

# From Organotransition-Metal Chemistry toward Molecular Electronics: Electronic Communication between Ligand-Bridged Metals<sup>†</sup>

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The molecular sciences of the transition metals have potential applications in a new fascinating field: molecular electronics.<sup>1,2</sup> This hope is based “*inter alia*” on the fact that the oxidation states of transition metals can be varied to a great extent and thus that many electron-transfer processes can result.<sup>2</sup> By suitable molecular engineering, it should become possible to assemble and tune molecular devices including transition metals and organize their interface with the macroscopic world. The interplay between light, electron transfer, and magneto-optic properties will then provide efficient and precise molecular sensors for the various needs of future technology.<sup>1–5</sup>

In this context, we wish to examine the electronic properties of simple bimetallic model systems and the electronic communication between the two metals across a delocalized bridging ligand in these molecules. This is the subject of the present Account, which will address the following questions: (i) Can one design simple ligand-bridged bimetallic complexes as good models for molecular conductors? (ii) What factors control the electronic communication between the two metals across a delocalized ligand? (iii) What are the consequences and applications of single- and multiple-electron transfers in such systems? (iv) Can the molecular electronics of hydrocarbon-bridged bimetallic complexes be, in turn, useful for their organometallic chemistry (i.e., synthesis, catalysis, and mechanistic studies)?

Electron-transfer processes between two redox centers have been examined with various linkers: simple inorganic atoms or ligands such as, for instance, pyrazine, 4,4'-bipyridine,<sup>6</sup> polyenes including  $\beta$ -carotene,<sup>7</sup> polyphenyls,<sup>8</sup> polyynes,<sup>9</sup> and polyaromatics.<sup>10</sup> Long-range electron-

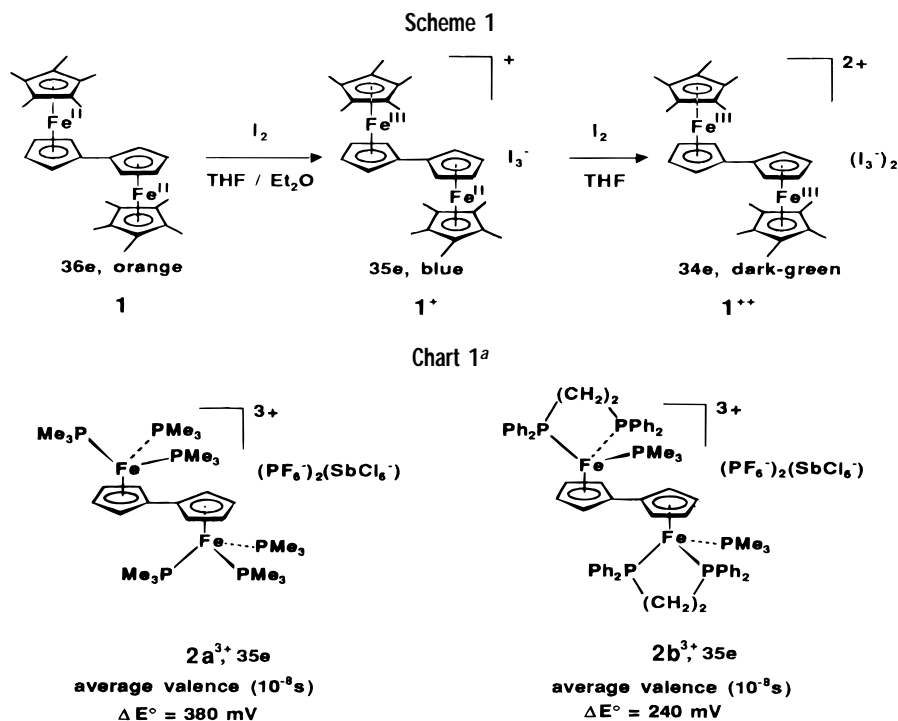
transfer studies have been especially useful for biological systems<sup>11</sup> including DNA;<sup>11f</sup> photoinduced electron-transfer studies have played a key role in providing high driving forces to test Marcus theory.<sup>12,13</sup> The pioneering work in the area of electronic communication between two metals has been reported by Taube with a series of diruthenium complexes following the famous pyrazine-bridged Creutz–Taube ion which allowed the distinction between trapped (class II) and detrapped (class III) mixed-valence compounds.<sup>6</sup> The second example, biferrocene,<sup>14</sup> is already a relatively good example for us to start with, having a single fulvalenyl bridge. Indeed, we will concentrate on

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<sup>†</sup> Abbreviations: Cp,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>; Cp\*,  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>; Fv,  $\mu_2, \eta^5, \eta^5$ -fulvalenyl unless noted otherwise.

- (1) (a) Balzani, V.; Scandola, F. *Supramolecular Chemistry*; Ellis Horwood: New York, 1991. (b) Balzani, V.; Moggi, L.; Scandola, F. In *Supramolecular Photochemistry*; Balzani, V., Ed.; Reidel: Dordrecht, The Netherlands, 1987; p 1. (c) *Molecular Electronics*; Launay, J.-P., Ed.; New J. Chem. **1991**, 15, 97.
- (2) (a) Astruc, D. *Electron Transfer and Radical Processes in Transition-Metal Chemistry*; VCH: New York, 1995. (b) Reference 2a, Chapter 4: Molecular Electronics.
- (3) (a) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995; Chapter 8: Devices.
- (4) (a) *Photochromism: Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990. (b) Czarnik, A. W. *Acc. Chem. Res.* **1994**, 27, 302. (c) James, T. J.; Limnane, P.; Shinkai, S. *Chem. Commun.* **1996**, 281.
- (5) (a) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993; Chapter 4. (b) Edmonds, T. E. *Chemical Sensors*; Blackie: Glasgow, U.K., 1988. (c) Atwood, J. L.; Holman, K. T.; Steed, J. W. *Chem. Commun.* **1996**, 1401.
- (6) (a) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, 95, 1086. (b) Taube, H. *Electron-Transfer Reactions of Complex Ions in Solution*; Academic Press: New York, 1970. (c) Taube, H. *Angew. Chem., Int. Ed. Engl.* **1984**, 23, 329. (d) Taube, H. *Science* **1984**, 226, 1028. (e) Creutz, C. In *Prog. Inorg. Chem.* Lippard, S. J., Ed.; Wiley: New York **1983**, 30, 1. (f) Reference 2, Chapter 1.
- (7) (a) Slama-Schwok, A.; Blanchard-Desce, M.; Lehn, J.-M. *J. Phys. Chem.* **1990**, 94, 3894. (b) Kanis, D. R.; Lacroix, P. G.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, 116, 10089. (c) Marder, S. R.; Cheng, L. T.; Tiemann, B. G.; Friedli, A. C.; Blanchard-Desce, M.; Perry, J. W.; Skindhoj, J. *Science* **1994**, 263, 511. (d) Etzenhouser, B. A.; Cavanaugh, M. D.; Spurgeon, H. N.; Sponsler, M. B. *J. Am. Chem. Soc.* **1994**, 116, 2221.
- (8) (a) Benniston, A. C.; Goulle, V.; Harriman, A.; Lehn, J. M.; Marczinke, B. *J. Phys. Chem.* **1994**, 98, 7798. (b) Collin, J. P.; Lainé, P.; Launay, J.-P.; Sauvage, J.-P.; Sour, A. *J. Chem. Soc., Chem. Commun.* **1993**, 434. (c) Sutter, J. P.; Grove, D. M.; Beley, M.; Collin, J. P.; Veldman N.; Spek, A. L.; Sauvage, J.-P.; van Koten, G. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 1282.
- (9) (a) Brady, M.; Weng, W.; Zhou, Y.; Seyler, J.; Amaroso, A. J.; Arif, A. M.; Böhme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, 119, 775. (b) Coat, F.; Lapinte, C. *Organometallics* **1996**, 15, 478. (c) Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, 117, 7129. (d) Harriman, A.; Ziessel, R. *Chem. Commun.* **1996**, 1707. (e) Bunz, U. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 969. (f) Lang, H. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 969.
- (10) (a) Crossley, M. J.; Burns, P. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1569. (b) Bänerle, P. *Adv. Mater.* **1992**, 4, 102.
- (11) (a) Beratan, D. N.; Betts, J. N.; Onuchic, J. N. *Science* **1991**, 252, 1285. (b) *Tunneling in Biological Systems*; Chance, B., De Vault, D., Frauenfelder, H., Marcus, R., Schrieffer, J., Sutin, N., Eds.; Academic Press: New York, 1979. (c) *Large-Range Electron Transfer in Biology, Structure and Bonding*; 1991; Vol. 75. (d) *Electron Transfer in Inorganic, Organic and Biological Systems*; Bolton, J. R.; Mataga, N., McLendon, G., Eds.; Advances in Chemistry Series 228; American Chemical Society: Washington, DC, 1991. (e) *Electron Transfer in Biology and the Solid State*; Johnson, M. K.; King, P. B.; Kurtz, D. M.; Kuttal, C.; Norton, M. L.; Scott, R. A., Eds.; Advances in Chemistry Series 226; American Chemical Society: Washington, DC, 1990. (f) Barton, J. K.; Hall, D. B.; Holmlin, R. E.; Turro, N. F. *Nature* **1996**, 382, 731.
- (12) (a) *Photoinduced Electron Transfer*; Fox, A. M.; Chanon, M., Eds.; Elsevier: Amsterdam, 1988. (b) Julliard, M.; Chanon, M. *Chem. Rev. (Washington, D.C.)* **1983**, 83, 425.
- (13) Reviews: (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, 811, 265. (b) Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **1988**, 27, 1227.
- (14) (a) Cowan, D. O.; Kaufman, F. *J. Am. Chem. Soc.* **1970**, 92, 219. (b) Mueller-Westerhoff, U. T. *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 702.

