Ferromagnetic interactions between triphenylmethyl radicals through an organometallic coupler

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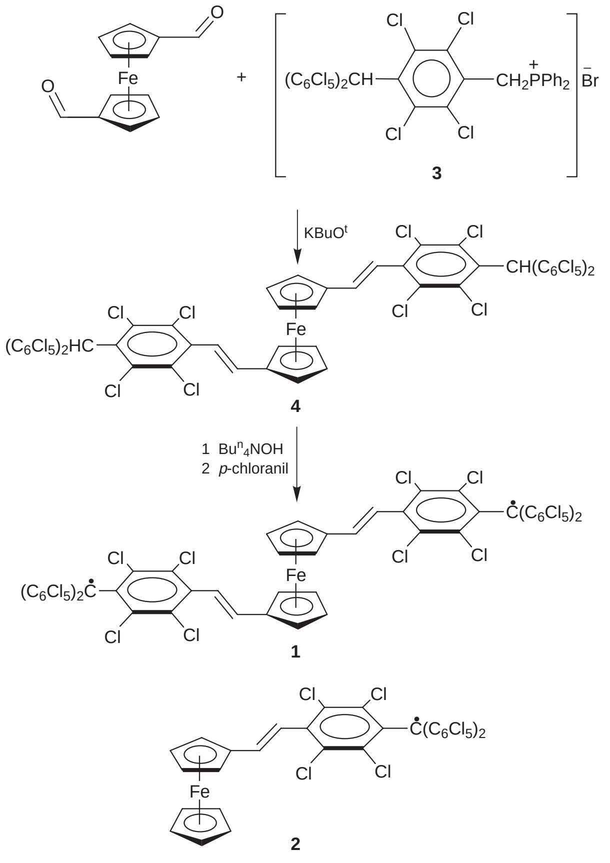
A diradical consisting of two polychlorinated triphenylmethyl radical units connected by a 1,1′-metallocenylendivinylene bridge has been synthesized and characterized; EPR frozen solution experiments down to liquid helium temperature showed that the organometallic unit acts as a ferromagnetic coupler.

In the last few years, the development and study of new coupling units that promote ferromagnetic interactions between pure organic radicals has been a subject of great interest.[1] Metallocenes are excellent candidates to be used as magnetic couplers not only because of their rich chemistry but also because they are electroactive species whose oxidation state can be controlled by means of a chemical or electrochemical stimulus; moreover their oxidized states are of open-shell character. However, although such complexes have been successfully used as building blocks of molecular solids promoting intermolecular magnetic exchange interactions,[2] their use as intramolecular magnetic couplers is new. Recently, we have reported a novel family of compounds consisting of two purely organic α-nitronyl aminoxyl radicals connected by different 1,1′-metallocenylene bridges where the metallocene units were shown to act as effective magnetic couplers that transmit the magnetic interactions through their skeletons.[3] However, the small spin density located on the metallocene units of these systems and the presence of intramolecular hydrogen bonds, which determines the existence of a direct intramolecular through-space magnetic interaction, lead to the appearance of an effective antiferromagnetic interaction between the two α-nitronyl aminoxyl radical units that is very sensitive to the molecular conformation.[4] For this reason, such complexes were not suitable candidates to study and rationalize the behaviour of 1,1′-metallocenylene bridges as magnetic couplers.

In order to overcome both these factors, diradical **1,** consisting of two polychlorinated triphenylmethyl radicals connected by a 1,1′-ferrocenylendivinylene bridge, was designed. The particular structure and topology of such a diradical leads to expectation of a non-negligible spin density on the ferrocene moiety making feasible the magnetic coupling between the two organic radical units.[5] In addition, the location of both radical units far away from each other avoids any possibility of having intramolecular contacts, and consequently, a significant direct through-space magnetic interaction. Here we report the synthesis and characterization of diradical **1.** The related monoradical **2** has also been synthesized and studied for comparison purposes.

