Lalonde, R. K. Müller, M. Scalone, G. Schoettel, U. Zutter, *Pure Appl. Chem.* **1996**, *68*, 131–138); c) (−)-Me-DuPHOS = (−)-1,2-bis((2*R*,5*R*)-2,5-dimethylphospholanyl)benzene (M. J. Burk, J. E. Feaster, W. A. Nugent, R. L. Harlow, *J. Am. Chem. Soc.* **1993**, *115*, 10125–10138); d) (−)-JOSIPHOS = (−)-(*R*)-(1)-[(*S*)-2-(diphenylphosphanyl)ferrocenyl]ethyldicyclohexylphosphane (A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, *J. Am. Chem. Soc.* **1994**, *116*, 4062–4066); e) (−)-*i*Pr-MeOBIPHEP stands for (−)-(*S*)-6,6′-dimethoxy-2,2′-bis(diisopropylphosphanyl)-1,1′-biphenyl (N. Feiken, P. S. Pregosin, G. Trabesinger, M. Scalone, *Organometallics* **1997**, *16*, 537–543; J. Foricher, R. Schmid (Hoffmann–La Roche AG), WO 9315091, **1993** [*Chem. Abstr.* **1993**, *119*, 271399k].

[6] R. R. Schrock, B. F. G. Johnson, J. Lewis, *J. Chem. Soc. Dalton Trans.* **1974**, 951–959.

[7] A. Currao, N. Feiken, A. Macchioni, R. Nesper, P. S. Pregosin, G. Trabesinger, *Helv. Chim. Acta* **1996**, *79*, 1587–1591.

[8] H. Takaya, T. Ohta, S. Inoue, M. Tokunaga, M. Kitamura, R. Noyori, *Org. Synth.* **1995**, *72*, 74–85.

[9] E. A. Broger, M. Karpf, U. Zutter (Hoffmann–La Roche AG), EP 643052 A2, **1993** [*Chem. Abstr.* **1995**, *122*, 290712k]; see also R. Schmid, M. Scalone in *Comprehensive Asymmetric Catalysis, Vol. 1+3* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, **1999**, chap. 41.2.

[10] K. Mashima, T. Hino, H. Takaya, *J. Chem. Soc. Dalton Trans.* **1992**, 2099–2107.

[11] That there are three solvento ligands is assumed by analogy with $[\mathrm{Ru}((+)\text{-BINAP})(\mathrm{H})(\mathrm{MeCN})_n(\mathrm{sol})_{3-n}](\mathrm{BF}_4)$ ($n = 0-3$).[4a]

[12] a) F. Bouachir, B. Chaudret, I. Tkatchenko, *J. Chem. Soc. Chem. Commun.* **1986**, 94–96; b) F. Bouachir, B. Chaudret, F. Dahan, I. Tkatchenko, *New J. Chem.* **1987**, *11*, 527–529; c) F. Bouachir, B. Chaudret, F. Dahan, F. Agbossou, I. Tkatchenko, *Organometallics* **1991**, *10*, 455–462.

[13] a) P. Pertici, G. Vitulli, *Inorg. Synth.* **1983**, *22*, 176–179; b) K.-M. Frosin, L. Dahlenburg, *Inorg. Chim. Acta* **1990**, *167*, 83–89; c) P. Pertici, G. Vitulli, *Comments Inorg. Chem.* **1991**, *11*, 175–194, and references therein.

[14] K. Hafner, A. Stephan, C. Bernhard, *Liebigs Ann. Chem.* **1961**, *650*, 42–62; see also note [12] in ref. [3].

[15] $[\mathrm{Ru}((-)\text{-Me-DuPHOS})_2(\mathrm{H})](\mathrm{PF}_6)$: M. Schlaf, A. J. Lough, R. H. Morris, *Organometallics* **1997**, *16*, 1253–1259.

