Enantioselective Self-Assembly of Bimetallic $[Mn^{II}\ (\Delta)\text{-}Cr^{III}(C_2O_4)_3]^-$ and $[Mn^{II}\ (\Lambda)\text{-}Cr^{III}(C_2O_4)_3]^-$ Layered Anionic Networks Templated by the Optically Active (*Rp*)- and (*Sp*)-$[1\text{-}CH_2N(n\text{-}C_3H_7)_3\text{-}2\text{-}CH_3{-}C_5H_3Fe{-}C_5H_5]^+$ Ions

**Michel Gruselle,*[a] René Thouvenot,[a] Bernard Malézieux,[a] Cyrille Train,[a]
Patrick Gredin,[b] Tatiana V. Demeschik,[c] Ludmila L. Troitskaya,[c] and
Viatcheslav I. Sokolov[c]**

Abstract: The ferrocenic ammonium (*Rp*)- and (*Sp*)-$[1\text{-}CH_2NR_3\text{-}2\text{-}CH_3{-}C_5H_3Fe{-}C_5H_5]$ iodide salts with R = CH_3, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, were synthesized starting from the (*Rp*)- and (*Sp*)-$[1\text{-}CH_2N(CH_3)_2\text{-}2\text{-}CH_3{-}C_5H_3Fe{-}C_5H_5]$ amines obtained in their optically active forms through asymmetric cyclopalladation of $[C_5H_5Fe{-}C_5H_4CH_2N(CH_3)_2]$. ^1H NMR studies of these planar chiral 1,2-disubstituted ferrocenic ammonium iodide salts in the presence of the (Δ)-(tris(tetrachlorobenzenediolato)phosphate(v) anion), [(Δ)-Trisphat] support the formation of specific diastereomeric ion pairs. Such intermolecular interactions can be related to the self-assembly of the two-dimensional optically active compounds $\{[(Sp)\text{-}1\text{-}CH_2N(n\text{-}C_3H_7)_3\text{-}2\text{-}CH_3{-}C_5H_3Fe{-}C_5H_5][Mn\ (\Delta)\text{-}Cr(C_2O_4)_3]\}$ and $\{[(Rp)\text{-}1\text{-}CH_2N(n\text{-}C_3H_7)_3\text{-}2\text{-}CH_3{-}C_5H_3Fe{-}C_5H_5][Mn\ (\Lambda)\text{-}Cr(C_2O_4)_3]\}$ starting from the resolved (*Rp*)- and (*Sp*)-$[1\text{-}CH_2N(n\text{-}C_3H_7)_3\text{-}2\text{-}CH_3{-}C_5H_3Fe{-}C_5H_5]^+$ ion associated to the racemic anionic building block *rac*-$[Cr(C_2O_4)_3]^{3-}$ and Mn^{2+}. Both enantiomeric forms of the networks behave as ferromagnets with a Curie temperature of 5.7 K.

Keywords: chirality · molecular magnets · NMR spectroscopy · oxalate · self-assembly

Introduction

We are currently developing the enantioselective synthesis of bimetallic $\{Cat[M^{II}M^{III}(C_2O_4)_3]\}$ (where Cat stands for a monocation and M^{II}, M^{III} for two transition metal ions) oxalate-based magnets possessing a Cotton effect[1] to investigate the recently discovered magneto-chiral dichroism (MChD).[2]

Over the last few years the groups of Okawa,[3] Decurtins,[4] Day,[5] Coronado,[6] Ovanesyan,[7] and Kahn[8] have thoroughly investigated two- (2D) and three-dimensional (3D) networks prepared from the reaction of a tris(oxalato)-metalates, $[M_1^{III}(C_2O_4)_3]^{3-}$ (M^{III} = Cr, Co, Fe, Ru) associated in tandem with a metallic ion M_2 such as an alkali metal cation (Li^+, Na^+) or a transition-metal ion (Mn^{2+}, Ni^{2+}, Fe^{2+}…) in presence of a cationic entity C, according to reaction (1).

$$[M_1^{III}(C_2O_4)_3]^{3-} + M_2^{(3-x)+} + C^{x+} = \{C[M_1M_2(C_2O_4)_3]\} \qquad (1)$$

The bimetallic networks $\{C[M_1M_2(C_2O_4)_3]\}$ (termed $[M_1, M_2]$) are composed of an anionic sublattice $[M_1M_2(C_2O_4)_3]^{x-}$ and a cationic counterpart C^{x+} (x = 1,2). In the anionic sublattice each tris(oxalato)metalate ion possesses a propeller-like chirality and exists as a Δ or Λ configuration (noted (Δ)-M or (Λ)-M). The relative configurations of these connected metallic centers are closely related to the 2D or 3D architectures. A homochiral arrangement [(Δ)-M_1, (Δ)-M_2] or [(Λ)-M_1, (Λ)-M_2] induces a helical organization of the connected metallic ions, and a resulting 3D network is obtained.[9,10] A heterochiral arrangement [(Δ)-M_1, (Λ)-M_2] or [(Λ)-M_1, (Δ)-M_2] leads to a 2D honeycomb anionic network

---

[a] Prof. M. Gruselle, Prof. R. Thouvenot, Dr. B. Malézieux, Dr. C. Train
Laboratoire de Chimie Inorganique et Matériaux Moléculaires
UMR-CNRS 7071, Université Pierre et Marie Curie
4 place Jussieu, case courrier 42, 75252 Paris Cedex 05 (France)
Fax: (+33) 1-44273841
E-mail: gruselle@ccr.jussieu.fr

[b] Dr. P. Gredin
Laboratoire de Cristallochimie du Solide
Université Pierre et Marie Curie
4 place Jussieu, case courrier 176, 75252 Paris Cedex 05 (France)

[c] Dr. T. V. Demeschik, Dr. L. L. Troitskaya, Prof. V. I. Sokolov
A.N. Nesmeyanov Institute of Organo-Element Compounds
RAS, 28 Vavilov Street, 119991 Moscow (Russia)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. The χT versus T in 100 G and M versus H at 2 K curves for **7**.

DOI: 10.1002/chem.200305760

(Figure 1). The cationic moieties are located between the anionic layers. In 2D bimetallic oxalate-bridged networks, a large variety of cations can be accommodated in the interlayers space.[12–14,5b,6b,6c] Recently, some of us have shown that achiral ferrocenic ammonium ions such as $[C_5H_5FeC_5H_4CH_2NR_3]^+$ with R = C_2H_5, n-C_3H_7, n-C_4H_9, are able to template the formation of such 2D networks.[12]

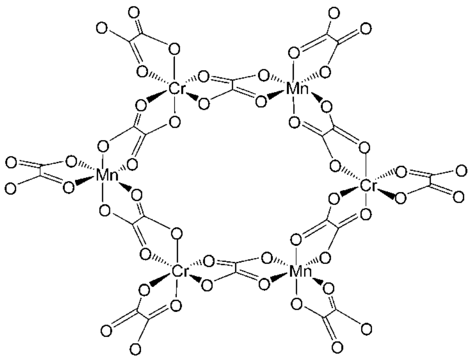


Figure 1. Schematic drawing of a heterochiral $[(\Delta)\text{-Mn}(\Lambda)\text{Cr(ox)}_3]^-$ honeycomb layer.

