°$(red)	i_c/i_a	$E°$(red)	i_c/i_a
$[Fe_2Fv(dppe)_2(NCMe)_2]^{2+}(PF_6^-)_2$ (**2a**$^{2+}$)	+0.77	0.2	+1.12	0.1	(−1.46)	0		
$[Fe_2Fv(dppm)_2(NCMe)_2]^{2+}(PF_6^-)_2$ (**2b**$^{2+}$)	+0.70	0.2	(+1.05)	0	(−1.53)	0		
$[Fe_2Fv(dppe)_2(CO)_2]^{2+}(PF_6^-)_2$, (**3a**$^{2+}$)					−1.20	1	−1.32	1
$[Fe_2Fv(dppm)_2(CO)_2]^{2+}(PF_6^-)_2$ (**3b**$^{2+}$)					−1.35	1	−1.47	1
$[Fe_2Fv(dppe)_2(PMe_3)]^{2+}(PF_6^-)_2$ (**4**$^{2+}$)	+0.71	1	+0.95	0.9	−1.58	0.3	(−1.80)	0
$[Fe_2Fv(PMe_3)_6]^{2+}(PF_6^-)_2$ (**8**$^{2+}$)	+0.70	1	+1.08	0.9	(−1.65)	0	(−2.0; −2.2)	0

[a] $E°_{values}$ (V) are taken as the average value between E_{p_a} and E_{p_c} when the wave is at least partially reversible. For totally irreversible waves, E_p (V) is given in parentheses. The voltammograms were recorded for DMF solutions containing 0.1 M n-$Bu_4N^+BF_4^-$ at −30 °C with Pt as the working electrode, Ag as the reference electrode, $FeCp_2$ as an internal reference; scan rate 400 mV s^{-1}. For reversible or partially reversible waves, $E_{p_a} - E_{p_c}$ values were found between 50 and 70 mV. (The theoretical Nernstian value at −30 °C is $E_{p_a} - E_{p_c}$ = 48 mV for electrochemically reversible waves; since no shift of E_p was observed, all the partially reversible waves are also electrochemically reversible.[55])



4^{2+}

4^{3+}

(12)

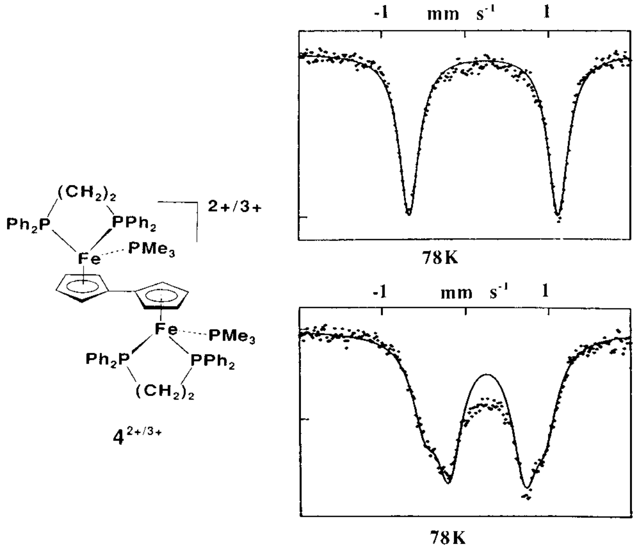
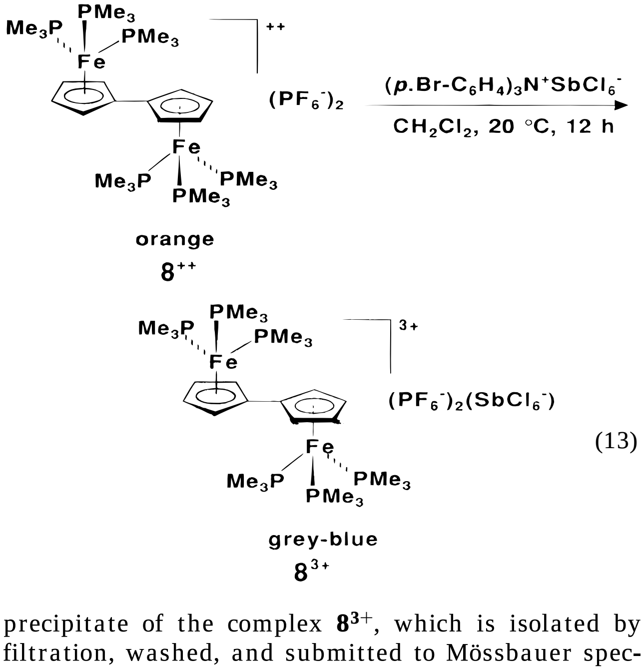


Figure 4. Mössbauer spectra of **4**$^{2+}$ (top) and of the average-valence complex **4**$^{3+}$ containing the starting Fe^{II}-Fe^{II} dicationic precursor (bottom, external doublet), in addition to the internal doublet corresponding to the major product **4**$^{3+}$.

The monoelectronic oxidation of the hexakis(trimethylphosphine) dicationic complex **8**$^{2+}$ is more facile, since both **8**$^{2+}$ and $(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$ are soluble in CH_2Cl_2 (eq 13). The reaction rapidly gives a gray-blue precipitate of the complex **8**$^{3+}$, which is isolated by filtration, washed, and submitted to Mössbauer spectroscopy. Again, only one doublet is found (besides another one due to **8**$^{2+}$), the parameters being close to those indicated above for **4**$^{3+}$ and consistent with a delocalized mixed-valence $Fe^{II}Fe^{III}$ complex[63,65] (at 77 K, IS = 0.33 vs Fe; QS = 1.03 mm s^{-1}) (eq 13).



orange
8^{++}

grey-blue
8^{3+}

(13)

Using 2 equiv of $(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$, the oxidation of **4**$^{2+}$ and **8**$^{2+}$ leads to decomposition, visually evident in the reaction medium and observed in the Mössbauer spectrum as some inorganic Fe^{III}. Under these conditions, it is difficult to establish the presence of the Fe^{III}-Fe^{III} complexes, which are at least somewhat unstable at 20 °C. In the case of the oxidation of **4**$^{2+}$, a Mössbauer doublet with parameters IS = 0.38 mm s^{-1} vs Fe and QS = 0.91 mm s^{-1} is observed, along with the doublet of the decomposition products (inorganic Fe^{III}). This doublet is possibly due to some $Fe^{III}Fe^{III}$ complex **4**$^{4+}$.