[16] Suitable crystals of **1** were obtained by liquid–liquid diffusion of $\mathrm{Et_2O}$ into a saturated 1,2-dichloroethane solution. $\mathrm{C_{26}H_{39}BF_4P_2Ru}$, $M_r = 601.39$, light-green plate ($0.25 \times 0.23 \times 0.05$ mm), monoclinic, space group $P2_1$, $a = 8.4489(2)$, $b = 14.2536(4)$, $c = 11.1539(3)$ Å, $V = 1315.52$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.518\ \mathrm{g\,cm^{-3}}$, $2\theta_{\max} = 50.12°$, $\mathrm{Mo_{K\alpha}}$, $\lambda = 0.71073$ Å, scan mode $= \omega$, $T = 173(2)$ K, 6640 reflections measured, 4445 independent, 4089 with $I > 2\sigma(I)$ included in refinement, absorption correction: SADABS (Sheldrick, 1996), ($\mu = 0.760\ \mathrm{mm^{-1}}$, max./min. transmission 1.00/0.793), direct methods structure solution using SHELXTL-V5.0, 315 parameters varied. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The hydride ligand was refined as an isotropic atom. $R(\mathrm{F}) = 0.0349$ (observed data), wR_2 (F^2) $= 0.0807$ (all data). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143502. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[17] B. R. James, D. K. W. Wang, *Can. J. Chem.* **1980**, 245–250; M. Jiménez-Tenorio, M. C. Puerta, P. Valerga, *Inorg. Chem.* **1994**, *33*, 3515–3520; K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, *Angew. Chem.* **1997**, *109*, 297–300; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 285–288; G. Trabesinger, A. Albinati, N. Feiken, R. W. Kunz, P. S. Pregosin, M. Tschoerner, *J. Am. Chem. Soc.* **1997**, *119*, 6315–6323.

[18] T. V. Ashworth, A. A. Chalmers, D. C. Liles, E. Meintjies, E. Singleton, *Organometallics* **1987**, *6*, 1543–1552.

[19] D. D. Pathak, H. Adams, N. A. Bailey, P. J. King, C. White, *J. Organomet. Chem.* **1994**, *479*, 237–245; N. Feiken, P. S. Pregosin, G. Trabesinger, A. Albinati, G. L. Evoli, *Organometallics* **1997**, *16*, 5756–5762.

[20] Attempts to grow suitable crystals of **14** and **15** to confirm the gross structures and to determine the exact structures by X-ray diffraction have failed to date.

[21] We recommend careful tuning at both stages when other $\widehat{\mathrm{PP}}$ are to be incorporated into the catalyst precursors and catalysts. For example, while **17** with sol = THF could be readily generated, **5** with sol = THF could not.

[22] For example, we have developed related methodology starting out from "$[\mathrm{Ru}(\mathrm{H})(\eta^5\text{-2,4-dimethylpentadienyl})_2](\mathrm{BF}_4)$" (T. D. Newbound, L. Stahl, M. L. Ziegler, R. D. Ernst, *Organometallics* **1990**, *9*, 2962–2972); see the patents listed in footnote [9] in ref. [3]. After submission of this paper, we learned that parallel work is in print (A. Bauer, U. Englert, S. Geyser, F. Podewils, A. Salzer, *Organometallics* **2000**, *19*, 5471–5476).

[23] The cluster centered around m/z 801 corresponds to the cluster expected for the cation of **14** − 2 mu (mass units). We also observe some of the cluster for the cation of **1** − 2 mu under these conditions.

A New Photomagnetic Molecular System Based on Photoinduced Self-Assembly of Radicals[**]

Imma Ratera, Daniel Ruiz-Molina,
José Vidal-Gancedo, Klaus Wurst, Nathalie Daro,
Jean-François Létard, Concepció Rovira, and
Jaume Veciana[*]

Dedicated to Professor Fred Wudl
on the occasion of his 60th birthday

The synthesis and characterization of supramolecular magnetic materials based on the self-assembly of open-shell molecules are currently of great interest.[1] The construction of such solids requires that the structural subunits exhibit noncovalent interactions that can be controlled in a predictable manner. The noncovalent intermolecular interactions that have been used to date for the assembly of such molecular subunits are hydrogen bonding,[2] transition metal