Several structural studies of racemic 2D networks based on single-crystal X-ray diffraction have been reported.[4a,15,16] For example, when the template cation is $[N(n\text{-}C_4H_9)_4]^+$, the crystal structure of the resulting $\{N(n\text{-}C_4H_9)_4[MnCr(C_2O_4)_3]\}$ was found to belong to the achiral $R3c$ space group.[15] Nevertheless, in a recent paper, some of us[17] have published the X-ray structure of $\{N(n\text{-}C_5H_{11})_4[MnFe(C_2O_4)_3]\}$ for which the space group was found to be enantiomorphous ($C222_1$). The loss of symmetry in the crystal results from a chiral twisted conformation of the alkyl chains, associated to an enantiomeric anionic layer configuration (all the chromium centers exhibit one configuration, while the manganese have the opposite one). This leads to anionic layers of the type $[(\Lambda)\text{-Mn }(\Delta)\text{-Fe}(C_2O_4)_3]^-$ or $[(\Delta)\text{-Mn }(\Lambda)\text{-Fe}(C_2O_4)_3]^-$. This result highlights that the reaction leading to single crystals from racemic tris(oxalato)ferrate(III) in the presence of Mn^{2+} and $[N(n\text{-}C_5H_{11})_4]^+$, evolves towards a spontaneous resolution of $\{[N(n\text{-}C_5H_{11})_4][(\Delta)\text{-Mn }(\Lambda)\text{-Fe}(C_2O_4)_3]\}$ and $\{[N(n\text{-}C_5H_{11})_4][(\Lambda)\text{-Mn }(\Delta)\text{-Fe}(C_2O_4)_3]\}$. This spontaneous resolution was also encountered for $\{[N(n\text{-}C_5H_{11})_4][MnCr(C_2O_4)_3]\}$ (space group: $C222_1$)[11a] and {DAZOP[$MnCr(C_2O_4)_3$]} (space group $P2_1$)[18] (DAZOP = 4-[4-(*N*,*N*-dimethylamino)phenylazo]-1-methylpyridinium). In each case the resulting configurations ([(Δ)-Mn, (Λ)-Cr] or [(Λ)-Mn, (Δ)-Cr]) of the anionic sublattice and that of the cations in the cationic sublattice are closely correlated. Therefore, one can imagine that a well-selected chiral cation used under its enantiomeric forms should be able to induce the formation of such optically active 2D networks.

For this purpose we decided to synthesize a series of optically active ferrocenic salts having a planar chirality, namely, the (*Rp*)- and (*Sp*)-[1-CH_2NR_3-2-CH_3–C_5H_3Fe–C_5H_5] iodide salts with R = CH_3 (**2I**), C_2H_5 (**3I**), n-C_3H_7 (**4I**), n-C_4H_9 (**5I**) (Figure 2). The enantiomeric excesses of (*Rp*)- and (*Sp*)-**2I** were determined by ^{1}H NMR measurements using as chiral shift reagent the [(Δ)-Trisphat] anion.[19]

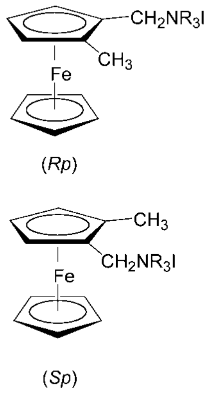
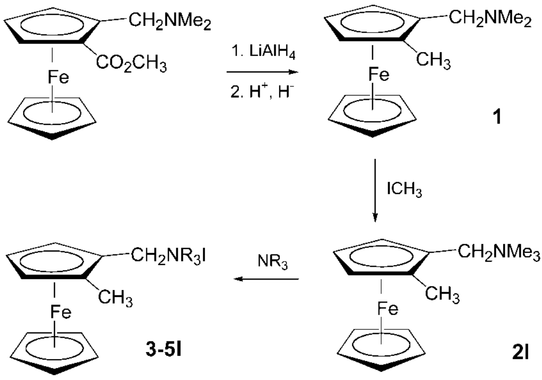


Figure 2. View of (*Rp*)- and (*Sp*)-[1-CH_2NR_3-2-CH_3–C_5H_3Fe–C_5H_5]I with R = Me (**2I**), Et (**3I**), *n*Pr (**4I**), and *n*Bu (**5I**).

We then describe the enantioselective synthesis of the [(*Rp*)-1-$CH_2N(n\text{-}C_3H_7)_3$-2-CH_3–C_5H_3Fe–C_5H_5][Mn (Λ)-$Cr(C_2O_4)_3$] [(*Rp*), (Λ)]-**7**, [(*Sp*)-1-$CH_2N(n\text{-}C_3H_7)_3$-2-CH_3–C_5H_3Fe–C_5H_5][Mn (Δ)-$Cr(C_2O_4)_3$] [(*Sp*), (Δ)]-**7** and discuss the circular dichroism (CD) and magnetic properties of these compounds.

Results and Discussion

Synthesis of (*Rp*)- and (*Sp*)-2I, 3I, 4I and 5I: These compounds were synthesized starting from the (*Rp*)- or (*Sp*)-[1-$CH_2N(CH_3)_2$-2-CH_3–C_5H_3Fe–C_5H_5] (**1**) amino compounds obtained through the classical asymmetric cyclopalladation reaction.[21] According to Scheme 1, the carboxylic ester function is converted to the methyl group in two reduction steps using first $LiAlH_4$ hydride and then the couple ($NaBH_4$, CF_3CO_2H) according to a modified version of the Kursanov–Parnes reaction.[23]



Scheme 1. Synthetic pathway to **2I**–**5I**.

The compounds (*Rp*)- and (*Sp*)-{[1-$CH_2N(CH_3)_3$-2-CH_3–C_5H_3Fe–C_5H_5]I} **2I** result from the quantitative reaction of methyl iodide with (*Rp*)- and (*Sp*)-**1**. The absolute configurations of the two enantiomers are secured by CD, which shows a positive Cotton effect at 263 and 421 nm for (*Rp*)-**2** and a negative Cotton effect for the (*Sp*)-**2** compounds (Figure 3). The corresponding **3I**, **4I**, and **5I** salts are obtained by replacement of the NMe_3 group of **2I** by NR_3 with $R = C_2H_5$, *n*-C_3H_7, *n*-C_4H_9, respectively.