Discussion

1. Substitution Reactions in $[Fe_2Fv(C_6H_6)_2]^{0/2+}$. Both photolysis of the 36e precursor $[Fe_2Fv(C_6H_6)_2]^{2+}$ in acetonitrile and mild reactions of the 38e neutral diradicals $[Fe_2Fv(C_6H_6)_2]$ provide synthetically useful pathways to a variety of organoiron fulvalenyl compounds. Mono- and dimetallic fulvalenyl complexes with or without metal−metal bonds, and of various oxidation states (Fe^0, Fe^I, Fe^{II}), are accessible in this

Table 2. Comparison of Mössbauer Data (77 K) for Fe^{II}, $Fe^{II}Fe^{II}$, Fe^{III}, and Mixed-Valence $Fe^{II}Fe^{III}$ Complexes (PF_6 Salts)[a]

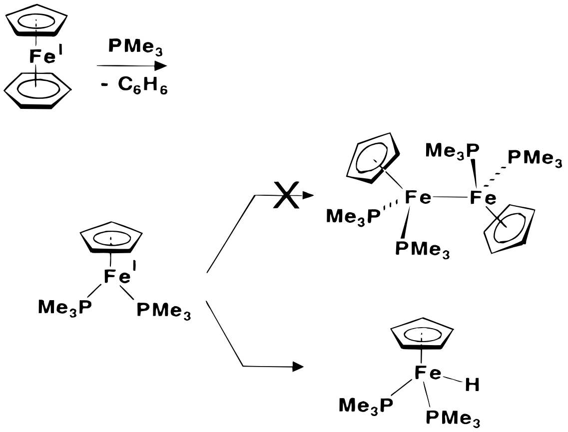
	IS (mm s^{-1})	QS (mm s^{-1})
$[Fe^{II}Cp(PMe_3)_3]^+$	0.31	1.87
$[Fe_2Fv(dppe)_2(PMe_3)_2]^{2+}$ (**4**$^{2+}$)	0.35	1.80
$[Fe^{II}{}_2Fv(PMe_3)_6]^{2+}$ (**8**$^{2+}$)	0.32	1.76
$[Fe^{III}Cp(PMe_3)_3]^{2+}$	0.31	0.63
$[Fe_2Fv(dppe)_2(PMe_3)_2]^{3+}$ (**4**$^{3+}$)	0.37	1.37
$[Fe_2Fv(PMe_3)_6]^{4+}$ (**8**$^{4+}$)	0.33	1.03

[a] All compounds give only one quadrupole doublet. IS values are given vs Fe metal, at room temperature.

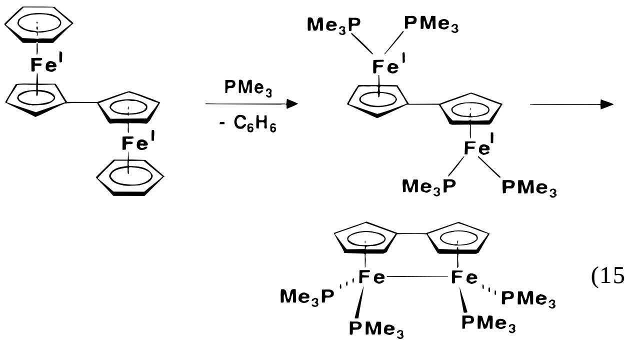
way. For instance, the neutral form of the fulvalenyl ligand is found in the hexacarbonyl Fe^0 complex **7**, whereas, with PMe_3, the metal−metal-bonded structure is preferred in **9**.[67]

The two routes are complementary for the synthesis of the piano-stool complexes $[Fe_2FvL_6]^{2+}$. The photolysis route brings in one acetonitrile ligand on each iron, which then can easily be displaced by another ligand. However, this photolytic reaction fails with PMe_3, whereas the route via the 36e complex directly gives the hexakis-PMe_3 complex. One possible reason for the failure of the photolytic reaction which works in mononuclear chemistry is that PMe_3, a good nucleophile, can add to the very electron poor benzene ligand of the dication, **1**$^{2+}$ to give a phosphonium cyclohexadienyl dication as phosphines do by adding to $[Fe(C_6H_6)_2]^{2+}$.[67]

The disproportionation reaction (eq 10) parallels that found in the mononuclear chemistry. Actually, both the photolytic reaction and the disproportionation reaction of Fe^I work in mononuclear chemistry to give $[FeCp(PMe_3)_3]^+$.[41] The best way to make this mononuclear compound is electron-transfer-chain catalysis using a catalytic amount of Fe^I under ambient conditions,[41] but again this reaction does not work in fulvalenyldiiron chemistry. Electron transfer to the 36e dication **1**$^{2+}$ gives the 37e average-valence complex in which delocalization provides sufficient stability to avoid arene displacement by a phosphine. Since neither the electrocatalytic nor the photolytic pathway is efficient in the diiron fulvalenyl compound, it is fortunate that the disproportionation of Fe^I still works and leads to **8**$^{2+}$. It is important to recall that this is only due to the presence of $Na^+PF_6^-$ in stoichiometric amounts since, in the absence of this salt, the two $[FeCp(PMe_3)_2]^{\bullet}$ radicals couple through the metal centers. This coupling is due to the entropy effect provided by the fulvalenyl ligand bridging the two iron centers in proximity, whereas the mononuclear compound undergoes another radical reaction, H atom abstraction, under the same conditions (compare eqs 14 and 15).



(14)



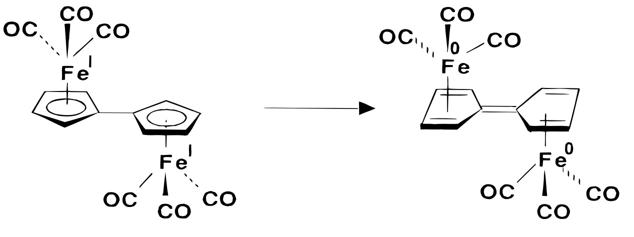
(15)

The disproportionation of Fe^I to Fe^{II} and Fe^0 is induced by $Na^+PF_6^-$ in both the reactions with CO and those with PMe_3. However, the electronic properties of this incoming ligand determine whether the disproportionation is intramolecular or intermolecular. Indeed, the extremely efficient electronic communication between the two metal centers via the fulvalenyl bridge makes intramolecular electron transfer highly favorable if the thermodynamic properties of the metal centers allow it. The CO ligand is electron-withdrawing, so that the replacement of one benzene ligand by CO's in **1** considerably unbalances the electronic properties of the two metal centers. The oxidation potential of a $[Fe^I$-Cp(arene)] unit is very negative, on the order of −1.5 V vs SCE, which is more negative than the reduction potential of the 17e $[FeCp(CO)_2]^{\bullet}$ radical to the 18e anion $[FeCp(CO)_2]^-$. The irreversible reduction of the dimer $[FeCp(CO)_2]_2$ occurs around −1.5 V vs SCE, but the reduction potential of the 17e radical is less negative because the above value takes into account the cleavage of the Fe−Fe bond. Thus, intramolecular electron transfer from the $[Fe^ICp(arene)]$ unit to the $[Fe^ICp(CO)_2]$ unit is at least isoergonic. The alternative is rapid exchange of benzene by CO's at the second iron center. In the absence of salt, full coordination of 6 CO's onto the two centers accompanied by intramolecular coupling within the fulvalenyl ligand saturates the coordination sphere of these iron centers to 18 electrons. It is interesting that intramolecular coupling within the fulvalenyl ligand occurs in the hexacarbonyl complex, not in the bis(benzene) complex; *i.e.*, the benzene ligands stabilize the diiron diradical whereas the CO's do not (compare eqs 16−18).[66]