---

[*] Prof. J. Veciana, I. Ratera, Dr. D. Ruiz-Molina, Dr. J. Vidal-Gancedo, Dr. C. Rovira
Institut de Ciencia de Materials de Barcelona (CSIC)
Campus Universitari de Bellaterra
08193, Cerdanyola (Spain)
Fax: (+34) 93-580-57-29
E-mail: vecianaj@icmab.es

N. Daro, Dr. J.-F. Létard
Institut de Chimie de la Matière Condensée (ICMCB)
Lab. des Sciences Moléculaires
Château Brivazac 87 Avenue du Docteur A. Schweitzer
UPR CNRS No 9048, 33608 Pessac Cedex (France)

Dr. K. Wurst
Institut für Allgemeine, Anorganische und Theoretische Chemie
Universität Innsbruck
Innrain 52a, 6020, Innsbruck (Austria)

[**] This work was supported by grants from DGI (project MAT 2000-1388-C03-01), CIRIT (project 2000 SGR00114), the 3MD Network of the TMR program of the EU (contract ERBFMRX CT980181), and the ESF program Molecular Magnets. D.R.-M. thanks the Generalitat de Catalunya for a postdoctoral grant, and I.R. thanks the CSIC-Carburos Metálicos and ESF for fellowships.

ligation,[3] stack-type alignment,[4] and bridging of ion radicals by their counterions.[5] Among these interactions, hydrogen bonding has emerged as a particularly useful and efficient tool. Indeed, transmission of magnetic interactions through hydrogen bonds was first observed with transition metal complexes.[6] Since then, several hydrogen-bonded organic magnets have been reported.[2] However, to the best of our knowledge, hydrogen-bonded supramolecular magnetic materials whose properties may be systematically tuned and/or controlled by external stimuli have so far not been reported despite the enormous interest in switchable magnetic materials.

Light is a particularly efficient stimulus for inducing changes in the magnetic properties of a given material. In fact, examples of photomagnetism in inorganic magnetic systems and in covalently linked organic polyradicals have already been reported. For instance, Hashimoto et al. reported photoinduced magnetization changes in a cobalt–iron cyanide complex,[7] which confirmed the possibility of modifying long-range magnetic ordering by photons. Furthermore, photoinduced magnetic changes in pure organic materials have also been described, for example, as in the photoisomerization of a carbene[8] and in the spin isomerism of a non-Kekulé diradical.[9] More recently, Irie and Matsuda described a photochromic system that interconverts reversibly between a singlet and a triplet high-spin ground state,[10] and Iwamura et al. reported a diradical species bearing two stable nitroxide radicals connected through an isomerizable unit.[11]

Herein we report a new photomagnetic system based on the photoinduced *trans*→*cis* isomerization of **1**. The *trans*-**1** isomer exists in solution as a monomeric species, whereas the *cis*-**1** isomer aggregates in solution through the formation of hydrogen bonds to give a thermodynamically stabilized diradical dimer with strong antiferromagnetic interactions. Although numerous photochromic supramolecular systems have been described up to now,[12] this photoinduced self-assembly process represents the first example of a photomagnetic system based on a supramolecular phenomenon.

The ferrocenyl Schiff base polychlorotriphenylmethyl radical (**1**) was obtained by a condensation reaction between the (4-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical and ferrocene monocarboxaldehyde. Since the condensation reaction is not stereoselective, the *trans* and *cis* isomers of compound **1** were present in the reaction product. Both isomers, *trans*-**1** and *cis*-**1**, were isolated as stable species in solution and in the solid state, and were characterized by different techniques such as elemental analysis, matrix-assisted laser desorption time-of-flight (MALDI-TOF) mass spectrometry, HPLC, cyclic voltammetry, FT-IR, UV/Vis/NIR, and ESR spectroscopy.

