idealized trigonal-bipyramidal geometry.

The energy values obtained for both electronic states at different levels of calculation are presented in Table IV. It must be remarked that all these energy values have been obtained by keeping the geometrical parameters optimized at the HF level unchanged by using the minimal basis set (see Figures 3 and 4). In the case of the triplet, although the optimization has been carried out at the ROHF level of calculation, electron correlation has been introduced over one UHF determinant, this procedure being the one implemented in the GAUSSIAN 86 system of programs. In these UHF calculations the spin contamination is very small, since the values of $S^2$ are 2.06 or 2.07 depending on the basis set which is used.

Let us first examine the results obtained with the minimal basis set. As was to be expected, the introduction of electron correlation stabilizes the singlet $^1A_1$ state more than the $^3B_2$ state. As a consequence the singlet state is the most stable at the MP2 level although the situation is again reversed when third-order corrections are taken into account. This difference in the relative stability of both states at the MP2 and MP3 levels is probably due to the fact that MP2 calculations overestimate the energy lowering. Given that the energy gap is only of about 3 kcal/mol at the MP3 level, these calculations permit only the conclusion that both states lie very close in energy.

The results obtained with the double-$\zeta$ quality basis set are qualitatively very similar. In this case, calculations at the MP3 level have not been carried out since they are not feasible with the facilities available in our laboratory. However, given that the singlet state is only 2 kcal/mol lower at the MP2 level, the triplet state is again expected to be more stable if third-order corrections are introduced. Calculations at a much higher level would be necessary to obtain a definitive answer about which is the ground state of this molecule.

## Conclusion

In this work we have carried out a quantitative conformational study of the $Cl_4W{=}CH_2$ complex in its $^1A_1$ electronic state. We have found that in a trigonal-bipyramidal structure the equatorial parallel ($eq_{\parallel}$) conformation is the most stable one. A preliminary study of different triplet states has also shown that there is a low-lying $^3B_2$ state very close in energy to the singlet $^1A_1$ state. So, calculations at a much higher level of calculation would be necessary to obtain a definitive answer about which is the ground state of this molecule.

**Acknowledgment.** Financial support from CICYT through project PB86-0529 is gratefully acknowledged.

**Registry No.** $Cl_4WCH_2$, 85236-42-6.

---

# Binuclear Organometallic Electron Reservoirs: Syntheses and Electrochemistry of the Fulvalene Complexes $[Fe_2(\mu_2,\eta^{10}\text{-}C_{10}H_8)(arene)_2]^{n+}$[1]

Marie-Hélène Desbois and Didier Astruc*

*Laboratoire de Chimie Organique et Organométallique, U.A. CNRS No. 35, Université de Bordeaux I, 351 Cours de la Libération, 33405 Talence Cêdex, France*

*Received July 27, 1988*

Ligand exchange reaction between biferrocene (1) and $C_6Me_6$ in the presence of $AlCl_3$ and Al powder in decahydronaphthalene (140 °C) provides $[Fe_2(Fv)(HMB)_2]^{2+}$ (2, (Fv = $\mu_2,\eta^{10}$-$C_{10}H_8$, HMB = $\eta^6$-$C_6(CH_3)_6$) isolated as a $PF_6^-$ crystalline salt, as well as analogues containing other arenes ($C_6H_6$ (bz), 3; $C_6H_5CH_3$ (tol), 4; $C_6H_5CH_2CH_3$ (Etbz), 5; $C_6H_3(CH_3)_3$ (mes), 6). The dissymmetric dicationic complex $[Fe_2(Fv)(bz)(HMB)]^{2+}(PF_6^-)_2$ (7) is made from $[Fe_2(Fv)(Cp)(bz)]^+PF_6^-$ (8) and HMB (Cp = $\eta^5$-$C_5H_5$). Permethylation of 2 using potassium *tert*-butoxide and methyl iodide in THF gives the perethylated complex $[Fe_2(Fv)(HEB)_2]^{2+}(PF_6^-)_2$ (HEB = $\eta^6$-$C_6(CH_2CH_3)_6$) (9) (one-pot formation of 12 C–C bonds). The cyclic voltammograms (CV) of 2 in DMF at −35 °C at Hg cathode show three reversible waves and a fourth, quasi-reversible one ($i_a/i_c$ close to unity, charge-transfer coefficient $\alpha = 0.5$; heterogeneous rate constant $k_s \simeq 10^{-3}$ cm s$^{-1}$). The other dicationic complexes $[Fe_2(Fv)(arene)_2]^{2+}$ (arene = bz, tol, Etbz, mes) including the dissymmetric complex $[Fe_2(Fv)(C_6H_6)(HMB)]^{2+}$ (7) show an analogous electrochemical behavior. The chemical reversibility of the waves increases with the number of methyl groups on the arene ligands (20 °C). The comproportionation constants for the formation of the mixed-valence $Fe^IFe^{II}$ complexes (arene = HMB (10), benzene (11), toluene (12), ethylbenzene (13), and mesitylene (14) and complex 15) and $Fe^0Fe^I$ species were estimated from $\Delta E$ values.

## Introduction

Sandwich compounds have recently received considerable attention in material science for the design of molecular ferromagnets,[2] for energy conversion,[3] and in stoichiometric[4a] and catalytic electron transfer processes.[4b] Many studies have already been performed.[5,6] The bi-

---

[1] (a) *Organometallic Electron Reservoirs*. 34. For part 33, see: Morrow, J.; Catheline, D.; Desbois, M.-H.; Manriquez, J.-M.; Ruiz, J.; Astruc, D. *Organometallics* **1987**, *6*, 2605. (b) This paper overlaps with parts of the third cycle thesis of M.-H.D..

[2] (a) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. (b) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Acc. Chem. Res.* **1988**, *21*, 114.

[3] Mueller-Westerhoff, U. T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 702.

[4] (a) Astruc, D. *Chem. Rev.* **1988**, *27*, 643. (b) Astruc, D. *Angew. Chem.* **1988**, *100*, 602; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 643.

0276-7333/89/2308-1841$01.50/0

ferrocene sandwich and its derivatives have been extensively studied and include recent works on the problems of mixed-valence delocalization.[7-9] The present dicationic complexes offer five redox states discernible by cyclic voltammetry, three of them being isolable. However, their stabilization requires the arene ligands to be alkylated. In this paper, we describe the syntheses of the title complexes with peralkylated arenes and their electrochemistry. We give detailed information on the 37e and 38e reduced states in a separate paper.[7l,m]