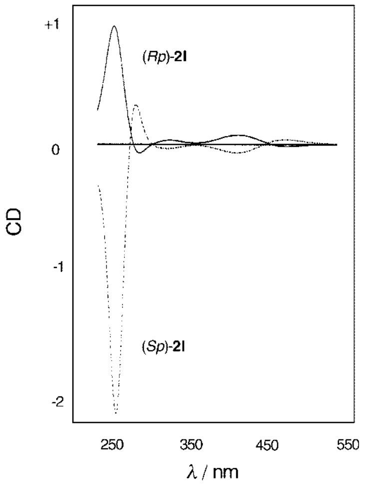
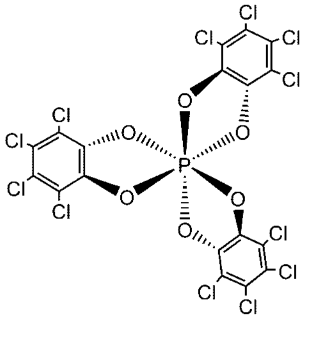


Figure 3. Circular dichroism (CD) of (*Rp*)-**2I** (full line) and (*Sp*)-**2I** (broken line).

^{1}H NMR experiments and determination of the enantiomeric excesses of 2I: There are few reports concerning diastereomeric interactions between anions of D_3 symmetry and planar chiral cations. Lacour et al., Kündig et al., and Rose et al.[25] have shown that the D_3-symmetric [(Δ)-Trisphat] anion acts as an efficient NMR chiral reagent to differentiate between enantiomers of neutral and cationic planar chiral metal complexes. On the other hand, we have also shown that this optically pure anion allows one to discriminate between the two enantiomers of propeller-like cobalt complexes.[26]

To gain a better understanding of the role of the template cation in the synthesis of optically active networks, we decided to investigate by ^{1}H NMR spectroscopy the chiral recognition between the cations **2**–**5** by the enantiopure [(Δ)-Trisphat] anion (Figure 4). For this purpose ^{1}H NMR spectra of the ammonium ferrocenyl iodides (*rac*)-**2I**–**5I**, (*Rp*)-**2I** and (*Sp*)-**2I** in CD_2Cl_2 solution were studied.



(Δ)

Figure 4. Structure of the [(Δ)-Trisphat] anion.

For *rac*-**2I** to *rac*-**5I**, additions of the [(Δ)-Trisphat] anion in increasing amounts (from 0.2 to 2.5 equivalents) lead to significant changes in the ^{1}H NMR spectrum as shown in Figure 5.

- The triplet signals corresponding to the protons of the terminal methyl group of $N(CH_2)_n\mathbf{CH_3}$ (with $n = 1$ to 3) are slightly shifted. For *rac*-**2I** the singlet assigned to the methyl groups $N(CH_3)_3$ is shifted to low frequencies by 60 ppb upon addition of 2.5 equivalents of the [(Δ)-Trisphat] anion.
- The two protons of the CH_2 methylene group tethering the nitrogen atom to the cyclopentadienyl ring, are diastereotopic and give rise to an AB spin system in the 4.5 ppm region. When adding [(Δ)-Trisphat] (2.5 equiv) these signals are strongly shielded by values of up to 50 ppb for *rac*-**2I** and 20 ppb for the *rac*-**3I** to **5I**. Moreover, for *rac*-**2I** the diastereomeric pairing leads to two AB sets as shown.
- Analysis of the effects for the protons of the substituted cyclopentadienyl ring is not straightforward becuase opposite induced shifts lead to overlap of the different multiplets.
- The analysis is easier for the singlet located around $\delta =$ 2.0 ppm corresponding to the CH_3 group borne by the cyclopentadienyl ligand. Addition of [(Δ)-Trisphat] leaves this signal almost unchanged for *rac*-**3I** to *rac*-**5I**. However, in the case of *rac*-**2I** a slight splitting occurs:

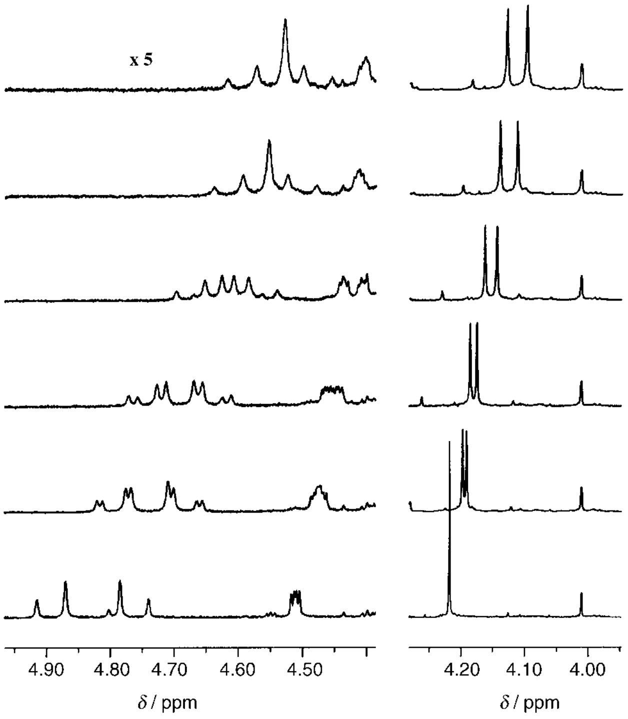


Figure 5. Evolution of the ^{1}H NMR spectrum (300.13 MHz) of *rac*-**2I** through addition of $[N(nBu_4)][(\Delta)Trisphat]$ (0.025 mol L^{-1} in CD_2Cl_2, 300 K, spectral width 2200 Hz, flip angle 60°, time domain 32 K points, acquisition time 7.47 s, 64 transients without relaxation delay). Fourier transform of the unapodized FID without zero filling leads to a digital resolution of 0.134 Hz per point. Number of [(Δ)-Trisphat] equivalents: from bottom to top, 0.0, 0.5, 1.0, 1.5, 2, 2.5.

the line shifts to lower frequency by 10 ppb upon the addition of 2.5 equivalents of [(Δ)-Trisphat]).

- The singlet located around $\delta = 4.2$ ppm corresponds to the five protons of the non-substituted cyclopentadienyl ring. This signal shifts progressively to low frequency by addition of [(Δ)-Trisphat]. This shift reaches 100 ppb for 2.5 equivalents. For *rac*-**2I**, the splitting occurs after the addition of the chiral anion, showing the formation of diastereomeric pairs. At the maximun splitting (31 ppb) obtained for 2 equivalents of [(Δ)-Trisphat]) the two signals are base line separated and can be integrated. The signal for *(Sp)*-**2I** is observed at high frequency with respect to that for *(Rp)*-**2I** (Figure 6).