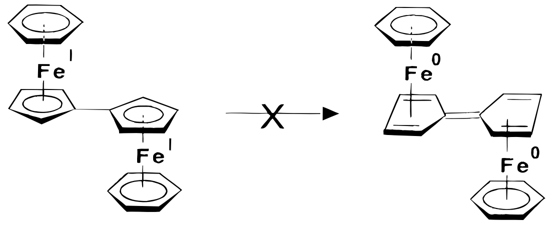
In the presence of $Na^+PF_6^-$, however, no hexacarbonyl complex is found, and intramolecular electron transfer to form the zwitterion is preferred. It is probable that $Na^+PF_6^-$ dislocates the intermediate intimate ion pair which is formed by intramolecular disproportionation. In this intramolecular ion pair, the two metals are in *cisoid* positions, whereas dislocation favors a *transoid* form which may subsequently irreversibly lose the $Fe(CO)_2$ fragment. The mononuclear fulvalenyl complex is a rare example of this class. It may be useful to synthesize heteronuclear fulvalenyl complexes by coordination of the Cp^- unit. The presence of $Na^+PF_6^-$ in

---

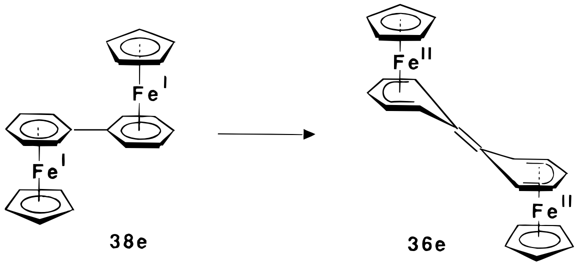
(67) (a) Davies, S. G.; Gelfand, L. S.; Sweigart, D. A. *J. Chem. Soc., Chem. Commun.* **1979**, 762. (b) Astruc, D. Tetrahedron Report No. 157. *Tetrahedron* **1983**, *39*, 4027.



38e **36e** (16)

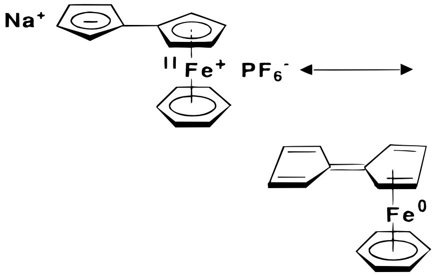


38e **36e** (17)



(18)

the complex confirms the crucial role of this salt in the formation of this complex and its zwitterionic structure (eq 19).

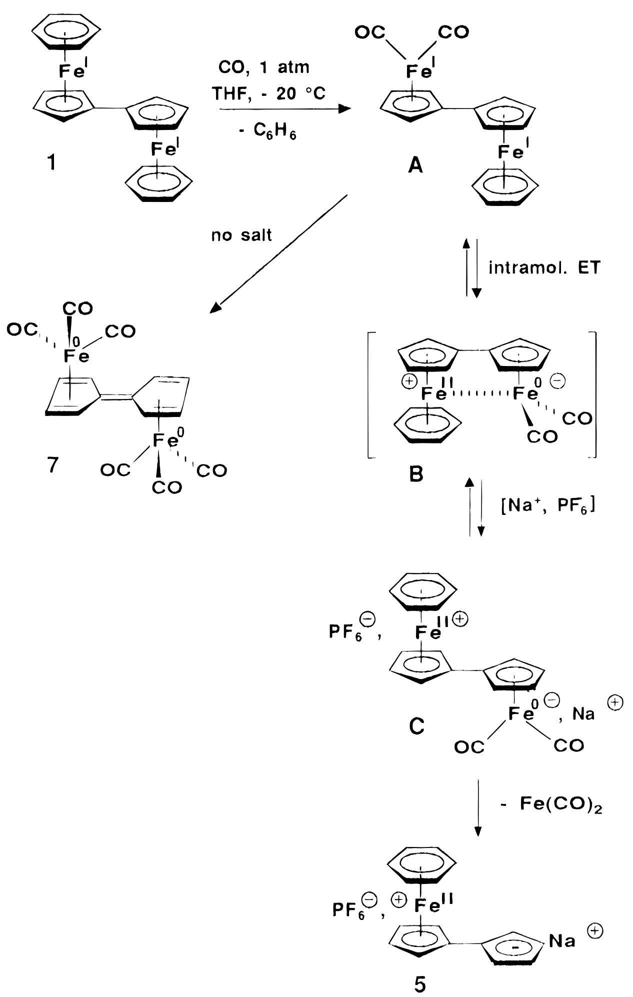


(19)

Again, the Fe^{II} state is preferred to an electron-rich Fe^0 form (compare with eqs 16–18, for instance). The only role of CO which is not retained in the product is to favor intramolecular electron transfer, since reduction of $[Fe^ICp(C_6H_6)]$ to $[Fe^0Cp(C_6H_6)]^-$, which requires a potential of −2.0 V vs SCE, would otherwise be highly endergonic.

This reduction of the mixed Fe^I sandwich unit to its 20e anionic form is indeed what happens in the disproportionation of Fe^I in the presence of PMe_3. At this time, PMe_3, in contrast to CO, is a more electron-releasing ligand than benzene (because it is not a good π acceptor). The 19e radical unit $[FeCp(PMe_3)_3]^\bullet$ has an oxidation potential of about −2.0 V vs SCE, which is sufficient to reduce $[Fe^ICp(C_6H_6)]$. This dismutation, known in mononuclear chemistry, is also efficient here and follows the same mechanism. It is driven in the presence of $Na^+PF_6^-$ because, once more, the organometallic ion pair $[Fe^{II}Cp(PMe_3)^+,Fe^0Cp(arene)^-]$ is dislocated by $Na^+PF_6^-$. This dislocation leads to two new ion pairs, one of which is destabilized: in the 20e anion $[Fe^0Cp(arene)]^-$, the large organometallic countercation slows down decomposition whereas the small ion Na^+ does not. Thus, in the reactions with both CO and PMe_3, the role of $Na^+PF_6^-$ is to dislocate a relatively stable ion pair to generate an unstable one whose rapid decomposition drives the overall electron-transfer reaction (disproportionation, Scheme 2).

