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Pronounced effect of interannular trimethylene bridges on the rate of intramolecular electron-transfer in mixed-valence biferrocenium salts. A novel electronic ground state of ferrocenium cations

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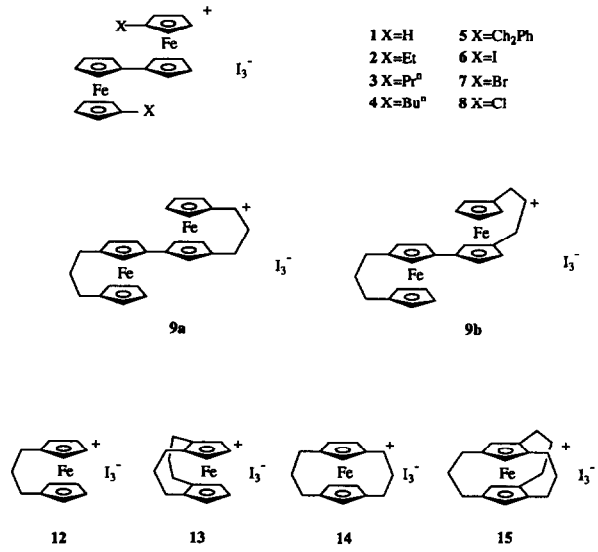
Abstract

X-ray structure determinations of two new constitutional isomers of biferrocene, the effects of interannular trimethylene bridges on intramolecular electron-transfer rates in the solid state, and characterization of the electronic ground state of a series of ferrocenium cations are reported.

Recently, there has been considerable progress in understanding the factors which control the rate of intramolecular electron transfer in the solid state for mixed-valence compounds [1–9]. The rates of electron transfer in mixed-valence cations **1–8** (Scheme 1) can be sensitively controlled by environmental factors. A recent interesting finding is that there is a significant influence on the electron-transfer rate in the mixed-valence biferrocenium salt **9** when the cyclopentadienyl (Cp) rings in each ferrocenyl moiety are linked by an interannular bridge [8,10]. Such a structural modification of the parallel relation between the two Cp rings around the Fe ion would lead to greater metal–ligand interactions as the rings tilt. However, there still remains one important question. At temperatures below 5 K compound **9** shows two doublets in the ^{57}Fe Mössbauer spectrum, one with a quadrupole splitting (ΔE_Q) of ~ 1.36 mm s^{-1} and the other with $\Delta E_Q = \sim 1.88$ mm s^{-1} [11]. There are two possible explanations for this ^{57}Fe Mössbauer spectrum. First, the Mössbauer results indicate that the valence state of iron atoms in compound **9** is localized on the Mössbauer time-scale (10^7 s^{-1}) in the solid state at 4.2 K. A second possibility is that the Mössbauer sample contained both **9a** and



Scheme 1.

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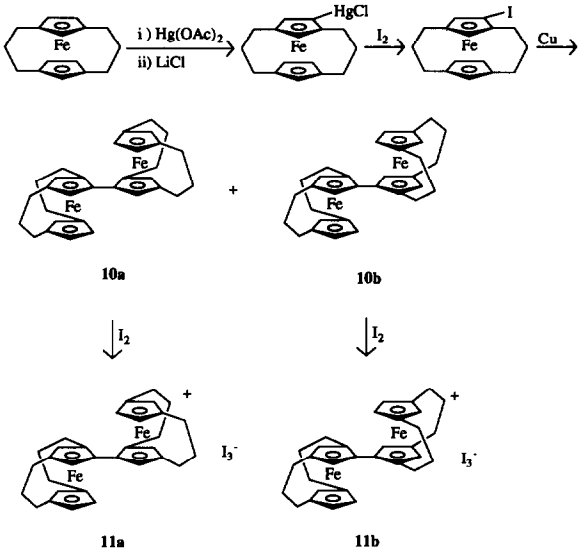

Scheme 2.

9b constitutional isomers in a 1 : 1 ratio. Unfortunately, a suitable crystal of **9** for X-ray determination could not be obtained. To study the effects of interannular bridges, we have prepared two new constitutional isomers **11a** and **11b** (Scheme 2), and determined the crystal structures of **10a**, **10b**, and **11a** (see Experimental section). We now show that there is a dramatic difference in electron-transfer rates between **9** and **11**. Additionally, the unusual physical properties of **11** are explained in terms of structural characteristics.