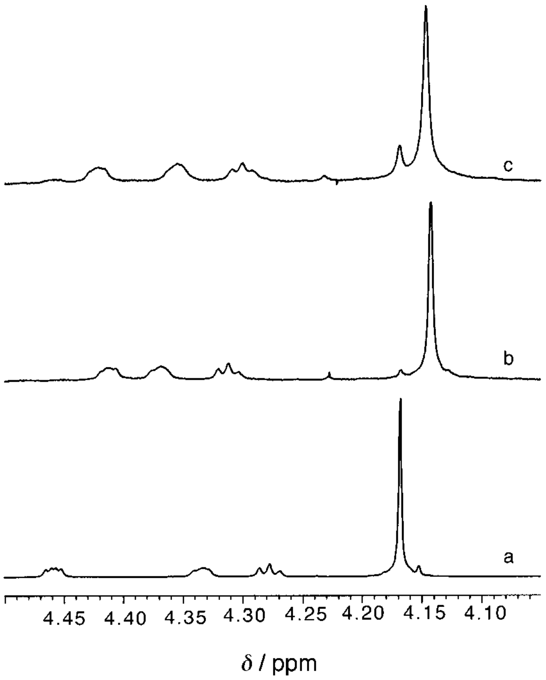


Figure 6. ^{1}H NMR spectra (300.13 MHz) of (*Sp*)-**2I** (a) (*Rp*)-**2I** (b) (*Rp*)-**2I** + about 0.2 equivalents of *rac*-**2I** (c) recorded under the same experimental conditions as in Figure 5.

The increase of the splitting with increasing [(Δ)-Trisphat] concentrations is related to the dynamic diastereomeric ions pairing between the planar chiral cation and the D_3-symmetry anion. The integration of the signals arising from diastereomeric pairs allows one to determine the enantiomeric excesses for the (*Rp*)-**2I** and (*Sp*) -**2I**. For (*Rp*) -**2I** and (*Sp*)-**2I** the enantiomeric excesses are found to be 0.95.

Synthesis of [(*Rp*)]-6, [(*Sp*)]-6, [(*Rp*), (Λ)]-7 and [(*Sp*),(Δ)]-7: The optically active (*Rp*) or (*Sp*) iodide ammonium salts **2I**–**5I** were used in an attempt to template the formation of 2D networks using $K_3[rac\text{-}\{Cr(C_2O_4)_3\}]\cdot 3H_2O$ and $MnCl_2\cdot 4H_2O$ as building blocks. Two-dimensional networks were obtained for **3I** and **4I**. These results have to be compared with those previously obtained with an achiral ferrocenic ammonium salt.[12] In the latter case, the synthesis of 2D networks was possible for $R = C_2H_5$, n-C_3H_7, and n-C_4H_9 using bromide salts which are much more soluble than iodide salts. The n-C_4H_9 derivative **5I**, in particular, precipitates from the water–methanol mixture, rendering the formation of the network impossible. The IR spectra show a strong band at 1632 and 1628 cm^{-1} for **6** and **7**, respectively, which is attributed to a stretching vibration of the bridging oxalate ligand.[24]

The poor crystallinity of samples **7** in its racemic or optically active forms does not permit a definitive conclusion on the crystal structure from the X-ray powder diffraction pattern. Nevertheless, the general diffractogram looks like those found with the $[N(n\text{-}C_4H_9)_4]^+$ ion, which is very well known to possess a 2D structure.[5a] Moreover, according to IR, normalized circular dichroism (NCD), and ferromagnetic properties, which are very similar to those previously published for achiral $\{C_5H_5FeC_5H_4{-}CH_2NR_3[MnCr(C_2O_4)_3]\}$ networks,[12] it is possible to assume the layered structural organization of these compounds.

A dramatic difference is observed for the networks obtained from the optically active ferrocenic ammonium salts **3I** and **4I**. Using **3I** the resulting networks (*Rp*)-**6** and (*Sp*)-**6** do not have optical activity corresponding to the d–d transition of the chromium, as is the case for the networks [(*Rp*), (Λ)]-**7** and [(*Sp*), (Δ)]-**7** obtained starting from **4I**.

The achiral[12] and chiral ferrocenic ammonium cations template the formation of the bimetallic anionic network for ethyl and propyl alkyl chains. On the contrary, tetraethylammonium cannot template the formation of such networks, whereas tetrapropylammonium does.[4c,11b] This emphasizes the role of the ferrocenic moiety in the templating activity of such ammonium cations.

The most striking difference between the templating activity of **3** and **4** is that **4** can induce the enantioselective self-assembly of the anionic network, whereas **3** cannot. A reasonable hypothesis is that the propyl chain of **4** penetrates the cavity of the honeycomb layers, whereas the ethyl chain of **3** does not. This weaker interaction between the cation **3** and the anionic network does not allow the transfer of chirality from the resolved cation to the bimetallic network.

Normalized CD for [(*Rp*), (Λ)]-7 and [(*Sp*),(Δ)]-7: The CD spectra for (*Rp*)-**4I** and (*Sp*)-**4I** show an intense positive (or negative, respectively) signal at 260 nm and 421 nm. The CD spectra for [(*Rp*), (Λ)]-**7** and [(*Sp*),(Δ)]-**7** show intense positive (or negative, respectively) signals at 260 nm and 570 nm (Figure 7).

The signal at 260 nm observed for **4I** and **7** is attributed to the π→π* transition of the cyclopentadienyl groups of the ferrocenic ammonium. The signal at 575 nm observed for **7** is attributed to the d–d transition of the tris(oxalato)-chromate(III) moiety.[1a] A positive (negative, respectively) circular dichroic signal at this wavelength is associated to a (Δ)- ((Λ)-, respectively) configuration of the tris(bis-chelated)chromium(III) ion.[12]

The opposite Cotton effects observed for (*Rp*)-**4I** and (*Sp*)-**4I** give indications of the enantiomeric character of the synthetic process leading to the template cations. This holds for the synthesis of [(*Rp*), (Λ)]-**7** and [(*Sp*),(Δ)]-**7** starting from (*Rp*)-**4** and (*Sp*)-**4** as well. In this case, the most impor-