Scheme 1



This type of salt effect was first disclosed by Winstein and called “special salt effect”,[68,69] but it was not applied to electron-transfer reactions at that time. Special salt effects are especially important in organometallic chemistry[69−71] because transition metals can undergo redox changes very easily and the special salt effect often completely changes the course of the reactions,[69−71] as, for instance, in the present case. We have found in several examples of such a special salt effect that $Na^+PF_6^-$ is the most efficient salt. The reason is that it combines a very small cation Na^+ , which considerably perturbs the energy of ion pairs that it forms by

---

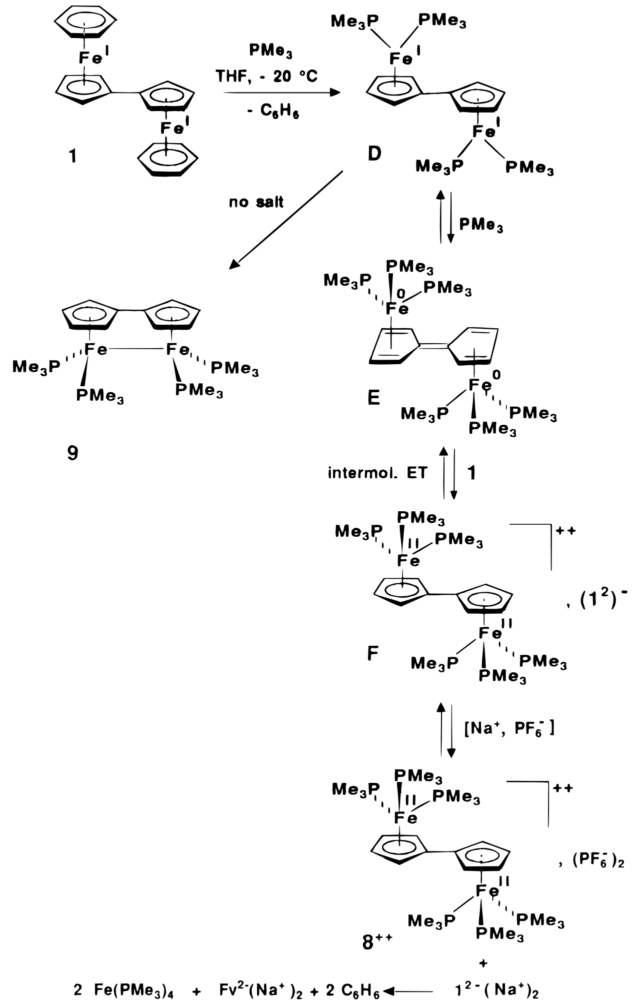
(68) Winstein, S.; Clippinger, E.; Fainberg, A. H.; Heck, R.; Robinson, G. C. *J. Am. Chem. Soc.* **1956**, *78*, 328.

(69) For a recent review of special salt effects, see: Loupy, A.; Tchoubar, B.; Astruc, D. *Chem. Rev.* **1992**, *92* , 1141.

(70) For an excellent book on salt effects see: Loupy, A.; Tchoubar, B. *Salt Effects in Organic and Organometallic Chemistry*; VCH: Weinheim, Germany, 1992.

(71) For reviews of salt-effect-induced electron-transfer reactions, see refs 43 and 69. For other examples, see also refs 41 and 43, and ref 4, Chapter 5, and: Astruc, D. *Acc. Chem. Res.* **1986**, *19*, 377.

Scheme 2



dislocation of other ion pairs, with the anion PF_6^-, which gives very stable organometallic salts.[43] The special salt effect of $Na^+PF_6^-$ can even sometimes be catalytic if all the substrates and products are soluble.[41,43]

2. Redox Properties of $[Fe_2FvL_6]^{2+}$ and Mixed Valency. The Fe_2Fv moiety provides a delocalized electron-sink system which is extremely versatile for redox changes, depending on the other ligands in the piano-stool structures. With acetonitrile ligands, the odd-electron states are not very stable even on the electrochemical time scale and these complexes are the least interesting from this point of view. Rather, they are useful precursors to other complexes. The dicarbonyl complexes are too electron-poor to give $Fe^{II}Fe^{III}$ within the current electrochemical window, as for the precursor $\mathbf{1}^{2+}$, but their reduction is noteworthy. The fact that there are two close, reversible waves indicates that the $Fe^{I}Fe^{II}$ and $Fe^{I}Fe^{I}$ series are stable on the time scale of cyclic voltammetry. Preliminary attempts to synthesize the reduced neutral complex **4** led to decomposition, but further low-temperature studies might be envisaged to examine the electronic structure of the Fe^{I}-Fe^{II} mixed valency and the direduced states.[72] The very small separation between the two waves ($\Delta E = 120$ mV) might indicate, however, that the mixed-valence species $Fe^{I}Fe^{II}$ is localized (class II). This is not necessarily so, since the gain of energy in the direduced state due to the intramolecular electronic rearrangement may shift the second reduction potential toward less negative values. Such an example is known (see eq 18) for which the mixed valence is delocalized, although the difference between the two reduction waves is only 120 mV.[61b,73,74] Note that $\mathbf{1}^{2+}$ and $\mathbf{3a}^{2+}$ have about the same reduction potential, signifying that the dppe + CO ligands have the same donicity as the benzene ligand in $\mathbf{1}^{2+}$. However, in the example of $\mathbf{1}^{2+}$, the two reduction waves are separated by almost $^1/_2$ V, and the mixed valency is delocalized (class III) in $\mathbf{1}^+$ on the Mössbauer and infrared time scales.[31]

Scheme 3 helps in explaining the observed reversibility. It appears that, given the electronic flexibility demonstrated for the fulvalenyl bridging ligand (compare eqs 16 and 17), the reduced states do not need to depart very much from the stable 36e state upon mono- and dielectronic reduction. The electronic rearrangement within the fulvalenyl ligand must be extremely fast, *i.e.* faster than all electrochemical time scales. The full reversibility in CV is observed only when CO is the coligand. Indeed, CO is an additional electron sink which can help accommodate the incoming electrons even in the Fe^0 direduced state. When only phosphine ligands are present as legs of the piano stool, the first reduction wave is either partially reversible ($\mathbf{4}^{2+}$) or totally irreversible ($\mathbf{8}^{2+}$). This partial or total chemical irreversibility must be due to the decoordination of a phosphine ligand, which is somewhat retarded by chelation and/or the better π-acceptor properties of the dppe ligand as compared to PMe_3. This irreversibility means that the hexaphosphine equivalent of the direduced species **3a** of Scheme 3 is not accessible, whereas the hexacarbonyl equivalent was synthesized by reaction of CO with **1**. The stable ternary $[FeFv(PMe_3)_x]$ complexes have an oxidation state of at least 1, as in **9**.

The triphosphine complexes $\mathbf{4}^{2+}$ and $\mathbf{8}^{2+}$ are more interesting for their oxidation which is accessible at potentials above +0.70 V vs SCE. They both show two reversible waves in their CVs, separated by 0.24 V for $\mathbf{4}^{2+}$ and 0.38 V for $\mathbf{8}^{2+}$. This situation resembles that found for biferrocene, which has two oxidation waves at +0.20 and +0.50 V vs SCE,[75] *i.e.* at less positive potentials. The biferrocenium monocation is thus easily accessible by mild oxidation and has been the subject of many studies (including many dialkyl derivatives), as the mixed valency oscillates between class II and class III on the Mössbauer time scale.[6,75-77] For $\mathbf{4}^{2+}$ and $\mathbf{8}^{2+}$, however, the oxidation compounds are much more difficult to synthesize than in the biferrocene series because (i) the oxidation potentials are more than $^1/_2$ V more positive than in biferrocenes, (ii) the starting

---

(72) Geiger has studied the mixed valency in fulvalenyldimetal carbonyl complexes in which the two metals are also bridged by a diphosphine: Geiger, W. E.; Atwood, C. G.; Chin, T. T. In *Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds*; Pombeiro, A. J. L., McCleverty, J. A., Eds.; NATO Series C, No. 385; Kluwer: Dordrecht, The Netherlands, 1993; p 549.