Our crystallographic study of **10a** shows that there are two crystallographically independent molecules in the unit cell and one of the molecular structures is shown in Fig. 1. There are very similar geometrical arrangements in the two independent molecules. In the case of **10b**, there are four crystallographically independent molecules in the unit cell. The average values of the dihedral angles between the two Cp rings of each ferrocene moiety in **10a** and **10b** are 10.3(2)° and 9.9(4)°, respectively. Furthermore, the two Cp rings in **10a** and **10b** are nearly eclipsed with an average staggering angle of 0.4(3)° and 1.4(5)°, respectively. The average distances from the iron atom to the centre of mass (COM) of the Cp ring are 1.604(3) and 1.606(4) Å for **10a** and **10b**, respectively. These values agree well with that in ferrocene (1.65 Å) [12]. An interesting finding is that the two Cp rings in the fulvalenide bridge are not coplanar. The average dihedral angles between the two Cp rings of the fulvalenide ligand in **10a** and **10b** are 56.1(2)° and 50.2(4)°, respectively. In the case of **1–8**, a *trans* conformation with a planar fulvalenide bridge has been observed [3,5,9]. We believe that this difference is mainly due to the steric effect of the interannular trimethylene bridge.

As shown in Fig. 1, the cation in **11a** has two dimensionally inequivalent metallocene units. The Fe^{II} moiety in the cation has an average iron–COM distance of 1.608(6) Å and the Fe^{III} moiety has an average distance of 1.658(6) Å. In agreement with the Mössbauer data for **11a** (*vide infra*), this suggests that the cation in **11a** is composed of Fe^{II} and Fe^{III} units. The dihedral angles between the Cp rings associated with atoms Fe1 and Fe2 are 11.2(5)° and 14.6(5)°, respectively. The two Cp rings of the Fe^{II} and Fe^{III} moieties are nearly eclipsed with an average staggering angle of 0.8(7)° and 2.1(7)°, respectively. Similarly, the two Cp rings in the fulvalenide ligand are not coplanar, with a dihedral angle of 42.0(5)°. The single-crystal

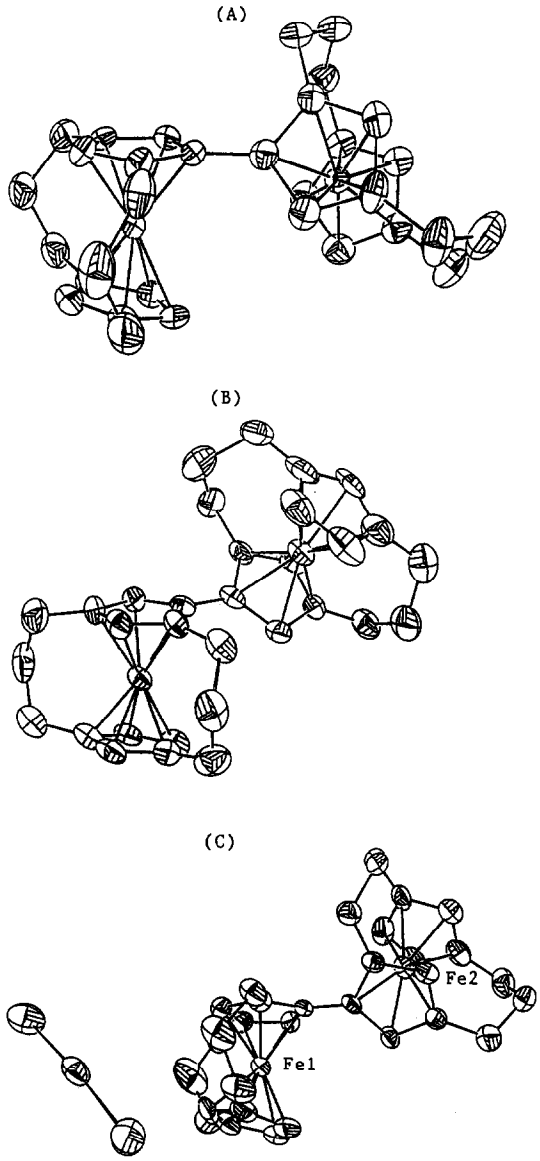

Fig. 1. Molecular structure of **10a** (A), **10b** (B) and **11a** (C).

