# Binuclear Electron Reservoir Complexes.[1] Syntheses, Reactivity, and Electronic Structure of the 35-, 36-, and 37-Electron Fulvalene Complexes $[Fe_2(\mu_2,\eta^{10}\text{-}C_{10}H_8)(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6R_6)]^{n+}$ ($n$ = 0, 1, 2; R = H, Me)

Marie-Hélène Desbois,[†] Didier Astruc,[†,*] Jacques Guillin,[‡] and François Varret[‡]

*Laboratoire de Chimie Organique et Organométallique, U.A. CNRS No. 35, Université de Bordeaux I, 351 Cours de la Libération, 33405 Talence Cêdex, France, and Groupe de Physique et Chimie du Solide, U.A. CNRS No. 807, Université du Maine, 72017 Le Mans Cêdex, France*

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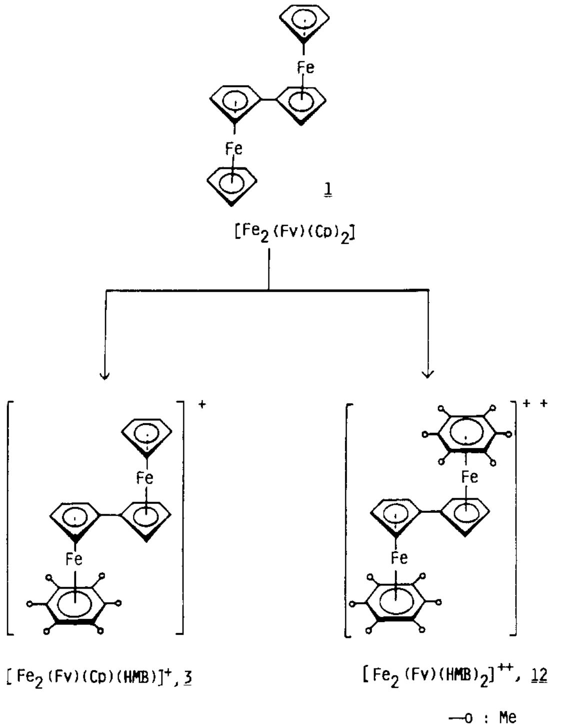
The dissymmetric binuclear organometallic fulvalene sandwiches $[Fe_2(Fv)(Cp)(C_6R_6)]^+PF_6^-$ (Fv = $\mu_2,\eta^{10}\text{-}C_{10}H_8$; R = H, Me) have been synthesized in modest yields from biferrocene (1) and the corresponding aromatic. Their cyclic voltammograms (CV) show four reversible waves at −35 °C in DMF (0.1 M $[n\mathrm{Bu}_4N][BF_4]$) corresponding to the 35e to 38e complexes. The 35e, 36e, and 37e complexes were obtained by using classical redox reagents whereas the 38e form (18e + 20e) is only reversibly observed by CV at low temperature. The 35e complexes are stable for both R = H and Me, whereas only the 37e complex with R = Me is stable at 20 °C. Both 35e and 37e series are localized, class I, mixed-valence complexes ($Fe^{II}Fe^{III}$ and $Fe^IFe^{II}$). Their Mössbauer and ESR behavior resembles those of the monomeric sandwiches ($[Fe^{III}(Cp)_2]^+$) and $[Fe^I(Cp)(Ar)]$. However, the coupling between the Jahn–Teller distortion and the lattice in the latter brings about a specific dependence of the quadrupole splitting with temperature (a phase transition is observed) in the 37e complex series.