(73) Astruc, D.; Lacoste, M.; Toupet, L. *J. Chem. Soc., Chem. Commun.* **1990**, 558.

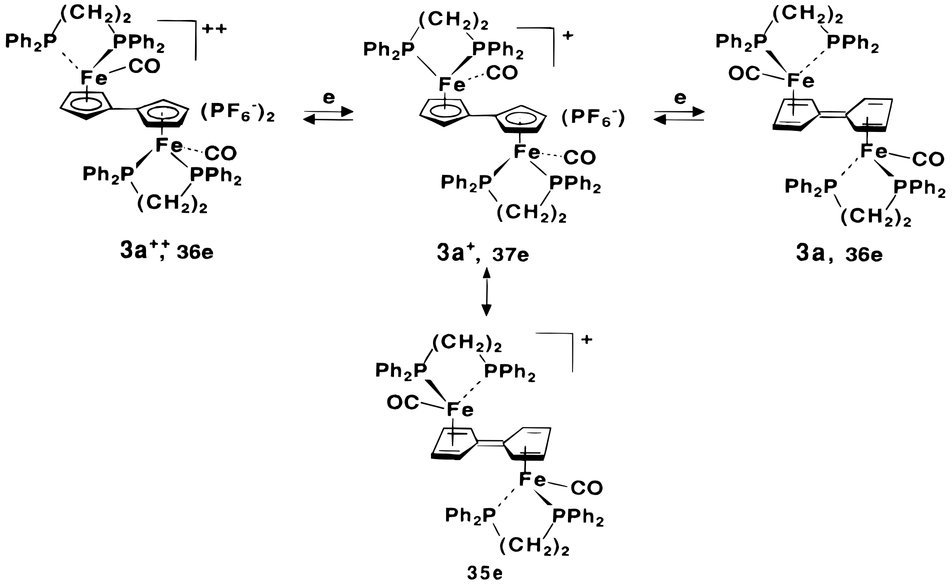
(74) Rittinger, S.; Buchholz, D.; Delville-Desbois, M.-H.; Linarès, J.; Varret, F.; Boese, R.; Zolnai, L.; Huttner, G.; Astruc, D. *Organometallics* **1992**, *11*, 1454.

(75) Matsumoto, T.; Sato, M.; Ichimura, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1720.

(76) Delville, M.-H.; Robert, F.; Gouzerh, P.; Linarès, J.; Boukheddaden, K.; Varret, F.; Astruc, D. *J. Organomet. Chem.* **1993**, *451*, C10.

(77) The nature of the alkyl group in dialkylbiferrocenium salts as well as that of the counteranion has a crucial role in the trapped or detrapped nature of the mixed valency. See ref 4, Chapters 1, 6, and 7.

Scheme 3



complexes are dicationic and the expected oxidation products are tri- or tetracationic, and (iii) the separation between the two oxidation potentials is smaller than for biferrocenes, rendering selective oxidation to the mixed-valence complexes more difficult. This last point is especially crucial if the dioxidized product is unstable, which is the case here, because it prevents synthesizing the mixed-valence complex by comproportionation, an efficient method when the two potentials are very close.[71] Ideally, one should use an excess of an oxidizing reagent which selectively oxidizes the dication to the trication, but not the tetracation, since at such a high potential, a stoichiometric amount of oxidant is apparently not sufficient. So far, we have only used (p-$BrC_6H_4)_3N^+SbCl_6^-$, which can oxidize the dication to either the tri- or tetracation. However, the use of 1 equiv of this oxidant leaves some starting material and the use of excess oxidant (3 equiv) to synthesize the tetracation leads to at least partial decomposition of the latter. Thus, under these conditions, we can generate the trications without any decomposition but the samples are always contaminated with starting materials which are observed in the Mössbauer spectra. However, only one Mössbauer doublet is observed beside that of the starting dication for both $\mathbf{4}^{3+}$ and $\mathbf{8}^{3+}$. Moreover, the QS values of the doublets are intermediate between those of Fe^{II} and Fe^{III} with the same geometrical environment, which is a clear indication of average valence $Fe^{II}Fe^{III}$ systems on the Mössbauer time scale for both $\mathbf{4}^{3+}$ and $\mathbf{8}^{3+}$. This result is in accord with the difference in potential between the two reversible oxidation waves observed in the CV's of $\mathbf{4}^{3+}$ and $\mathbf{8}^{3+}$.[78] It can tentatively be explained by the forced *transoid* geometry of the complexes $\mathbf{4}^{3+}$ and $\mathbf{8}^{3+}$. As can be seen from Figure 1, there is considerable bulk around each iron center due to the large phosphine cone angles and the fulvalenyl ligand is kept flat in this way, favoring good electronic communication in the trications. This situation is in contrast with that of biferrocene, in which rotation about the ferrocenyl−ferrocenyl C−C bond is free, possibly restricting electronic communication in the mixed-valence biferrocenium.

Conclusion

(1) The substitution of the benzene ligands by CO and phosphines using visible-light photolysis in $[Fe_2Fv(C_6H_6)_2]^{2+}$ ($\mathbf{1}^{2+}$) (easily available from biferrocene) or mild thermal reactions in the 38e direduced form **1** provides a variety of fulvalenyl complexes with one or two iron atoms, with several oxidation states (Fe^0, Fe^I, Fe^{II}, Fe^{III}), and with or without Fe−Fe bonds. The two methods are complementary. For instance, $[Fe_2Fv(PMe_3)_6]^{2+}$ ($\mathbf{8}^{2+}$), whose synthesis failed using photolysis of $\mathbf{1}^{2+}$, can be made from **1**.

(2) The photolytic method is efficient in synthesizing the dications $[Fe_2Fv(diphos)(NCMe)]^{2+}$ ($\mathbf{2}^{2+}$) in acetonitrile, and further thermal replacement of the acetonitrile ligands leads to $[Fe_2Fv(diphos)L_2]^{2+}$ (L = CO ($\mathbf{3}^{2+}$), PMe_3 ($\mathbf{4}^{2+}$)).

(3) The thermal reactions of **1** dramatically depend on the presence of $Na^+PF_6^-$ and on the donicity of the incoming ligand (CO or PMe_3). In the absence of $Na^+PF_6^-$, these ligand-substitution reactions give $[Fe^0_2Fv(CO)_6]$ (**7**) (no Fe−Fe bond) and $[Fe^I_2Fv(PMe_3)_4]$ (**9**) (with an Fe−Fe bond). On the other hand, in the presence of a stoichiometric amount of $Na^+PF_6^-$, electron transfer is induced by this salt due to dislocation of intermediate ion pairs to give unstable Na^+ salts, thereby driving the reactions. With CO, intramolecular electron transfer ultimately gives the rare monometallic zwitterionic fulvalenyl complex $[Fe^+Fv^-(C_6H_6),Na^+PF_6^-]$ (**5**), whereas with PMe_3, $\mathbf{8}^{2+}$ is obtained by intermolecular electron transfer.