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bimetallic compounds bridged by a single planar hydrocarbon ligand such as fulvalenyl, biphenyl, or a polyaromatic hydrocarbon.

## Bi-sandwich Fulvalenyl Complexes Involving Redox Cascades and Average-Valence Systems

Although biferrocene itself is a trapped (class II) mixed-valence complex,<sup>14</sup> Hendrickson's group showed that dialkyl derivatives are often detrapped on the Mössbauer time scale ( $10^{-8}$  s).<sup>15</sup> The balance between the two classes is subtle on this time scale and depends on the nature of the alkyl group and counteranion. In some rare occasions, the trapped mixed valency can be shown by X-ray crystallography<sup>15b,16</sup> as, in decamethylbiferrocenium triiodide (Figure 1).<sup>16</sup> In this series, even the 34-electron (34e)  $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}$  dication could be stabilized, in contrast to the parent compound (Scheme 1).

The Mössbauer spectrum of  $1^+$  confirmed the trapped mixed valency and that of  $1^{2+}$  showed a single quadrupole doublet at 4.2 K with parameters typical of  $\text{Fe}^{\text{III}}$  (isomer shift,  $\text{IS} = 0.537 \text{ mm}\cdot\text{s}^{-1}$  versus Fe; quadrupole splitting,  $\text{QS} = 0.237 \text{ mm}^{-1}$  at 293 K) with a small antiferromagnetic coupling ( $\theta = -5.58 \text{ K}$ ).<sup>16</sup> On the other hand, when the fulvalenyl ligand bridges piano-stool units with three phosphine ligands as legs of each piano stool, the Mössbauer spectra of the mixed-valence  $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$  complexes shows only one quadrupole doublet with QS values intermediate between those of  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  complexes with similar geometries and ligands. These complexes ( $2\text{a}^{3+}$  and  $2\text{b}^{3+}$ , Chart 1) are thus detrapped on the Mössbauer time scale.<sup>17</sup> The complexes  $2^{2+}$  show two

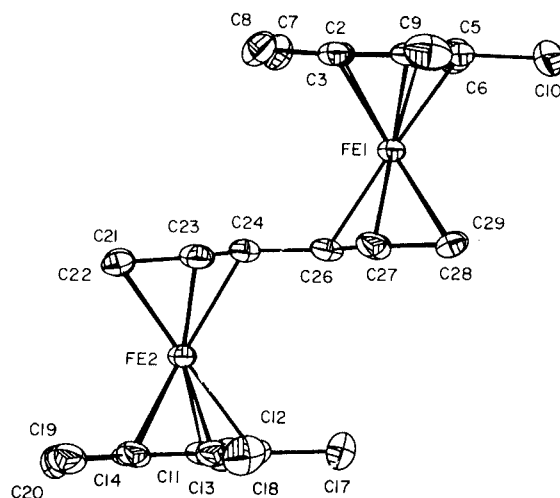


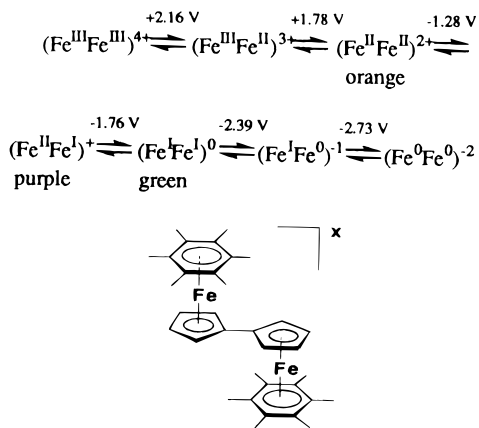
FIGURE 1. ORTEP drawing of the decamethylbiferrocenium salt  $1^+\text{I}_3^-$  at 295 K. The metrical details of the two metallocene moieties are inequivalent. Distances from the iron atoms to the least-squares mean planes of the two  $\text{C}_5\text{Me}_5$  rings are 1.669 and 1.712 Å; those from the iron atoms to the  $\text{C}_5\text{H}_4$ - rings are 1.651 and 1.697 Å. These are significantly different, indicating two distinct oxidation states for the iron in the dimer.

reversible oxidation waves, but the two reduction waves are partly ( $2\text{b}^{2+}$ ) or totally ( $2\text{a}^{2+}$ ) irreversible.<sup>18</sup>

When diiron-fulvalenyl complexes bear a third type of co-ligand, arenes, their redox chemistry is richer<sup>19</sup> than with the two above series  $1$  and  $2^{2+}$ , and these mixed-sandwich complexes show cascades of six single-electron waves, i.e., seven oxidation states ( $3\text{b}^x$ , Scheme 2) by cyclic voltammetry (CV).

- (15) (a) Hendrickson, D. N.; Oh, S. M.; Dong, T. Y.; Kambara, T.; Cohn, M. J.; Moore, M. F. *Commun. Inorg. Chem.* **1985**, 4, 329. (b) Dong, T. Y.; Kambara, T.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1986**, 108, 4423, 5857.  
(16) Delville, M.-H.; Robert, F.; Gouzerh, P.; Linarès, J.; Boukheddaden, K.; Varret, F.; Astruc, D. *J. Organomet. Chem.* **1993**, 451, C10.

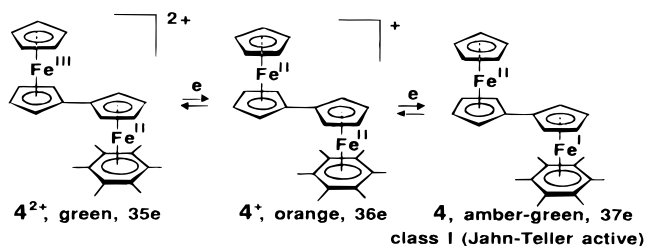
- (17) Lacoste, M.; Astruc, D.; Garland, M.-T.; Varret, F. *Organometallics* **1988**, 7, 2253.  
(18) Lacoste, M.; Delville, M.-H.; Ardoin, N.; Astruc, D. *Organometallics* **1997**, 16, 2343.  
(19) Desbois, M.-H.; Astruc, D.; Guillin, J.; Mariot, J.-P.; Varret, F. *J. Am. Chem. Soc.* **1985**, 107, 52.

Scheme 2<sup>a</sup>**3b : x = +4 to -2**

<sup>a</sup>  $E^\circ$  vs SCE, Pt,  $\text{SO}_2$  for oxidation of  $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ , DMF for reduction of  $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ , 0.1 M  $n\text{-Bu}_4\text{NPF}_6$  (refs 20 and 23b).