## Introduction

The synthesis of various oxidation states of fulvalene-bridged bimetallic complexes offers the opportunity of studying the electronic interaction between the two metal centers through a delocalized organic ligand. This approach can also be realized by using polyaromatic ligands, but the results are very different in terms of coupling interaction.[2,3] The information we wish to obtain from this study should be useful for the design of unstable polyelectronic redox catalysts and of stacked sandwich materials.[4]

Ligand exchange reactions between biferrocene and $C_6R_6$ (R = H or Me) give rise to the exchange of either one or two $C_5H_5$ rings. In this way, two series of arene complexes are available: a dissymmetric one, **3**,[6,8] and a symmetric one, **12**[5,7] (R = Me) (Scheme I). In several papers, we have reported the syntheses and electronic structures of a series of complexes, including delocalized mixed-valence 37e complexes and antiferromagnetically coupled 38e biradicals.[7,9] We now wish to detail studies on the dissymmetric series **3** which contains a ferrocenyl unit linked to a [Fe(Cp)(arene)] unit via the Cp ligand. This work has been the subject of a preliminary communication.[9]

**Scheme I**



## Experimental Section

**General Data.** See preceding paper in this issue.

**Preparations.** The following abbreviations will be used for the ligand formula: $\eta^5\text{-}C_5H_5$, Cp; $\mu_2,\eta^{10}\text{-}C_{10}H_8$, Fv; $\eta^6\text{-}C_6Me_6$, HMB; $\eta^6\text{-}C_6H_6$, bz. The synthesis of biferrocene is described in the preceding paper in this issue.

1. **$[Fe_2(Fv)(Cp)(HMB)]^+PF_6^-$ (3).** Biferrocene (2 g, 5.4 mmol), $C_6Me_6$ (4.38 g, 27 mmol), aluminum chloride (3.6 g, 27 mmol), Al powder (0.146 g, 5.4 mmol), and water (0.097 g, 5.4 mmol) were mixed under argon and stirred for 23 h in 50 mL of refluxing heptane. After hydrolysis at 0 °C, aqueous ammonia

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[†] Laboratoire de Chimie Organique et Organométallique, Université de Bordeaux I.

[‡] Laboratoire de Physique et Chimie du Solide, Université du Mans. Preliminary synthetic studies were effected in the Laboratoire de Chimie des Organométalliques, University of Rennes I, Rennes Cedex, France.

(1) Organometallic Electron Reservoirs. 35. For part 34 see ref 9a.

(2) Rieke, R. D.; Milligan, S. N.; Schulte, L. D. *Organometallics* **1987**, *6*, 699.

(3) (a) Lacoste, M.; Varret, F.; Toupet, L.; Astruc, D. *J. Am. Chem. Soc.* **1987**, *109*, 6504. (b) Lacoste, M.; Toupet, L.; Varret, F.; Ardoin, N.; Astruc, D. *Organometallics* **1989**, *10*, 000.

(4) Desbois, M.-H.; Michaud, P.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1985**, 450.

(5) Morrison, W. H.; Ho, E. Y.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 500.

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was added to the aqueous layer in order to precipitate aluminum hydroxide; aqueous $HPF_6$ was then added to the filtrate which precipitated the desired salt and $[Fe(Cp)(HMB)]^+PF_6^-$ (**9**) which was also formed during the reaction. The crude product was washed with a 1:1 mixture THF/ether to solubilize (**3**). Recrystallization from hot THF gave 0.300 g (9% yield) of red microcrystals of **3** after the solution was cooled and allowed to stand overnight at −21 °C: $^1H$ NMR ($CD_3COCD_3$, 20 °C) $\delta$ 4.40 (m, Fv, 8 H), 3.93 (s, Cp, 5 H), 2.33 (s, $CH_3$, 18 H); $^{13}C$ NMR ($CD_3CN$, 20 °C) $\delta$ 99.8 ($C_6$ ring), 96.9, 78.2, 75.9, 72.2, 69.9, 69.1 (Fv), 71.0 (Cp), 17.6 ($CH_3$); Mössbauer data (mm/s vs Fe at room temperature, 293 K) IS 0.39, QS 2.27 ([Fe(Fv)(Cp)]; IS 0.43, QS 1.89 ($[Fe(Fv)(HMB)]^+PF_6^-$); electrochemical data (DMF; 0.1 M [*n*$Bu_4N$][$BF_4$], 20 °C; sweep rate = 0.5 V/s) (a) oxidation (Pt anode) $E°$ (V vs SCE) = +0.61, (b) reduction (Hg cathode) $E°$ (V vs SCE) = −1.58 and −2.36. Anal. Calcd for $C_{27}H_{31}Fe_2PF_6$: C, 52.97; H, 5.10; Fe, 18.30. Found: C, 52.95; H, 5.13; Fe, 17.69.