As outlined in Scheme 1, the synthetic route for preparing these radical derivatives is based on two main steps. First, a Wittig reaction between the phosphonium bromide precursor **3** and the corresponding ferrocene carbaldehyde derivative; *i.e.* ferrocene 1,1′-biscarbaldehyde and ferrocene monocarbaldehyde for radicals **1** and **2**, respectively. Second, a subsequent deprotonation and oxidation to yield the desired radicals. In the first step of the synthesis of **1**, the substituted phosphonium bromide, α,α-bis(pentachlorophenyl)-2,3,5,6-tetrachloro-α′-(triphenylphosphonium)-*p*-xylene bromide **3**, was suspended in dry THF and treated with an equimolar amount of KOBu^t. The resulting yellow ylide suspension was stirred for *ca.* 1 h and after this time ferrocene 1,1′-biscarbaldehyde was added and stirred for a further 72 h. The reaction mixture was quenched with HCl and extracted with $CHCl_3$ to give 1,1′-bis{4-[bis(pentachlorophenyl)methyl]-2,3,5,6-tetrachlorostyryl}ferrocene **4** after chromatographic purification from *n*-hexane–$CHCl_3$ (1 : 1). Finally, a THF solution of **4** was treated with an excess of tetra(*n*-butyl)ammonium hydroxide. The solution, which immediately turned purple, was stirred at room temperature for 4 h. Subsequent oxidation of the resulting dianion with *p*-chloranil yielded the 4,4′-(1,1′-ferrocenylenedivinylene)di[α,α-bis(pentachlorophenyl)-2,3,5,6-tetrachlorobenzyl] diradical **1**, which was isolated as a clathrate ($\mathbf{1}\cdot 2C_6H_6$) after chromatographic purification (*n*-hexane–CCl_4, 1 : 1) and recrystallization from C_6H_6. This diradical is completely stable in air both in the solid state and in dilute solutions. The related monoradical derivative, the 4-(ferrocenylvinylene)-α,α-bis(pentachlorophenyl)-2,3,5,6-tetrachlorobenzyl radical **2** was prepared following the same procedure, from the phosphonium bromide derivative **3** and ferrocene carbaldehyde. Both radicals were obtained as dark green microcrystals and were characterized by elemental analysis, cyclic voltammetry, IR, UV–VIS and EPR spectroscopies.



Scheme 1

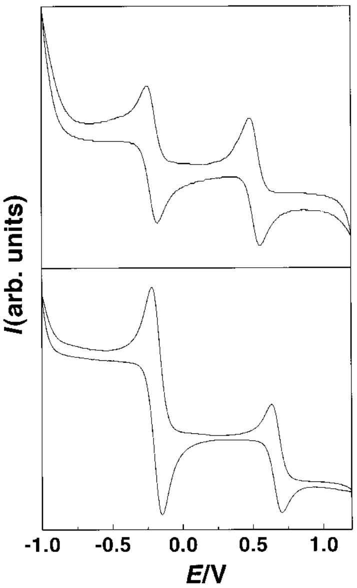


Fig. 1 Cyclic voltammograms recorded in a CH_2Cl_2 solution containing NBu_4PF_6 (0.l M) of (a) monoradical **2** and (b) diradical **1**.

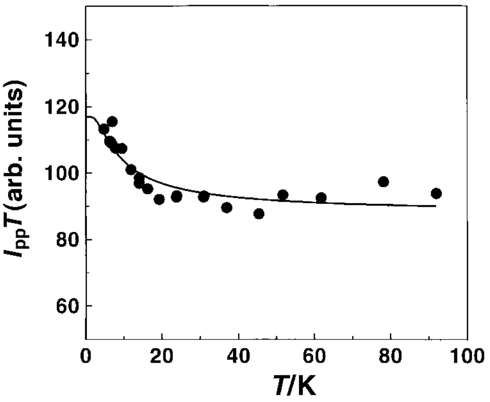


Fig. 2 Temperature dependence of $I_{pp}T$ of diradical **1**. The closed circles represent the experimental data and the continuous line the fit of experimental data to the Bleaney–Bowers equation.

