Angewandte Chemie

DOI: 10.1002/anie.200801124

Mixed Valency

Synthesis of the Prototypical Cyclic Metallocene Triad: Mixed-Valence Properties of [(FeCp)$_3$(trindenyl)] Isomers[**]

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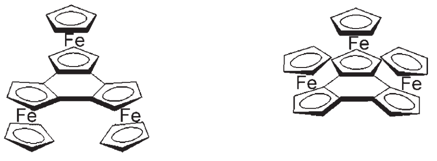
Mixed-valence compounds, which have at least two redox sites in different oxidation states linked by a bridging ligand that promotes electron transfer from one site to the other, are excellent benchmarks for the study of intramolecular electron transfer.[1] Transition metal complexes that display multielectron redox chemistry are therefore attracting much interest due to their potential applications in molecular materials for catalysis and electronics.[2] In particular, compounds containing multiple ferrocene (Fc) units are suitable models since these units display versatile organic chemistry and a well-defined redox behavior.[3–5]

Although there have been many reports of biferrocenyl complexes,[1c,3,5] experimental[6] and theoretical[7] studies on oligoferrocene systems are relatively scarce despite their potential to highlight those factors that influence the mechanistic pathway of intercomponent electron transfer.

A powerful probe for evaluating the magnitude of the metal–metal interaction in mixed-valence compounds involves analysis of the intervalence-transfer (IT) absorption bands in the near-IR region.[8] Specifically, investigations on the three families (linear, cyclic, and star-shaped) of triferrocenyl systems[9] should provide a means of bridging the gap between the interpretation of the electron-transfer process in simple bimetallic molecules and that in multi-component systems. However, very few electrochemical and spectroscopic studies have been reported on cyclic ferrocenyl triads in which rigid, two-dimensional C_3-arrays are defined by directly linking three cyclopentadienyl (Cp) groups.[10]

The trindene trianion (Td), the smallest C_3-symmetric polycyclic conjugated hydrocarbon, was synthesized by Katz and Ślusarek in 1980.[11] The use of Td as a metal bridging ligand is particularly favorable because strain is minimal as a consequence of the presence of only five- and six-membered rings. In spite of this, no trimetallocene complexes of Td have been reported[11] and only a handful of homo- and heterotrimetallic derivatives of [Re(CO)$_3$],[12] [Mn(CO)$_3$],[12] and [Rh(cod)][13] have been synthesized and studied by cyclic voltammetry (CV).[14]

Herein we report the synthesis of the first cyclic trimetallocene complexes of the trindenyl ligand, which is the prototypical cyclic metallocene triad. The two possible isomers, namely *syn,syn,anti*-[(FeCp)$_3$Td] (**1**) and *syn,syn,syn*-[(FeCp)$_3$Td] (**2**; Scheme 1) were obtained in a $^3/_1$ isomer ratio by an exchange reaction between K$_3$Td and [FeCp(η^6-fluorenyl)]. Crystals of **1** suitable for an X-ray analysis were obtained, while **2** was identified from the NMR spectra of the mixture.



1 **2**

Scheme 1. The *syn,syn,anti*-[(FeCp)$_3$Td] (**1**) and *syn,syn,syn*-[(FeCp)$_3$Td] (**2**) isomers.

The X-ray structure of **1**[15] and the calculated structure of **2** are shown in Figure 1. The structure of **1** shows that two ferrocenyl groups are disposed in a mutual *syn* orientation while the third is *anti* to them. The Cp rings are eclipsed in the *anti* ferrocenyl unit but are almost in a staggered conformation in the *syn* metal groups and are tilted by 5–7°. The highly resonant Td system is expected to be rigorously planar with a net aromatic geometry of the central phenyl ring. In contrast, the dihedral angles defined by the penta- and hexa-atomic

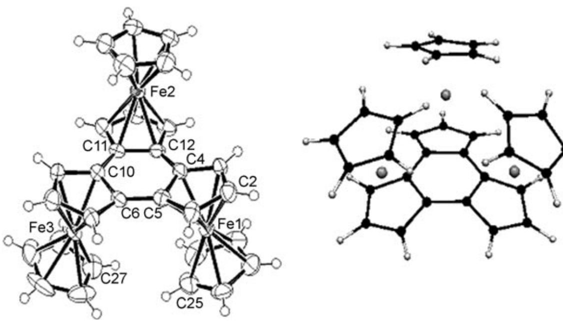


Figure 1. X-ray crystallographic structure of **1** (left) and DFT calculated geometry of **2** (right; white H, black C, gray Fe).