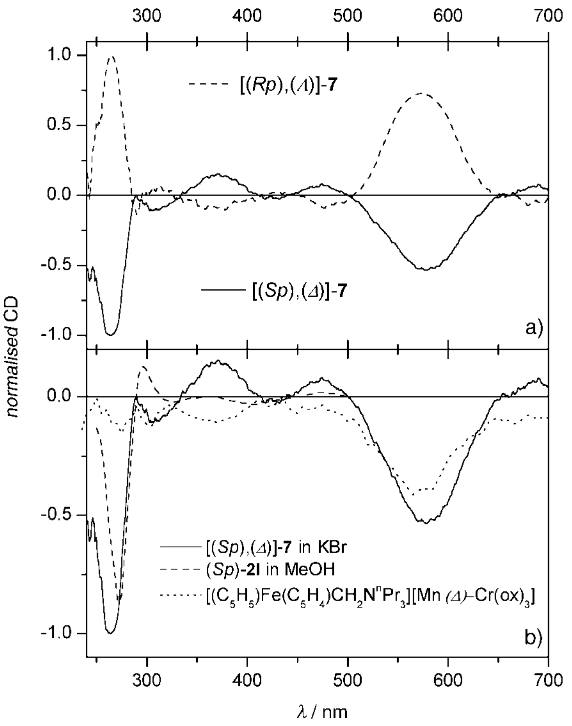


Figure 7. a) CD curves for [(*Sp*),(Δ)]-**7** and [(*Rp*),(Λ)]-**7** in KBr pellets. b) CD curves for [(*Sp*),(Δ)]-**7** and [(C_5H_5)Fe(C_5H_4)$CH_2N(C_3H_7)_3$][Mn (Δ)-Cr(C_2O_4)$_3$] in KBr pellets, and for (*Sp*)-**2I** in MeOH.

tant feature is the appearance of a dichroic signal associated with the chromium(III) ions inserted in the honeycomb layers though $[Cr(ox)_3]^{3-}$ that has been introduced in the reaction mixture in its racemic form. Moreover the absolute configuration of the chromium(III) ion is ruled by the absolute configuration of the template cation. Thus, thanks to the use of a resolved template cation, the self-assembly of the anionic network is enantioselective.

Magnetic properties: To study the magnetic ground state of compounds in which the chromium(III) ion can exhibit optical activity, SQUID magnetization measurements were performed on **7** both in its enantiomeric and racemic forms. The molar susceptibility χ_M has been measured in a magnetic field of 0.1 T between 2 and 300 K. In all cases, the $\chi_M T$ product increases monotonically when the temperature is decreased and then diverges at the low temperature. The χ_M^{-1} versus T curves are linear between 50 and 300 K and can be fitted using a Curie–Weiss law $\chi_M^{-1}=(T-\Theta)/C$, where Θ and C are the Weiss and Curie constants, respectively (Figure 8a). Θ equals 8.6, 8.3, and 8.7 K and C equals 6.19, 6.31, and 6.23 emu K mol^{-1} for [(*Rp*), (Λ)]-**7**, [(*Sp*),(Δ)]-**7**, and *rac*-**7**, respectively. The C values are close to the spin-only value (6.25 emu K mol^{-1}). The small variations of the Weiss constants are within the error. We thus exclude any quantitative interpretation of the small variations observed with the optical purity of the samples. The behavior of **7** in the paramagnetic state confirms the ferromagnetic nature of the exchange interaction between the metal ions.[3a]

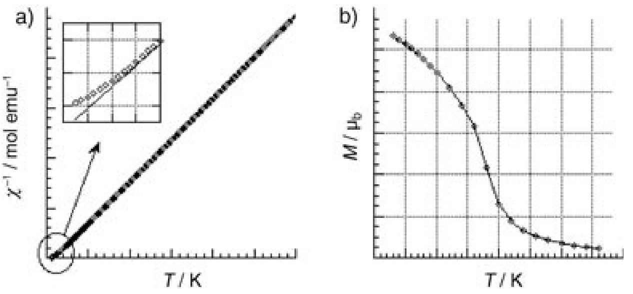


Figure 8. Plot of experimental (open diamonds) χ^{-1} versus T curve and its Curie–Weiss fit (solid line) (a), and field cooled in 0.01 T (b) for [(*Rp*), (Λ)]-**7**.

Complex **7** exhibits long-range magnetic order at low temperature (Figure 8b); its Curie temperature is 5.4 K. It is the same for both enantiomers and for the racemic compound as well. They compare well with those previously observed for the racemic analogues.[3a,12] At 2 K, the magnetization reaches rapidly a saturation value of 7.50 μ_b which is close to the spin-only value for two ferromagnetically coupled Mn^{II} and Cr^{III} ions.

These results compare well with those previously published. They confirm that the nature of the exchange coupling within the planes and hence the magnetic ordering temperature are not very sensitive to the nature of the countercation[3,6,11,14] nor to the optical activity of the compound.[12]

Conclusion

Oxalate-based 2D networks can be obtained in their optically active forms, leading to materials possessing both a Cotton effect and magnetic ordering. The optically active 2D networks are available by two routes: resolved (Δ)- or (Λ)-tris(oxalato)metalates(III) can be used as starting materials.[1a,12] Alternatively, the more general approach presented here relies on the enantioselective self-assembly of the anionic network thanks to the chiral templating activity of a resolved cation. Using ^{1}H NMR spectroscopy in solution, we have demonstrated that planar chiral ammonium ions form diastereomeric ion pairs with D_3-symmetric anions. In the case of 2D oxalate-based networks, the enantioselective self-assembly process could be initiated by the formation of such diastereomeric ion pairs followed by the incorporation of M^{II} cations as a new hexacoordinate element, the configuration of which is determined by the resolved starting materials.

Through these two different methods to control the configuration of magnetically ordered 2D networks, we are now able to synthesize a wide variety of optically active oxalate-based magnets even if the tris(oxalato)metalate building block does not exist or if the resolution is not known.[27] This versatility, together with the other strategies developed towards chiral magnets,[28–30] is a valuable tool to understand the very microscopic factors that govern magneto-chiral effects.[2]

Experimental Section

The IR spectra were recorded on a Bio-Rad IR-FT spectrometer as KBr pellets in the 4000–250 cm^{-1} region. Elemental analyses were performed at the SIARE-UPMC (Paris) and Nesmeyanov Institute (Moscow). Circular dichroism curves were recorded in the 240–700 nm region on a Jasco J-810 spectropolarimeter as KBr pellets (2 mg of product in 100 mg of KBr) or in MeOH. To afford comparison, the spectra were normalized and corrected for baseline deviation. Optical rotations were measured on an EPO1 (0.5 cm cell) or Ameria AA5 (10 cm cell) polarimeter.

The ^1H NMR spectra (300 MHz) were obtained at room temperature in 5 mm o.d. tubes on a Bruker AC 300 spectrometer equipped with a QNP probehead (CD_2Cl_2 solution, $c=0.025$ $mol\,L^{-1}$). Chemical shifts are given according to the IUPAC convention with respect to $SiMe_4$.

Magnetic measurements were performed with a Quantum Design MPMS-5S SQUID magnetometer in the DC mode for an external magnetic field up to 5 T for temperatures ranging between 2 and 300 K.