## Experimental Section

**General Data.** Reagent grade tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), diethyl ether, and pentane were predried on Na foil and distilled from sodium benzophenone ketyl under argon just before use. Benzene, toluene, heptane, and decahydronaphthalene were treated identically and stored under argon. Acetonitrile was stirred under argon overnight over phosphorus pentoxide, distilled from sodium carbonate, and stored under argon. Methylene chloride was distilled from calcium hydride just before use. All other chemicals were used as received. All manipulations were done by Schlenk techniques or in a nitrogen filled Vacuum Atmosphere drylab. Infrared spectra were recorded with Pye-Unicam SP 1100 and Perkin Elmer 1420 ratio recording infrared spectrophotometers which were calibrated with polystyrene. Samples were examined in solution (0.1-mm cells with NaCl windows) or between NaCl disks in Nujol. $^1$H NMR spectra were recorded with continuous Hitachi R24B (60 MHz) and Brücker AC 200 (200 MHz) spectrometers. $^{13}$C NMR were obtained in the pulsed Fourier transform mode at 20.115 MHz with a Brücker WP 90 spectrometer and at 50.327 MHz with a Brücker AC 200 spectrometer. All chemical shifts are reported in parts per million ($\delta$, ppm) with reference to tetramethylsilane ($Me_4Si$) and were measured relative to the solvent or $Me_4Si$. Electronic spectra (visible and near-infrared) were recorded between −50 °C and +25 °C with Cary 14 and Cary 219 spectrophotometers with 10-mm quartz cells. Cyclic voltammetry data were recorded with a PAR 273 potentiostatic galvanostat. Care was taken in cyclic voltammetry experiments to minimize the effects of solution resistance on the measurements of peak potentials (the use of positive feedback $iR$ compensation and dilute solutions ($\simeq 10^{-4}$ mol L$^{-1}$) kept currents around 1–2 $\mu$A). Thermodynamic potentials were recorded with reference to an aqueous SCE segregated from the test solution by a fine frit containing a DMF solution ($[nBu_4N][BF_4]$, 0.1 M). The diffusion coefficients were obtained from analysis of the chronoamperometric $i$–$t$ transient. The area of the electrode was calibrated by using external references as indicated in the text. Elemental analyses were performed by the Centre of Microanalyses of the CNRS (Lyon-Villeurbanne, France).

**Preparations.** The following abbreviations will be used for the ligand formula: $\eta^5$-$C_5H_5$, Cp; $\mu_2,\eta^{10}$-$C_{10}H_8$, Fv; $\eta^6$-$C_6Me_6$, HMB; $\eta^6$-$C_6H_6$, bz; $\eta^6$-1,3,5-$C_6H_3Me_3$, mes; $\eta^6$-$C_6H_5CH_3$, tol; $\eta^6$-$C_6H_5CH_2CH_3$, Etbz.

1. **Bifferocene (1).** Biferrocene was prepared in 50–70% yield from the reaction of iodoferrocene with copper bronze as described by Rausch[21] except that the product was purified by column chromatography instead of using fractional crystallizations. The crude product, as a concentrated solution in toluene, was placed on an alumina column. After elution with ether to remove impurities such as ferrocene and iodoferrocene, biferrocene was obtained by elution with toluene.

2. **$[Fe_2(Fv)(HMB)_2]^{2+}(PF_6^-)_2$ (2).** Biferrocene (2 g, 5.4 mmol), HMB (8.75 g, 54 mmol), aluminum trichloride (7.2 g, 54 mmol), Al powder (0.146 g, 5.4 mmol), and water (0.097 mg, 5.4 mmol) were mixed under argon and stirred for 16 h in 50 mL of decahydronaphthalene at 140 °C. After hydrolysis at 0 °C, aqueous ammonia was added to the aqueous layer in order to precipitate aluminum hydroxide; aqueous $HPF_6$ (6 mmol) was then added to the filtrate which precipitated the desired bication and $[Fe(Cp)(HMB)]^+PF_6^-$ (**24**) also formed. After precipitation, the crude product was washed three times with 50 mL of acetone in order to eliminate $[Fe(Cp)(HMB)]^+PF_6^-$. The residue was then extracted with acetonitrile and chromatographed on an activated acidic alumina column. The solution was then concentrated, and recrystallization from an acetonitrile/ethanol mixture gave 0.646 g (14%) of orange microcrystals: $^1$H NMR ($CD_3CN$, 20 °C) $\delta$ 4.86 (t, Fv, 4 H), 4.84 (t, Fv, 4 H), 2.20 (s, $CH_3$, 36 H); $^{13}$C NMR ($CD_3CN$, 20 °C) $\delta$ 100.5 ($C_6$ ring), 86.5, 80.9, 75.4 (Fv), 17.3 ($CH_3$). Anal. Calcd for $C_{34}H_{44}Fe_2P_2F_{12}$: C, 47.77; H, 5.20. Found: C, 47.74; H, 5.50.

3. **$[Fe_2(Fv)(Ar)_2]^{2+}(PF_6^-)_2$ (Ar = bz, tol, Etbz, mes).** All these cations were prepared according to the literature[12] (bz (**3**), mes (**6**)) except for the following modifications: (i) 1 equiv of distilled water added, (ii) reaction time was 16 h, (iii) $[Fe(Cp)(Ar)]^+PF_6^-$ was separated from $[Fe_2(Fv)(Ar)_2]^{2+}(PF_6^-)_2$ by washing the crude product with acetone (Ar = HMB) or dichloromethane (Ar = bz, mes, tol, Etbz). A second purification was operated by the passage through an alumina column as in preparation 2. Recrystallization from an acetonitrile/ethanol mixture gave the desired cations in improved yields (Ar = bz, 45% yield; Ar = mes, 25% yield). The cations were identified by comparison with the literature data[12] for Ar = bz and mes.

**(a) $[Fe_2(Fv)(tol)_2]^{2+}(PF_6^-)_2$ (4):** $^1$H NMR ($CD_3CN$, 20 °C) $\delta$ 6.00 (s, $C_6H_5$, 5 H), 5.43 (t, Fv, 4 H), 5.26 (t, Fv, 4 H), 2.16 (s, $CH_3$, 3 H); $^{13}$C NMR ($CD_3CN$, 20 °C) $\delta$ 105.80 ($C_q$), 90.48 ($C_o$ (Ar)), 89.84 ($C_m$ (Ar)), 89.41 ($C_p$ (Ar)), 87.79, 78.94, 75.38 (Fv), 20.36 ($CH_3$). Anal. Calcd for $C_{24}H_{24}Fe_2F_{12}P_2$: C, 40.36; H, 3.38. Found: C, 39.99; H, 3.47.

**(b) $[Fe_2(Fv)(Etbz)_2]^{2+}(PF_6^-)_2$ (5):** $^1$H NMR ($CD_3CN$, 20 °C) $\delta$ 5.88 (s, $C_6H_5$, 10 H), 5.28 (t, Fv, 4 H), 5.13 (t, 4 Fv, 4 H), 2.63, 2.50, 2.36, 2.25 (q, $CH_2$, 4 H), 1.25, 1.13, 1.00 (t, $CH_3$, 6 H); $^{13}$C NMR ($CD_3CN$, 20 °C) $\delta$ 110.77 ($C_q$ (Ar)), 89.73 ($C_o$ (Ar)), 89.25 ($C_m$ (Ar)), 88.65 ($C_p$ (Ar)), 87.63, 78.62, 75.11 (Fv), 28.13 ($CH_2$), 15.02 ($CH_3$). Anal. Calcd for $C_{26}H_{28}Fe_2P_2F_{12}$: C, 42.08; H, 3.80. Found: C, 42.39; H, 3.81.