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[**] This work was supported by the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR) within PRAT 2006. CINECA (Consorzio di calcolo del Nord-Est, Casalecchio di Reno) is gratefully acknowledged for allowing access to its computational facilities (IBM SP5). Cp = C$_5$H$_5$.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200801124.

ring planes of Td (10.0(2)°, 2.56(2)°, and 13.3(2)° for Fe1, Fe2, and Fe3, respectively; Figure 1) show a notable deviation from the predicted planarity, mainly due to the need to relieve repulsive nonbonding interactions between the two ferrocenyl groups in the *syn* orientation. Rather short contact distances persist between the atoms despite these distortions (C27–C25 3.55 and H27–H25 2.39 Å). An inspection of the C–C distances of the central six-membered ring reveals a bond length alternation, with the C4–C5, C6–C10 (1.436(2) Å), and C11–C12 (1.435(2) Å) bonds being shorter than C5–C6 (1.471(2) Å), C10–C11 (1.456(2) Å), and C4–C12 (1.458(2) Å). Among the latter, the C5–C6 bond connecting the *syn* ferrocene moieties is consistently longer due to steric reasons, although electronic effects due to the triferrocene system cannot be excluded.

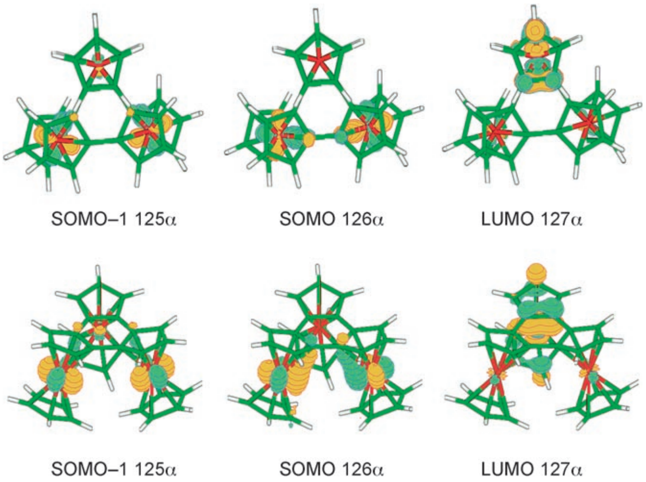

Figure 2. Kohn–Sham frontier molecular spin-orbitals of **1**$^+$ (above) and **2**$^+$ (below), the α levels are shown with their numbers. The density is 0.05 $(e a_0^{-3})^{1/2}$.

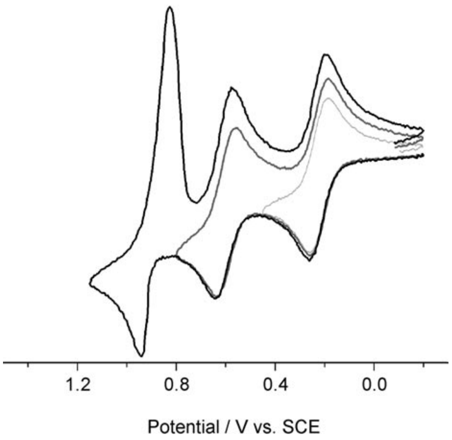

Figure 3. CVs at different potential scan reversals of 1.0×10^{-3} M **1** in CH_2Cl_2 at a Au disk electrode ($d = 0.5$ mm); scan rate: 0.5 V s^{-1}; T: 20 °C.