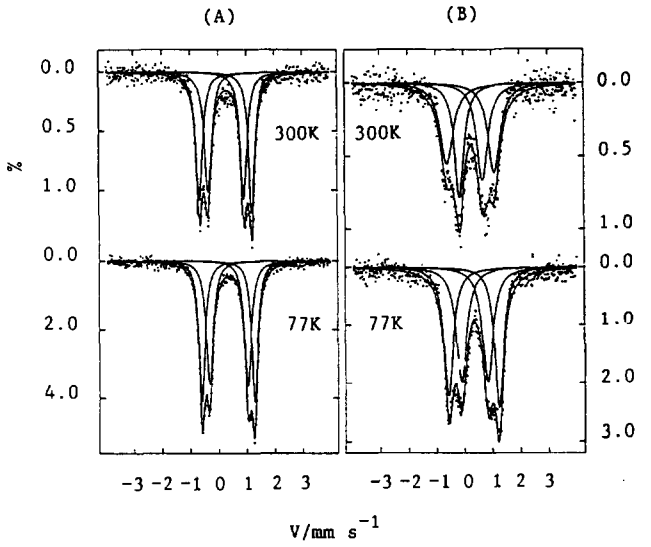

Fig. 2. ^{57}Fe Mössbauer spectra of **11a** (A) and **11b** (B).

X-ray determination of the structure of **11a** indicates that this mixed-valence cation has a localized electronic state. This is also consistent with our Mössbauer results.

As shown in Fig. 2, the Mössbauer results indicate that the valence states of the iron atoms in compounds **11a** and **11b** are localized on the Mössbauer time-scale (10^7 s^{-1}) in the solid state at 300 K. At temperatures below 300 K, the cations of **11a** and **11b** show two doublets in the ^{57}Fe Mössbauer spectra, one corresponding to the Fe^{II} and the other to the Fe^{III} site. Thus, there is a dramatic difference in electron-transfer rates between **9** and **11**. This is mainly due to the difference of coplanarity of the two Cp rings in the fulvalenide ligand in **9** and **11**. In **11** the π interaction between the two ferrocenyl moieties is destroyed as the linking bond of the two ferrocenyl units is twisted. From the Mössbauer studies, we can conclude that compound **9** has a localized electronic ground state at 4.2 K (electron-transfer rate $< 10^7$ s^{-1}). Of course, it is necessary to discuss why the ferrocenium moiety in **9** and **11** has an unusually large quadrupole splitting of ~ 1.37 mm s^{-1}. In general, ferrocenyl groups (electronic ground state $^1A_{1_g}$) give spectra characterized by large quadrupole splitting (ΔE_Q) in the range of 2.0 ~ 2.2 mm s^{-1}, while the spectra of the ferrocenium cations (electronic ground state $^2E_{2_g}$) are characterized by small or vanishing quadrupole splitting [3]. To study the influence of interannular trimethylene bridge on the electronic ground state of ferrocenium cation, we have prepared a series of model compounds **12–15** (Scheme 1). Surprisedly, a large quadrupole splitting is seen in the Mössbauer spectra of **13–15** at 300 K. The ΔE_Q values of **12–15** are 0.1484, 0.9357, 0.5414, and 0.6268 mm s^{-1}, respectively. The Mössbauer data clearly indicate that the electronic ground state of **13–15** is not a pure $^2E_{2_g}$ state. In compounds **12–15**, the Cp rings are tilted from the parallel geometry for ferrocenium. Bending back the Cp rings leads to an increase of $d_{x^2-y^2}$, d_{xy}-ring overlap. In other words, the metal nonbonding orbitals start to interact with the ligand π orbitals. Under these circumstances the iron ions lose some degree of their Fe^{III} character, and this results in an increase in ΔE_Q because each iron ion is closer to Fe^{II} in its properties. This is what we observe for compounds **9**, **11**, **13**, **14**, and **15**.