The powder diffraction patterns were collected at room temperature on a Philips PW-1050 goniometer using the Bragg–Brentano configuration and Mn-filtered $Fe_{K\alpha}$ radiation. The X-ray powder patterns were analyzed by the EVA program[20] to check for the absence of the starting compounds, the crystallinity of the material, and to calculate *d* spacings.

Synthesis of (*Rp*)- and (*Sp*)-*N,N*-dimethylaminomethyl)-2-methylferrocene (1): Optically active (*Rp*)- and (*Sp*)-**1** were obtained by an asymmetric cyclopalladation reaction adapted from the literature.[21] A solution of 1-methoxycarbonyl-2-dimethylaminomethylferrocene (2 g, 6.6 mmol in diethyl ether (50 mL)) resulting from the asymmetric cyclopalladation followed by carbonylation, was added dropwise to a suspension of $LiAlH_4$ (0.25 g, 6.6 mmol) in diethyl ether (100 mL). After the mixture had been stirred for one hour at room temperature, it was treated with water. The organic layer was extracted with diethyl ether to give the corresponding amino alcohol (1.54 g; 85 % yield). $NaBH_4$ (1.19 g, 8.84 mmol) and CF_3CO_2H (0.68 mL, 8.84 mmol) were added to a cooled (−40 °C) CH_2Cl_2 solution (250 mL) of the amino alcohol over 15 min. After the addition, the mixture was poured into a beaker containing ice and Na_2CO_3. A solution of Na_2SO_3 was then added to reduce the ferricinium compounds. Extraction using diethyl ether gave (*Rp*)- or (*Sp*)-**1** (1.2 g) in 82 % yield. NMR and IR spectra of the enantiomers are identical to those recorded for *rac*-**1**.[22]

$[\alpha]_D^{20}$ (+)-(*Rp*)-**1** = +37 ($c=0.117$, EtOH); $[\alpha]_D^{20}$ (−)-(*Sp*)-**1** = −35 ($c=0.173$, EtOH).

Synthesis of 2I, 3I, 4I and 5I: *General procedure*: These compounds were prepared by exchange reaction starting from the (*N,N*-dimethylaminomethyl)-2-methylferrocene (**1**) precursor previously treated with an excess of methyl iodide in acetone. The precipitating salt (**2I**) and was washed with diethyl ether.

The optically active iodide salts (*Rp*)- and (*Sp*)-**2I** were obtained starting from (*Rp*)- and (*Sp*)-(*N,N*-dimethylaminomethyl)-2-methylferrocene (**1**), respectively.

rac-**2I**: ^1H NMR (300 MHz, 0.025 $mol\,L^{-1}$, CD_2Cl_2, TMS): $\delta=4.82$ (AB system, $J=13.6$ Hz, 2H), 4.51 (m, 1H), 4.33 (m, 1H), 4.30 (m, 1H), 4.22 (s, 5H), 3.22 (s, 9H), 2.16 ppm (s, 3H); elemental analysis calcd (%) for $C_{15}H_{22}FeIN$: C 45.14, H 5.56, N 3.51; found: C 45.33, H 5.71, N 3.67; NCD: (2.5×10^{-4} $mol\,L^{-1}$, CH_3OH): (*Rp*)-**2I**: 263(+), 294(−), 331(+), 421(+), 485(−); NCD (1.66×10^{-4} $mol\,L^{-1}$, CH_3OH): (*Sp*)-**2I**: 263(−), 294(+), 331(−), 421(−), 485(+).

The corresponding *N,N,N*-trialkyl salts were obtained by refluxing the methyl iodide salt of the precursor **2I** (1.5 g, 3.4 mmol) with a (10 fold) excess of the corresponding trialkylamine (5 mL) in acetonitrile (20 mL) for two days. The expected *N,N,N*-trialkyl iodide salt was obtained as a (3:1) mixture with the methyl iodide precursor salt **2I** and was recovered after three fractional crystallizations from acetone/diethyl ether mixtures.

The optically active iodide salts (*Rp*)- and (*Sp*)-**3I**, -**4I**, -**5I** were prepared from optically active (*Rp*)-**2I** $[\alpha]_D^{20}=+40.1$ (c = 0.087, CH_2Cl_2; 95 % *ee*) and (*Sp*)-**2I** $[\alpha]_D^{20}=-41.0$ (c = 0.098, CH_2Cl_2; 95 % *ee*).

Compound **3I**, yield 60 % (*Rp*) $[\alpha]_D^{20}=+38.0$ ($c=0.132$, CH_2Cl_2); (*Sp*) $[\alpha]_D^{20}=-41.0$ ($c=0.098$, CH_2Cl_2); elemental analysis calcd (%) for $C_{18}H_{28}FeIN$: C 49.00, H 6.40, N 3.17; found: C 48.96, H 6.42, N 3.11.

Compound **4I**, yield 63 % (*Rp*) $[\alpha]_D^{20}=+47.0$ ($c=0.122$, CH_2Cl_2) and (*Sp*) $[\alpha]_D^{20}=-45.0$ ($c=0.220$, CH_2Cl_2); elemental analysis calcd (%) for $C_{21}H_{34}FeIN$: C 52.19, H 7.09, N 2.90; found: C 51.97, H 7.08, N 2.83.

Compound **5I**, yield 54 % (*Rp*) $[\alpha]_D^{20}=+29.0$ ($c=0.038$, CH_2Cl_2) and (*Sp*) $[\alpha]_D^{20}=-27.0$ ($c=0.029$, CH_2Cl_2); elemental analysis calcd (%) for $C_{24}H_{40}FeIN$: C 54.87, H 7.67, N 2.67; found: C 54.73, H 7.76, N 2.84.

Synthesis of {*rac*-[1-$CH_2N(C_2H_5)_3$-2-CH_3-C_5H_3Fe-C_5H_5][$MnCr(C_2O_4)_3$]} (6): {*rac*-[1-$CH_2N(C_2H_5)_3$-2-CH_3−C_5H_3Fe−C_5H_5]I} (**3I**) (30 mg, 0.068 mmol) was dissolved in methanol (0.20 mL) in a 10-mL tube, while in another tube K_3[*rac*-{$Cr(C_2O_4)_3$}]·3H_2O (33 mg, 0.068 mmol) and $MnCl_2\cdot4H_2O$ (14 mg, 0.068 mmol) were dissolved in a mixture of water (0.25 mL) and acetone (0.10 mL). The latter solution was added to the alcoholic one with a Pasteur pipette; a continuous scratching of the walls of the tube was carried out to facilitate the precipitation. The solution was filtered off on a 0.4 μm polycarbonate membrane. The precipitate was washed with methanol (2×3 mL) and with pure diethyl ether. A pale greenish microcrystalline powder was recovered (27 mg, 0.04 mmol, 58 % yield). IR (KBr disk): 1632 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{28}O_{12}NFeCrMn$: C 42.07, H 4.12, N 2.04; found: C 40.62, H 4.10, N 2.15.