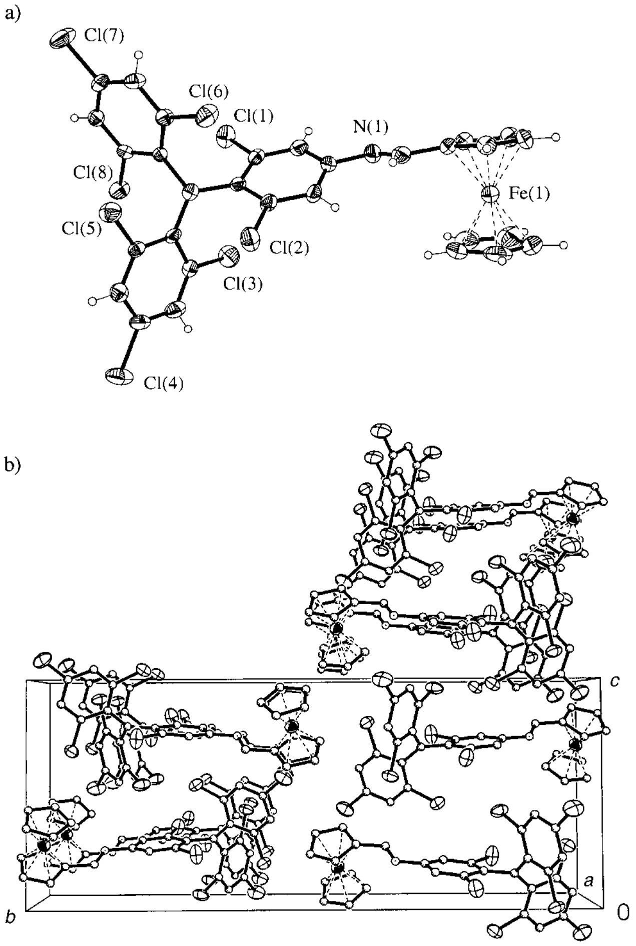
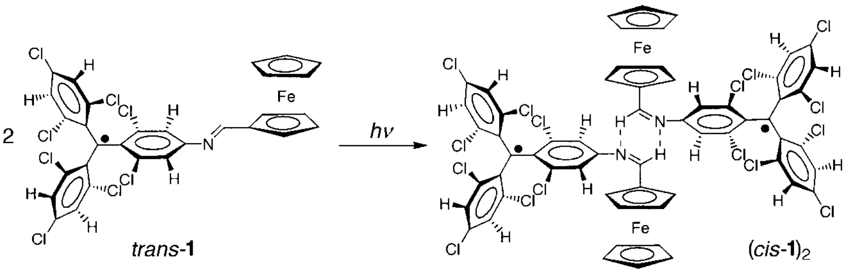


Figure 1. Molecular structure (with 50% ellipsoids; top) and crystal packing (bottom) of *trans*-**1**.

Single crystals for the X-ray structure analysis of *trans*-**1** were grown by slow evaporation from a carbon tetrachloride/hexanes (1/1) mixture.[13] The structure of *trans*-**1** (Figure 1; ORTEP view) reveals almost eclipsed cyclopentadienyl rings and a *trans* configuration at the CH=N double bond. Despite the available resonance pathway and the *trans* configuration, the η-C_5H_4 and the $C_6H_2Cl_2$ rings are twisted by an angle of about 28°. Presumably, the steric interactions between the hydrogen atom of the CH=N group one of the *ortho* hydrogen atoms of the benzene ring prevents a planar arrangement. The solid-state packing of *trans*-**1** is best described as enantiomerically related pairs of molecules (see Figure 1b). Stacking of these related pairs occurs with continuous staggering along the *c* axis and with a head-to-tail pairing along the *b* axis. The relative arrangement and the considerably large distances between neighboring molecules excludes the presence of hydrogen bonds among neighboring CH=N units. Under these circumstances, the largest driving forces for such molecular packing are dipole–dipole and van der Waals interactions, which lead to an efficient filling of space. Unfortunately, despite the use of different crystallization techniques, we have been unable to obtain crystals suitable for determining the X-ray structure of the *cis*-**1** isomer.[14]