4. **$[Fe_2(Fv)(bz)(HMB)]^{2+}(PF_6^-)_2$ (7).** $[Fe_2(Fv)(Cp)(bz)]^+PF_6^-$ (0.2 g, 0.379 mmol), HMB (0.613 g, 3.79 mmol), aluminum chloride (0.505 g, 3.79 mmol), Al powder (0.010 g, 0.379 mmol) and water (0.007 g, 0.379 mmol) were mixed and stirred for 16 h in 10 mL

---

(5) (a) Buet, A.; Darchen, A.; Moinet, C. *J. Chem. Soc., Chem. Commun.* **1979**, 447. (b) Román, E.; Dabard, D.; Moinet, C.; Astruc, D. *Tetrahedron Lett.* **1979**, *16*, 1433. (c) Connelly, N. G.; Geiger, W. E., Jr. *Adv. Organomet. Chem.* **1984**, *23*, 1. (d) Geiger, W. E., Jr.; Connelly, N. G. *Ibid.* **1985**, *24*, 87. (e) Dessy, R. E.; Bares, L. A. *Acc. Chem. Res.* **1972**, *5*, 415. (f) de Montauzon, D.; Poilblanc, R.; Lemoine, P.; Gross, M. *Electrochim. Acta* **1978**, *23*, 1247. (g) Denisovitch, L. I.; Gubin, S. P. *Russ. Chem. Rev.* (*Engl. Transl.*) **1977**, *46*, 27. (h) Chu, C. T.-W.; Lo, F. Y.-K.; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 3409. (i) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978. (j) Darchen, A. *J. Chem. Soc., Chem. Commun.* **1983**, 768.

(6) (a) Astruc, D.; Dabard, R.; Laviron, E. *C.R. Acad. Sci., Ser. C* **1969**, *88*, 471. (b) Nesmeyanov, A. N.; Denisovitch, L. T.; Gubin, S. P.; Vol'kenau, N. A.; Sirotkina, F. I.; Bolesova, I. N. *J. Organomet. Chem.* **1969**, *20*, 169. (c) Astruc, D.; Dabard, R. *Bull. Soc. Chim. Fr.* **1976**, 228. (d) El Murr, N. *J. Chem.* Soc., *Chem. Commun.* **1981**, 219. (e) El Murr, N. *J. Chem. Soc., Chem. Commun.* **1981**, 251. (f) Finke, R. G.; Voegell, R. H.; Laganis, E. D.; Boekelheide, V. *Organometallics* **1983**, *2*, 347. (g) Bowyer, W. J.; Geiger, W. E., Jr.; Boekelheide, V. *Organometallics* **1984**, *3*, 1079. (h) Plitzko, K. D.; Boekelheide, V. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 700.

(7) (a) Morrison, W. H.; Hendrickson, D. N. *J. Chem. Phys.* **1973**, *59*, 380. (b) Cowan, D. O.; Collins, R. L.; Kaufman, F. *J. Phys. Chem.* **1971**, *75*, 2025. (c) Morrison, W. H.; Krogsud, S.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 1998. (d) Cowan, D. O.; Candela, G. A.; Kaufman, F. *J. Am. Chem. Soc.* **1971**, *93*, 3889. (e) Kaufman, F.; Cowan, D. O. *Ibid.* **1970**, *92*, 6198. (f) Cowan, D. O.; Park, J.; Barber, M.; Swift, P. *J. Chem. Soc., Chem. Commun.* 1971, 1444. (g) Cowan, D. O.; Levanda, C.; Park, J.; Kaufman, F. *Acc. Chem. Res.* **1973**, *6*, 1. (h) Rudie, A. W.; Davison, A.; Frankel, R. B. *J. Am. Chem. Soc.* **1979**, *101*, 1629. (i) Morrison, W. H.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 2331. (j) Iijima, S.; Saida, R.; Motoyama, I.; Sano, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1375. (k) Motoyama, I.; Suto, K.; Katada, M.; Sano, H. *Chem. Lett.* **1983**, 1215. (l) Desbois, M.-H.; Astruc, D.; Guillin, J.; Mariot, J.-P.; Varret, F. *J. Am. Chem. Soc.* **1985**, *107*, 5270. (m) Desbois, M.-H.; Astruc, D.; Guillin, J.; Varret, F.; Trautwein, A. X.; Villeneuve, G. *J. Am. Chem. Soc.* **1989**, *111*, 5800.

(8) For a recent, comprehensive review, see: Mueller-Westerhoff, U. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 702.

(9) (a) Hendrickson, D. N.; Oh, S. M.; Dong, T.-Y.; Moore, M. F. *Comments Inorg. Chem.* **1985**, *4*, 329 and references cited therein. (b) Dong, T. Y.; Hendrickson, D. N.; Pierpont, C. G.; Moore, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 963. (c) Dong, T. Y.; Kambara, T.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1986**, *108*, 4423. (d) Dong, T. Y.; Hendrickson, D. N.; Iwai, K.; Cohn, M. J.; Geib, S. J.; Rheingold, A. L.; Sano, H.; Motoyama, I.; Nakashima, S. *J. Am. Chem. Soc.* **1985**, *107*, 7996.

of decahydronaphthalene at 140 °C. The same procedure as in preparation 2 allowed the precipitation of the desired salt. The crude product was extracted with acetonitrile and passed through an alumina column using acetonitrile as the eluant. Recrystallization from acetonitrile/ethanol gave 0.07 g (24% yield) of a crystalline orange powder: $^1$H NMR ($CD_3CN$, 20 °C) $\delta$ 6.13 (s, bz, 6 H), 5.50 (t, Fv, 4 H), 5.36 (t, Fv, 4 H), 2.26 (s, HMB, 18 H); $^{13}$C NMR ($CD_3CN$, 20 °C) $\delta$ 100.34 ($C_6$ (HMB)), 90.23 ($C_6$ (bz)), 87.00, 86.00, 80.90, 78.66, 75.41, 74.91 (Fv), 17.34 ($CH_3$). Anal. Calcd for $C_{28}H_{32}Fe_2P_2F_{12}$: C, 43.63; H, 4.19. Found: C, 43.48; H, 4.30.

**5. $[Fe_2(Fv)(HEB)_2]^{2+}(PF_6^-)_2$ (9).** To a 100-mL three-necked flask equipped with a reflux condenser and containing 0.449 g of **2** (0.5258 mol) and 5.888 g of potassium *tert*-butoxide (predried in vacuo, overnight at 60 °C) (52.58 mmol) was added a solution of 7.47 g of methyl iodide (52.58 mmol) in 4 mL of dimethoxyethane. A strong reflux immediately occurred with the appearance of a red-brown color persistent for 20 min. The mixture was stirred at 50 °C for 29 h. DME was then removed in vacuo; the orange pale solid was washed with 50 mL of distilled water, filtered, extracted with dichloromethane, and chromatographed on an activated acidic alumina column. Three orange bands were observed. The first one was concentrated, and recrystallization from a dichloromethane/ethanol mixture gave 0.154 g (29% yield) of the desired product **9**. The other two bands corresponded to complexes still containing Me groups. The reaction of the two last fractions with more methyl iodide and potassium *tert*-butoxide also gave the desired dicationic alkylated complex **9**: $^1$H NMR ($CD_3CN$, 20 °C) $\delta$ 4.63 (m, Fv, 8 H), 2.48 (q, $CH_2$, 24 H), 1.16 (t, $CH_3$, 36 H); $^{13}$C NMR ($CD_3CN$, 20 °C) $\delta$ 106.3 ($C_6$ ring), 87.3, 79.9, 75.5 (Fv), 24.0 ($CH_2$), 16.3 ($CH_3$). Anal. Calcd for $C_{46}H_{68}Fe_2P_2F_{12}$: C, 54.02; H, 6.70. Found: C, 53.50; H, 6.67.