Synthesis of {(*Rp*)-1-$CH_2N(C_2H_5)_3$-2-CH_3-C_5H_3Fe-C_5H_5[$MnCr(C_2O_4)_3$]} [(*Rp*)]-6 and {(*Sp*)-1-$CH_2N(C_2H_5)_3$-2-CH_3-C_5H_3Fe-C_5H_5[$MnCr(C_2O_4)_3$]} [(*Sp*)]-6: The experimental procedure was the same as for the racemic compound except for the starting ferrocenic moiety that was the corresponding (*Rp*)- or (*Sp*)-**3I** enantiomer. NCD studies led us to conclude that no optical activity is observed for the d–d chromium transition.

Synthesis of {*rac*-1-$CH_2N(n\text{-}C_3H_7)_3$-2-CH_3-C_5H_3Fe-C_5H_5[$MnCr(C_2O_4)_3$]} (7): {*rac*-[1-$CH_2N(n\text{-}C_3H_7)_3$-2-CH_3−C_5H_3Fe−C_5H_5]I} (**4I**) (140 mg, 0.30 mmol) was dissolved in methanol (1.2 mL) in a 10-mL tube, while in another tube K_3[*rac*-{$Cr(C_2O_4)_3$}]·3H_2O (120 mg, 0.246 mmol) and $MnCl_2\cdot4H_2O$ (60 mg, 0.30 mmol) were dissolved in water (1 mL). The aqueous solution was added to the alcoholic one with a Pasteur pipette; a continuous scratching of the walls of the tube was carried out to facilitate the precipitation. The solution was filtered on a 0.4 μm polycarbonate membrane. The precipitate was washed with a methanol–water (3:1) mixture (2×4 mL) and filtered, then washed with pure methanol (2×5 mL) and once with diethyl ether. A pale greenish microcrystalline powder was recovered (75 mg, 0.10 mmol, 42 % yield). IR (KBr disk): 1628 cm^{-1}; elemental analysis calcd (%) for $C_{27}H_{34}O_{12}NFeCrMn$: C 44.59, H 4.71, N 1.93; found: C 43.78, H 4.82, N 1.91.

Synthesis of {(*Rp*)-1-$CH_2N(n\text{-}C_3H_7)_3$-2-CH_3-C_5H_3Fe-C_5H_5[Mn (Λ)-$Cr(C_2O_4)_3$]} [(*Rp*), (Λ)]-7 and {(*Sp*)-1-$CH_2N(n\text{-}C_3H_7)_3$-2-CH_3-C_5H_3Fe-C_5H_5[Mn (Δ)-$Cr(C_2O_4)_3$]} [(*Sp*),(Δ)]-7: The experimental procedure was the same as for the racemic compound except for the starting ferrocenic moiety that was the corresponding (*Rp*)- or (*Sp*)-**4I** enantiomer.

[(*Rp*), (Λ)]-7: NCD: 260(+),315(+), 365(−), 420(+), 480(−), 575(+).

[(*Sp*),(Δ)]-7: NCD: 260(−), 315(−), 365(+), 420(−), 480(+), 575(−).

Acknowledgments

This work was supported by the French CNRS and the Université Pierre et Marie Curie (Paris, France) and benefited from Russian financial support (RFBR grant 02–03–33355).

---

[1] a) R. Andrés, M. Gruselle, B. Malézieux, M. Verdaguer, J. Vaissermann, *Inorg. Chem.* **1999**, *38*, 4637–4646; b) R. Andrés, M. Brissard, M. Gruselle, C. Train, J. Vaissermann, B. Malézieux, J. P. Jamet, M. Verdaguer, *Inorg. Chem.* **2001**, *40*, 4633–4640; c) M. Gruselle, R. Andrés, B. Malézieux, M. Brissard, C. Train, M. Verdaguer, *Chirality* **2001**, *13*, 712–714.

[2] a) L. D. Barron, *Nature* **2000**, *405*, 895–896; b) G. L. J. A. Rikken, E. Raupach, *Nature* **1997**, *390*, 493–494; c) G. L. J. A. Rikken, E. Raupach, *Nature* **2000**, *405*, 932–935; d) E. Raupach, G. L. J. A. Rikken, C. Train, B. Malézieux, *Chem. Phys.* **2000**, *261*, 373–380.

[3] a) H. Tamaki, Z. J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto, H. Okawa, *J. Am. Chem. Soc.* **1992**, *114*, 6974–6979; b) H. Tamaki, *Chem. Lett.* **1992**, 1975–1978.

[4] a) S. Decurtins, H. W. Schmalle, H. R. Oswald, A. Linden, J. Ensling, P. Gütlich, A. Hauser, *Inorg. Chim. Acta* **1994**, *216*, 65 – 73; b) S. Decurtins, H. W. Schmalle, P. Schneuwly, J. Ensling, P. Gütlich, A. Hauser, *J. Am. Chem. Soc.* **1994**, *116*, 9521 – 9528; c) R. Pellaux, H. W. Schmalle, R. Huber, P. Fischer, T. Hauss, B. Ouladdiaf, S. Decurtins, *Inorg. Chem.* **1997**, *36*, 2301 – 2308.

[5] a) P. Day, *J. Chem. Soc. Dalton Trans* **1997**, 701 – 705; b) M. Kurmoo, A. W. Graham, P. Day, S. J. Coles, M. Hursthouse, J. L. Caulfield, J. Singleton, F. L. Pratt, W. Hayes, L. Ducasse, P. Guionneau, *J. Am. Chem. Soc.* **1995**, *117*, 12209 – 12217.

[6] a) E. Coronado, Galan-J. R. Mascaros, C. J. Gomez-Garcia, J. M. Martinez-Agudo, *Inorg. Chem.* **2001**, *40*, 113 – 120; b) E. Coronado, J. R. Galan-Mascaros, C. J. Gomez-Garcia, V. Laukhin, *Nature* **2000**, *408*, 447 – 449; c) E. Coronado, J. R. Galan-Mascaros, C. J. Gomez-Garcia, J. M. Martinez-Agudo, *Adv. Mater.* **1999**, *11*, 558 – 561.

[7] a) N. S. Ovanesyan, G. V. Shilov, L. O. Atovmyan, R. N. Lyubovskaya, A. A. Pyalling, Y. G. Morozov, *Mol. Cryst. Liq. Cryst.* **1995**, *273*, 175 – 179; b) N. S Ovanesyan, G. V. Shilov, A. A. Pyalling, N. A. Sanina, L. O. Atovmyan, L. Bottyan, *Mol. Cryst. Liq. Cryst.* **1999**, *335*, 91 – 104; c) N. S. Ovanesyan, A. A. Pyalling, N. A. Sanina, A. B. Kashuba, L. Bottyan, *Hyperfine Interactions* **2000**, *126*, 149 – 154.