All the CV waves are chemically reversible. The last electron transfer is slow (heterogeneous electron-transfer rate constants are around  $10^{-3} \text{ cm}^2 \cdot \text{s}^{-1}$  with various arene ligands) which signifies stereoelectronic reorganization with partial decoordination of at least one of the ligands in the course of the reduction step  $3^+ \rightarrow 3^{2+}$ . It is remarkable that the framework remains intact upon such a series of five single-electron transfers. It is also noteworthy that the comproportionation constants  $K$  are very large for all the mixed-valence species ( $K > 10^5$ ),<sup>20</sup> which means that they are all detrapped. For instance, for the comproportionation  $3b^{2+} + 3b \rightleftharpoons 2 3b^+$ ,  $K = [3b^+]^2/[3b^{2+}] \times [3b] = (E_1 - E_2)F/RT = 1.5 \times 10^{10}$  at 293 K. The green 38e  $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$  and the purple 37e  $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$  complexes, synthesized from the  $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$  dicationic precursors by Na/Hg reduction, are thermally stable at 20 °C when the arene ligands are peralkylated ( $\text{C}_6\text{Me}_6$  or  $\text{C}_6\text{Et}_6$ ). The Mössbauer parameters are intermediate between those of  $\text{Fe}^{\text{I}}$  and  $\text{Fe}^{\text{II}}$ , which shows that the mixed-valence  $\text{Fe}^{\text{I}}/\text{Fe}^{\text{II}}$  monocations  $3^+$  are detrapped on the time scale of  $10^{-8} \text{ s}$ , with most spin density on the metals (for instance 42% on each Fe for  $3b^+$ ) without Jahn–Teller activity (vide infra). The green neutral complexes are genuine  $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$  biradicals (triplets) with, for **3b**, an antiferromagnetic transition coupled with a phase transition around 37 K.<sup>21</sup> The comparative study of the binding mode of the perpendicular C–H vibration of cyclopentadienyl rings by infrared spectroscopy for the  $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ ,  $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$ , and  $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$  complexes showed that the  $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$  complex  $3b^+$  only has a band at  $790 \text{ cm}^{-1}$ , an average position between those found for the  $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$  complex  $3b^{2+}$  ( $840 \text{ cm}^{-1}$ ) and the  $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$  complex **3b** ( $758 \text{ cm}^{-1}$ ), and therefore that the  $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$  complexes  $3^+$  are average-valence complexes (class III) even on the infrared time scale ( $10^{-13} \text{ s}$ ). In fact, from the difference between the redox potentials involved,<sup>22</sup> we noted that permethylation of the  $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$  system increases the delocalization, contrary to what happens in the ferrocenium series<sup>23c</sup> (vide supra, Scheme 1).

Scheme 3



In the series  $4^{n+}$  ( $n = 0-2$ ), the three oxidation states including the two mixed-valence  $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$  compounds are stable and could be isolated (Scheme 3). The ESR and Mössbauer spectra show class I mixed valency (i.e., the two redox centers have very different environments). Relatively little electronic communication proceeds via the fulvalenyl bridge and **4** is Jahn–Teller active, i.e. the lower level of Kramer's doublet is singly occupied. The Jahn–Teller activity is observed inter alia by the variation of the Mössbauer QS with temperature which corresponds to a thermal population of the upper level.<sup>24</sup>

These studies show that, with the same situation in complexes **1–4**, i.e. only one fulvalenyl bridge between two iron centers, the electronic communication can be extremely different from one case to the other, with the nature of the mixed valency being controlled by the co-ligands:

$4^{2+}$  and **4** (Cp, arene): class I  $< 1^+$  (2 Cp\*); class II  $< 2^+$  (6 PR<sub>3</sub>); class III ( $10^{-8} \text{ s}$ ,  $\Delta E^\circ = 0.24-0.38 \text{ V}$ )  $< 3^+$  (2 arenes); class III ( $10^{-13} \text{ s}$ ,  $\Delta E^\circ = 0.4-0.5 \text{ V}$ ).

## Bi-sandwich Biphenyl Complexes Involving $\text{Fe}^{\text{I}}$ : How to Understand and Design Fast Two-Electron Transfers (Scheme 4)

Although  $[\text{Fe}_2(\mu_2, \eta^{10}\text{-biphenyl})\text{Cp}_2]^{2+}$  (**5a**<sup>2+</sup>) is isoelectronic to, and an isomer of, **3a**<sup>2+</sup>, its CV is intriguingly simple (Figure 3, top), containing only a single wave at  $-30^\circ \text{C}$ , which contrasts with the redox cascade found for **3a**<sup>2+</sup> (Scheme 2). This wave is chemically and electrochemically reversible and corresponds to two electrons ( $\Delta E_p = 28 \text{ mV}$ ) by comparison with ferrocene or biferrocene. However, with the Cp\* analogue, **5b**<sup>2+</sup>, this wave is split into two close, reversible single-electron waves ( $\Delta E^\circ = 130 \text{ mV}$ ). The two-electron reduction (in THF) of **5a**<sup>2+</sup> using  $\text{LiAlH}_4$  at  $-30^\circ \text{C}$  and of **5b**<sup>2+</sup> using Na/Hg at  $20^\circ \text{C}$  gives deep-blue neutral diamagnetic complexes **5** (Scheme 4). The X-ray crystal structure of **5b** (Figure 2, left) shows that the biphenyl ligand has rearranged upon reduction to a bicyclohexadienylidene ligand coordinated in an  $\eta^5$  fashion to both iron atoms with a full double bond ( $1.37 \text{ \AA}$ ) between the two C<sub>6</sub> rings and a folding angle of  $25^\circ$ .<sup>25</sup> Although the two waves are close, the comproportionation constant is high enough ( $K = 172$  at  $20^\circ \text{C}$ ) to synthesize the mixed-valence complex **5b**<sup>+</sup> by reaction between **5b**<sup>2+</sup>

(20) Desbois, M.-H.; Astruc, D. *Organometallics* **1989**, *8*, 1841.

(21) Desbois, M.-H.; Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 460.

(22) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.

(23) (a) Delville, M.-H.; Rittinger, S.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1992**, 519. (b) Ruiz, J.; Astruc, D. Unpublished data.

(24) Desbois, M.-H.; Astruc, D.; Guillin, J.; Varret, F. *Organometallics* **1989**, *8*, 1848.

(25) (a) Lacoste, M.; Varret, F.; Toupet, L.; Astruc, D. *J. Am. Chem. Soc.* **1987**, *109*, 6504. (b) Astruc, D.; Lacoste, M.; Desbois, M.-H.; Varret, F.; Toupet, L. In *Paramagnetic Organometallic Species in Activation Selectivity and Catalysis*; Chanon, M., Ed.; Kluwer: Dordrecht, The Netherlands, 1988; p 245.