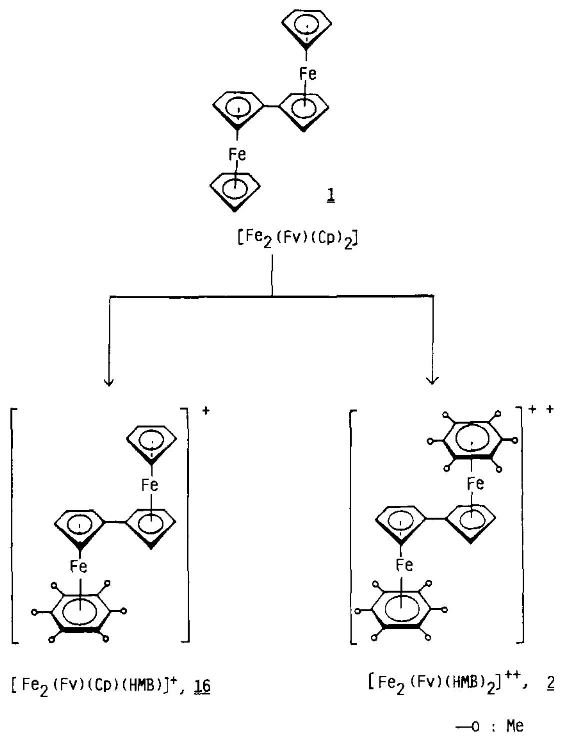
## Results

**Syntheses.** Reactions between biferrocene and a 10-fold excess of $C_6Me_6$ and of $AlCl_3$ in decahydronaphthalene in the presence of aluminum powder give a reproducible 14% yield of **2** after metathesis, chromatographic purification, and recrystallization. Extreme care must be exercised at the start of the reaction and during hydrolysis to avoid traces of air. This Nesmeyanov-type[10,11] ligand exchange proceeds much more easily with benzene.[12] Thus, the influence of the bulk of the arene is clear on the double ligand exchange reaction. The yield progressively decreases (with benzene, 35%[12]) as the arene bulk increases, although, in the mononuclear series, the electron-releasing property of the Me groups increases the reaction yield.

When biferrocene and a fivefold excess of $C_6Me_6$ and of $AlCl_3$ are reacted under the same conditions, the yield of **3** is optimum, 9% and, as above, lower than with other arenes bearing no or less than six Me groups. In fact, there are discrepancies from one reaction to the other because of the heterogeneous nature of the medium, even using trisublimed aluminum trichloride.

Besides the benzene and mesitylene complexes which are already known in both the mono- and dicationic series,[12] we have synthesized the new toluene (**4**), ethylbenzene (**5**), hexamethylbenzene (**2**), and hexaethylbenzene (**9**) dicationic complexes, the latter with the aim to obtain stable and more soluble reduced derivatives. Contrary to the other dicationic systems, complex **9** was not obtained by using the classical ligand exchange reaction between biferrocene and $C_6Et_6$ in order to avoid problems of dealkylation which have already been observed when the cyclopentadienyl ring is substituted.[13] A much more convenient route was the peralkylation of the dicationic precursor **2**, using an excess of base and alkylating reagent according to the general scheme used in the mononuclear series:[13a-c]

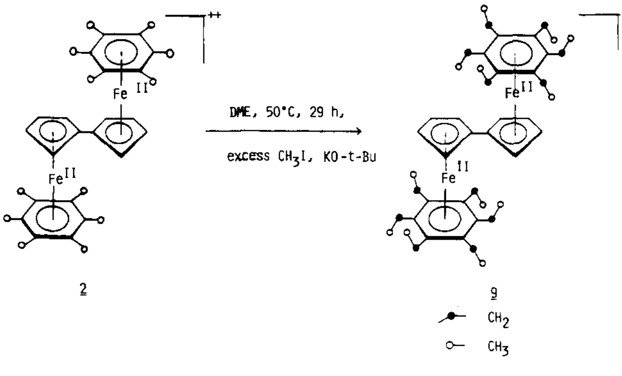
Scheme I



$$[Fe(Cp)(C_6Me_6)]^+PF_6^- \xrightarrow[\text{base}]{RX} [Fe(Cp)(C_6(CH_2R)_6)]^+PF_6^-$$

R = Me, $PhCH_2$, $CH_2CHCH_2$; X = halogen; base = KO-*t*Bu

Indeed, the dicationic precursor **2** was treated with an excess of KO-*t*Bu and $CH_3I$ to give the perethylated complex **9** in 29% yield.



It is also possible to effect a stepwise ligand exchange of the two free Cp rings of **1** allowing the introduction of two distinct arene ligands. For the synthesis of the mixed complex **7**, the benzene ligand is introduced first, giving **8**; reaction of the isolated $PF_6$ salt of **8** with $C_6Me_6$ provides the complex $[Fe_2(Fv)(bz)(HMB)]^{2+}(PF_6^-)_2$ (**7**) in 24% yield.

**Electrochemistry.** The cyclic voltammograms of all the complexes were performed under the same conditions

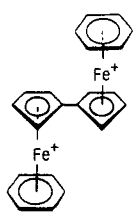
---

(10) (a) Astruc, D.; Hamon, J.-R.; Althoff, G.; Román, E.; Batail, P.; Michaud, P.; Mariot, J.-P.; Varret, F.; Cozak, D. *J. Am. Chem. Soc.* **1979**, *101*, 5445. (b) Hamon, J.-R.; Astruc, D.; Michaud, P. *Ibid.* **1981**, *103*, 758. (c) Astruc, D. *Tetrahedron Report* No. 157. *Tetrahedron* **1983**, *39*, 4027.

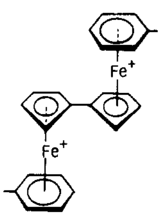
(11) Nesmeyanov, A. N. *Adv. Organomet. Chem.* **1972**, *10*, 1.

(12) Lee, C. C.; Demchuk, K.; Sutherland, R. G. *Synth. React. Met.-Org. Chem.* **1978**, *8*, 361.

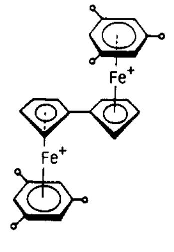
(13) (a) Astruc, D.; Hamon, J.-R.; Román, E.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 7502. (b) Hamon, J.-R.; Saillard, J.-Y.; Le Beuze, A.; Mc Glinchey, M. J.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 7549. (c) Moulines, F.; Astruc, D. *Angew. Chem., Int Ed. Engl.* **1988**, *100*, 1394. (d) Hamon, J.-R.; Astruc, D. *Organometallics* **1989**, *8*, 000.