2. **$[Fe_2(Fv)(Cp)(bz)]^+PF_6^-$ (2).** This cation was prepared in a manner analogous to that already reported,[6] except for the following modifications: (i) 1 equiv of distilled water was added to the reactants before reflux, (ii) heptane was used as the refluxing solvent, (iii) the reaction time was 16 h, (iv) the separation between $[Fe_2(Fv)(Cp)(Bz)]^+PF_6^-$ and $[Fe(Cp)(Bz)]^+PF_6^-$ (**8**) was operated by washing the crude product with a THF/ether mixture (70:30), which allowed the solubilization of **2** and not of **8**. The chromatography on alumina column was done by using THF as eluant. Yields obtained were analogous to those given in the literature.[6] The cation was identified by its known $^1H$ NMR spectrum. Mössbauer parameters (mm/s vs Fe at room temperature, 293 K): IS 0.43, QS 2.26 ([Fe(Fv)(Cp)]); IS 0.45, QS 1.52 ($[Fe(Fv)(bz)]^+PF_6^-$). Electrochemical data (DMF; 0.01 M [*n*$Bu_4N$][$BF_4$]; −30 °C, sweep rate = 0.5 V/s): (a) oxidation (Pt anode) $E°$ (V vs SCE) = +0.65; (b) reduction (hanging Hg electrode) $E°$ (V vs SCE) = −1.31 and −2.13.

3. **$[Fe_2(Fv)(Cp)(HMB)]$ (5).** A 0.71-g sample of $[Fe_2(Fv)(Cp)(HMB)]^+PF_6^-$ (**3**) (1.16 mmol) in 50 mL of THF was stirred with 13.34 g of Na/Hg amalgam (1%, 5.80 mmol) for 2 h at room temperature under argon. THF was then removed in vacuo, and the residue was extracted and recrystallized from a pentane solution at −80 °C giving 0.433 g of extremely air-sensitive ivory-green crystals of the complex $[Fe_2(Fv)(Cp)(HMB)]$ (**5**) (0.927 mmol, 80% yield): Mössbauer data (mm/s vs Fe, room temperature) IS 0.43 (293 K), QS 2.31 (293 K, 77 K, 4.2 K) (Fe(Fv)(Cp)), IS 0.78, QS 1.47 (4.2 K), IS 0.81, QS 1.39 (77 K), IS 0.72, QS 0.78 (300 K), ([Fe(Fv)(HMB)]). For ESR results see Table I. Anal. Calcd for $C_{27}H_{31}Fe_2$: C, 69.41; H, 6.68; Fe, 23.90. Found: C, 69.59; H, 6.17; Fe, 24.16.

4. **$[Fe_2(Fv)(Cp)(bz)]$ (4).** A 0.1-g sample of $[Fe_2(Fv)(Cp)(bz)]^+PF_6^-$ (0.189 mmol) in 5 mL of THF was stirred with 0.72 g of $LiAlH_4$ (18.9 mmol) for 2 or 3 min at −80 °C under argon. The green solution was then transferred into an ESR tube at −80 °C: ESR (THF, 77 K) see Table I.

5. **$[Fe_2(Fv)(Cp)(bz)]^{2+}(PF_6^-)(BF_4^-)$ (6).** A 1-g sample of **2** as the $PF_6^-$ salt (1.89 mmol) in 20 mL of THF was stirred with 0.22 g of $NOBF_4$ for 30 min at −40 °C under argon. A greenish precipitate progressively appeared; THF was then removed in vacuo, and the residue was very rapidly extracted with acetone and precipitated with ether giving 0.80 g (70% yield) of the desired product: Mössbauer data (mm/s vs Fe at room temperature 293 K) IS 0.50, QS 0.12 ($Fe^{III}$), IS 0.53, QS 1.69 ($Fe^{II}$). For ESR results see Table I. Anal. Calcd for $C_{21}H_{19}Fe_2BPF_{10}$: C, 41.02; H, 3.11. Found: C, 41.31; H, 3.66.