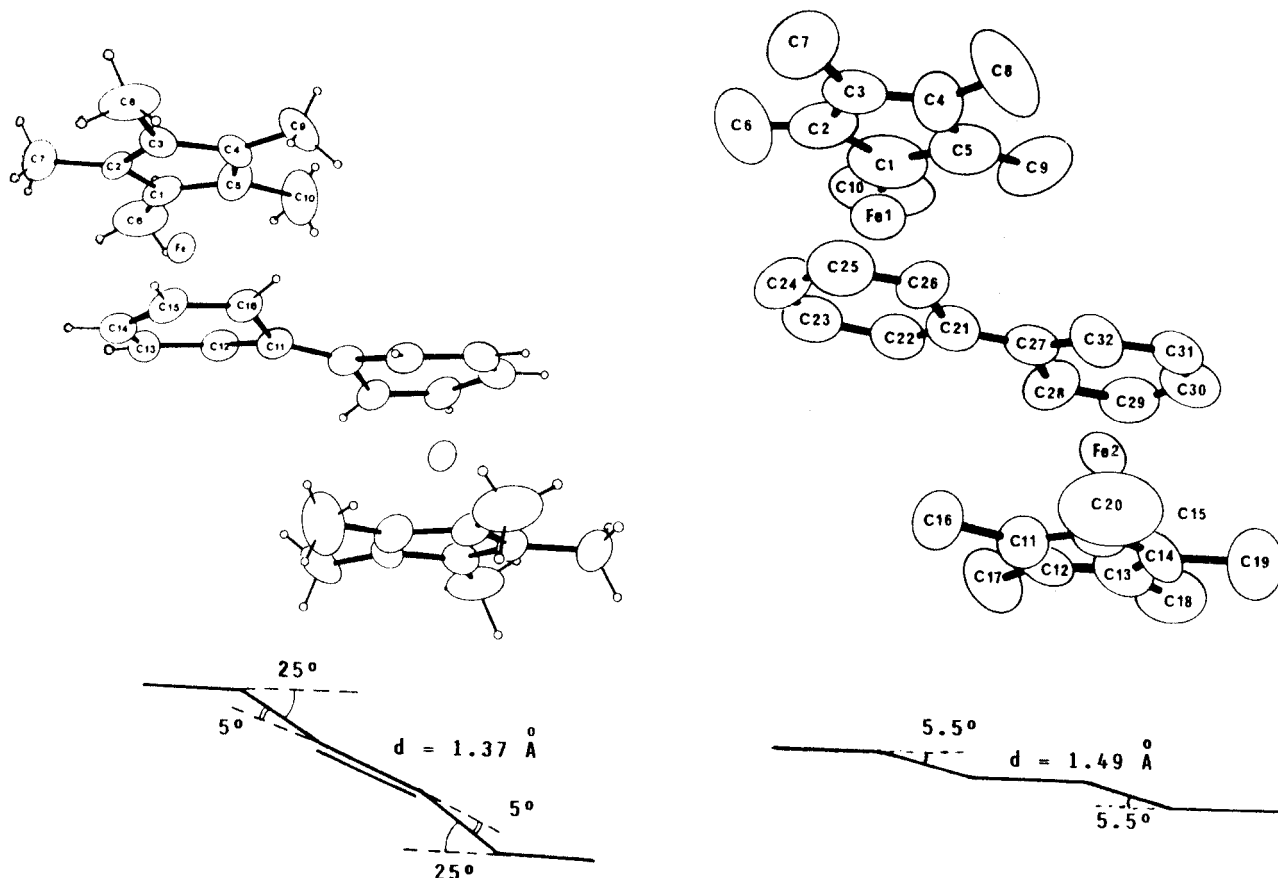
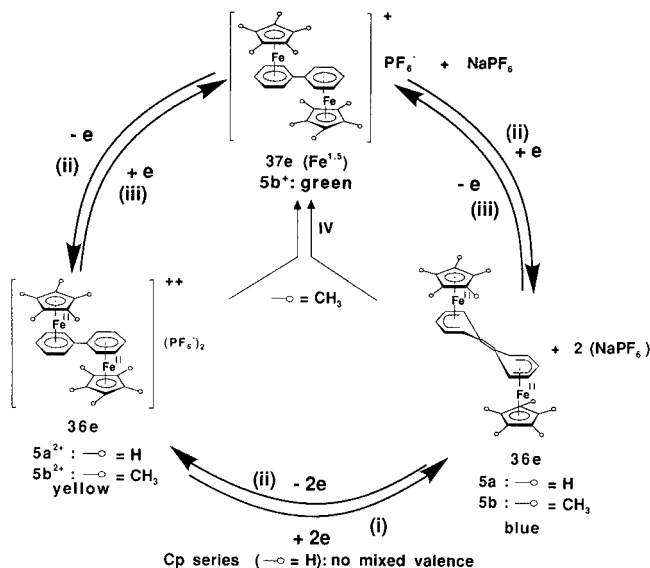


FIGURE 2. X-ray molecular structure of **5b** and **5b<sup>+</sup>** showing the distortion of the biphenyl ligands. Reproduced from ref 26a. Copyright 1990 American Chemical Society.

Scheme 4. ET Processes of Biphenyl Diiron Complexes in THF<sup>a</sup>



<sup>a</sup> (i) LiAlH<sub>4</sub>, -80 °C; (ii) O<sub>2</sub>, NaPF<sub>6</sub>; (iii) Na/Hg, 20 °C; (iv) comproportionation, 20 °C.

and **5b**. The X-ray crystal structure of the resulting green complex shows an almost completely flat biphenyl ligand coordinated  $\eta^6$  to both iron atoms (Figure 2, right). The zero-field Mössbauer spectrum of **5a<sup>+</sup>** shows only one doublet whose parameters are intermediate between those of Fe<sup>II</sup> and Fe<sup>I</sup>. Thus, **5b<sup>+</sup>** is a detrapped average-valence Fe<sup>I</sup>Fe<sup>II</sup> complex as is **3<sup>+</sup>**, and the rearrangement of the biphenyl ligand intervenes only in the second electron-transfer step **5b<sup>+</sup>**  $\rightarrow$  **5b** (Scheme 4).<sup>25,26</sup>

This structural reorganization proceeding in the course of the second electron transfer **5<sup>+</sup>**  $\rightarrow$  **5** stabilizes the neutral complexes **5**, and the stabilization energy shifts the standard redox potential  $E^\circ$  of the second CV wave toward a less negative value. To estimate this reorganization energy, we compare the CVs of **5a<sup>2+</sup>** and **5b<sup>2+</sup>** to those of **2a<sup>2+</sup>** and **2b<sup>2+</sup>**, which do not rearrange upon bielectronic reduction to **2**. The difference between the potential  $E^\circ$  of the first and second waves in the absence of rearrangement in **2a<sup>2+</sup>** is  $\Delta E^\circ = 0.32$  V and corresponds to the electrostatic energy. It is fully compensated by the rearrangement energy in **5a**, but not quite so in **5b**. For **5a**, the reorganization energy can thus be estimated at 0.32 V ( $\Delta G^\circ = -7.4$  kcal·mol<sup>-1</sup> = -30.9 kJ·mol<sup>-1</sup>). For **5b**, it is appropriate to compare the CV to that of [Fe<sub>2</sub>Fv(C<sub>6</sub>-Me<sub>6</sub>)<sub>2</sub>]<sup>2+</sup>, **3b<sup>2+</sup>**, for which  $\Delta E^\circ_2 = 0.48$  V. In the CV of **5b<sup>2+</sup>**,  $\Delta E^\circ_1 = 0.13$  V and we estimate the reorganization energy for **5b** to be  $\Delta E^\circ_2 - \Delta E^\circ_1 = 0.35$  V ( $\Delta G^\circ = -8.1$  kcal·mol<sup>-1</sup> = 33.9 kJ·mol<sup>-1</sup> (Figure 3)). The combination of X-ray data and CV's allows us to understand for the first time how a reversible, fast two-electron transfer is working in **5a<sup>2+</sup>**  $\rightarrow$  **5a** with the model **5b<sup>2+</sup>**  $\rightarrow$  **5b** which can be fully analyzed using the comparison with the pure electron-cascade models **3<sup>2+</sup>**  $\rightarrow$  **3**.<sup>25-27</sup> Previous organometallic examples of such fast two-electron transfers were known, but no

- (26) (a) Lacoste, M.; Rabaã, H.; Astruc, D.; Ardoïn, N.; Varret, F.; Saillard, J.-Y. Le Beuze, A. *J. Am. Chem. Soc.* **1990**, *112*, 9548. (b) Astruc, D.; Desbois, M.-H.; Lacoste, M.; Ardoïn, N.; Toupet, L.; Varret, F. *Mixed Valency Systems: Applications in Chemistry, Physics and Biology*; Prassides, K., Ed.; Kluwer: Dordrecht, The Netherlands, 1991; p 107. (27) Astruc, D.; Lacoste, M.; Toupet, L. *J. Chem. Soc., Chem. Commun.* **1990**, 558.