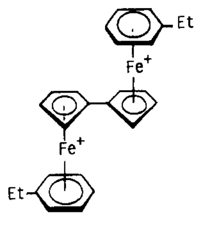
$[Fe_2(Fv)(bz)_2]^{++}$, 3



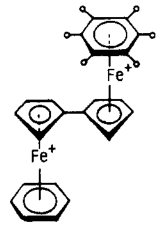
$[Fe_2(Fv)(tol)_2]^{++}$, 4



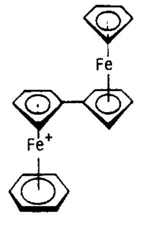
$[Fe_2(Fv)(mes)_2]^{++}$, 6



$[Fe_2(Fv)(Etbz)_2]^{++}$, 5



$[Fe_2(Fv)(bz)(HMB)]^{++}$, 7



$[Fe_2(Fv)(Cp)(bz)]^{+}$, 8

of temperatures (room temperature or −35 °C), solvents (DMF), electrodes (hanging mercury or platinum electrodes), and conducting salt ($[nBu_4N][BF_4]$, 0.1 M), except when specifically mentioned. On the Hg cathode, the bications all present four one-electron reduction waves (Figure 1). The electrode material had no influence on the first three waves which are chemically and electrochemically reversible at −35 °C for all the complexes of this series. Consistent results were obtained on both platinum and mercury. The switching potential $E_{sp}$ was chosen enough far away from the cathodic peak potential (at least 150 mV) so that its effect remained small. DMF was preferred to acetonitrile because of the lack of chemical reversibility of the waves in the latter solvent. Diffusion-controlled ET were checked ($i_{pc}/v^{1/2}$ is constant over a wide scan range). Half-wave potentials ($E°_i$) for the dimers as measured by cyclic voltammetry are given in Table I.

The reversibility was determined, for each wave, by the peak separation ($\Delta E_{pi}$) and the ratio of the anodic to cathodic peak current ($i_{pa}/i_{pc}$). In fact, the $\Delta E_p$ values were slightly larger than the theoretical one (47 mV). Anyway, problems of uncompensated solution resistance between the reference and working electrodes were avoided by using low concentration and current values (1–2 μA). Note that under the present experimental conditions, both ferrocene/ferricinium and $[Fe(Cp)(HMB)]^+PF_6^-/[Fe(Cp)(HMB)]$ couples had also larger $\Delta E_p$ of 60 and 65 mV, which were used as criteria of reversibility. No variation of the $E_{pc}$ and $|E_{pa} - E_{pc}|$ values with scan rates was observed.[14] Figure 1 shows the general shape of such voltammograms.

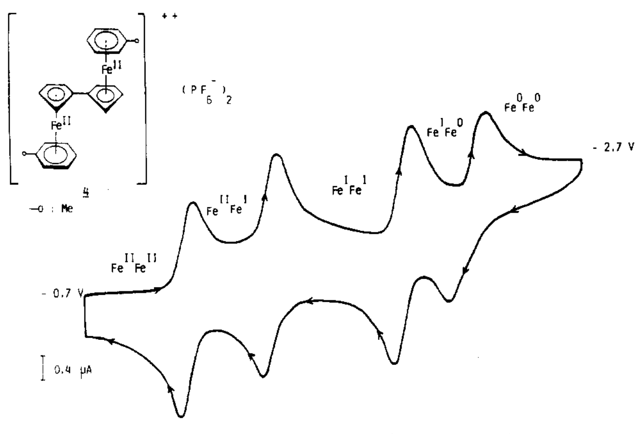


**Figure 1.** Cyclic voltammogram of 3.3 × $10^{-5}$ M DMF solution of $[Fe_2(Fv)(tol)_2]^{2+}(PF_6^-)_2$ (0.1 M $[nBu_4N][BF_4]$ at Hg cathode; scan rate = 0.4 V/s; − 35 °C; $E°$ (V vs SCE) = −1.160, −1.530, −2.120, and −2.450).

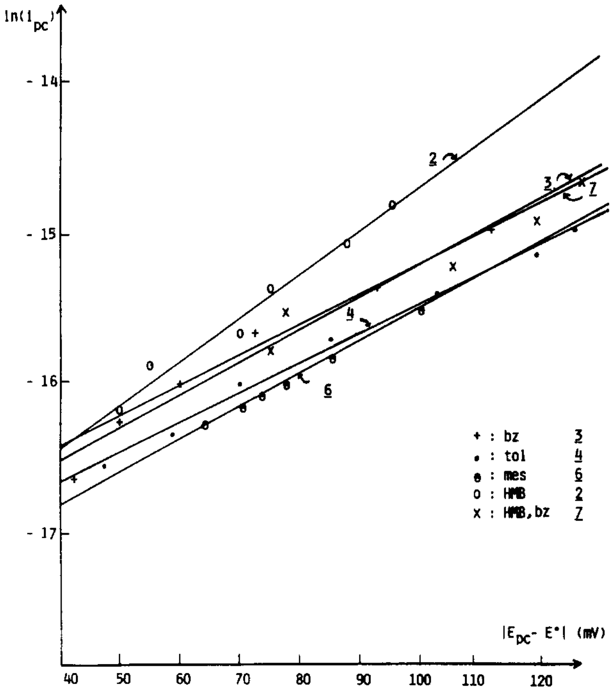


**Figure 2.** Plot of the current ln ($i_{pc}$) vs ($E_{pc} - E°$) varying scan rate for the different complexes in DMF (0.1 M $[nBu_4N][BF_4]$ at − 35 °C).

The four one-electron reduction waves are well separated, and the comparison of the potentials with those of respective monomers[10] outlines the electron-withdrawing effect of the positive charge of the second iron center, shifting the potentials to more positive values. The role of electron-donating methyl substituents is also illustrated upon the comparison of the different potentials for the series: Ar = bz, tol, Etbz, mes, HMB. The difference of potentials between the two first waves in these dimers is relatively large, up to 480 mV for 2. It is slightly lower between the last two waves. These differences, $E°_i$ (where $E°_i$ is the standard potential of wave number $i$ ($i$ = 1, 2, 3, 4)), can be attributed to strong exchange interactions between the two iron centers propagated throughout the orbitals of the fulvalene ring (direct iron–iron exchange interactions are excluded because of the arene bulk[18]). The stabilization of the $Fe^IFe^{II}$ states is shown by the very high values of the comproportionation constants (Table II).

The fourth wave observed only on mercury cathode between −2.3 and −2.7 V vs SCE is chemically reversible ($i_{pa}/i_{pc}$ close to unity) but not electrochemically reversible.

---

(14) (a) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; Chapter 6. (b) Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969; p 124 and p 214 ff.