The cyclic voltammetric response of *trans*-**1** and *cis*-**1** show one reversible oxidation process at +0.61 and +0.72 V, respectively, and one reversible reduction process at −0.66 and −0.67 V, respectively (vs. a Ag/AgCl electrode in CH_2Cl_2). The reversible oxidation process arises, in both cases, from the oxidation of the iron atom of the ferrocene unit, while the reversible reduction process is associated with the reduction at the triphenylmethyl radical unit to the corresponding carbanion; as ascertained by UV/Vis and ESR spectroelectrochemical experiments. ESR spectroscopy provides more detailed and definitive information about the molecular and electronic structure of both isomers in solution. Thus, the isotropic X-band ESR spectrum of the radical *trans*-**1** in toluene/dichloromethane (1/1; $c = 10^{-5}\,\text{mol}\,\text{L}^{-1}$) at 220 K, is concentration-independent and shows the lines corresponding to the coupling of the unpaired electron with the different nuclei with nonzero magnetic moments; that is, with ^{1}H, ^{14}N, and naturally abundant ^{13}C isotopes at the α and aromatic positions. Computer simulation gave the isotropic g values (g_{iso}) and the isotropic hyperfine coupling constants (a_{i}). The g_{iso} value is 2.0030, which is very close to the values for other polychlorotriphenylmethyl radicals.[15] The values of the coupling constants of *trans*-**1** are: $a(^{14}\text{N}) = 1.18$ G; $a(^{1}\text{H}_{meta}) = 1.06$ G; $a(^{1}\text{H}_{trans}) = 0.25$ G; $a(^{13}\text{C}_{\alpha}) = 28.5$ G; $a(^{13}\text{C}_{bridge}) = 12.5$ G; $a(^{13}\text{C}_{ortho}) = 10.3$ G.[16] At 160 K, its spectrum shows a single broad line characteristic of an isolated free radical in a rigid medium with a low magnetic anisotropy. This fact clearly shows that the *trans*-**1** isomer exists in solution as a monomeric species. Surprisingly, the X-band ESR spectrum of the *cis*-**1** radical in toluene/dichloromethane (1/1) at 220 K did not show the lines corresponding to the coupling of the unpaired electron with the different magnetic nuclei, but the characteristic fine structure of a triplet species. The zero-field splitting parameters obtained by computer simulation of the spectra obtained at 160 K are $|D'| = 25.2$ G and $|E'| = 0$. This behavior has been attributed to the formation of a dimeric species which is held together by intermolecular C-H $\cdots$ N hydrogen bonds between the CH=N groups of two different molecules (Scheme 1). Semiempirical ZINDO/1 calculations[17] revealed that the H-bonded dimeric form of *cis*-**1** corresponds to an energy minimum, while for the *trans*-**1** isomer similar H-bonded dimeric or polymeric species do not correspond to energy minima; probably because of the steric hindrance developed in such species. These calculations also revealed that the dimeric species (*cis*-**1**)$_2$ are more stable than the monomeric species *trans*-**1** by 7 kcal mol^{-1}. The forbidden $\Delta m_{\text{s}} = \pm 2$ transition characteristic of triplet species was also observed at the half-field region of the spectrum of *cis*-**1** and the intensity of the corresponding signal (I_{pp}), obtained by double integration, was measured in the 4–100 K temperature range. Since the experimental value of $I_{\text{pp}}T$ is proportional to the population in the triplet state, the fact that $I_{\text{pp}}T$ decreases with decreasing temperature indicates that the ground state of the dimeric species is the singlet state and the triplet state should be associated with a thermally accessible excited state. A separation of 54 ± 2 K (38 cm^{-1}) between both states was obtained from the fitting of the experimental data to a Bleaney–Bowers equation.[18]



Scheme 1. Photoinduced *trans* → *cis* isomerization of **1**.