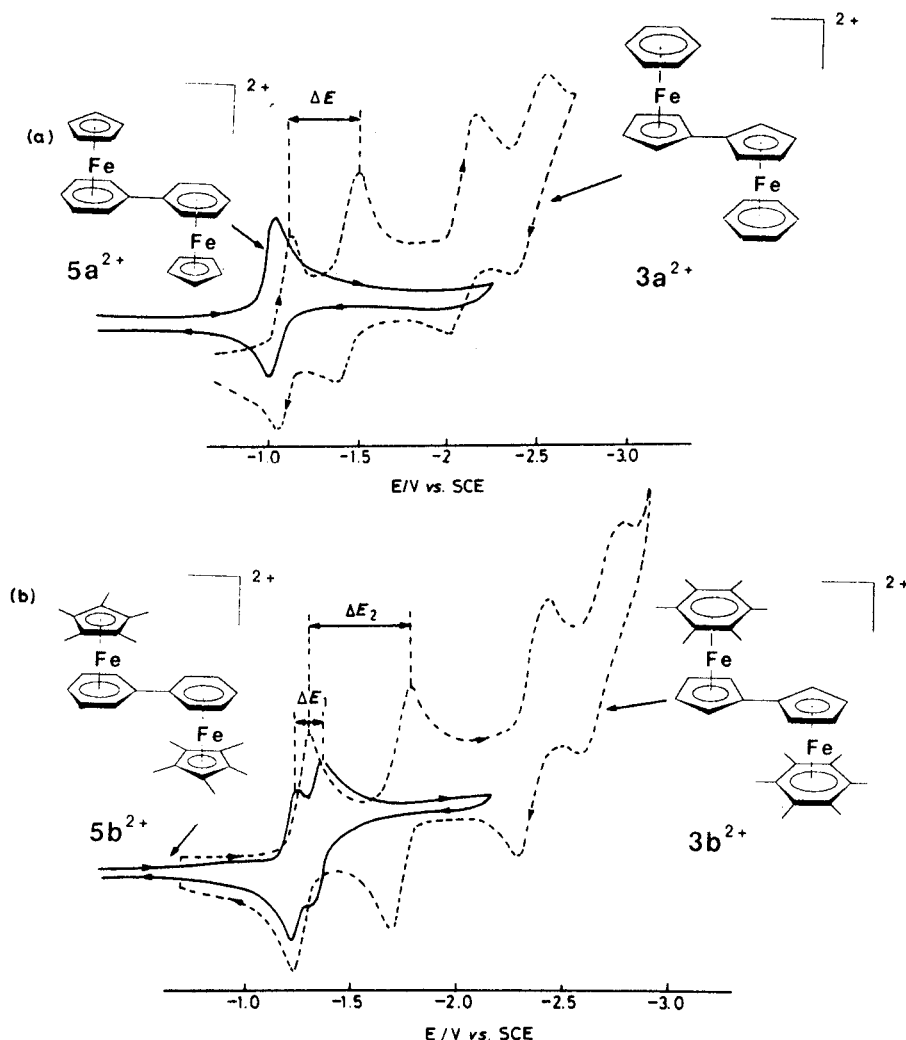
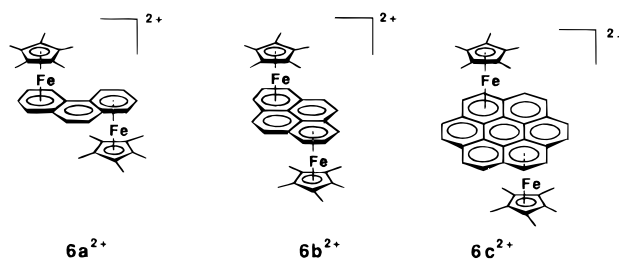


FIGURE 3. CV of (a) parent series,  $5a^{2+}$  (—) and  $3a^{2+}$  (---), and (b) permethylated series  $5b^{2+}$  (—) and  $3b^{2+}$  (---) ( $3.3 \times 10^{-5}$  M DMF solution; 0.1 M  $[n\text{-Bu}_4\text{N}]^+[\text{BF}_4]^-$ ; Hg cathode; scan rate  $0.4 \text{ V}\cdot\text{s}^{-1}$ ;  $-35^\circ\text{C}$ ). Rearrangement energy [parent series (a)] and  $\Delta E_2 - \Delta E_1$  [permethylated series (b)]. Reproduced with permission from ref 27. Copyright 1990 Royal Society of Chemistry.

X-ray data of intermediate mixed-valence systems could shed such light on the intimate mechanism.<sup>28–31</sup> Indeed, in a very similar example,  $[\text{Cr}_2(\mu_2, \eta^{10}\text{-biphenyl})(\text{CO})_6]^{2+}$ , it had been suggested<sup>28</sup> that the same rearrangement as in **5b** intervenes in the course of the first electron transfer  $[36e]^{2+} \rightarrow [35e]^+$ . Two fast, nearly simultaneous, one-electron-transfer processes play key roles in redox catalysis, for instance, in energy-conversion devices and biological systems.<sup>32</sup> Their understanding<sup>33</sup> and control should contribute to the design of new devices.

- (28) Milligan, S. N.; Riecke, R. D. *Organometallics* **1983**, 2, 171; **1987**, 6, 699.
- (29) (a) Finke, R. G.; Voegeli, R. H.; Laganis, E. D.; Boekelheide, V. *Organometallics* **1983**, 2, 347. (b) Plitzko, K. D.; Boekelheide, V. *Angew. Chem., Int. Ed. Engl.* **1987**, 26, 700.
- (30) Bowyer, W. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1985**, 107, 5657.
- (31) A 19e intermediate in a fast + slow electron-transfer couple has been observed by  $^1\text{H}$  NMR: Merkert, J.; Nielson, R. M.; Waever, M. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1989**, 111, 7084.
- (32) (a) Collman, J. P.; Wagenknecht, P. S.; Hutchinson, J. E. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 1537. (b) Kiwi, J.; Kalyanasundaran, K.; Grätzel, M. *Struct. Bonding* **1982**, 49, 37.
- (33) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, 24, 966. (b) Kojima, H.; Bard, A. J.; Wong, H. N. C.; Sondheimer, F. *J. Am. Chem. Soc.* **1976**, 98, 5560. (c) Ebersson, L. *Electron Transfer in Organic Chemistry*; Springer-Verlag: Berlin, 1987; p 101. (d) Katakis, D.; Gordon, G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1987; Chapter 7.10. (e) Lappin, G. *Redox Mechanisms in Inorganic Chemistry*; Ellis Horwood: New York, 1994; Chapter 5. (f) Reference 2, Chapter 7.

Chart 2



## Electronic Communication and Switch across Polyaromatic Ligands

Like fulvalene complexes  $3^{2+}$ , but contrary to the closely related biphenyl complexes  $5^{2+}$ , diiron polyaromatic complexes **6**<sup>2+</sup> (Chart 2) show extended redox cascades in their CV's, including the electrochemically irreversible fourth wave  $[\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}] \rightarrow [\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}]^{2+}$ , indicating some decoordination (**6a**<sup>2+</sup>, **6b**<sup>2+</sup>). Again, the purple mixed-valence  $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$  cationic complexes are stabilized by permethylation of the Cp ligands and detrapped on the Mössbauer time scale. The direduced neutral complexes are thermally stable up to  $-10^\circ\text{C}$ , and their ESR and Mössbauer spectra show that they are triplets ( $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$  biradicals). SCF MS-X $\alpha$  calculations, effected for the