**Table I. Electrochemical Data of $[Fe_2(Fv)(Ar)_2]^{2+}$ $(PF_6^-)_2$ (Ar = bz, tol, mes, HMB, Etbz) in DMF (0.1 M $[nBu_4N][BF_4]$; −35 °C; Hanging Hg Cathode; Sweep Rate = 400 mV/s)[a]**

| | $Fe_2(Fv)(Ar)_2^{2+}$, Ar = | | | | | |
|---|---|---|---|---|---|---|
| | bz | tol | mes | HMB | bz, HMB | Etbz |
| $E_1$[b] | −1.130 | −1.160 | −1.230 | −1.280 | −1.150 | −1.150 |
| $E_2$[b] | −1.460 | −1.530 | −1.630 | −1.760 | −1.670 | −1.520 |
| $E_3$[b] | −2.055 | −2.120 | −2.280 | −2.390 | −2.115 | −2.120 |
| $E_4$[b] | −2.330 | −2.450 | −2.630 | −2.740 | −2.710 | −2.380 |
| $(E_{pc} - E_{pa})_1$[c] | 60 | 60 | 70 | 60 | 60 | 55 |
| $(E_{pc} - E_{oa})_2$[c] | 70 | 65 | 70 | 60 | 60 | 60 |
| $(E_{pc} - E_{pa})_3$[c] | 75 | 80 | 80 | 90 | 70 | 65 |
| $(E_{pc} - E_{pa})_4$[c] | 185 | 205 | 170 | 175 | 255 | 120 |
| $(i^\circ_a/i^\circ_c)_1$ | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| $(i^\circ_a/i^\circ_c)_2$ | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| $(i^\circ_a/i^\circ_c)_3$ | 0.91 | 1.00 | 1.00 | 0.98 | 1.00 | 0.97 |
| $(i^\circ_a/i^\circ_c)_4$ | 0.90 | 0.97 | 0.88 | 0.97 | 0.98 | 0.94 |
| $E^\circ_2 - E^\circ_1$[c] | 330 | 370 | 400 | 480 | 520 | 370 |
| $E^\circ_4 - E^\circ_3$[c] | 280 | 330 | 350 | 350 | 600 | 260 |

[a] $E^\circ_i$ are given in V vs SCE. $i^\circ_a/i^\circ_c = i_{pa}/i_{pc} + 0.485(i_{sp}/i_{pc}) + 0.086$ ($i_{pa}$ = anodic peak current; $i_{pc}$ = cathodic peak current; $i_{sp}$ = switching peak current). [b] In V vs SCE (±5 mV). [c] In mV (±10 mV).

**Table II. Comproportionation Constants at 238 K for the First Two Waves ($Fe^{II}Fe^{II} + Fe^IFe^I \rightarrow 2Fe^{II}Fe^I$) and the Last Two Waves ($Fe^0Fe^0 + Fe^IFe^I \rightarrow 2Fe^0Fe^I$)[a]**

| | bz | tol | mes | HMB | bz, HMB | Etbz |
|---|---|---|---|---|---|---|
| $\Delta E_1^\circ$[b] | 330 | 370 | 400 | 480 | 520 | 370 |
| $Kc_1$ | $1.0 \times 10^7$ | $7.0 \times 10^7$ | $3.0 \times 10^8$ | $1.5 \times 10^{10}$ | $1.8 \times 10^{10}$ | $7.0 \times 10^7$ |
| $\Delta E_2^\circ$[b] | 280 | 330 | 350 | 350 | 600 | 260 |
| $Kc_2$ | $9.0 \times 10^5$ | $1.0 \times 10^7$ | $3.0 \times 10^7$ | $2.6 \times 10^7$ | $4.4 \times 10^{12}$ | $3.2 \times 10^5$ |

[a] $\ln Kc_i = (n_1E^\circ_i - n_2E^\circ_{i+1})F/RT$ with $n_1 = n_2 = 1$. [b] $\Delta E^\circ_i$ in mV (±10 mV).

**Table III. Experimental Data Obtained for 2, 3, 4, 5, 6, and 7 from the Plots $\ln (i_{pc}) = -(n\alpha F(E_{pc} - E^\circ)/RT) + \ln (0.227nFACo^*k_s)$**

| | **3** (bz) | **4** (tol) | **6** (mes) | **2** (HMB) | **7** (bz, HMB) | **5** (Etbz) |
|---|---|---|---|---|---|---|
| corr coeff | 0.983 | 0.996 | 0.988 | 0.984 | 0.964 | 0.998 |
| $a$ | 21.37 | 19.37 | 21.36 | 28.66 | 19.70 | 24.51 |
| $\alpha$ | 0.44 | 0.40 | 0.44 | 0.56 | 0.40 | 0.50 |
| $b$ | −15.38 | −15.44 | −15.66 | −15.59 | −15.20 | −14.45 |
| $10^7Co^*$, mol $cm^{-3}$ | 6.32 | 5.37 | 6.71 | 5.10 | 2.38 | 38.72 |
| $10^3k_s$, cm $s^{-1}$ | 1.90 (±0.5) | 2.20 (±0.4) | 1.40 (±0.3) | 1.90 (±0.3) | 1.50 (±0.3) | 0.8 (±0.5) |

Indeed, looking at $\Delta E_p$ values, we can assume that the electron-transfer rate is slow enough so that Nernstian equilibrium is not established at the electrode but fast enough so that both cathodic and anodic contributions are important; then a quasi-reversible charge-transfer kinetic is observed.[14,15] The systems have been considered as one-component ones given the sufficiently large difference of potentials between the third and the fourth waves. To study the electrochemical irreversibility of the waves, the following criteria were applied: (i) the variation of $\Delta E_p$ ($|\Delta E_p| = |E_{pc} - E_{pa}|$) with scan rate is significant; (ii) the widths of the CV waves ($E_p - E_{p/2}$), where $E_{p/2}$ is measured at half the current maximum, were observed to be significantly greater than the 47 mV expected at this temperature for reversible systems (see Table SI (supplementary material)); (iii) the variation of the peak potential with the CV scan rate gave linear plots with slopes around 40 mV (Table SII (supplementary material)). These latter criteria allowed evaluation of the charge-transfer coefficient: ≃0.5 for all the complexes, as qualitatively indicated by the symmetric shape of the quasi-reversible cathodic waves. Different attempts were made to calculate the electron-transfer rate constants ($k_s$) for these waves. We first used the equation defined by Nicholson and Shain[16] giving the expression of the intensity of the peak current as a function of the heterogeneous rate constant (eq 1)

$$i_{pc} = 0.227nFACo^*k_s \exp(-\alpha nF/RT)(E_{pc} - E^\circ) \quad (1)$$

where $\alpha$ is the coefficient defined above, $n$ the number of electrons transferred in the rate-limiting step, and $Co^*$ the bulk concentration. Experimental data are given in Table III, and plots of $\ln (i_{pc})$ vs $(E_{pc} - E^\circ)$ for different scan rates are shown on Figure 2, giving straight lines with the slopes proportional to $n$ and the intercepts to $\ln k_s$. It should be noted that eq 1 has been applied to irreversible electrode processes. However, it is possible to determine $\alpha$ and $k_s$ thereof, although not so accurately as with the other methods. Moreover, the $k_s$ values found here are close to those obtained by the latter ones (vide infra).