6. **$[Fe_2(Fv)(Cp)(HMB)]^{2+}(PF_6^-)(I^-)$ (7).** A 0.5-g sample of **3** as the $PF_6^-$ salt (0.816 mmol) in 20 mL of $CH_2Cl_2$ was stirred with 0.104 g of $I_2$ (0.408 mmol) for 1 h. A greenish precipitate formed; $CH_2Cl_2$ was then removed in vacuo, and the residue was extracted with acetone and precipitated with ether giving 0.48 g (0.65 mmol, 79.5%) of the desired product: Mössbauer data (mm/s vs Fe at room temperature 293 K) IS 0.48, QS 0.13 ($Fe^{III}$), IS 0.50, QS 2.36 ($Fe^{II}$). For ESR results see Table I. Anal. Calcd for $C_{27}H_{31}Fe_2PF_6I$: C, 43.87; H, 4.22. Found: C, 44.09; H, 3.99.

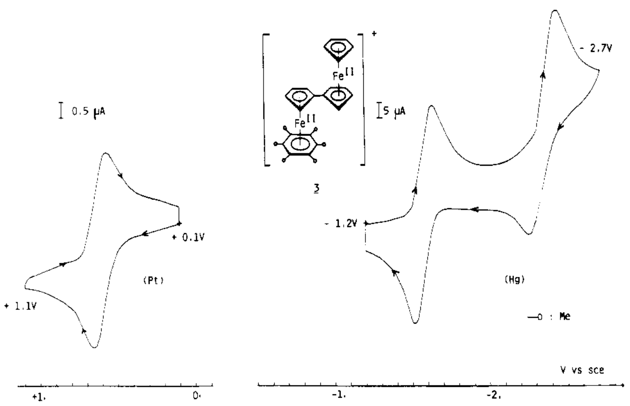

**Figure 1.** Cyclic voltammogram of $[Fe_2(Fv)(Cp)(HMB)]^+PF_6^-$ in DMF (0.1 M [*n*$Bu_4N$][$BF_4$]; V vs SCE; 20 °C; scan rate = 0.5 V/s): (a) oxidation, Pt anode, $E°$ = 0.160; (b) reduction, Hg cathode, $E°$ = −1.580 and −2.360.

**7** and **8** could both be reduced by using $^1/_2$ equiv of $Na_2S_2O_3$ in 10 mL of $CH_2Cl_2$ under argon (15 min) to give back their monocationic precursors, respectively (80–85% yield in recrystallized complexes), identified by comparison with authentic samples.

## Results and Discussion

**Syntheses.** The syntheses of the monocations $[Fe_2(Fv)(Cp)(arene)]^+$ proceed better with benzene then with bulkier arenes such as HMB, and the yields are only very modest in the latter case. The reaction is subjected to discrepancies due to the heterogeneous nature of the medium. The use of fresh aluminum trichloride and the absence of traces of air are crucial. The Nesmeyanov-type ligand exchange reactions lead to either single or double arene exchange depending on the excess of arene and $AlCl_3$ (see Experimental Section).

**Electrochemistry.** The voltammograms in DMF on the Hg cathode show three reversible waves at +20 °C for **2** and **3** (Figure 1). One corresponds to the oxidation of the ferrocene unit to a ferricinium one; the other two correspond to the reduction of the $[Fe^{II}(Cp)(arene)]^+$ unit to $Fe^I$ and then to $Fe^0$ as already shown.[11] The oxidation of the ferrocene unit is shifted toward positive potentials by 100 mV for complex **3** and 150 mV for complex **2** relative to ferrocene because the cationic substituent is electron-withdrawing. The reduction of the $[Fe^{II}(Cp)(arene)]^+$ unit is shifted by 50 mV for complex **3** (relative to $[Fe(Cp)(HMB)]^+$) and only 20 mV for complex **2** (relative to $[Fe(Cp)(bz)]^+$) toward more negative values because the ferrocene substituent is electron-releasing. Among the four oxidation states shown, three are isolable. The fourth one is at a too negative potential and shows some character of chemical irreversibility ($i_{pa}/i_{pc} < 1$) at room temperature. This tendency is more marked for the reduced form of **2** than for that of **3**.