Complexes **1** and **2** were fully optimized at the B3LYP/SDD,6-31G(d,p) level of theory starting from the crystallographic structure and from a model molecule, respectively. The conformation of the Cp rings, the tilting of the *syn* {FeCp} groups (8°), and the bending of the aromatic Td ligand (5–6°) calculated for **1** are in agreement with the X-ray structure. In **2**, the Cp rings are all staggered, the {FeCp} groups are tilted by approximately 5°, and the Td ligand is bent by approximately 8°. The distances between the Fe atoms and the centroids of the coordinated Cp moieties are predicted to be only slightly longer in **2** than in **1** (0.01 Å). The Kohn–Sham frontier MOs in **1** are strongly metal centered, similar to those described for the bimetallic [(CpFe)$_2$(*as*-indacenediide)] isomers.[3b] The HOMO is formed mainly by $d_{x^2-y^2}$ and d_{xy} Fe atomic orbitals, while d_{xz} and d_{yz} contribute to the LUMO. The contribution of the Td π system to the HOMO and LUMO is limited to the lobes localized on the C atoms shared between the benzene and the *syn* ferrocenyl groups, which are combined in an antibonding and a bonding fashion, respectively. A similar composition of the frontier MOs is found for **2**. The most significant structural changes in **1** upon oxidation occur in the *anti* ferrocenyl unit, which suggests that the electron is removed from the d orbitals of this Fe atom. The Fe–Cp distance increases by around 0.05 Å; no variation is observed for the *syn* ferrocenyl groups. The spin density in **1**$^+$ is localized in the *anti* Fe nucleus (1.50 vs. −0.026 and −0.027) and an appreciable charge separation is also found ($\Delta q = 0.43$ and 0.49).

The Fe–Cp distance in **2**$^+$ increases in only one Fc unit (by around 0.07 Å), and the spin density values (1.51 vs. −0.028 and −0.027) and the charge separation ($\Delta q = 0.24$ and 0.25) are similar to those computed for **1**$^+$. Mixing of the frontier energy levels occurs in both **1**$^+$ and **2**$^+$, but the frontier spin-orbitals are still strongly metal d-based (Figure 2). These results indicate that the cations are valence-trapped species similar to the bis-iron indacenyl and fulvalenyl complexes.[3b]

The CV scan of **1** in CH_2Cl_2/[N*n*Bu$_4$][PF$_6$] proceeds in two well-defined and reversible (chemically and electrochemically) one-electron steps at $E_{1/2} = 0.23$ and 0.61 V vs. SCE due to the redox couples **1**/**1**$^{1+}$ and **1**$^{1+}$/**1**$^{2+}$. These steps are followed by a chemically irreversible and nondiffusion-controlled process ($E_p = 0.94$ V) with a typical stripping peak as its cathodic counterpart, thus showing that the trication **1**$^{3+}$ precipitates on the Au electrode (Figure 3). The value of $(\Delta E_{1/2})^{1+/2+}$ (380 mV) is indicative of the thermodynamic stability of the cationic species and the related value of K_c^1 [Eq. (1)] of the order of 10^6 suggests the possibility of being able to characterize the mixed-valence cation **1**$^+$ in solution.

$$[\mathrm{Fe^{II}{-}Fe^{II}{-}Fe^{II}}] + [\mathrm{Fe^{III}{-}Fe^{III}{-}Fe^{II}}] = 2\,[\mathrm{Fe^{II}{-}Fe^{III}{-}Fe^{II}}] \qquad (1)$$

In fact, stable solutions of **1**$^+$ in CH_2Cl_2, obtained by chemical oxidation with an equimolar amount of [FeCp$_2$][BF$_4$], could be analyzed at room temperature by optical spectroscopy. Two strong absorption bands with apparent maximum at around 5300 and 3490 cm^{-1} appear in the near-IR/IR spectral region (Figure 4). The assignment of these bands to **1**$^+$ was confirmed by stepwise spectroelectrochemical oxidation of **1** in the range 0.0–0.3 V. The chemical stability and reversibility (≥ 95 %) were verified by spectral recovery in an anodic/cathodic scan reversal.