An alternative method for the evaluation of $k_s$[16b] requires the fitting of the values of $\Delta E_p$ to a working curve in order to obtain the values of a function, $\psi$, defined as $\psi = k_s(\pi DnvF/RT)^{-1/2}$. The evaluation of $k_s$ by Nicholson's method applies to the range of peak separations between 45 and 200 mV at −35 °C, during which the electrode process is progressing from reversible to irreversible. In order to obtain the accurate value of $\psi$ for a given $\Delta E_p$, a polynomial interpolation was achieved by using Atken's algorithm and a fourth-order polynomial to decrease oscillations and obtain better accuracy of the results. Detailed data are given in supplementary material (Table III). The third and last method employed to obtain other $k_s$ values independently was currently used to provide the

---

(15) For a leading reference, see: Geiger, W. E., Jr. *Prog. Inorg. Chem.* **1985**, *23*, 275.

(16) (a) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706. (b) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

**Table IV. Study of the Fourth Wave for $[Fe_2(Fv)(Ar)_2]^{2+}(PF_6^-)_2$**[a]

| | $10^{-3}Z$, cm s$^{-1}$ | $10^3k_s$, cm s$^{-1}$ | | | $\Delta G^*$, kcal mol$^{-1}$ | | |
|---|---|---|---|---|---|---|---|
| | | i | ii | iii | i | ii | iii |
| bz | 282 | 1.9 (±0.5) | 2.1 (±0.4) | 2.1 (±0.3) | 6.7 (±0.1) | 6.7 (±0.1) | 6.7 (±0.1) |
| tol | 272 | 2.2 (±0.4) | 1.7 (±0.2) | 1.9 (±0.3) | 6.6 (±0.1) | 6.7 (±0.1) | 6.5 (±0.1) |
| mes | 256 | 1.3 (±0.3) | 2.0 (±0.3) | 2.4 (±0.3) | 6.9 (±0.1) | 6.7 (±0.1) | 6.7 (±0.1) |
| HMB | 236 | 1.9 (±0.3) | 1.9 (±0.3) | 2.5 (±0.3) | 6.6 (±0.1) | 6.6 (±0.1) | 6.6 (±0.1) |
| bz, HMB | 256 | 1.5 (±0.3) | 0.7 (±0.3) | 0.9 (±0.3) | 6.8 (±0.2) | 7.2 (±0.2) | 7.0 (±0.2) |
| Etbz | 264 | 0.8 (±0.5) | 4.1 (±0.5) | 1.6 (±0.5) | 7.1 (±0.3) | 6.3 (±0.3) | 6.8 (±0.2) |

[a] Calculated electron transfer rates ($k_s$) and activation barriers to electron transfer ($\Delta G^*$) obtained by three different ways (scan rate range = 0.025–0.800 V/s): (i) $k_s$ from the plot $\ln (i_{pc}) = -n\alpha F(E_{pc} - E°)/RT + \ln (0.227nFACo^*k_s)$; (ii) $k_s = \psi(\pi Dn\upsilon F/RT)^{1/2}$; (iii) $k_s = 2.18(D\alpha nF/RT)^{1/2} \exp(-\alpha^2nF(E_{pa} - E_{pc})/RT)$. $\Delta G^*$ is obtained as follows: $\Delta G^* = -RT \ln (k_s/Z)$, where $Z$ is the heterogeneous collision frequency and is calculated from $Z = (RT/2\pi M)^{1/2}$ ($M$ = molar weight of the species).

rate constant of electron transfer at the CV peak potential for totally irreversible electrochemical processes[14,16] (eq 2). However, it was also shown to be convenient to directly obtain $k_s$ defined as in eq 2 for chemically reversible systems[17]

$$k(E) = k_s \exp(\alpha nF(E - E°)/RT) \qquad (2)$$

where $E$ is the electrode potential; all other coefficients were defined earlier. The method anyway consists of applying eq 3 which gives the peak potential as a function of $k_s$.

$$E_p = E° + (RT/\alpha nF)(0.780 + \ln (D\alpha n\mathrm{F}v/RT)^{1/2} - \ln k_s) \qquad (3)$$

The algebraic rearrangement of eq 3 to eq 4 provides another expression of $k_s$.

$$k_s = 2.18(D\alpha nF/RT)^{1/2} \exp(-\alpha nF(E_p - E°)/RT) \qquad (4)$$

Indeed, Klinger and Kochi have shown how sweep-induced irreversibility of a CV wave can be used to determine the rate constant $k_s$. The expression given in eq 4 for irreversible waves has been modified[17] to give eq 5 after algebraic rearrangement:

$$k_s = 2.18(D\alpha nFv/RT)^{1/2} \exp(-\alpha^2nF(E_{pa} - E_{pc})/RT) \qquad (5)$$

This relationship indicates that $k_s$ can easily be obtained from the difference in the CV peak potentials and the sweep rate (experimental data are given in supplementary material (Table IV)). The results obtained from the three methods are summarized in Table IV as well as the corresponding activation free energy $\Delta G^*$, calculated by using the known eq 6, where $Z$ is the collision frequency ($Z$ =

$$\Delta G^* = -RT \ln (k_s/Z) \qquad (6)$$

$(RT/2\pi M)^{1/2}$; $M$ = molecular weight). The electrode area and the diffusion coefficients $D$ were obtained from the analysis of the chronoamperometric $i$–$t$ transient according to the relationship $it^{1/2} = nFACo^*(D/\pi)^{1/2}$ as described by Adams.[14b] The assumption of a semi-infinite linear diffusion was made. The area of the electrode A was calibrated with both ferrocene (in which the diffusion coefficient $D = 1.6 \times 10^{-6}$ cm$^2$ s$^{-1}$ in DMF at −35 °C) and $[Fe_2(Fv)(HMB)_2]^{2+}(PF_6^-)_2$ (in which $D = 2.8 \times 10^{-6}$ cm$^2$ s$^{-1}$ under the same conditions).

## Discussion

This dicationic series posed challenging synthetic problems because bulky arenes did not give any reaction product until the optimal conditions were found. Perethylbenzene complexes were made in order to increase markedly the solubility of the reduced states and thus allow physical studies. An intriguing question was the following: how many oxidation states could be observed and what is their structure? The isolation of three isostructural oxidation states is consistent with the chemical and electrochemical reversibilities observed for the two first waves. The third one, also reversible, might indicate that no structural rearrangement occurred during the third ET, generating $[Fe_2(Fv)(arene)_2]^-$. This species cannot be observed, and thus this hypothesis cannot be verified either. There are, anyway, many examples of structural rearrangements that are concomitant with fast (reversible) ET in organometallic chemistry.[5c,d,22]

A more convincing argument against stereoelectronic rearrangement is the fact that the wave $Fe^IFe^I \rightarrow Fe^IFe^0$ is found as expected on the potential scale. It is not shifted toward a less negative value by the gain of energy provided by a structural rearrangement. In any case, the possibility of a structural rearrangement involving little energy cannot be discarded.

Whereas there is little probability that a deep structural rearrangement intervenes in the third ET, this is not the case for the fourth ET which is not electrochemically reversible and only chemically reversible at −35 °C for the overall series. Depending on definitions, the heterogeneous ET of the fourth wave is quasi-reversible or irreversible, i.e. slow.[15,19] The Marcus theory states that deep structural rearrangement, concomitant with ET, slows it down (the internal reorganization term $\lambda_i$ is important[20]). However, there are examples of slow heterogeneous electron transfer which are not due to structural rearrangements[15] (possibility of double-layer effect and influence of the electrode material). In any case, the possibility that a structural rearrangement causes the slowing down of the ET cannot be discarded. There is also increasing driving force to intramolecular coupling as the number of valence electrons over 18 increases on each metal in the sandwich unit.