**Localized $Fe^IFe^{II}$ and $Fe^{II}Fe^{III}$ Mixed-Valence Complexes.** Reduction of **3** with sodium amalgam in THF at 20 °C in 2 h provides an 80% yield of **5**, an ivory-green,

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[6] Lee, C. C.; Demchuk, K.; Sutherland, R. G. *Synth. React. Met.-Org. Chem.* **1978**, *8*, 361.

[7] Desbois, M.-H.; Astruc, D.; Guillin, J.; Mariot, J.-P.; Varret, F. *J. Am. Chem. Soc.* **1985**, *107*, 5280.

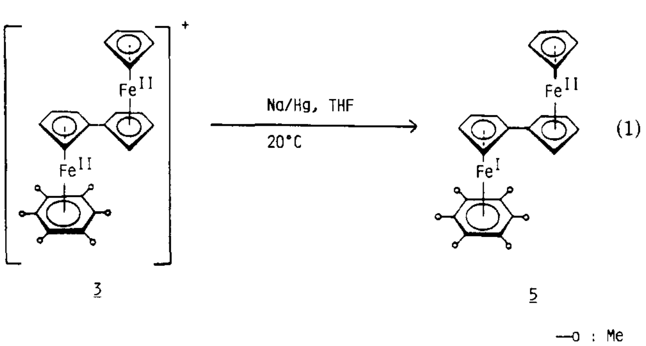
[8] Desbois, M.-H.; Guillin, J.; Mariot, J.-P.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1985**, 447.

[9] (a) Desbois, M.-H.; Astruc, D. *Organometallics*, preceding paper in this issue. (b) Desbois, M.-H.; Astruc, D.; Guillin, J.; Varret, F.; Trautwein, A. X.; Villeneuve, G. *J. Am. Chem. Soc.* **1989**, *111*, 5800.

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

[11] (a) Astruc, D.; Hamon, J.-R.; Althoff, G.; Român, 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. (d) Bowyer, W. J.; Geiger, W. E.; Boekelheide, V. *Organometallics* **1984**, *3*, 1679 and references cited therein.

stable $Fe^{I}$ complex with a ferrocene substituent (eq 1).



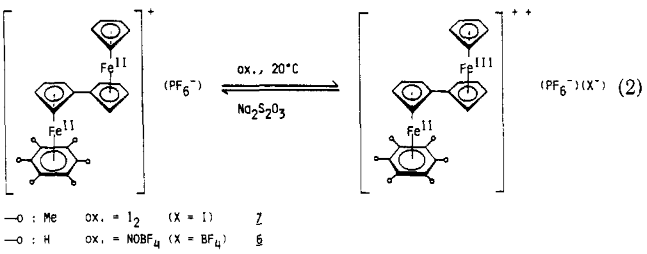
(1)

The permethylation of the arene is responsible for the stabilization that always occurs in the $Fe^{I}$ series. This localized mixed-valence $Fe^{I}Fe^{II}$ complex is very air ($O_2$) sensitive because the electron-releasing ferrocene substituent renders the $Fe^{I}$ center even more electron-rich than [Fe(Cp)(HMB)] (**11**).

