

First Delocalization of a Mono-Fulvalene-bridged Mixed-valence Diiron Complex on the Infrared Time Scale

Marie-Hélène Delville, Stefan Rittinger and Didier Astruc

Laboratoire de Chimie Organique et Organométallique, URA CNRS 35, 351 Cours de la Libération, 33405 Talence Cédex, France

Measurement of the infrared $\nu_{\text{CH}(\text{Cp})}$ stretch around 800 cm^{-1} of the $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ ($q = 2$), $\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}$ ($q = 1$) and $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ ($q = 0$) states of $[\text{Fe}_2\text{Fv}(\text{C}_6\text{Me}_6)_2]^{q+}$ (Fv = fulvalene) and $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ ($q = 0$), $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ ($q = 1$) and $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}$ ($q = 2$) states of $[\text{Fe}_2\text{Fv}(\text{C}_5\text{Me}_5)_2]^{q+}$ shows that $\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}$ is delocalized whereas $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ is localized; the electrochemical E° values indicate that the cyclopentadienyl permethylation increases the delocalization in the arene series whereas it decreases it in the C_5Me_5 one.

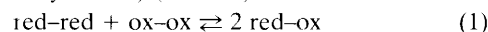
Mixed-valence states play an important role in many fields such as biochemistry, energy storage, molecular electronic materials and high temperature superconductivity and have attracted a renewed interest.^{1a} Since the establishment of the famous Robin and Day classification² based on the extent of the overlap between the metal orbitals containing the unpaired electron and the orbitals of the bridging ligand, there has been difficulty in assigning symmetrical dinuclear complexes as class II (localized) or class III (delocalized) as exemplified by the long controversy about the Creutz-Taube ion^{1c-e} $[\text{Ru}(\text{NH}_3)_5]_2(\mu^2\text{-pyz})$ (pyz = pyrazine). This is essentially due to the armada of specific techniques with various time scales which concerns *various states of samples*. It is indeed known that the cooperativity effects of solitons dramatically increase the tunnelling mechanism to overcome the intervalence barrier.³ Thus, according to the hypothesis suggested by Hush⁴ and illustrated by Hendrickson,³ infrared spectroscopy is considered as one of the most reliable criteria to distinguish between trapped class II and detrapped class III systems since the time scale is relatively short (10^{-12} s). Therefore, it has been employed to study valence localization in mixed-valence biferrocenes.^{3b} The perpendicular cyclopentadienyl C–H bending mode, for a Fe^{II} metallocene, typically occurs in a range from 805 to 815 cm^{-1} . The corresponding band for a Fe^{III} metallocene is found between 840 and 850 cm^{-1} . Thus, a trapped mixed-valence complex that has an appreciable potential energy barrier for intramolecular electron transfer would show perpendicular C–H bending bands for both oxidation states. Only one band is expected for detrapped valences.

Whereas considerable information,^{3,5} including excellent comprehensive reviews,^{5d} has appeared on the $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ biferrocene systems, only Mössbauer spectroscopy (10^{-7} s) has been applied to the $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$ systems. Indeed, the reduction of the g -tensor anisotropy, $\Delta g = g_{\parallel} - g_{\perp}$ for dimers as compared to monomers could not be used since the orbital angular momentum is already considerably reduced for CpFe^{I} arene (three g values very close to 2.0^6). As shown with the biferrocene series, Mössbauer spectroscopy can provide the conclusion of localization, delocalization or transition between the two at the 10^{-7} s time scale depending on the counter-anion, the mode of crystallization and the nature of the Cp substituents. Thus, it does not give the required intrinsic information on the molecular cationic biferrocenium system. Further, it has been demonstrated that compounds which transfer electrons faster than the Mössbauer time scale at 4.2 K are nevertheless found to be trapped on the infrared time scale.^{3b}

We now wish to report that the fulvalene bridged $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$ bisandwich complex $[\text{Fe}_2\text{Fv}(\text{C}_6\text{Me}_6)_2]^+\text{BF}_4^-$ is not only delocalized on the Mössbauer⁷ as already known but also on the infrared time scales. We also compare this later result with the infrared spectrum of the C_5 -permethylated analogue $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ complex $[\text{Fe}_2\text{Fv}(\text{C}_5\text{Me}_5)_2]^+\text{I}_3^-$ (ref. 8) and discuss the permethylation effect on the localization in each case.

In order to measure the infrared bending mode in the perpendicular C–H vibration region of Cp rings for the three oxidation states in the two $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$ and $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ series, we have synthesized them (red–red, red–ox, ox–ox) with counter-anions as BF_4^- and I_3^- salts^{7,8} to avoid any other stretches in the region under study. The results are gathered in Table 1.