Thus, if one may propose that the structure of the monoanion is the same as those of the dication, the monocation, and the neutral complex, there is a good probability that the dianion has a different structure; i.e., is not a 40e

---

[17] Klinger, R. J.; Kochi, J. K. *J. Phys. Chem.* **1981**, *85*, 1731.

[18] Hendrickson, D. N.; Russell, C. L.; Yeong, T. H.; Hsiu-Rong, C. *Bio. Inorg. Cop. Chem.* **1985**, 223.

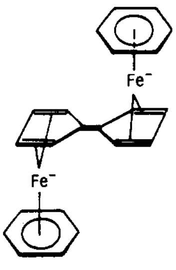
[19] (a) Savéant, J.-M. *Acc. Chem. Res.* **1980**, *13*, 323. (b) Kochi, J. K. *J. Organomet. Chem.* 1986, *300*, 139. (c) Chanon, M.; Tobe, M. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 1.

[20] (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966. (b) For a recent, comprehensive review, see: Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

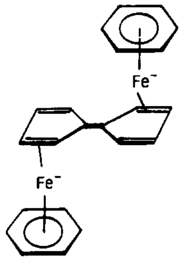
[21] Rausch, M. D. *J. Org. Chem.* **1961**, *25*, 1802.

[22] (a) Moraczewski, J.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 4779. (b) Bowyer, W. J.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5657. (c) Tulyathan, B.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5960.

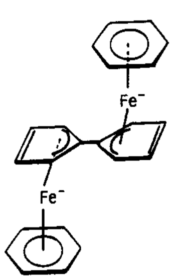
$Fe^0Fe^0$ species.[15] Possibilities of "geometrical" rearrangement are (i) intramolecular coupling in the fulvalene ligand with or without slippage, (ii) $\eta^5 \rightarrow \eta^3$ slippage of one double bond in one or two Cp ligands, and (iii) $\eta^6 \rightarrow \eta^4$ slippage of one or two arene ligands. The first mode provides an $Fe^{-I}Fe^{-I}$, 38e complex if no decoordination occurs, 34e if only one double bond remains coordinated. The two other modes also give 38e $Fe^{-I}Fe^{-I}$ species.



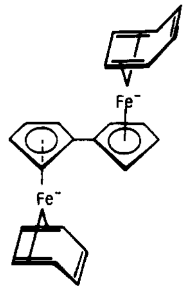
38 e⁻



34 e⁻



36 e⁻



36 e⁻

Note that, in monomers, the heterogeneous ET 19e → 20e is electrochemically reversible and thus generally provides a perfect sandwich isoelectronic with the 20e nickelocene complex.[23] This indicates that the arene decoordination is not likely and that rearrangement presumably involves the fulvalene ligand.

## Concluding Remarks

1. The symmetric binuclear sandwiches $[Fe_2(Fv)(C_6R_6)_2]^{2+}(PF_6^-)_2$ have been synthesized in modest yields by using carefully controlled conditions. The synthesis of the hexaethylbenzene complex requires the formation of 12 C–C bonds. Mixed-arene compounds are also accessible.

2. The CV's of all the dications show an extended electrochemical series of five oxidation states. The first three ET are chemically and electrochemically reversible; the fourth one is slow.

3. Kinetic studies of the fourth ET have been done by using several methods. The hypothesis of a structural rearrangement in the course of this fourth ET has been examined. This electrochemical behavior is exactly similar to that of the $[Fe_2(Cp^*)_2(\text{polyaromatic})]^{2+}$ series which is reported elsewhere.

**Acknowledgment.** We thank Drs. N. Ardoin, F. Moulines, (Laboratoire de Chimie Organique et Organomētallique, Universitē de Bordeaux I) for experimental help, J. Morand for his help in recording some electrochemical experiments in our early Bordeaux days, and J. Guillin and F. Varret (Laboratoire de Physique et de Chimie du Solide, Le Mans) for Mössbauer experiments. A DGRST grant to M.-H. D. in the preliminary stage of the study at the Laboratoire de Chimie des Organometalliques (University of Rennes) is gratefully acknowledged.

**Registry No.** **1**, 1287-38-3; **2**, 121268-57-3; **3**, 53702-59-3; **4**, 121268-59-5; **5**, 121268-61-9; **6**, 68531-52-2; **7**, 121268-62-0; **8**, 68499-72-9; **9**, 121268-64-2; HMB, 87-85-4; bz, 71-43-2; tol, 108-88-3; Etbz, 100-41-4; mes, 74-86-2; $[Fe(Cp)(HMB)]^+PF_9^-$, 53702-66-2; $[Fe_2(Fv)(bz)_2]^-$, 121268-65-3; $Fe_2(Fv)(bz)_2$, 78398-48-8; $[Fe_2(Fv)(bz)_2]^+$, 97431-21-5; $[Fe_2(Fv)(tol)_2]^-$, 121268-66-4; $Fe_2(Fv)(tol)_2$, 78379-00-7; $[Fe_2(Fv)(tol)_2]^+$, 121268-67-5; $[Fe_2(Fv)(mes)_2]^-$, 121268-68-6; $Fe_2(Fv)(mes)_2$, 121268-69-7; $[Fe_2(Fv)(mes)_2]^+$, 121268-70-0; $[Fe_2(Fv)(HMB)_2]^-$, 121268-71-1; $Fe_2(Fv)(HMB)_2$, 97431-22-6; $[Fe_2(Fv)(HMB)_2]^+$, 97431-20-4; $[Fe_2(Fv)(bz)(HMB)]^-$, 121268-72-2; $Fe_2(Fv)(bz)(HMB)$, 121268-73-3; $[Fe_2(Fv)(bz)(HMB)]^+$, 121268-74-4; $[Fe_2(Fv)(Etbz)_2]^-$, 121268-75-5; $Fe_2(Fv)(Etbz)_2$, 121268-76-6; $[Fe_2(Fv)(Etbz)_2]^+$, 121268-77-7.

**Supplementary Material Available:** Table SI, electrochemical study of the fourth wave for the symmetric series $[Fe_2(Fv)(Ar)_2]^{2+}(PF_6^-)_2$ in DMF (0.1 M $[n\text{Bu}_4\text{N}][\text{BF}_4]$; −35 °C; Hg cathode; determination of the charge-transfer coefficient $\alpha$), Table SII, linear variation of peak potential with $v$: determination of $\alpha$ using the slope ($a$) of plots obtained ($a = RT/F\alpha n$; $\epsilon$ = correlation coefficient for experimental values), Table SIII, calculated values of $k_s$ using $k_s = \psi\,(\pi DnFv/RT)^{1/2}$, and Table SIV, calculated values of $k_s$ at different scan rates using eq 5 (3 pages). Ordering information is given on any current masthead page.

---

[23] Sharp, P.; Raymond, K. N.; Smart, J. C.; Mc Kinney, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 753.