Complex **5** shows three *g* values close to 2 by ESR spectroscopy (THF, 77 K), as for other $Fe^{I}$ and $Fe^{I}Fe^{II}$ complexes (Table I). Mössbauer spectra show two quadrupole doublets. One doublet is due to the ferrocene derivative and does not depend on temperature; the other doublet has a quadrupole splitting that depends on temperature. However, this dependence does not follow a regular law of thermal population of the upper Kramers' level because of the strong perturbation introduced in the lattice by the presence of the ferrocenyl group. This phenomenon is known for some other $Fe^{I}$ complexes such as **11**.[11] In particular, it allows the observation of phase transitions when discontinuities arise in the variation of the quadrupole splitting. In Figure 2 this kind of discontinuity indeed can be observed between 200 and 220 K for **5**.

The parent complex **2** can also be reduced to a $Fe^{I}Fe^{II}$ complex by $LiAlH_4$ at −80 °C in THF to give the green complex **4**, which shows by ESR spectroscopy (THF, 77 K) three *g* values characteristic of the rhombic distortion in $Fe^{I}$ systems (Table I).

The bimetallic monocations **2** and **3** can also be oxidized to give localized $Fe^{II}Fe^{III}$ mixed-valence complexes. The oxidation of **3** best proceeds by using $I_2$ and that of **2** by using $NOBF_4$. The mixed-valence dications **7** and **6** are obtained in good yields as greenish microcrystals. They can be reduced back to **3** and **2** by using $Na_2S_2O_3$ (eq 2).



(2)

Mössbauer spectra show two temperature-independent doublets, one with the parameters of a ferricinium derivative[12a] and the other with the parameters of a $[Fe(Cp)(arene)]^+$ cation.[12c] The ESR spectra of **6** and **7** are characteristic of those of ferricinium derivatives with three largely anisotropic *g* values[12b,13] (Figure 3). The difference of symmetry between the two sites and this large anisotropy of the **g** tensor depict a class I behavior for these complexes (Table I).[13]

**Table I. ESR Spectroscopic Results for $Fe^{II}Fe^{I}$ (THF, $3 \times 10^{-4}$ mol/L, 77 K) and $Fe^{III}Fe^{II}$ (Solid-State Samples, 4.2 K) Complexes in the Dissymetric Series**

| [Fe₂(Fv)(Cp)(Ar)] | | $g_x$ | $g_y$ | $g_z$ | $\mu$, $\mu_B$ |
|---|---|---|---|---|---|
| $[Fe_2(Fv)(Cp)(bz)]$ | $Fe^{II}Fe^{I}$ | 2.005 | 2.063 | 1.859 | 1.713 |
| | $Fe^{III}Fe^{II}$ | 1.539 | 1.518 | 3.873 | 2.218 |
| $[Fe_2(Fv)(Cp)(HMB)]$ | $Fe^{II}Fe^{I}$ | 2.005 | 2.065 | 1.853 | 1.712 |
| | $Fe^{III}Fe^{II}$ | 1.578 | 1.528 | 3.834 | 2.209 |
| $[Fe(Cp)(HMB)]^a$ | $Fe^{I}$ | 2.000 | 2.063 | 1.864 | 1.712 |
| $[Fe(Cp)(bz)]^a$ | $Fe^{I}$ | 1.896 | 1.962 | 1.789 | 1.631 |

$^a$From: Rajasekharan, M. V.; Giezynski, S.; Ammeter, J. H.; Oswald, N.; Michaud, P.; Hamon, J.-R.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 2400.

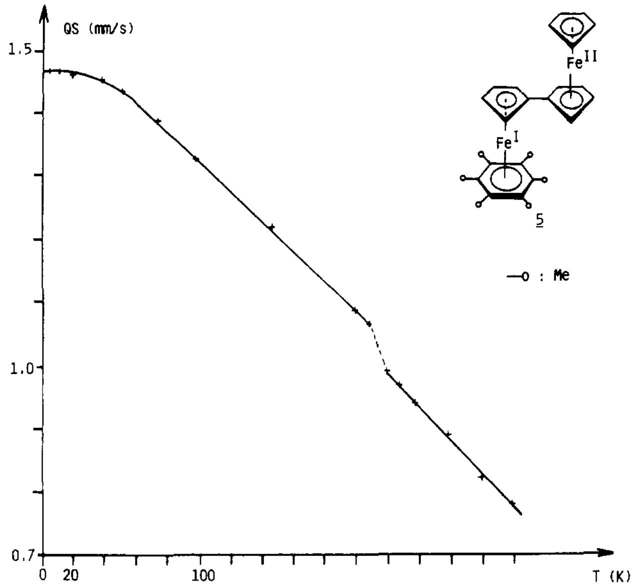


**Figure 2.** Temperature dependence of the quadrupole splitting for the localized mixed-valence $Fe^{II}Fe^{I}$ complex **5**.