(4) The diiron fulvalenyl piano-stool complexes have a rich redox chemistry. In cyclic voltammetry $[Fe_2Fv(diphos)(CO)_2]^{2+}$ ($\mathbf{3a}^{2+}$) gives two close reversible monoelectronic reductions ($\Delta E° = 120$ mV), whereas $[Fe_2Fv(dppe)(PMe_3)_2]^{2+}$ ($\mathbf{4}^{2+}$) and $[Fe_2Fv(PMe_3)_6]^{2+}$ ($\mathbf{8}^{2+}$) give two reversible monoelectronic oxidations ($\Delta E° = 0.24$ and 0.38 V, respectively). The bielectronic reduction $\mathbf{3a}^{2+} \rightarrow \mathbf{3a}$ and the bielectronic oxidations $\mathbf{4}^{2+} \rightarrow \mathbf{4}^{4+}$ and $\mathbf{8}^{2+} \rightarrow \mathbf{8}^{4+}$ leads to decomposition on the synthetic scale

---

(78) For the relationship between the difference of potential between the two waves and the mixed valency, see: Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017. See also ref 4, Chapter 1.

at 20 °C using redox reagents, but monoelectronic oxidations $\mathbf{4}^{2+} \rightarrow \mathbf{4}^{3+}$ and $\mathbf{8}^{2+} \rightarrow \mathbf{8}^{3+}$ using $(p\text{-BrC}_6H_4)_3N^+SbCl_6^-$ give stable average-valence complexes (class III) on the Mössbauer time scale (10^{-7} s).

Experimental Section

1. General Data. All manipulations of air-sensitive materials were conducted in a Vacuum Atmospheres Corp. argon Dri-Lab or under argon in a Schlenk apparatus connected to a double manifold. Reagent grade tetrahydrofuran, pentane, and toluene were predried over Na foil and distilled from sodium benzophenone ketyl under argon. All other chemicals were used as received. ^{1}H NMR spectra were obtained with Bruker AC 200 (200 MHz) or AC 250 (250 MHz) spectrometers, and ^{13}C NMR spectra were recorded with Bruker AC 200 (50.3 MHz) or Bruker AC 250 (67.9 MHz) spectrometers. NMR spectra were referenced to Me_4Si (^{1}H) or the appropriate deuterated solvent (^{13}C). Cyclic voltammetry studies were performed with a Princeton Applied Research 273 potentiostat. Mössbauer spectra were recorded with a 25 mCi ^{57}Co source on Rh. The Mössbauer spectrometer operated in the constant-acceleration mode; typically, the reliability of the velocity scale is 0.2%. The instrumental line width is 0.215 mm s^{-1}. For all the Mössbauer data, see Table 2. Elemental analyses were performed by the CNRS Center of Microanalyses at Lyon-Villeurbanne, France. Care was taken in the CV experiments to minimize the effects of solution resistance on the measurements of peak potentials (the use of positive-feedback *iR* compensation and dilute solutions ($\sim 10^{-3}$ mol L^{-1}) maintained currents between 1 and 10 μA). The additional redox couple ferrocene/ferrocenium was used when possible as a control for *iR* compensation. Thermodynamic potentials were recorded with reference to an aqueous SCE in DMF (0.1 M n-Bu_4NBF_4). When necessary, the reference electrode was an Ag quasi-reference electrode (QRE). The silver wire was pretreated by immersion in 10 M HNO_3 for 5 min before use. The counter electrode was platinum. The working electrode was a polished platinum disk embedded in glass (7.85×10^{-3} cm^2) treated first with 0.1 N HNO_3 solution and then with a saturated ammonium iron sulfate hexahydrate solution. The QRE potential was calibrated by adding the reference couple (FcH/FcH$^+$; FcH = ferrocene). The value of $E°$(FcH/FcH$^+$) in DMF was checked by verifying that $iv^{1/2}$ was constant (cyclic voltammetry), and chemical reversibility was checked using chronoamperometry by verifying that $i_r(2\tau/i_f(\tau)) = 0.293$ (i_r and i_f being the return and forward current intensities, respectively, and τ the time after which the current is switched; see p 102 in ref 4). The i_{p_a}/i_{p_c} ratio was determined graphically from the absolute anodic value $(i_{p_a})_0$ of the anodic peak and the cathodic intensity value $(i_{p_c})_0$ at the return point using the equation $i_{p_a}/i_{p_c} = (i_{p_a})_0/i_{p_c} + 0.485/i_{p_c} + 0.086$ (see p 98 in ref 4)

2. [Fe$_2$Fv(dppe)(NCMe)$_2$]$^{2+}$(PF$_6^-$)$_2$ (2a^{2+}). A 100 mL portion of a yellow MeCN solution of $\mathbf{1}^{2+}$ (1 g, 1.5 mmol), containing partially soluble dppe (1.16 g, 3 mmol), in a Schlenk flask was degassed and photolyzed for 12 h at −15 °C with a 150 W visible lamp located 1 cm from the Schlenk flask. The solution progressively turned red while the suspended solid disappeared. The solution was then concentrated to 20 mL, and addition of 100 mL of ether precipitated the complex $\mathbf{2a}^{2+}$. Recrystallization in acetone provided 1.82 g (88.7% yield) of air-stable red crystals of $\mathbf{2a}^{2+}$. Anal. Calcd for $C_{66}H_{62}N_2Fe_2P_6F_{12}$: C, 56.25; H, 4.40. Found: C, 55.98; H, 4.31. ^{1}H NMR (CD_3CN, TMS; δ, ppm): 7.56 (m, 40 H, C_6H_5), 5.06 and 3.70 (2t, 8 H, Fv), 2.60 (m, 8 H, CH_2), 2.04 (s, 6 H, CH_3). ^{31}P NMR (C_3D_6O, H_3PO_4; δ, ppm): +94.90 (s, dppe).

3. [Fe$_2$Fv(dppm)(NCMe)$_2$]$^{2+}$(PF$_6^-$)$_2$ (2b^{2+}). The above procedure applied to dppm yielded 86% of the air-stable complex $\mathbf{2b}^{2+}$. Anal. Calcd for $C_{64}H_{58}N_2Fe_2P_6F_{12}$: C, 55.65; H, 4.20. Found: C, 55.39; H, 4.25. ^{1}H NMR (CD_3CN, TMS; δ, ppm): 7.54 (m, 40 H, C_6H_5), 5.10 and 4.15 (2t, 8 H, Fv), 2.70 (m, 4 H, CH_2). ^{31}P NMR (C_3D_6O, H_3PO_4; δ, ppm): +34.24 (s, dppm).