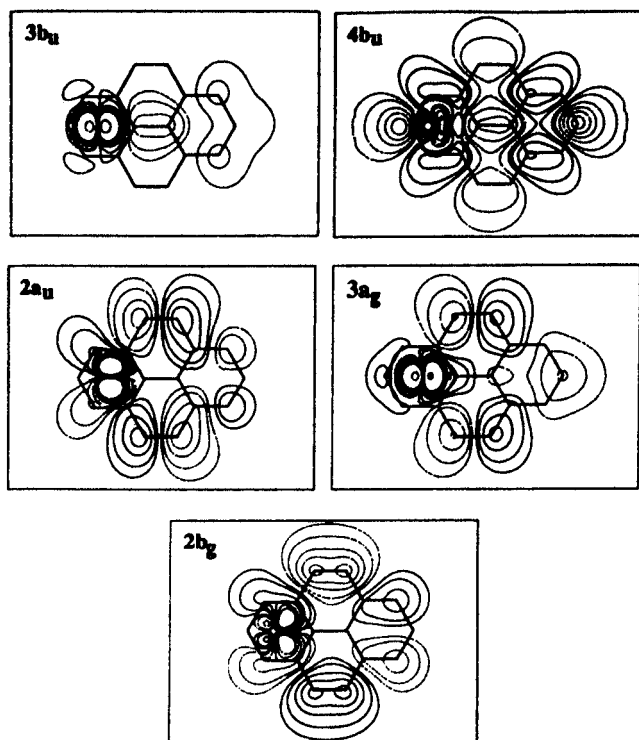


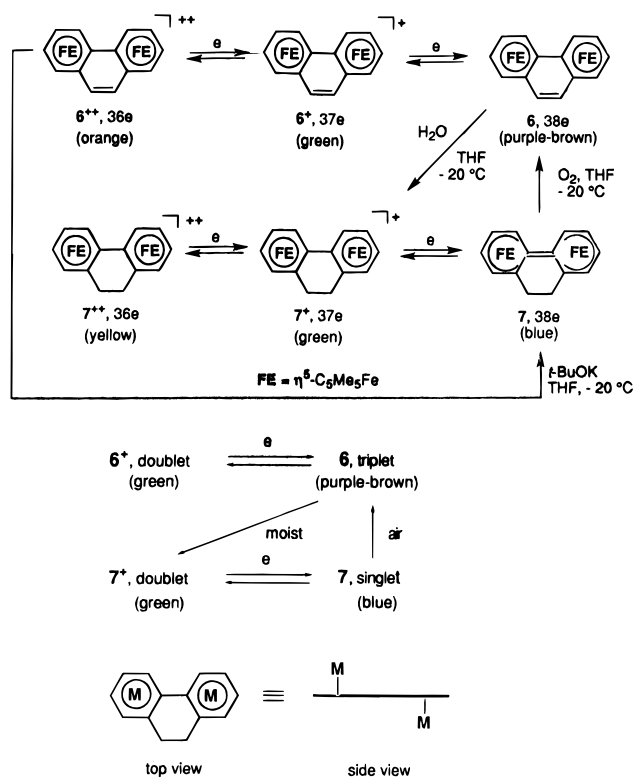
FIGURE 4. Contour plots of the HOMO and some lower unoccupied orbitals of  $6b^{2+}$  in a plane parallel to the pyrene ligand and situated midway between this ligand and one Fe atom. Reproduced from ref 34. Copyright 1995 American Chemical Society.

fulvalenyl, biphenyl, and pyrene complexes, are in accord with the proposed electronic structures (Figure 4).

The  $3a_g$  LUMO of the pyrene complexes  $6b^{2+}$  is equally distributed between the metals and the pyrene bridge, indicating that the unpaired electron(s) have both iron and pyrene character, as confirmed by the Mössbauer data.<sup>34,35</sup> This corroborates electrochemical and theoretical studies on the monoiron polyaromatic  $Fe^I$  complexes which show that the ligand character of the orbital of the unpaired electron increases as the polyaromatic ligand is more extended, thereby lowering its orbital energy levels.<sup>36</sup>

The borderline between the direduced biphenyl-type complexes, for which intramolecular ligand coupling to bicyclohexadienylidene occurs, and the direduced polyaromatic complexes  $6^{2+}$ , which show antiferromagnetic coupling, is found for the pair of ligands, dihydroanthracene (biphenyl group)/anthracene (polyaromatic group). Electronic communication, established between the two iron centers across the phenanthrene ligand, can be switched off by hydrogenation of **6** using water and THF in the dihydrophenanthrene complex **7** and switched on again by dehydrogenation of **7** with  $O_2$  (from air), giving back **6a** (Scheme 5).<sup>35</sup> Although the mechanism of the reaction  $6 \rightarrow 7^+$  has not been studied in detail, we believe that initial protonation of **6** at an  $Fe^I$  center by water is

Scheme 5. Redox Reactions of the Diiron–Phenanthrene Complexes<sup>a</sup>



<sup>a</sup> FE stands for the  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>Fe moiety.

followed by H shift from  $Fe^{III}$  to the closest benzylic phenanthrene carbon, and H atom abstraction from THF by the resulting radical.

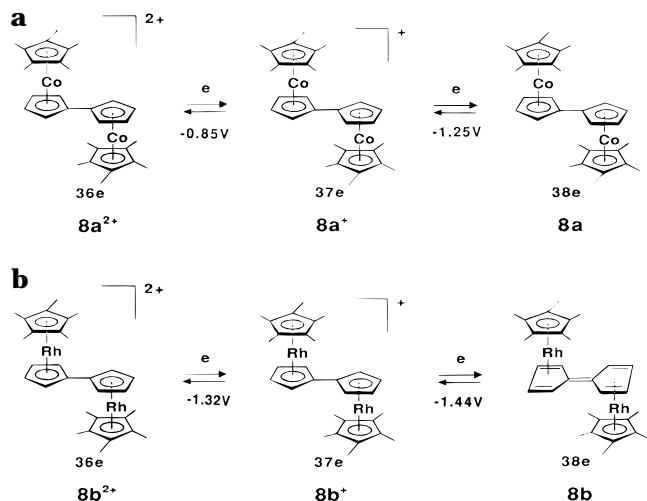
“Vertical” communication could also occur along the sandwich axis in the thermally unstable pink mixed-valence  $[Fe_2(2,2-p\text{-cyclophane})Cp_2]^{+}$ ,<sup>37</sup> attempts to synthesize the  $Cp^*$  analogue from the dicationic precursor gave instead intramolecular C–C bond formation<sup>36,38</sup> between the two arene ligands, favoring the diamagnetic direduced state as in **5**.<sup>36</sup>

## Electronic Flexibility: Fulvalenyl versus Fulvalene Bridging Ligand

From the fulvalenyl complexes **3**, we know that the fulvalenyl ligand can be an excellent ancillary transmitter of electronic communication without being involved by stereoelectronic perturbation. On the contrary, the biphenyl ligand can undergo a considerable stereoelectronic rearrangement in the direduced state for **5** and **7**, switching off the electronic communication between the two metal centers. The difference in behavior is partly due to the fact that the fulvalene orbitals have high energy levels which do not let them intervene in the coupling process. Can this situation be reversed by other choices of metals and ligands? A means to monitor the intramolecular C–C coupling phenomenon is to observe the separation between the  $E^o$  values of the two CV reduction waves of the 36e dications (cf. comparison between  $3a^{2+}$

- (34) Rabaâ, H.; Lacoste, M.; Delville, M.-H.; Ruiz, J.; Gloaguen, B.; Ardoin, N.; Astruc, D.; Le Beuze, A.; Saillard, J.-Y.; Linares, J.; Varret, F.; Dance, J.-M.; Marquestaut, E. *Organometallics* **1995**, *14*, 5078.  
 (35) Astruc, D.; Ruiz, J.; Lacoste, M.; Gloaguen, B.; Ardoin, N.; Linares, J.; Varret, F. *J. Chem. Soc., Chem. Commun.* **1995**, 1565.  
 (36) (a) Lacoste, M.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1987**, 667.  
 (b) Lacoste, M.; Rabaâ, H.; Astruc, D.; Le Beuze, A.; Saillard, J.-Y.; Précigoux, G.; Courseille, C.; Ardoin, N.; Bowyer, W. *Organometallics* **1989**, *8*, 2233.

- (37) Bowyer, W. J.; Geiger, W. E.; Boekelheide, V. *Organometallics* **1984**, *3*, 1979.  
 (38) Plitztko, K.-D.; Rapko, B.; Gollas, B.; Wehrle, G.; Weakley, T.; Pierce, D. T.; Geiger, W. E.; Haddon, R. C.; Boekelheide, V. *J. Am. Chem. Soc.* **1990**, *112*, 6545.

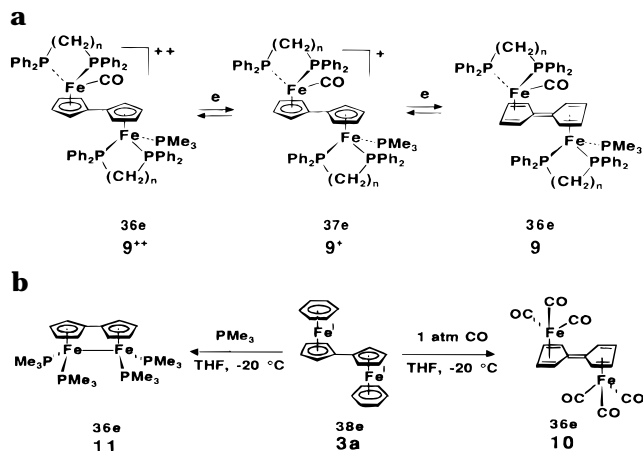
Scheme 6<sup>a</sup>

<sup>a</sup>  $E^\circ$  Values indicated below the arrows are given versus SCE using ferrocene as internal reference (Hg cathode, DMF, *n*-Bu<sub>4</sub>NBF<sub>4</sub>).