Our interest in compound **1** was considerably enhanced when it was found that the ESR spectrum of *trans*-**1** in methylcyclohexane exhibited a time dependence behavior under in situ irradiation at 415 nm,[19] a result that is consistent with the conversion from the *trans*-**1** to the *cis*-**1** isomer (Figure 2). After eight hours of irradiation a mixture with a *cis*:*trans* ratio ≥90:10 was obtained; as confirmed by computer simulation. The photoinduced *trans*-**1** → *cis*-**1** isomerization in methylcyclohexane at room temperature was also monitored by UV/Vis spectrosocopy. Indeed, the *trans*-**1** and *cis*-**1** isomers show characteristic UV/Vis absorption bands for the radical (377 nm) and conjugated ferrocene (408 nm) chromophores. The main difference lies in the relative intensity of both bands. The band at 377 nm for the *trans*-**1** isomer is less pronounced, whereas that at 408 nm is more intense than the corresponding bands for the *cis*-**1** isomer. This fact allowed us to study the effect of irradiation upon a solution of *trans*-**1** in methylcyclohexane by UV/Vis spectroscopy. The in situ irradiation of *trans*-**1** ($c = 10^{-5}\,\text{mol}\,\text{L}^{-1}$ in methylcylohexane) was carried out using 415 nm light in a quartz cell at room temperature for 2 h. During the irradiation of the *trans*-**1** solution, the absorption band at 377 nm increases, whereas the absorption band at 408 nm decreases; an isosbestic point occurs at 382 nm. This confirms a neat transformation from the *trans*-**1** to the *cis*-**1** isomer. Finally, it must be emphasized that irradiation of a *cis*-**1** solution ($c = 10^{-5}\,\text{mol}\,\text{L}^{-1}$) did not indicate the presence of the reverse photoisomerization process, either by ESR and/or by UV/Vis spectroscopy. Moreover, warming *cis*-**1** solutions in three different solvents (methylcyclohexane, toluene, and acetonitrile) up to 80 °C provided no evidence of a thermally induced backward *cis*-**1** → *trans*-**1** isomerization, while the *trans*-**1** → *cis*-**1** isomerization process takes place in the three studied solvents (Scheme 2).

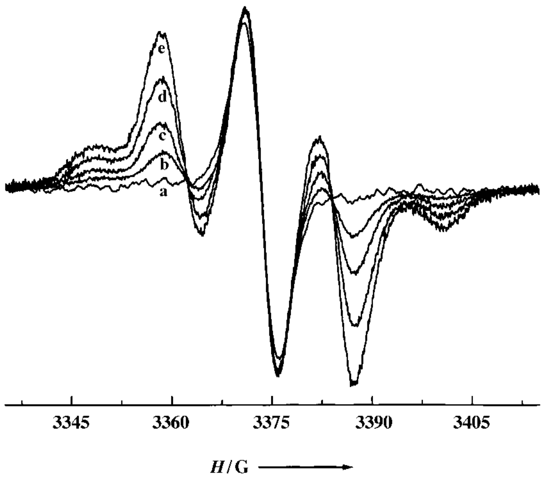
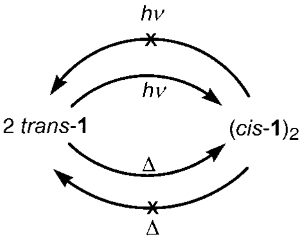


Figure 2. Photoinduced *trans* → *cis* isomerization of **1** monitored by ESR spectroscopy. $t = 0$ (a), 1 (b), 3 (c), 5 (d), 8 h (e).



Scheme 2. Overview of the photochemically and thermally possible isomerizations of **1**.

In summary, the photoinduced *trans* → *cis* isomerization of **1** has been monitored by UV/Vis and ESR spectrosocopy. Interestingly, the *cis*-**1** isomer aggregates in solution at low temperatures through the formation of hydrogen bonds to give thermodynamically stable diradical dimers with strong antiferromagnetic interactions. This one-way photoinduced self-assembly process represents an interesting example of a photomagnetic system based on a supramolecular phenomenon in which a doublet species is converted into a singlet one.