4. [Fe$_2$Fv(dppe)(CO)$_2$]$^{2+}$(PF$_6^-$)$_2$ (3a^{2+}). A 1,2-dichloroethane solution (30 mL) of $\mathbf{2a}^{2+}$ (1 g, 0.7 mmol) was degassed and refluxed under 1 atm of CO for 16 h. The red solution progressively turned yellow. The solvent was then removed under vacuum, and the solid residue was chromatographed on an alumina column with acetonitrile as the eluent. Recrystallization from acetone/ether provided 0.84 g (86% yield) of yellow microcrystals of $\mathbf{3a}^{2+}$. Anal. Calcd for $C_{64}H_{56}O_2Fe_2P_6F_{12}$: C, 55.57; H, 4.05. Found: C, 55.57; H, 3.99. ^{1}H NMR (C_3D_6O, TMS; δ, ppm): 7.69 (m, 40 H, C_6H_5), 6.04 and 5.05 (2t, 8 H, Fv), 3.05 (m, 8 H, CH_2). ^{31}P NMR (C_6D_6O, H_3PO_4; δ, ppm): +91.04 (s, dppe). Infrared (1,2-$C_2H_4Cl_2$): ν_{CO} 1960 cm^{-1}.

5. [Fe$_2$Fv(dppm)(CO)$_2$]$^{2+}$(PF$_6^-$)$_2$ (3b^{2+}). A 250 mL autoclave was loaded with 50 mL of 1,2-$C_2H_4Cl_2$ and 0.85 g (0.6 mmol) of $\mathbf{2b}^{2+}$. The solution was degassed, and CO was introduced (180 atm). The autoclave was then heated for 15 h at 100 °C. The resulting yellow solution contained crystals. The mixture was chromatographed and the eluate recrystallized as above, which provided 0.72 g (86% yield) of yellow microcrystals of $\mathbf{3b}^{2+}$. Anal. Calcd for $C_{62}H_{52}O_2Fe_2P_6F_{12}$: C, 54.95; H, 3.98. Found: C, 54.84; H, 3.88. ^{1}H NMR (C_3D_6O, TMS; δ, ppm): 7.52 (m, 40 H, C_6H_5), 5.86 and 5.35 (2t, 8 H, Fv), 4.50 (m, 4 H, CH_2). ^{31}P NMR (C_3D_6O, H_3PO_4; δ, ppm): +25.56 (s, dppm). ^{13}C NMR (C_3D_6O; δ, ppm): 216.3 (CO), 134.4, 133.5, 131.5, and 129.5 (C_6H_5), 92.0 (C, Fv), 84.0 and 81.3 (CH, Fv), 43.2 (CH_2). Infrared (1,2-$C_2H_4Cl_2$): ν_{CO} 1970 cm^{-1}.

6. [Fe$_2$Fv(dppe)(PMe$_3$)$_2$]$^{2+}$(PF$_6^-$)$_2$ (4^{2+}). In 40 mL of 1,2-$C_2H_4Cl_2$, 0.6 g of $\mathbf{2a}^{2+}$ was dissolved, and 2 equiv of PMe_3 was added under argon. The reaction mixture was allowed to react at 20 °C for 2 days, and the color progressively turned from dark red to pink. The solvent was removed under vacuum, and these operations were repeated twice to displace MeCN completely. The resulting complex $\mathbf{4}^{2+}$ (40% yield) was washed with ether. Anal. Calcd for $C_{68}H_{74}Fe_2P_8F_{12}$: C, 55.20; H, 5.00. Found: C, 54.95; H, 5.11. ^{1}H NMR (CD_3CN, TMS; δ, ppm): 7.50 (m, 40 H, C_6H_5), 4.70 and 4.00 (2m, 8 H, Fv), 2.10 (m, 8 H, CH_2), 0.65 (d, 18 H, PMe_3). ^{13}C NMR (DMSO; δ, ppm): 137.6 (C_q, C_6H_5), 131.7, 130.1, and 125.9 (C_6H_5), 89.2 (C_q, Fv), 78.3 and 78.0 (Fv), 27.8 (CH_2), 18.6 (PMe_3).

7. Reaction of 1 with CO in the Absence of Na$^+$PF$_6^-$: [Fe$_2$Fv(CO)$_6$] (7). A 0.3 g (0.44 mmol) sample of [Fe$_2$Fv(C_6H_6)$_2$]$^{2+}$(PF$_6^-$)$_2$ ($\mathbf{1}^{2+}$) in 20 mL of THF was reduced with 10 g of Na/Hg amalgam (1%, 8.8 mmol) for 8 h at −20 °C under argon. THF was removed under vacuum, and the crude product was extracted twice with 10 mL of cold freshly distilled oxygen-free toluene in order to eliminate both Na/Hg and Na$^+$PF$_6^-$ salt. The Schlenk tube was then put under 1 atm of CO by alternating a vacuum and a CO atmosphere at least six times. The solution was left 3 h at −20 °C and then warmed slowly (5 °C/h) until 0 °C. The solution progressively turned from green to purple-red. The toluene solution was completely red in 4 h at 0 °C. It slowly reacted further at room temperature to give a product insoluble in all common solvents and presenting bridging and terminal CO's. The red complex was also thermodynamically unstable in the solid state but could be identified as **7**. ^{1}H NMR ($CDCl_3$; δ, ppm): 5.34 (t, 4 H, $-C_5H_4$), 5.05 (t, 4 H, $-C_5H_4$). ^{13}C NMR ($CDCl_3$, δ, ppm): 218.6 (CO), 88.6 ($-C_5H_4$; C_q), 86.5 and 76.0 ($-C_5H_4$). Infrared (CH_2Cl_2 or toluene): ν_{CO} 2000, 1940 cm^{-1}.

8. Reaction of 1 with PMe$_3$ in the Absence of Na$^+$PF$_6^-$: [Fe$_2$Fv(PMe$_3$)$_4$] (9). The Na/Hg reduction of $\mathbf{1}^{2+}$ (0.250 g, 0.364 mmol) was carried out at −20 °C for 8 h in 10 mL of THF under argon. THF was removed *in vacuo*, and the crude green product was extracted twice with 10 mL of cold, freshly distilled oxygen-free toluene in order to eliminate the amalgam and the Na$^+$PF$_6^-$ salt; 12 equiv of PMe_3 (4.46 mmol) was added at −20 °C and allowed to react at this temperature for 4 h.

After reaction and evaporation of the solvent, the green solution gave an orange-red complex; 75 mg (38% yield) of **9** was obtained and revealed to be slightly unstable at room temperature. ^{1}H NMR ($C_6D_5CD_3$; δ, ppm): 365 (t, 4 H, $-C_5H_4$), 334 (t, $-C_5H_4$, 4 H), 146−99 (2m, 36 H, CH_3). ^{31}P NMR (C_6D_5-CD_3, H_3PO_4; δ, ppm): 26.70.