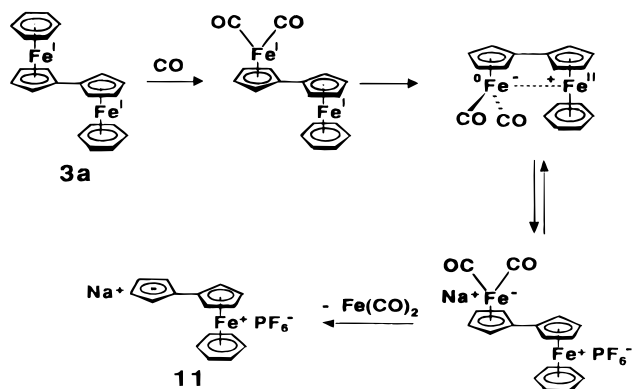
and 5<sup>2+</sup>). For instance, in the bicobaltocenium complex **8a**<sup>2+</sup>, we would expect a behavior similar to that of 3<sup>2+</sup> since 3<sup>2+</sup> and **8a**<sup>2+</sup> are isoelectronic. We indeed observe, for **8a**<sup>2+</sup>, a redox cascade similar to that of 3<sup>2+</sup> with large separation between the wave (also meaning stable, de-trapped average valences; Scheme 6a).<sup>39a</sup> On the contrary, for the analogous dirhodium complex **8b**<sup>2+</sup>, we know that one of the ligands bears the radical center, as in the single-electron reduction of rhodocenium cation, which is followed by dimerization via the Cp carbon bearing the radical center.<sup>39b</sup> Indeed, the two reversible single-electron reduction waves of **8b**<sup>2+</sup> are very close ( $\Delta E^\circ = 0.13$  V) as for 5b<sup>2+</sup>. This confirms that the electronic rearrangement  $\mu_2, \eta^{10}$ -fulvalenyl  $\rightarrow \mu_2, \eta^8$ -fulvalene intervenes in the course of the second single-electron step: **8b**<sup>+</sup>  $\rightarrow$  **8b**<sup>39a</sup> (Scheme 6b). The  $\mu_2, \eta^8$ -Fv ligand has already been characterized by X-ray in [Ni<sub>2</sub>Fv<sub>2</sub>].<sup>40a</sup> For this complex, one may retrospectively notice that its  $\Delta E^\circ$  value is indeed much lower ( $\Delta E^\circ = E^\circ(\text{Ni}_2\text{Fv}_2^{+/2+}) - E^\circ(\text{Ni}_2\text{Fv}^{0/+}) = 0.41$  V) than those of the Fe and Co bimetalloacenylene analogues ( $\Delta E^\circ = E^\circ(\text{Fe}_2\text{Fv}^{+/2+}) - E^\circ(\text{Fe}_2\text{Fv}^{0/+}) = 0.59$  V and  $\Delta E^\circ = E^\circ(\text{Co}_2\text{Fv}^{+/2+}) - E^\circ(\text{Co}_2\text{Fv}^{0/+}) = 0.87$  V).<sup>40b</sup> This keeps the same fulvalenyl ligands along the redox cascade, consistent with rearrangement fulvalenyl  $\rightarrow$  fulvalene for the dinickel sandwich only (Ni<sub>2</sub>Fv<sub>2</sub><sup>2+</sup>  $\rightarrow$  Ni<sub>2</sub>Fv<sub>2</sub>).

Even with the same metal (iron), it is possible to force this rearrangement by suitable choice of the co-ligands. The presence of at least one carbonyl ligand favors the Fe<sup>0</sup> oxidation state in **9** and **10** because it allows sufficient back-bonding, whereas the benzene ligands in **3** stabilize Fe<sup>I</sup> and let **3** escape the 18e rule. On the other hand, the  $\mu_2, \eta^8$ -Fv ligand would have allowed **3** to follow this rule. Thus, the CV of 9<sup>2+</sup> is analogous to that of 8b<sup>2+</sup> with two close single-electron reversible waves ( $\Delta E^\circ = 0.13$  V; Scheme 7a). Upon reaction with 1 atm CO at  $-20^\circ\text{C}$ , **3a** gives **9**, the substitution of the two benzene ligands by

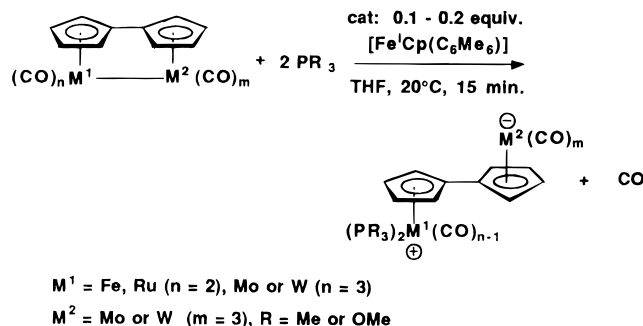
Scheme 7



Scheme 8



Scheme 9



six CO's being accompanied by the rearrangement of fulvalenyl to fulvalene (Scheme 7b). With PMe<sub>3</sub>, however, Fe<sup>0</sup> would be too electron-rich, and pseudo-Fe<sup>II</sup> is preferred in complex **11** (Scheme 7b, note that the fulvalenyl ligand forces the two 17e Fe<sup>I</sup> centers to couple to form **11**<sup>41a</sup> whereas, in the same reaction of [Fe<sup>I</sup>Cp(C<sub>6</sub>H<sub>6</sub>)], [Fe<sup>I</sup>-Cp(PMe<sub>3</sub>)<sub>2</sub>(H)] is obtained).

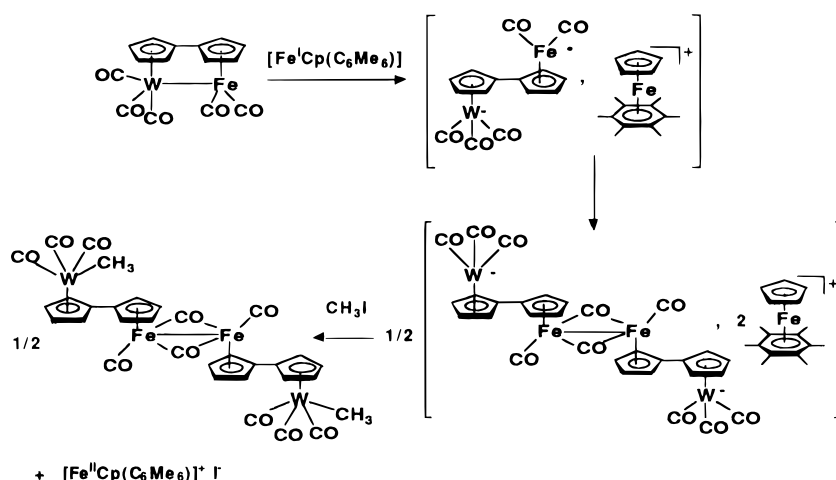
## Electron Transfer Across the Fulvalenyl Bridge between the Two Metal Centers in the Course of Reactions

**(a) Intramolecular Electron Transfer Induced by a Salt.** The reaction of **3a** with CO in Scheme 7b follows a totally

- (39) (a) Rittinger, S.; Buchholz, D.; Delville-Desbois, M.-H.; Linares, J.; Varret, F.; Boese, R.; Zolnai, L.; Huttner, G.; Astruc, D. *Organometallics* **1992**, *11*, 1454. (b) Fischer, E. O.; Wawersik, H. *J. Organomet. Chem.* **1966**, *5*, 559.
- (40) (a) Sharp, P. R.; Raymond, K. N.; Smart, J. C.; McKinney, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 753. (b) Geiger, W. E.; Connelly, N. G. *Adv. Organomet. Chem.* **1985**, *24*, 87.

- (41) (a) Delville-Desbois, M.-H.; Lacoste, M.; Astruc, D. *J. Am. Chem. Soc.* **1992**, *114*, 8310. (b) Astruc, D.; Delville, M.-H.; Ruiz, J. In ref 41c. (c) *Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds*; Pombeiro, A. J. L., Mc Cleverty, J. M., Eds.; NA ASI Series, Vol. 385; Kluwer: Dordrecht, The Netherlands, 1993; p 277. (d) Ruiz, J.; Lacoste, M.; Astruc, D. *J. Am. Chem. Soc.* **1990**, *112*, 5471.