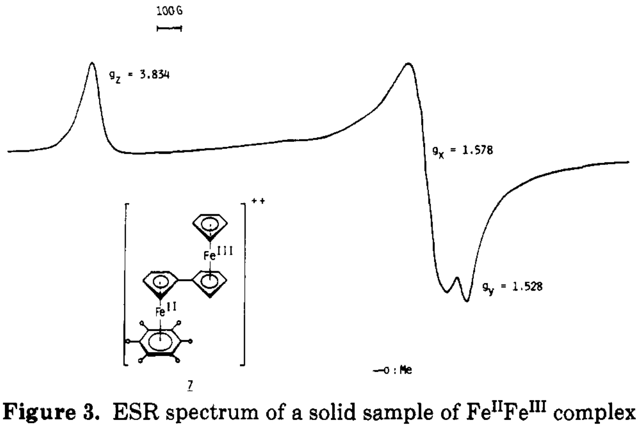


**Figure 3.** ESR spectrum of a solid sample of $Fe^{II}Fe^{III}$ complex **7** (4.2 K).

## Concluding Remarks

The dissymmetric series of dimeric sandwich complexes $[Fe_2(Fv)(Cp)(Ar)]^{n+}$ can be isolated in three redox forms,

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(12) The Mössbauer spectra of the $Fe^{II}Fe^{III}$ complexes are nearly the superposition of those of ferricinium[12a,b] and of $Fe^{II}(Cp)(arene)^+$;[12c] (a) Collins, R. L. *J. Chem. Phys.* **1965**, *42*, 1072. (b) Prins, R. *Mol. Phys.* **1970**, *19*, 603. (c) Stukan, R. A.; Vol'kenau, A. N.; Goldanskii, V. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, *8*, 1472.

(13) (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.

two of which (35e and 36e; $n$ = 1, 2) are thermally stable for Ar = $C_6H_6$, whereas arene permethylation also stabilizes the 37e form, as in the monometallic series. The fourth oxidation state, a 40e anion, is not isolable. It corresponds to an 18e ferrocenyl group attached to a 20e $[Fe(Cp)(Ar)]^-$ species.

In the class I mixed-valence complexes,[14] the electronic structures related to each oxidation state are already known.[13] The most remarkable feature is the cooperative interaction in the $Fe^IFe^{II}$ complexes in which the molecular $Fe^I$ structure is coupled with the lattice. This effect is observed in the variation of the quadrupole splitting with temperature. When no cooperative interaction is observed, i.e. in dilute frozen solutions or even in some solids, a Tanh law of thermal population of the upper Kramers' level is observed with a vibronic reduction factor of 0.2–0.3. On the other hand, many Jahn–Teller active $Fe^I$ compounds show deviation from the regular law, sometimes including breaks indicating phase transitions.[15] Indeed this is the case for **11** and **5**.

Finally, note that these dissymmetric dinuclear sandwich complexes are made of two units. The ferrocene/ferricinium fragment is an electrocatalyst for a number of organometallic reactions working with an oxidative induction.[16,17] The $[Fe(Cp)(Ar)]^{+/0}$ unit is an electrocatalyst for other inorganic and organometallic reactions proceeding by reductive induction.[16,18] Since photoexcited states are at the same time better oxidizing and reducing agents than the ground states, these bifunctional redox and electrocatalysts could find use in energy conversion devices.