Comparison of the results for monomers and dimers in both series illustrates the respective influences of the releasing and withdrawing substituents. The $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$ complex **1a**⁺ exhibits only one perpendicular bending mode at 790 cm^{-1} , a position intermediate between those of the parent dioxidized and direduced **1a**²⁺ and **1a**. This indicates that **1a**⁺ is delocalized valence (class III) on the IR time scale. On the other hand, **2a**⁺ exhibits a mixed valence behaviour (class II) since it shows two vibrations in the region studied at respectively 810 and 830 cm^{-1} , positions which are very close to those of **2a**²⁺ and **2a** (the electron releasing effect of the ferrocenyl group on the Fe^{III} moiety and the electron withdrawing effect of the ferrocenium group on the Fe^{II} sandwich are expected). So far, biferrocenium as well as substituted biferrocenium cations have all been found to be localized mixed-valence compounds exhibiting two infrared bending modes in the C-H_{\perp} region.³ Comparison of the localization magnitude in the present compound **2b**⁺ and on its permethylated analogue **2a**⁺ is of interest. Such information is available from the difference in standard potentials between the first and the second oxidation waves: $\Delta E^\circ = E^\circ(\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}) - E^\circ(\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}/\text{Fe}^{\text{I}}\text{Fe}^{\text{II}})$ determined by cyclic voltammetry. Indeed, four types of contribution to the free energy of disproportionation [eqn. (1)] have been recognized^{1d} [eqn. (2)]. All four factors are weak for class II but $\Delta G^\circ_{\text{D}}$ is large for class III: $\Delta G^\circ_{\text{D}} \approx F\Delta E^\circ \approx H_{\text{DA}}$ (adiabaticity matrix) (Table 2).



$$\Delta G^\circ_{\text{C}} = \Delta G^\circ_{\text{c}} + \Delta G^\circ_{\text{E}} + \Delta G^\circ_{\text{D}} + \Delta G^\circ_{\text{S}}$$

entropy electrostatic delocalization synergy

(2)

What emerges from Table 2 is that the permethylation of the ancillary ring increases the delocalization of the $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$ system and has an opposite effect on the delocalization of $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ complexes.

Table 1 Infrared bending mode in the 800 cm^{-1} region for **1a**^{q+} and **3a**^{q+} (Nujol) and **2a**^{q+} and **4a**^{q+} (KBr pellet) on a Perkin-Elmer 1450 spectrophotometer

$\nu_{\text{C-H}(\text{Cp}_{\perp})}/\text{cm}^{-1}$									
1a ²⁺	1a ⁺	1a	3a ⁺	3a	2a ²⁺	2a ⁺	2a	4a ⁺	4a
840	790	758	845	792	847	810 830	804	838	800

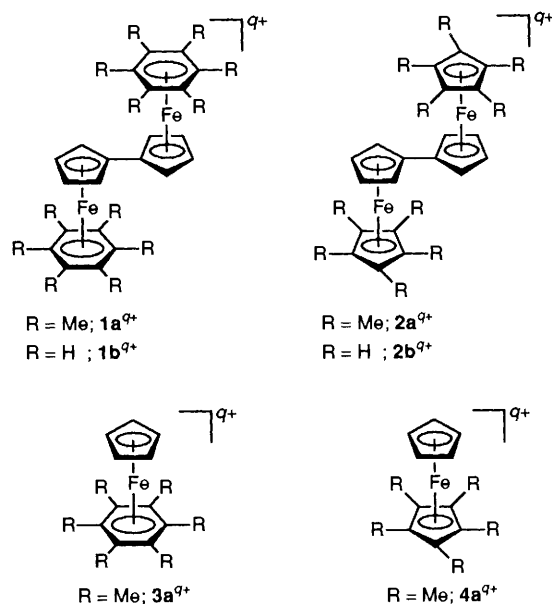


Table 2 Thermodynamic parameters for the comproportionation of $\mathbf{1a}^+$, $\mathbf{1b}^+$, $\mathbf{2a}^+$, $\mathbf{2b}^+$

	$\Delta E^\circ/\text{mV}$	K_C^c	$\Delta G_D/\text{kJ mol}^{-1}$
1a	480 ^a	1.31×10^8	46.32
1b	330 ^a	3.81×10^7	31.84
2a	240 ^b	1.14×10^4	23.16
2b	330 ^d	3.81×10^8	31.84

^a Ref. 7(b). ^b Ref. 8. ^c $\ln K_C = (n_1 E_1^\circ - n_2 E_2^\circ)F/RT [\Delta E^\circ (\pm 10 \text{ mV})]$.
^d Ref. 3(h).