Experimental Section

1: To a dry solution of (4-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical in toluene, which was obtained as previously described,[20] was added ferrocene monocarboxaldehyde in the presence of molecular sieves. The mixture was heated up to 60 °C and stirred for 48 h. After removal of the molecular sieves and evaporation of the solvent, a brown precipitate was obtained, which contained a mixture of *cis*- and *trans*-**1**. The *trans*-**1** isomer was isolated as a dark brown microcrystalline material by recrystallization from *n*-hexane, and the *cis*-**1** isomer was isolated as a dark green powder by flash chromatography (Florisil (magnesium silicate), carbon tetrachloride). *trans*-**1**: elemental analysis(%): calcd for $C_{30}H_{16}Cl_8NFe$: C 49.4, H 2.21, N 1.90; found: C 49.6, H 1.8, N 2.1; IR (KBr): $\tilde{\nu}_{max} = 3420$, 2967, 2913, 1631, 1556, 1536, 1465, 1371, 1261, 1225, 1182, 1137, 1104, 1021, 858, 809 cm^{-1}; UV/Vis (methylcyclohexane): $\lambda(\varepsilon) = 377$ (20300), 409 (14900), 565 nm (1863). *cis*-**1**: elemental analysis (%): calcd for $C_{30}H_{16}Cl_8NFe$: C 49.4, H 2.21, N 1.90; found: C 49.8, H 2.0, N 2.2; IR (KBr): $\tilde{\nu}_{max} = 3434$, 2925, 2849, 1715, 1631, 1552, 1526, 1487, 1383, 1371, 1292, 1227, 1182, 1134, 1076, 1057, 926, 858, 817, 788 cm^{-1}; UV/Vis (methylcyclohexane): $\lambda(\varepsilon) = 377$ (23300), 407 (13600), 578 nm (2940).

Received: July 18, 2000
Revised: November 10, 2000 [Z15478]

---

[1] a) *Magnetic Properties of Organic Materials* (Ed.: P. M. Lahti), Marcel Dekker, New York, **1999**; b) *Magneto Science: Molecules to Materials, Vol. 1* (Eds.: J. Miller, M. Drillon), Wiley-VCH, in press; c) J. Veciana, C. Rovira, D. B. Amabilino, *NATO ASI Ser. Ser. C* **1998**, *518*.

[2] a) J. Veciana, J. Cirujeda, C. Rovira, J. Vidal-Gancedo, *Adv. Mater.* **1995**, *7*, 221; b) E. Hernàndez, M. Mas, E. Molins, C. Rovira, J. Veciana, *Angew. Chem.* **1993**, *105*, 919; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 882; c) J. Cirujeda, L. E. Ochando, J. M. Amigó, C. Rovira, J. Rius, J. Veciana, *Angew. Chem.* **1995**, *107*, 99; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 55; d) M. M. Matsushita, A. Izuoka, T. Sugawara, T. Kobayashi, N. Wada, K. Takeda, M. Ishikawa, *J. Am. Chem. Soc.* **1997**, *119*, 4369; e) A. Caneschi, F. Ferraro, D. Gatteschi, A. Le Lirzin, M. Novak, E. Rentschler, R. Sessoli, *Adv. Mater.* **1995**, *7*, 476; f) F. M. Romero, R. Ziessel, M. Drillon, J.-L. Tholence, C. Paulsen, N. Kyritsakas, J. Fischer, *Adv. Mater.* **1996**, *8*, 826.

[3] a) K. E. Vostrikova, D. Luneau, W. Wernsdorfer, P. Rey, M. Verdaguer, *J. Am. Chem. Soc.* **2000**, *122*, 718; b) C. Rancurel, D. B. Leznoff, J.-P. Sutter, S. Golhen, L. Ouahab, J. Kliava, O. Kahn, *Inorg. Chem.* **1999**, *38*, 4753; c) M. Tanaka, K. Matsuda, T. Itoh, H. Iwamura, *Angew. Chem.* **1998**, *110*, 866; *Angew. Chem. Int. Ed.* **1998**, *37*, 810; d) A. Caneschi, D. Gatteschi, P. Rey, *Prog. Inorg. Chem.* **1991**, *39*, 331, and references therein.

[4] a) H. M. McConnell, *J. Chem. Phys.* **1963**, *33*, 1910; b) R. Breslow, B. Jaun, R. Q. Klutiz, C. Z. Xia, *Tetrahedron* **1981**, *38*, 863; c) J. Zhang, M. Baumgarten, *Chem. Phys.* **1997**, *222*, 1.

[5] a) N. Hirota, S. I. Weissman, *J. Am. Chem. Soc.* **1964**, *86*, 2538; b) M. Baumgarten, L. Gherghel, T. Wehrmeister, *Chem. Phys. Lett.* **1997**, *267*, 175, and references therein.

[6] B. N. Figgis, E. S. Kucharski, M. Vrtis, *J. Am. Chem. Soc.* **1993**, *115*, 176, and references therein.