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**Registry No.** **1**, 1287-38-3; **2**, 68499-72-9; **3**, 98162-01-7; **4**, 121072-54-6; **5**, 98162-02-8; **6**, 121072-55-7; **7**, 121072-56-8; **8**, 12176-31-7; **9**, 53702-66-2; $C_6Me_6$, 87-85-4.

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(14) (a) *Mixed Valence Compounds, Theory and Applications in Chemistry, Physics, Geology and Biology*; Brown, D. B.; Ed.; D. Reidel: Boston, 1980. (b) Allen, G. C.; Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 357. (c) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247. (d) Day, P. *Int. Rev. Phys. Chem.* **1981**, *1*, 149. (e) Wong, E. Y.; Schatz, P. N. *Prog. Inorg. Chem.* **1981**, *28*, 369. (f) Hush, N. S. *Mixed Valence Compounds*; Brown, D. B., Ed.; D. Reidel: Dordrecht, 1980; p 151.

(15) Varret, F.; Mariot, J.-P.; Hamon, J.-R.; Astruc, D. *Hyperfine Interact.* **1988**, *39*, 67.

(16) Astruc, D. *Angew. Chem.* **1988**, *100*, 662; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 643.

(17) (a) Desbois, M.-H.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1988**, 472. (b) Amatore, C.; Verpeaux, J.-N.; Madonik, A. M.; Desbois, M.-H.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1988**, 200.

(18) (a) Moinet, C.; Román, E.; Astruc, D. *J. Electroanal. Interfacial Electrochem.* **1981**, *121*, 241. (b) Darchen, A. *J. Chem. Soc., Chem. Commun.* **1983**, 768. (c) Ruiz, J.; Lacoste, M.; Astruc, D., in preparation. (d) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189.

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# Kinetic and Labeling Studies of the Formation and Trapping Reactions of Dimethylgermylene

Alan J. Shusterman,*,† Bruce E. Landrum, and Rebecca L. Miller

*Department of Chemistry, Pomona College, Claremont, California 91711*

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The kinetics of the thermal decomposition of 7,7-dimethyl-1,4,5,6-tetraphenyl-7-germabenzonorbornadiene (**1**) have been studied in the presence of excess styrene, 2,3-dimethylbutadiene, and $CCl_4$. At 78.3 °C the observed rate constant is $1.1 \times 10^{-3}\ s^{-1}$ and is independent of the initial concentrations of **1** and the other reagents indicating a first-order, unimolecular decomposition. The same rate constant is also obtained without any added reagents. Activation parameters for the decomposition are $\Delta H^{\ddagger} = 27.8 \pm 0.6$ kcal/mol and $\Delta S^{\ddagger} = 6.8 \pm 1.6$ eu. The parameters are consistent with rate-determining cleavage of a single bridgehead germanium–carbon bond to give a diradical intermediate. Generation of dimethylgermylene from **1** in the presence of excess (*E*)-2-deuteriostyrene yields cis and trans isomers of 2,5-dideuterio-1,1-dimethyl-3,4-diphenylgermacyclopentane. The site of the deuterium label is partially scrambled and can be rationalized by postulating acyclic diradical intermediates for the cycloaddition process.

## Introduction

Germylenes are logical intermediates for the synthesis of organogermanium compounds. A diverse set of germylenes are known, and they display high reactivity toward a variety of organic compounds.[1] Unfortunately, the mechanistic basis of germylene chemistry is still poorly understood making many germylene reactions unreliable for synthetic planning, including even the reaction of germylenes with alkenes. For example, one of the best studied germylenes, $GeCl_2$, reacts with alkenes by an unknown mechanism to give a variety of organogermanium products, including, in some cases, an alkene–germylene copolymer.[2]

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† Present address: Department of Chemistry, Reed College, 3203 S.E. Woodstock Blvd., Portland, OR 97202.

(1) (a) Satge, J.; Massol, M.; Riviere, P. *J. Organomet. Chem.* **1973**, *56*, 1. (b) Riviere, P.; Riviere-Baudet, M.; Satge, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 10.

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