This is understandable since different molecular orbitals are involved (e_1^* in Fe^{I} and e_2 in Fe^{III}). The former involves more ligand character than the latter which facilitates a super-exchange mechanism.

In conclusion we have demonstrated that besides the ferrocene series which needs *two* bridged fulvalene ligands to exhibit a delocalized behaviour on the infrared time scale, we have synthesized and fully characterized the first detrapped mixed-valence $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$ complex with only one bridge between the two monomers. We have noted the opposite effect permethylation of the ancillary ligand (C_5Me_5 or C_6Me_6) in the $\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}$ and $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ mixed valence complexes.

We thank the CNRS, the University Bordeaux I and the Région Aquitaine for financial support and the DFG for a post-doctoral fellowship to S. R.

Received, 30th December 1991; Com. 1/06469J

References

- (a) *Mixed Valence Systems: Application in Chemistry, Physics and Biology*, ed. K. Prassides, Kluwer Academic Press, Dordrecht, NATO ASI Series vol. 343, 1991; (b) H. Taube, *Pure Appl. Chem.*, 1985, **25**; (c) D. E. Richardson and H. Taube, *Coord. Chem. Rev.*, 1984, **60**, 107; (d) C. Creutz, *Prog. Inorg. Chem.*, 1983, **30**, 1; (e) A. Vogler and H. Kundely, *Comments Inorg. Chem.*, 1990, **9**, 201; (f) M. T. Pope and A. Muller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34; (g) S. B. Piepho, *J. Am. Chem. Soc.*, 1990, **112**, 4197.
- (a) M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **8**, 247; (b) P. Day, *Int. Rev. Phys. Chem.*, 1981, **1**, 149; (c) K. Y. Wong and P. N. Schatz, *Prog. Inorg. Chem.*, 1981, **28**, 369; (d) G. C. Allen and N. S. Hush, *Prog. Inorg. Chem.*, 1967, **8**, 357; (e) N. S. Hush, *Prog. Inorg. Chem.*, 1967, **8**, 391.
- (a) J. A. Kramer and D. N. Hendrickson, *Inorg. Chem.*, 1980, **19**, 3330; (b) T. Y. Dong, D. N. Hendrickson, C. G. Pierpont and M. F. Moore, *J. Am. Chem. Soc.*, 1986, **108**, 963; (c) R. J. Webb, A. L. Rheingold, S. J. Geid, D. L. Staley and D. N. Hendrickson, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1388; (d) R. J. Webb, S. J. Geig, D. L. Staley, A. L. Rheingold and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1990, **112**, 5031 and references cited therein; (e) D. N. Hendrickson, S. M. Oh, T. Y. Dong, T. Kambara, M. J. Cohn and M. F. Moore, *Comments Inorg. Chem.*, 1985, **4**, 329; (f) D. N. Hendrickson, *J. Am. Chem. Soc.*, 1991, **113**, 5031 and references cited therein; (g) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 1975, **14**, 955; (h) W. H. Morrison, S. Krogsrud and D. N. Hendrickson, *Inorg. Chem.*, 1973, **12**, 1998.
- (a) J. Baettie, N. S. Hush and P. Taylor, *Inorg. Chem.*, 1976, **15**, 992; (b) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, 1973, **95**, 1086.
- (a) D. O. Cowan and F. Kaufman, *J. Am. Chem. Soc.*, 1970, **92**, 1086; (b) D. O. Cowan and F. Kaufman, *J. Am. Chem. Soc.*, 1970, **92**, 6198; (c) I. Motoyama, K. Suto, M. Katada and H. Sano, *Chem. Soc. Jap., Chem. Lett.*, 1983, 1215; (d) for an electrochemical review, see W. E. Geiger and N. G. Connelly, *Adv. Organomet. Chem.*, 1985, **24**, 87 and references cited therein.
- (a) J.-R. Hamon, D. Astruc and P. Michaud, *J. Am. Chem. Soc.*, 1981, **103**, 758; (b) M. V. Rajesekharan, S. Giezynski, J. H. Ammeter, N. Ostwald, J.-R. Hamon, P. Michaud and D. Astruc, *J. Am. Chem. Soc.*, 1982, **104**, 2400.
- (a) M.-H. Desbois, D. Astruc, J. Guillin, F. Varret, A. X. Trautwein and G. Villeneuve, *J. Am. Chem. Soc.*, 1989, **111**, 5800; (b) M.-H. Desbois and D. Astruc, *Organometallics*, 1989, **8**, 1841.
- S. Rittinger, D. Buchholz, M.-H. Delville, J. Lineares, F. Varret, R. Boese, L. Zolnai, G. Huttner and D. Astruc, *Organometallics*, 1992, **11**, in press.