9. Reaction of 1 with CO in the Presence of $Na^+PF_6^-$: $[Fe^+Fv^-(C_6H_6),Na^+PF_6^-]$ (5). The Na/Hg reduction of **1**$^{2+}$ (0.50 g, 0.728 mmol) was carried out at −20 °C for 8 h in 10 mL of THF under argon. After the system was cooled to −50 °C to freeze the Na/Hg amalgam, the THF mixture was filtered into another Schlenk tube and put under a CO atmosphere at −40 °C, as in procedure 7. The solution was warmed to room temperature and turned progressively orange-red between −5 and 20 °C. THF was removed *in vacuo*, and the crude product was extracted with 20 mL of dry acetone and then purified by alumina chromatography. Rapid recrystallization gave 0.132 g (42% yield) of red microcrystals of **5**; **5** left in solution decomposed over 2 days upon standing even at −20 °C. ^{1}H NMR (CD_3COCD_3; δ, ppm): 6.10 (s, 6 H, C_6H_6), 5.24 (t, $-C_5H_4$, 2H), 5.08 (t, 2 H, $-C_5H_4$), 4.70 (t, $-C_5H_4$, 2H), 4.47 (t, $-C_5H_4$, 2H). ^{13}C NMR (CD_3COCD_3; δ, ppm): 89.6 (C_6H_6), 96.3 (C_q), 78.2 (C_q), 76.8, 73.6, 72.4, and 69.3 ($C_5H_4-C_5H_4$). Mössbauer parameters (mm s^{-1} vs Fe, 293 K): IS 0.52; QS 1.61. Electrochemical data (DMF, 0.1 M *n*-Bu_4NBF_4, Pt, 20 °C, sweep rate 0.4 V s^{-1}): $E°$ (V vs SCE) = −1.32 ($i_c/v^{1/2}$ constant; $i_a/i_c = 0.8$; $E_{p_a} - E_{p_c} = 90$ mV); $E_{p_c} = -2.23$ V ($i_c/v^{1/2}$ constant; $i_a/i_c = 0$); $E_{p_a} = +0.81$ V ($i_c/i_a = 0$). Electrochemical data (−50 °C): $E°$ (V vs SCE): −1.35 ($i_a/i_c = 1$); 2.19 ($i_a/i_c = 0.2$; $E_{p_a} - E_{p_c} = 170$ mV); +0.84 ($i_c/i_a = 0$). Anal. Calcd for $C_{16}H_{14}FeNaPF_6$: C, 44.68; H, 3.28. Found: C, 44.87; H, 3.30.

10. Reaction of 1 with PMe_3 in the Presence of $Na^+PF_6^-$: $[Fe_2Fv(PMe_3)_6]^{2+}(PF_6^-)_2$ (8^{2+}). A Schlenk tube under argon was charged with $[Fe_2Fv(C_6H_6)_2]^{2+}(PF_6^-)_2$ (**1**$^{2+}$; 0.5 g, 0.73 mmol), 1% Na/Hg (8 g, 3.6 mmol), and THF (50 mL) at −20 °C and stirred at −20 °C for 8 h. The mother liquor was filtered, PMe_3 (0.8 mL, 7 mmol) was added to it at −20 °C, and the mixture was stirred at −20 °C for 3 h, then warmed to 20 °C, and concentrated to 20% of its initial volume; 50 mL of toluene was added, and the remaining THF was evaporated, which precipitated **8**$^{2+}$ as a pink solid. Chromatographic purification (alumina, acetonitrile) followed by recrystallization from acetonitrile/ethanol gave **8**$^{2+}$ as pink microcrystals (0.316 g, 44% yield, maximum theoretical yield 50%). Anal. Calcd for $C_{28}H_{62}Fe_2P_8F_{12}$: C, 34.07; H, 6.28. Found: C, 34.50; H, 5.74. ^{1}H NMR (CD_3CN; δ, ppm): 5.04 and 4.63 (2m, 8 H, $C_5H_4-C_5H_4$), 1.55 (m, 54 H, Me). ^{31}P NMR (CD_3COCD_3; δ, ppm): 22.4. ^{13}C NMR (CD_3COCD_3; δ, ppm): 88.2 (C_q), 82.9 and 78.3 ($C_5H_4-C_5H_4$), 22.2 (m, $P(CH_3)_3$).

The filtrate was evaporated to dryness, and extraction using pentane gave the air-sensitive red complex $[Fe(PMe_3)_4]$ (**10**; 30% yield, maximum theoretical yield 50%), identified by comparison with the ^{1}H NMR data from the literature.[54]

11. Generation of $[Fe_2Fv(dppe)_2(PMe_3)_2]^{3+}(PF_6^-)_2$-$(SbCl_6^-)$ (4^{3+}). A Schlenk tube under argon was charged with $[Fe_2Fv(dppe)_2(PMe_3)_2]^{2+(PF}{}_6{}^-)_2$ (**4**$^{2+}$; 70 mg, 0.05 mmol), (*p*-$BrC_6H_4)_3N^+SbCl_6^-$ (39 mg, 0.05 mmol), and CH_2Cl_2 (10 mL). When the mixture was stirred, the color changed from pink to brown and, after 1 h, the color change was over. The brown precipitate was washed with CH_2Cl_2 several times, dried under vacuum, and submitted to Mössbauer spectroscopy.

12. Generation of $[Fe_2Fv(PMe_3)_6]^{3+}(PF_6^-)_2(SbCl_6^-)$ (8^{3+}). The same procedure as in paragraph **11** was applied to $[Fe_2Fv(PMe_3)_6]^{2+}(PF_6^-)_2$ (**8**$^{2+}$). The blue-gray precipitate was also submitted to elemental analysis. Anal. Calcd for $C_{28}H_{62}Fe_2P_8F_{12}SbCl_6$: C, 25.44; H, 4.69. Found: C, 26.70; H, 4.61. The higher percentage of C found is consistent with the finding of a minor amount of starting material **8**$^{2+}$ in the Mössbauer spectrum.

13. Generation of $[Fe_2Fv(dppe)_2(PMe_3)_2]^{4+}(PF_6^-)_2$-$(SbCl_6^-)_2$ and $[Fe_2Fv(PMe_3)_6]^{4+}(PF_6^-)_2(SbCl_6^-)_2$. The same procedure as in paragraphs **11** and **12** was used, with 3 equiv of (*p*-$BrC_6H_4)_3N^+SbCl_6^-$. Insoluble dark brown solids were obtained, washed with CH_2Cl_2, dried *in vacuo*, and submitted to Mössbauer analysis. The Mössbauer spectra all indicated the formation of inorganic Fe^{III} (Fe_2O_3), besides minor amounts of organometallic $Fe^{III}Fe^{III}$ compounds.

Acknowledgment. We are grateful to the Institut Universitaire de France, the Université Bordeaux I, the Centre National de la Recherche Scientifique (CNRS), and the Région Aquitaine for financial support. We thank Professor F. Varret (Université de Versailles) for recording and discussing the Mössbauer spectra. NMR assistance by Drs. M. Pétreau and B. Barbe (CESAMO, Université Bordeaux I) is also gratefully acknowledged.

OM961060+