[8] J. Larionova, B. Mombelli, J. Sanchiz, O. Kahn, *Inorg. Chem.* **1998**, *37*, 679 – 684.

[9] A. Hernandez-Molin, F. Lloret, C. Ruiz-Perez, M. Julve, *Inorg. Chem.* **1998**, *37*, 4131 – 4135.

[10] R. Pellaux, S. Decurtins, H. W. Schmalle, *Acta Cryst. C* **1999**, *55*, 1075 – 1079.

[11] a) S. G. Carling, C. Mathonière, P. Day, K. M. Abdul Malik, S. J. Coles, M. B. Hursthouse, *J. Chem. Soc. Dalton Trans.* **1996**, 1839 – 1844; b) C. Mathonière, C. J. Nutall, S. G. Carling, P. Day, *Inorg. Chem.* **1996**, *35*, 1201 – 1206.

[12] B. Malézieux, R. Andrés, M. Brissard, M. Gruselle, C. Train, P. Herson, L. L. Troitskaya, V. I. Sokolov, S. T. Ovseenko, T. V. Demeschik, N. S. Ovanesyan, I. A. Mamed'yarova, *J. Organomet. Chem.* **2001**, *637–639*, 182 – 190.

[13] CléR. ment, S. Decurtins, M. Gruselle, C. Train, *Montashefte für Chemie* **2003**, *134*, 117 – 135

[14] S. Bénard, P. Yu, J. P. Audière, R. Clément, J. Guilhem, L. Tchertaniv, K. Nakatani, *J. Am. Chem. Soc.* **2000**, *12*, 9444 – 9454.

[15] L. O. Atovmyan, G. V. Shilov, R. N. Lyubovskaya, E. L. Zhilyaeva, N. S. Ovanesyan, S. I. Pirumova, I. G. Gusakoskaya, Y. G. Morozov, *J. E. T. P. Lett.* **1993**, *58*, 766 – 769.

[16] J. Larionova, B. Monbelli, J. Sanchez, O. Kahn, *Inorg. Chem.* **1998**, *37*, 679 – 684.

[17] G. V. Shilov, N. S. Ovanesyan, N. A. Sanina, L. O. Atovmyan, M. Gruselle, *Russ. J. Coord. Chem.* **2001**, *27*, 605 – 611.

[18] J. S. O. Evans, S. Bénard, P. Yu, R. Clément, *Chem. Mater.* **2001**, *13*, 3813 – 3816.

[19] J. Lacour, S. Torche-Haldimann, J. J. Jodry, C. Ginclinger, F. Favarger, *Chem. Commun.* **1998**, 1733 – 1734.

[20] a) P. Caussin, J. Nusinovici, D. W. Beard, *Adv. X-ray anal.* **1988**, *31*, 423 – 430; b) P. Caussin, J. Nusinovici, D. W. Beard, *Adv. X-ray anal.* **1989**, *32*, 531 – 538.

[21] a) V. I. Sokolov, L. L. Troitskaya, *Chimia* **1978**, *32*, 122 – 123; b) V. I. Sokolov, L. L. Troitskaya, O. A. Reutov, *J. Organomet. Chem.* **1979**, *182*, 537 – 540; c) V. I. Sokolov, *Pure Appl. Chem.* **1983**, *55*, 1837 – 1842.

[22] L. A. Troitskaya, T. V. Demeshchik, V. I. Sokolov, I. A. Mamed'yarova, B. Malézieux, M. Gruselle, *Russian Chem. Bull. Int. Ed.* **2001**, *50*, 497 – 503.

[23] MaléB. zieux, M. Gruselle, L. L. Troitskaya, V. I. Sokolov, J. Vaissermann, *Organometallics* **1994**, *13*,2979 – 2986.

[24] J. Vaissermann, *PhD*, Université Pierre et Marie Curie, Paris, **1974**.

[25] a) J. Lacour, C. Ginclimer, C. Grivet, G. Bernardinelli, *Angew. Chem.* **1997**, *109*, 660 – 662; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 608 – 610; b) J. G. Plana, D. Prim, E. Rose, F. M. Rose-Munch, D. Monchaud, J. Lacour, *Organometallics* **2001**, *20*, 4107 – 4110; c) H. Ratni, J. J. Jodry, J. Lacour, E. P. Kundig, *Organometallics* 2**000**, *19*, 3997 – 3999.

[26] a) H. Amouri, R. Thouvenot, M. Gruselle, *C. R. Chimie* **2002**, *5*, 257 – 262; b) H. Amouri, R. Thouvenot, M. Gruselle, B. Malézieux, J. Vaissermann, *Organometallics* **2001**, *20*, 1904.

[27] F. Pointillart, C. Train, M. Gruselle, F. Villain, H. W. Schmalle, D. Talbot, P. Gredin, S. Decurtins, M. Verdaguer, *Chem. Mater.* **2004**, *16*, 832 – 841.

[28] a) K. Inoue, K. Kikuchi, M. Ohba, H. Okawa, *Angew. Chem.* **2003**, *115*, 4958 – 4961; *Angew. Chem. Int. Ed.* **2003**, *42*, 4810 – 4813; b) K. Inoue, H. Imai, P. S. Ghalsasi, K. Kikuchi, M. Ohba, H. Okawa, J. V. Yakhmi, *Angew. Chem.* **2001**, *113*, 4372 – 4375; *Angew. Chem. Int. Ed.* **2001**, *40*, 4242 – 4245.

[29] a) E. Coronado, C. Gimenez-Saiz, J. M. Martinez-Agudo, A. Nuez, F. M. Romero, H. Stoeckli-Evans, *Polyhedron* **2003**, *22*, 2435 – 2440; b) E. Coronado, C. J. Gomez-Garcia, A. Nuez, F. M. Romero, E. Rusanov, H. Stoeckli-Evans, *Inorg. Chem.* **2002**, *41*, 4615 – 4617.

[30] a) M. Minguet, D. Luneau, C. Paulsen, E. Lhotel, A. Gorski, J. Waluk, D. B. Amabilino, J. Veciana, *Polyhedron* **2003**, *22*, 2349 – 2354; b) M. Minguet, D. Luneau, E. Lhotel, V. Villar, C. Paulsen, D. B. Amabilino, J. Veciana, *Angew. Chem.* **2002**, *114*, 606 – 609; *Angew. Chem. Int. Ed.* **2002**, *41*, 586 – 589.

Received: November 28, 2003
Revised: May 26, 2004