The cyclic voltammetric response of **2** shows one oxidation and one reduction process. The reversible process at +587 mV arises from the oxidation of the ferrocene unit while the reversible reduction process occurring at -177 mV is associated with the reduction of the triphenylmethyl radical unit. Cyclic voltammetry of diradical **1** (Fig. 1) shows one reversible oxidation process at +666 mV and one reversible reduction process at -181 mV that involves the simultaneous transfer of two electrons. The oxidation process was assigned, as in the monoradical species, to the oxidation of the ferrocene unit, while the reduction process was assigned to the reduction of both triphenylmethyl radical units. The fact that the oxidation process of the ferrocene unit of diradical **1** appears at a higher potential value than those observed for monoradical **2** and the unsubstituted ferrocene is the first direct evidence for the presence of an electronic interaction between the radical and the ferrocene units. Nevertheless, EPR spectroscopy provides more detailed and definitive information about the electronic structure as well as of the intramolecular electron–electron interactions in these compounds. X-Band EPR isotropic spectra of radicals **1** and **2** were obtained in toluene–CH_2Cl_2 (1 : 1). The spectra of both complexes at room temperature showed lines corresponding to the coupling of the unpaired electrons with the different nuclei with non-zero magnetic moments; *i.e.* with ^1H and naturally abundant ^{13}C isotope at the α and aromatic positions. Computer simulation gave the isotropic g-values (g_{iso}) and the isotropic hyperfine coupling constants (a_i) of the unpaired electrons with the different nuclei with non-zero magnetic moments. The g_{iso} values for diradical **1** and monoradical **2** were 2.0028 and 2.0033, respectively which are very close to that observed for other polychlorotriphenylmethyl radicals.[6] More interesting is the comparison of the isotropic hyperfine coupling constant values with the hydrogen atoms of the ethylene moieties and some of the carbon nuclei of the triphenylmethyl unit. The values of the coupling constant of diradical **1**, $a_1(^1H) \approx 0.80$ G (2H), $a_2(^1H) \leqslant 0.30$ G (2H) and $a(^{13}C) \approx 13.0$ G (1 C_α) are approximately half those found for monoradical **2**, $a_1(1^1H) \approx 1.77$ G (1H), $a_2(1^1H) \approx 0.57$ G (1H) and $a(^{13}C) \approx 29.0$ G (1 C_α) . It is then possible to conclude that the two electrons in diradical **1** are interacting with a magnetic exchange coupling constant, J, that fulfills $J >> a_i$. It is also worth noting that the coupling constants of diradical **1** are not exactly half of those observed for the monoradical **2** when measured under identical experimental conditions, suggesting that both molecules have small differences in the conformations of their bridges. The spectrum of diradical **1** in frozen toluene–CH_2Cl_2 (1 : 1) showed the characteristic fine structure of a triplet species and appeared to be symmetrical, indicating that this complex has a low (if any) anisotropy. The forbidden $\Delta m_s = \pm 2$ transition characteristic of a triplet species, was also observed at the half-field region of the spectrum and the intensity of the corresponding signal (I_{pp}), obtained by double integration, was measured in the range 4–100 K. The reproducibility of the results was confirmed by two independent experiments. Since the quantity $I_{pp}T$ is proportional to the population in the triplet state, the fact that $I_{pp}T$ (Fig. 2) increases with decreasing temperature indicates that the ground state of **1** is the triplet state and the singlet state should be regarded as a thermally accessible excited state.[7] A separation of +10 ±2 K (7 cm^{-1}) between both states was obtained from the fitting of the data in Fig. 2 to a Bleaney–Bowers equation.[8]

In conclusion, we have shown that 1,1′-ferrocenylene bridges can act as ferromagnetic couplers when radical units with a suitable topology are connected to them. This concept can be extended to the synthesis of novel metallocene complexes bearing other organic and inorganic units providing a valuable access to this interesting class of materials.

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Notes and references

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4 The spin density on the metallocene units linked to the α-carbon atom of α-nitronyl aminoxyl radicals is very small because the SOMO orbital has a node on this carbon atom and therefore the spin density is transmitted only by a spin polarization mechanism.

5 By contrast, for diradical **1** both unpaired electrons can be delocalized by conjugation onto the ferrocene unit according to the particular topology of the diradical promoting a larger magnetic coupling.

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7 To obtain accurate temperature measurements that ensure the validity of the experimental results, the spectrometer was equipped both with a flowing-helium Oxford ESR-900 cryostat (4.2–100 K), controlled by an Oxford ITC4 temperature control unit, and with a calibrated custom-made double temperature control system for determining accurately the sample temperature. Additional precautions to avoid undesirable saturation effects and spectral line broadening were also taken.

8 R. L. Carlin, *Magnetochemistry*, Springer-Verlag, Berlin, 1986, p. 71.

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