Considerable complexity may be expected in the theoretical analysis of IT transitions in trinuclear complexes due to

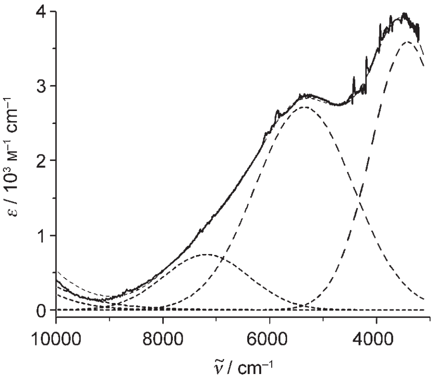

Figure 4. Near-IR/IR spectrum of the $\mathbf{1}^+$ cation in CH_2Cl_2 (solid line) and Gaussian deconvolution (dashed lines).

the presence of multiple electronically coupled redox centers. Classical and semi-classical models have both been widely applied to weakly coupled (localized) systems.[16] However, as the electronic coupling increases significantly (to almost delocalized and delocalized), the scenario of the classical model is no longer suitable and trinuclear complexes have been shown to manifest new properties that are definitely distinct from those of their corresponding dinuclear analogs[7] due to the possibility of itinerant "extra" electron hopping over the coupled sites.[17] More importantly, the influence of the third metal is such that within the three-site classical model the localized-to-delocalized transition is favored relative to the two-site case,[8a] although this effect has not been verified experimentally.[7]

Analysis of the spectrum of $\mathbf{1}^+$ (Figure 4) showed that the two observed bands correspond to the overlay of three IT bands, as shown by Gaussian deconvolution using the minimum number of sub-bands. Similarly, three IT bands have very recently been observed for Class II–III diiron[18] and diruthenium[1a] systems. The inclusion of the strong absorption band present in the visible spectrum at 615 nm (16260 cm^{-1}), whose tail is partially superimposed on that of the near-IR spectrum, significantly improved the fit and gave the $\tilde{\nu}_{max}$ values reported in Table 1.

As expected for an almost delocalized Class II–III mixed-valence system, the IT bands of $\mathbf{1}^+$ appear at low energy and are narrow and solvent-independent, as proved by marginal variations of the $\tilde{\nu}_{max}$ values upon changing the solvent polarity (see the Supporting Information). A Class II behavior has been observed for the structurally related bimetallic $[(CpFe)_2($*as*-indacenediide$)]$ isomers.[3b] The results for $\mathbf{1}^+$ suggest that introduction of the third fused Fc favors the localized-to-delocalized transition.

Table 1: Near-IR/IR data for cations $\mathbf{1}^+$ and $\mathbf{2}^+$ in CH_2Cl_2.

Complex	$\tilde{\nu}_{max}$ [cm^{-1}]	ε_{max} [M^{-1} cm^{-1}]	$(\Delta\tilde{\nu}_{1/2})_{obsd}$ [cm^{-1}]	$(\Delta\tilde{\nu}_{1/2})_{calcd}$ [cm^{-1}]	Γ
$\mathbf{1}^+$	3430	3590	1380	2790	0.51
	5310	2715	1740	3470	0.50
	7030	745	1780	3990	0.55
$\mathbf{2}^{+[a]}$	10480	1050	3350	4865	0.31

[a] Data obtained for a $^3\!/_2$ mixture of $\mathbf{1}^+$ and $\mathbf{2}^+$.

The value of the half-bandwidth $(\Delta\tilde{\nu}_{1/2})$ for binuclear, symmetrical and weakly coupled mixed-valence systems can be calculated by using the Hush relationship [Eq. (2)][16a] where E_0 represents the redox asymmetry. It has been reported that Equation (2) is applicable to oligoferrocenes.[19] Moreover, oxidation of the structurally correlated bimetallic isomers *anti*-$[(FeCp)_2($indacenediide$)]$ and *syn*-$[(FeCp)_2($indacenediide$)]$ occurs at almost identical potential.[3b] We can therefore assume with confidence that E_0 is almost zero for $\mathbf{1}^+$.

$$(\Delta\tilde{\nu}_{1/2})_{calcd}\ (\mathrm{cm}^{-1}) = [16\,RT\ln 2(\tilde{\nu}_{max}-E_0)]^{1/2} \qquad (2)$$

