

A New Valence Tautomerism Example in an Electroactive Ferrocene Substituted Triphenylmethyl Radical

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Valence tautomeric complexes combining an acceptor and a donor group interconvert reversibly between two or more electronic isomers with different charge (and spin) distributions because of an intramolecular electron-transfer process.¹ Such a process takes place in response to different external stimuli, such as temperature, pressure, or irradiation, and gives rise to electronic isomers that show different optical and magnetic properties.² This fact converts valence tautomeric complexes as excellent candidates for molecular bistability.³ However, even though a large number of valence tautomeric complexes have been synthesized and studied, the variety of such compounds is fairly limited, since most of them are based on transition metal complexes with quinone or quinone-type redox active ligands.^{3,4} For this reason, and considering the enormous interest and perspectives of bistable molecular nano-objects, the synthesis of new valence tautomeric molecules has become an objective of current interest. Here we report for the first time a new type of valence tautomeric compound, the radical **1**, that combines an electron acceptor organic radical unit covalently linked, through an ethylenic spacer, to a ferrocene moiety that acts as the donor group. Reversible interconversion between the two distinct electronic isomers of the open-shell compound **1** (Scheme 1) is thermally induced, as ascertained by Mössbauer spectroscopy.

Radical **1** was obtained as a dark brown microcrystalline solid using the synthetic procedure previously reported.⁵ Additional characterization by different techniques such as MALDI-TOF/MS, HPLC, cyclic voltammetry, UV-vis-NIR, and X-ray diffraction was successfully completed. Single crystals were grown by slow evaporation from a dichloromethane/hexane (1:1) mixture and used for its X-ray crystal determination.⁶ An ORTEP view of **1** is shown in Figure 1. The structure reveals almost eclipsed cyclopentadienyl rings and a *trans* configuration for the CH=CH unit. Despite the available resonance pathway between the radical and ferrocene units and the *trans* configuration of the CH=CH spacer, the C₆Cl₄ ring is twisted by an angle of ~45° with respect to the spacer, probably because of the electronic interactions between the CH=CH hydrogen and the *ortho* chlorine atoms of the benzene ring causes this lack of planarity. Remarkable is the broad intervalence transition band shown by radical **1** at 1020 nm in the solid state, revealing that an intramolecular electron-transfer process is induced by light irradiation.

Our interest in compound **1** was considerably enhanced when it was found that the ⁵⁷Fe Mössbauer spectrum of **1** in solid state exhibited a temperature-dependent behavior in agreement with the observation of a temperature-dependent intramolecular electron

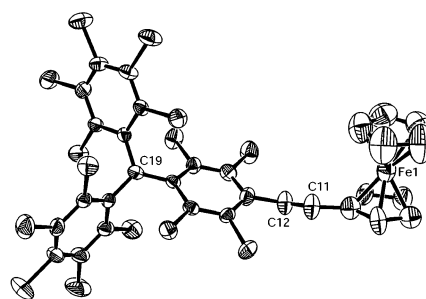
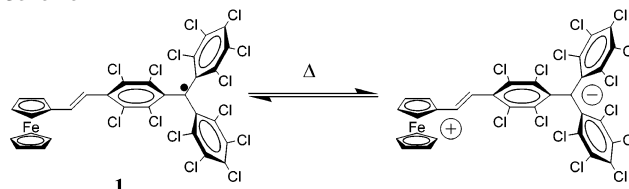


Figure 1. ORTEP view of radical **1**. Hydrogen atoms and solvent molecules have been omitted for clarity. Thermal ellipsoids are shown at 50% probability level.

Scheme 1



transfer. Selected Mössbauer spectra obtained in the temperature range of 293 to 4.2 K are shown in Figure 2. The spectrum recorded at the lowest temperature (4.2 K) shows the typical quadrupole doublet of ferrocene,⁷ the isomer shift, relative to α -iron, of 0.542 ± 0.002 mm s⁻¹ and the quadrupole splitting of 2.337 ± 0.002 mm s⁻¹. With increasing temperature a new quadrupole doublet with smaller splitting of 0.514 mm s⁻¹ (200 K), characteristic of the ferricinium cation,⁷ grows in at the expense of the ferrocene doublet.⁸ Clearly, this is indicative of a temperature-induced electron transfer from the ferrocene center to the radical as shown from left to right in Scheme 1. The conversion appears to be gradual up to room temperature and fully reversible as confirmed by repetitive temperature-variable Mössbauer experiments. The area fraction of the ferricinium doublet is 0.63 at 293 K and still rising as can be seen from a plot of the area fractions as function of temperature. Such a gradual interconversion was also noticed by subtle changes in the magnetization data for radical **1**. Indeed, magnetization data for radical **1** revealed that its μ_{eff} moment at 300 K was $2.28 \mu_{\text{B}}$ and recurrent measurements gave similar μ_{eff} moment values. Such a value is oversized to be justified just in terms of an organic radical contribution with $S = 1/2$, for which a theoretical $1.73 \mu_{\text{B}}$ value is expected. This result has been assigned to significant orbital contributions of the remnant [Fe^{III}Cp₂]⁺ fraction over the spin only value of $1.73 \mu_{\text{B}}$, as occurs for other [Fe^{III}Cp₂]⁺ derivatives.⁹ A decrease of the temperature reveals a steady decrease of the μ_{eff} , down to a value of $1.65 \mu_{\text{B}}$ at 15 K, whereupon the μ_{eff} moment