[7] O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, *Science* **1996**, *272*, 704.

[8] W. Sander, G. Bucher, F. Reichel, D. Cremer, *J. Am. Chem. Soc.* **1991**, *113*, 5311.

[9] L. C. Bush, R. B. Heath, J. A. Berson, *J. Am. Chem. Soc.* **1993**, *115*, 9830.

[10] a) K. Matsuda, M. Irie, *Tetrahedron Lett.* **2000**, 41, 2577; b) K. Matsuda, M. Irie, *Chem. Lett.* **2000**, 16–17.

[11] K. Hamachi, K. Matsuda, T. Itoh, H. Iwamura, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2937.

[12] a) M. S. Vollmer, T. D. Clark, C. Steinmen, M. R. Ghadiri, *Angew. Chem.* **1999**, *111*, 1703; *Angew. Chem. Int. Ed.* **1999**, *38*, 1598; b) H. Rau in *Photochromism, Molecules and Systems* (Eds.: H. Dürr, H. Bouas-Laurent), Elsevier, Amsterdam, **1990**, p. 165; c) V. Balzani, F. Scandola, *Supramolecular Photochemsitry*, Ellis Horwood, New York, **1991**, p. 355.

[13] X-ray crstal structure analysis: $C_{30}H_{16}Cl_8NFe$, monoclinic, space group $P2_1/n$ (no. 14), $a = 8.1900(4)$, $b = 29.539(2)$, $c = 12.1065(4)$ Å, $\beta = 91.021(3)°$, $V = 2928.4(3)$ Å^3, $Z = 4$, $T = 218(2)$ K, $\lambda(Mo_{K\alpha}) = 0.7173$ Å, $F(000) = 1460$, $\mu = 1.269$ mm^{-1}, $\rho_{calcd} = 1.656$ $g\,cm^{-3}$, brown platelet $0.2 \times 0.1 \times 0.015$ mm. Data collection: Nonius Kappa CCD, 5879 measured reflections were corrected with the program SCALEPACK. Structure solution and refinement: anisotropic refinement on F^2 (SHELXL 93), hydrogen atoms at calculated positions; *R* values for 361 parameters and 2191 observed reflections $[I > 2\sigma(I)]$ $R_1 = 0.0396$ and $wR_2 = 0.0703$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147245. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[14] A systematic searching on the Cambridge Crystallographic Structure Database (CSD) revealed the existence of several examples of imino derivatives in which the HC=N group adopts a *trans* configuration, whereas there is no example in which the same group adopts a *cis* configuration. This fact agrees with the experimental difficulties found in this work to crystallize the *cis* isomer.

[15] O. Armet, J. Veciana, C. Rovira, J. Riera, J. Castañer, E. Molins, J. Rius, C. Miravitlles, S. Olivella, J. Brichfeus, *J. Phys. Chem.* **1987**, *91*, 5608.

[16] Remarkable is the observation of the hyperfine coupling with ^{14}N nuclei, which indicates that the unpaired electron is not only delocalized in the triphenylmethyl unit but also into the imine group. This fact is expected to enhance the presence of intermolecular magnetic exchange interactions in the case in which CH=N groups are involved in intermolecular bonds, as it was confirmed by ESR frozen solution experiments for the *cis*-**1** isomer.

[17] ZINDO-1 semiempirical calculations were performed using the HyperChem 3 molecular modeling package.

[18] R. L. Carlin, *Magnetochemistry*, Springer, Berlin, **1986**, p. 71.

[19] Irradiation experiments (power 10 $mW\,cm^{-2}$) were performed by using fiber optic illuminator model 77501 (Quartz tungsten halogen lamp, ORIEL). *trans* → *cis* isomerization was achieved with an interference filter centered at 415 nm (bandwidth 60 nm). No evidence of *cis* → *trans* isomerization was observed by using various interference filters (centered from 350 to 450 nm).

[20] a) L. Teruel, Ll. Viadel, J. Carilla, Ll. Fajarí, E. Brillas, J. Sañé, J. Rius, L. Juliá, *J. Org. Chem.* **1996**, *61*, 6063.