The cation in each of the compounds **11–15** serves as a very sensitive probe of the microscopic structure of the electronic state. Characterization of the electronic ground state in these cations by magnetic susceptibility and EPR and investigation of the counteranion effects on the rate of electron transfer in solid state are underway. Studies of the electron-transfer rates of **11a** and **11b** in the solution state and MO calculations of the theoretical values of ΔE_Q in the cations of **11–15** are also in progress.

1. Experimental section

All new compounds gave satisfactory spectroscopic and analytical data. Selected physical data: **10a**, m.p. 242 ~ 243°C; M^+, m/z 530; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.12 (s, 2H, Cp), 4.07 (s, 2H, Cp), 3.79 (s, 2H, Cp), 3.73 (s, 2H, Cp), 3.59 (s, 2H, Cp), and 2.2–1.4 (m, 24H, $-CH_2-$). **10b**, m.p. 192 ~ 193°C; M^+, m/z 530; ^{1}H NMR (500 MHz, $CDCl_3$) δ3.99 (s, 4H, Cp), 3.82 (s, 2H, Cp), 3.73 (s, 2H, Cp), 3.47 (s, 2H, Cp), and 2.3–1.4 (m, 24H, –CH2–). Crystal data [298 K, Enraf-Nonius CAD-4 diffractometer, Mo Kα radiation ($\lambda = 0.70930$ Å)], no crystal decay, full-matrix least-squares refinement with Fe, C, and I atoms anisotropic, during the final cycles of refinement fixed hydrogen contributions with C–H bond length fixed at 1.08 Å. **10a**, $C_{32}H_{34}Fe_2$, M = 530.31, triclinic, space group $P\bar{1}$, $a = 9.1435(13)$, $b = 15.0514(20)$, $c = 17.844(4)$ Å, $\alpha = 106.39(3)$, $\beta = 91.730(17)$, $\gamma = 90.756(24)°$, $U = 2354.3(7)$ Å^3, $Z = 4$, $D_c = 1.496$ g cm^{-3}, $F(000) = 1112$, $\mu = 1.25$ mm^{-1}, specimen $0.29 \times 0.28 \times 0.34$ mm, 6139 unique reflections for a 2θ limit of 44.9°, 4458 with $F_o^2 > 2.0\sigma(F_o^2)$ used in the refinement where $\sigma(F_o^2)$ was estimated from counting statistics. An absorption correction was applied; $R = 0.04$ and $R_w = 0.046$. **10b**, $C_{32}H_{34}Fe_2$, M = 530.31, triclinic, space group $P1$, $a = 9.2089(14)$, $b = 24.1318(24)$, $c = 24.501(4)$ Å, $\alpha = 116.808(9)$, $\beta = 87.980(12)$, $\gamma = 91.577(10)°$, $U = 4856.2(12)$ Å^3, $Z = 8$, $D_c = 1.451$ g cm^{-3}, $F(000) = 2224$, $\mu = 1.21$ mm^{-1}, specimen $0.43 \times 0.18 \times 0.19$ mm, 9860 unique reflections for a 2θ limit of 44.9°, 5334 with $F_o^2 > 2.0\sigma(F_o^2)$

used in the refinement. An absorption correction was made; $R = 0.038$ and $R_W = 0.041$. **11a**, $C_{32}H_{34}Fe_2I_3$, M = 911.02, monoclinic, space group $P2_1/c$, a = 11.3628(17), b = 13.6655(15), c = 19.753(3) Å, β = 104.793(12), U = 2965.6(7) Å^3, $Z = 4$, $D_c = 2.04$ g cm^{-3}, $F(000) = 1748$, $\mu = 4.09$ mm^{-1}, specimen 0.20 × 0.13 × 0.25 mm, 3866 unique reflections for a 2θ limit of 44.9°, 2296 with $F_o^2 > 2.0\sigma$ (F_o^2) used in the refinement. An absorption correction was applied; $R = 0.039$ and $R_w = 0.043$.

2. Supplementary material available

Tables of atomic coordinates, bond lengths and angles, thermal parameters, and structure factors for **10a**, **10b** and **11a** (109 pages) are available from the authors.

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