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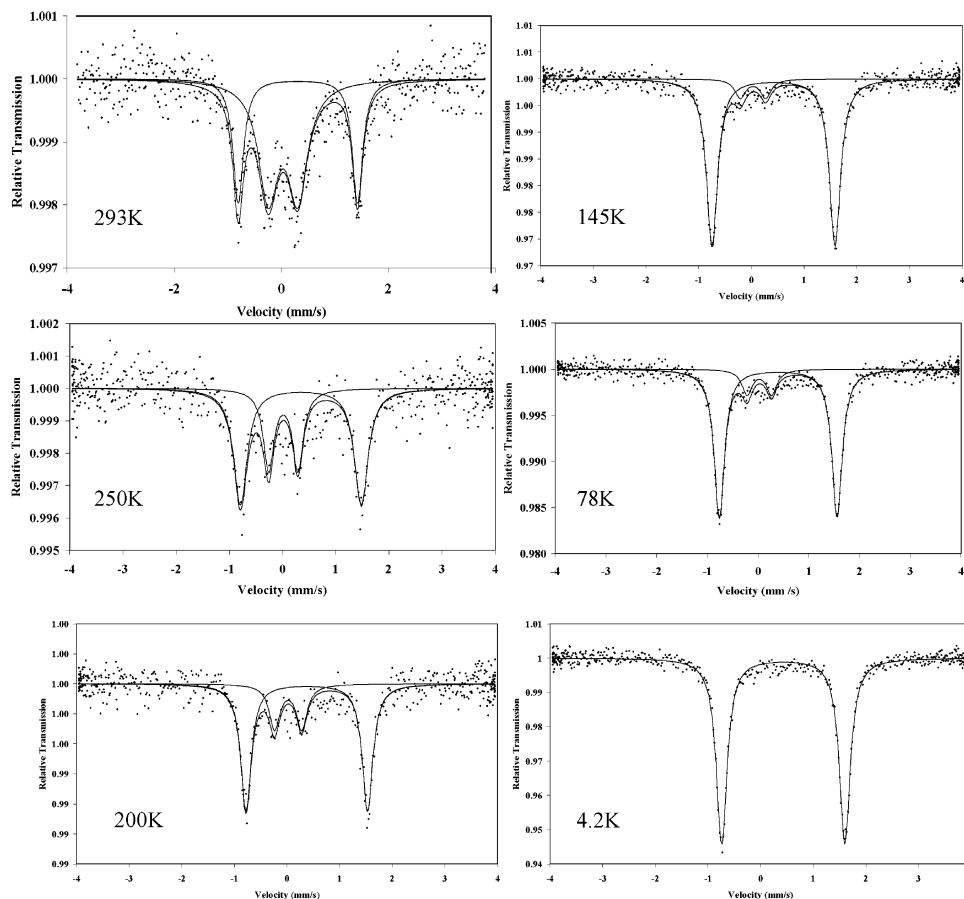


Figure 2. ^{57}Fe Mossbauer spectra of radical **1** as a function of temperature.

abruptly decreases probably due to the presence of weak intermolecular magnetic exchange interactions, as previously observed in related polychlorotriphenylmethyl radicals.¹⁰ The steady decrease of the μ_{eff} moment between 300 and 15 K suggests the presence of a fraction of an electronic isomer containing Fe^{III} whose population changes in accordance with a temperature-dependent intramolecular electron-transfer phenomenon between the ferrocene unit to the radical center, as depicted in Scheme 1. Finally, it is important to emphasize that although the interconversion is rather gradual, its T_{C} (temperature at which there equal amounts of both isomers) falls near room-temperature adding interest for potential future applications.

In summary, here we have described for the first time a novel valence tautomeric example combining an organic radical as acceptor unit and a ferrocene unit as the donor group. These findings should be useful in designing novel multifunctional switchable molecular systems that can be used as information storage devices at the nanoscopic scale. Detailed Mössbauer measurements to study hysteresis phenomena and additional light-induced electron-transfer experiments will be carried out in due course on ^{57}Fe enriched samples of radical **1**. The use of such enriched samples is required to minimize the very long recording times observed for compound **1**, arising from an apparently very low Debye temperature.

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Supporting Information Available: Crystallographic data of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (6) X-ray structure analysis. Crystal data: $\text{C}_{31}\text{H}_{11}\text{Cl}_{14}\text{Fe}\cdot 0.5\text{CH}_2\text{Cl}_2$, triclinic, space group $P\bar{1}$, $a = 8.8771(4)$, $b = 14.4198(8)$, and $c = 15.5546(7)$ Å, $\alpha = 109.200(2)$, $\beta = 97.008(3)$, and $\gamma = 102.408(2)^\circ$, $V = 1795.9(2)$ Å³, $Z = 2$, $T = 223(2)$ K, $\lambda = \text{Mo K}\alpha = 0.7173$ Å, $F(000) = 964$, $\mu = 1.562$ mm⁻¹, brown platelet $0.45 \times 0.25 \times 0.03$ mm. Data collection: Nonius Kappa CCD, 7774 measured reflections were corrected with the program DENZO and SCALEPACK. Structure solution and refinement: anisotropic refinement on F^2 (SHELXL 97), hydrogen atoms at calculated positions; R -values for 487 parameters and 3461 observed reflections [$I > 2\sigma(I)$] $R1 = 0.0425$ and $wR2 = 0.01059$. Refinement details: 3:2 disorder of the $\text{FeCp}_2\text{—C}(11)$ unit, which can be characterized by a reflection through a plane nearly perpendicular to the $\text{C}_6\text{Cl}_4\text{—C}(12)$ -ring system.
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