Scheme 10



different course in the presence of Na<sup>+</sup>PF<sub>6</sub><sup>-</sup>. Instead of **10**, **11** is obtained after intramolecular electron transfer (disproportionation driven by Na<sup>+</sup>PF<sub>6</sub><sup>-</sup>, which irreversibly dislocates the intermediate ion pair, Scheme 8). With PMe<sub>3</sub>, the Na<sup>+</sup>PF<sub>6</sub><sup>-</sup>-induced disproportionation is intermolecular as in the mono-Fe<sup>I</sup> series and gives [Fe<sub>2</sub>-Fv(PMe<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>(PF<sub>6</sub><sup>-</sup>)<sub>2</sub> and [Fe(PMe<sub>3</sub>)<sub>4</sub>].<sup>18,41</sup>

**(b) Intramolecular Electron Transfer Induced Electrocatalytically.** The homo- and heterodinuclear complexes [MM'Fv(CO)<sub>n</sub>] undergo cleavage of the metal–metal bond and intramolecular electron transfer across the fulvalene bridge by reaction with PMe<sub>3</sub> or P(OMe)<sub>3</sub>. These reactions give zwitterions (Scheme 9)<sup>42</sup> and are catalyzed by a cathode or an electron-reservoir complex [Fe<sup>I</sup>(C<sub>5</sub>R<sub>5</sub>)-(C<sub>6</sub>R'<sub>6</sub>)] (R, R' = H, Me).<sup>43</sup> The choice of the electron-reservoir complex (i.e., R and R') is crucial to the success of the reaction since the initiation step must be exergonic or about isoergonic. For instance, with the RuW complex and PMe<sub>3</sub> in THF, initiation by [Fe<sup>I</sup>Cp(C<sub>6</sub>Me<sub>6</sub>)] gives the monophosphine adduct [FvRu<sup>+</sup>(CO)<sub>2</sub>(PMe<sub>3</sub>)W(CO)<sub>3</sub>]<sup>-</sup>, whereas initiation with the stronger reductant [Fe<sup>I</sup>(C<sub>5</sub>-Me<sub>5</sub>)(C<sub>6</sub>Me<sub>6</sub>)] gives the diphosphine adduct [FvRu<sup>+</sup>(CO)-(PMe<sub>3</sub>)<sub>2</sub>W(CO)<sub>3</sub>]<sup>-</sup>.<sup>44</sup> The synthesis of such zwitterionic organobimetallic complexes is of interest for the field of nonlinear optics.

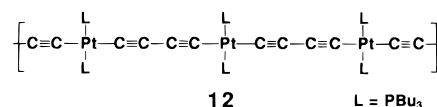
## Electronic Communication and Redox Recognition

The CVs of most homo- and heterobimetallic fulvalene carbonyl complexes show a single irreversible two-electron wave.<sup>40b,45</sup> Redox recognition upon reduction is observed, however, in the CV of [FeWFv(CO)<sub>5</sub>] (Fv = fulvalenyl, see Scheme 10), specifically generating the radical anion [Fe•W•Fv(CO)<sub>5</sub>].<sup>46</sup> This specificity is due to the regulation of the electronic communication between the two metals via the fulvalenyl bridge. Dimerization via the iron center

leads to the tetrametallic complex whose synthesis can be achieved using stoichiometric amounts of the electron-reservoir reagent [Fe<sup>I</sup>Cp(C<sub>6</sub>Me<sub>6</sub>)] (Scheme 10). A related strategy also led to the synthesis of tetrametallic Ru<sub>2</sub>W<sub>2</sub> derivatives.<sup>47</sup> Dimerization was known for the mononuclear complex [RhCp(CO)(PPh<sub>3</sub>)] whose oxidation forms [Rh<sub>2</sub>Fv(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>],<sup>48</sup> a series which has been further studied.<sup>49,50</sup>

## Conclusion and Prospects

Delocalized planar hydrocarbon ligands such as fulvalenyl, biphenyl, and polyaromatics provide an excellent electronic communication between two metals. The consequences of this electronic communication concern both the physical properties and the specific reactivity of the bimetallic complexes. With a suitable choice of co-ligands, delocalization of the mixed valences up to the infrared time scale can be observed. Under optimized conditions, these hydrocarbon-bridged bimetallic average-valence compounds are good models of molecular conductors. The design of molecular wires with long delocalized chains between two metals is an interesting extension, although the electronic coupling between the two metals always drops considerably as the hydrocarbon chain becomes longer. Perhaps the best solution for long molecular wires is to introduce metal relays with short hydrocarbon bridges as in the lyotropic Pt–alkyne polymers **12**.<sup>51</sup>



We have started to design organometallic switches with the phenanthrene system which are still at a rudimentary

- (42) Tilset, M.; Vollhardt, K. P. C.; Boese, R. *Organometallics* **1994**, *13*, 3136.  
 (43) Brown, D. S.; Delville, M.-H.; Boese, R.; Vollhardt, K. P. C.; Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 661.  
 (44) Brown, D. S.; Delville, M.-H.; Vollhardt, K. P. C.; Astruc, D. *Organometallics* **1996**, *15*, 2360.  
 (45) Moulton, R.; Weidman, T. W.; Vollhardt, K. P. C.; Bard, A. J. *Inorg. Chem.* **1986**, *25*, 1846.  
 (46) Delville-Desbois, M.-H.; Brown, D. S.; Vollhardt, K. P. C.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1991**, 1355.

- (47) Brown, D.; Delville-Desbois, M.-H.; Vollhardt, K. P. C.; Astruc, D. *New J. Chem.* **1992**, *16*, 899.  
 (48) McKinney R. J. *J. Chem. Soc., Chem. Commun.* **1980**, 603.  
 (49) (a) Connelly, N. G.; Lucy, A. R.; Payne, J. D.; Galas, A. M. R.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1983**, 1879. (b) Frieman, M. J.; Orpen, A. G.; Connelly, N. G.; Manners, I.; Raven, S. J. *Ibid.* **1985**, 2283. (c) Connelly, N. G. *Chem. Soc. Rev.* **1989**, *18*, 153.  
 (50) (a) Fonseca, E.; Geiger, W. E.; Bitterwolf, T. E.; Rheingold, A. L. *Organometallics* **1988**, *7*, 567. (b) Geiger, W. E.; Atwood, C. G.; Chin, T. T. In ref 41c, p 519.  
 (51) Kaharu, T.; Matsubara, H.; Takahashi, S. *J. Mater. Chem.* **1991**, *1*, 1 and references cited therein.



stage. Further coupling with light sensors, spin crossover systems, and other magnetic molecular materials will be challenging. It is now possible not only to observe redox cascades but also to turn them into polyelectronic steps, which should find applications in multielectron redox catalysis such as parts of energy-conversion devices. Another way to design molecular electron reservoirs with a large number of electrons provided at the same potential is the dendritic approach.<sup>52,53</sup> Finally, the electronic communication via delocalized ligands has consequences for the reactivity of these complexes, leading to the original synthetic applications indicated in the last sections. It is hoped that the bridges between organometallic chemistry

and molecular electronics will further inspire scientists to design new devices including catalysts and molecular materials with exceptional physical properties.

**Note Added in Proof:** An excellent review on metal–metal interactions in linked metallocenes very recently appeared: Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, 97, 637.

*This Account is dedicated to the memory of Dr. Nicole Ardoin (deceased April 12, 1997), an outstanding engineer and a major contributor in our research group since 1984. I also thank the talented researchers who are listed as coauthors of the publications emanating from this laboratory, especially Drs. M.-H. Delville-Desbois, M. Lacoste, and J. Ruiz (Bordeaux), Prof. F. Varret (Versailles), Prof. J. -Y. Saillard (Rennes), and Dr. D. Brown and Prof. K. P. C. Vollhardt (Berkeley). Financial support from the Institut Universitaire de France, the CNRS, the University Bordeaux I, the Région Aquitaine, the Humboldt Foundation, and Rhône-Poulenc is gratefully acknowledged.*

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- (52) (a) Ardoin, N.; Astruc, D. *Bull. Soc. Chim. Fr.* **1995**, 132, 875–909.  
 (b) Valério, C.; Fillaut, J.-L.; Ruiz, J.; Guittard, J.; Blais, J.-C.; Astruc, D. *J. Am. Chem. Soc.* **1997**, 119, 2588–2589.
- (53) Serroni, S.; Denti, G.; Campagna, S.; Juris, A.; Ciano, M.; Balzani, V. *Angew. Chem., Int. Ed. Engl.* **1992**, 31, 1493; *J. Am. Chem. Soc.* **1992**, 114, 2944.