If we apply Equation (2) to examine the bands of $\mathbf{1}^+$, the calculated values of $\Delta\tilde{\nu}_{1/2}$ are in the range 2800–4000 cm^{-1}, much higher than the experimental values (Table 1). The narrowness of the IT bands can be rationalized by the parameter $\Gamma = 1-(\Delta\tilde{\nu}_{1/2})_{obsd}/(\Delta\tilde{\nu}_{1/2})_{calcd}$, which has been proposed by Brunschwig, Creutz, and Sutin[16c] as a criterion for the classification of mixed-valence systems. The mean value (0.52 ± 0.02) obtained for the three bands supports the assignment of *syn,syn,anti* cation $\mathbf{1}^+$ as a Class II–III mixed-valence system. Taken as a whole, the experimental results for $\mathbf{1}^+$ are consistent with fast electron transfer and valence-averaging on the near-IR/IR timescale (i.e. of solvent motion), with a negligible contribution of the solvent to the reorganization energy. As expected for a Class II–III regime, the solvent is averaged and the spin density, according to DFT calculations with $\mathbf{1}^+$, is localized.

The spectrum of a $^3\!/_2$ mixture of $\mathbf{1}^+$ and $\mathbf{2}^+$ was obtained under the same conditions. Subtraction of the absorption of $\mathbf{1}^+$ from the spectrum of the mixture revealed a well-defined band for $\mathbf{2}^+$ at higher energy (10480 cm^{-1}) and broader than those of isomer $\mathbf{1}^+$ in the visible/near-IR region (Figure 5, Table 1). The value of $\Gamma = 0.31$ for this band is indicative of a weaker metal–metal electronic coupling when the three irons are in a *syn,syn,syn* configuration. A similar behavior has been observed for bimetallic $[(CpFe)_2($*as*-indacenediide$)]$ isomers.[3b] The lowest absorption bands can confidently be assigned, on the basis of the features of the frontier Kohn–Sham MOs of $\mathbf{1}^+$ and $\mathbf{2}^+$, to metal–metal charge-transfer

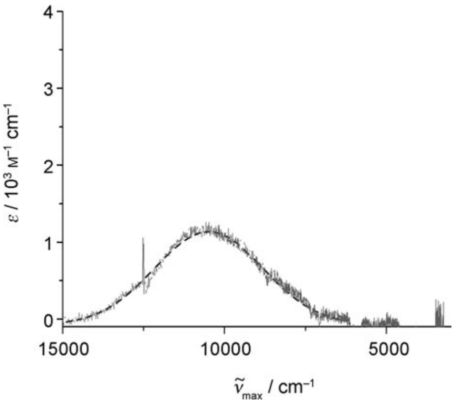

Figure 5. Visible/near-IR spectrum of $\mathbf{2}^+$ cation in CH_2Cl_2 (solid line) and Gaussian deconvolution (dashed line).

processes mainly involving the occupied SOMO and SOMO$-$1 and the empty LUMO (Figure 2).

In summary, the results reported herein provide important experimental evidence that the introduction of a third metal center increases the metal–metal interaction with respect to the structurally correlated binuclear systems.[3b] Moreover, the *syn*/*anti* isomerism of the third fused Fc group drives the Class II ($\mathbf{2}^{+}$) to borderline Class II–III ($\mathbf{1}^{+}$) transition.

Experimental Section

Full experimental details, including general and physical methods, the synthesis of **1**, **2**, $\mathbf{1}^{+}$, and $\mathbf{2}^{+}$, ESI mass and NMR spectra for **1** and **2**, UV/Vis and additional near-IR data for **1**, the packing diagram for **1**, relevant crystallographic interatomic distances and angles for **1**, the xyz coordinates of the DFT-optimized geometries, selected frontier Kohn–Sham MOs for **1**, **2**, $\mathbf{1}^{+}$, and $\mathbf{2}^{+}$, and computational details are available as Supporting Information.

Received: March 7, 2008
Revised: April 21, 2008

Keywords: anions · electron transfer · iron · metallocenes · mixed-valent compounds

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[15] CCDC 678528 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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