was obtained. Ligand **6**, derived from (–)-prolinol, also gives a very low ee (entry 17).

The results of these model studies[13] indicate that the concept of a chiral phosphorus ligand for organocopper reagents is, indeed, a workable hypothesis. Relevant are the following facts: (a) the addition of extra lithium salts is necessary; (b) 2 equiv of ligand is needed. We are presently extending these results to transferable groups other than nBu and other enones. Since it is easily possible to modify the chiral auxiliary on phosphorus, it seems that there is plenty of room for further improvement in this new class of chiral ligands to copper. Work is in progress toward this end.

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(13) Typical procedure: To a suspension of CuI (476 mg; 2.5 mmol) in THF (40 mL) is added ligand **1** (3.4 mL of a 1.5 N solution in toluene; 5.1 mmol) at –30 °C. The temperature is allowed to rise, and solubilization is usually observed around 10 °C. After stirring for 15 min, the solution is cooled to –40 °C and nBuLi (1.45 mL of a 1.6 M solution in hexane; 2.3 mmol) is added. The solution, which turns yellow, is warmed for 15 min at –5 °C and then cooled again to 78 °C, and 2-cyclohexenone **7** (200 μL; 2 mmol) in THF (5 mL) is introduced. The mixture is then slowly warmed to –30 °C (in 1 h) and stirred until the disappearance of **7**. Hydrolysis was carried out with 15 mL of 5 N HCl, and stirring is continued in the open air for 1 h in order to hydrolyze the ligand completely. The aqueous phase is extracted with two 100-mL portions of ether, and the combined organic phases were then washed twice with NH$_4$OH in order to remove the copper salts. The solvents were removed in vacuo, and the crude product was treated with (*R,R*)-2,3-butanediol in a Dean–Stark trap.[8] The final ketal **9** was purified by flash column chromatography and then by Kugelrohr distillation.

On the Mechanism of Spin Coupling in Metallocenium Charge-Transfer Salts: Ferromagnetism in Decamethylchromocenium Tetracyanoquinodimethanide

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The challenge of creating molecular-based ferro- or ferrimagnets has been addressed in several ways.[1–7] Among them, the search
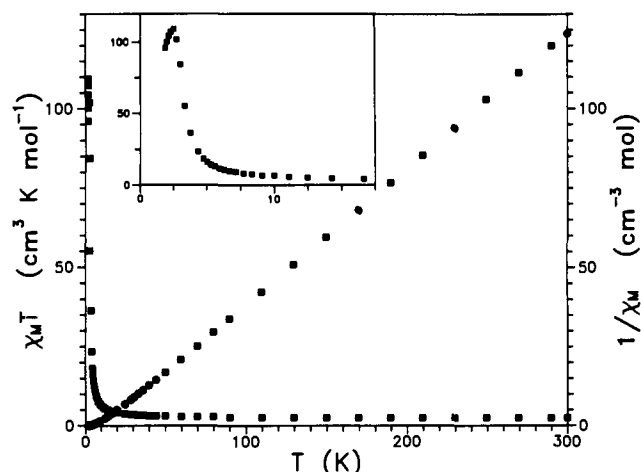
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Figure 1. Temperature dependence of $\chi_m T$ (squares) and χ_m^{-1} (circles) for polycrystalline **3** recorded at 250 G. Inset: expansion of the 1.9–15 K region of the $\chi_m T$ plot.

for ferromagnetic donor–acceptor (D$^+$A$^-$) charge-transfer (CT) salts[3–6] has been dominated by a "prescription"[3] inspired by McConnell's[2a] recognition that ferromagnetic spin coupling within an interacting D$^+$A$^-$ pair might arise through configuration mixing with a virtual CT state, provided that D$^+$ or A$^-$ possesses an orbitally degenerate ground state. The [Fe(C$_5$(CH$_3$)$_5$)$_2$]$^+$ ($S = 1/2$, $^2E_{2g}$) and [Mn(C$_5$(CH$_3$)$_5$)$_2$]$^+$ ($S = 1$, $^3E_{2g}$) cations have such a ground state.[8] Their mixed-stack, ...D$^+$A$^-$D$^+$A$^-$..., salts with orbitally nondegenerate paramagnetic counterions thus fulfill the requirements of the CT configuration mixing mechanism[3] and, indeed, typically display ferromagnetic behavior,[3a,4] with [Fe-(C$_5$(CH$_3$)$_5$)$_2$][TCNE][9] (**1**) and [Mn(C$_5$(CH$_3$)$_5$)$_2$][TCNQ][4a] (**2**) being bulk ferromagnets.

However, the behavior of the [M(C$_5$(CH$_3$)$_5$)$_2$]$^+$ CT salts where M = Fe or Mn does *not* validate this mechanism, for its predictions in these two cases coincide with those of alternate mechanisms for spin coupling, namely, Heisenberg exchange between electrons in orthogonal orbitals[10,11] and spin-polarization-based exchange.[2b,12] In contrast, CT configuration mixing would lead to antiferromagnetic D$^+$–A$^-$ coupling for the orbitally nondegenerate [Cr-(C$_5$(CH$_3$)$_5$)$_2$]$^+$ ($S = 3/2$, $^4A_{1g}$)[8] cation, whereas the alternate mechanisms would lead to ferromagnetic D$^+$–A$^-$ coupling. Thus, CT salts with M = Cr serve as a clear test of the spin-coupling mechanism in this class of materials. We report here that the 1:1 CT salt [Cr(C$_5$(CH$_3$)$_5$)$_2$][TCNQ] (**3**) not only displays fer-

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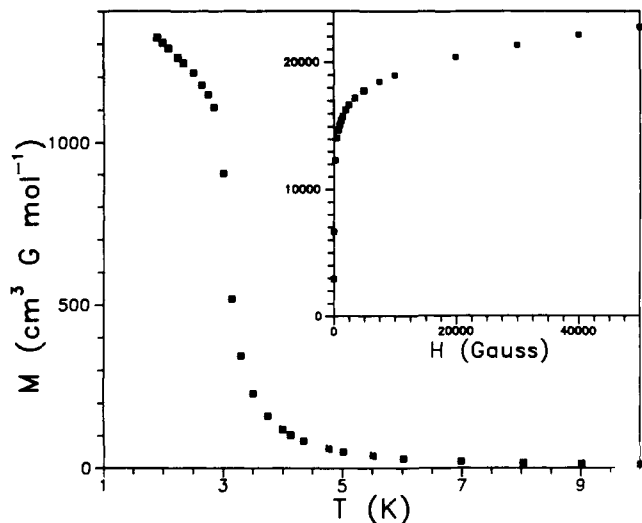
Figure 2. Field-cooled magnetization M of polycrystalline **3** in an external field of 15 G. Inset: field dependence of the magnetization for polycrystalline **3** recorded at 2 K.

romagnetic coupling among the spins but also is a bulk ferromagnet with T_c = 3.1 K, contrary to the prediction of the CT configuration-mixing mechanism[3] and to a previous report that **3** is a ferrimagnet.[13] The results presented here further support our proposal that the use of higher spin molecular ions should result in enhanced ferromagnetic interactions and, ultimately, increased critical temperatures in magnetic molecular materials.[4a,c,d] Specifically, in the classical limit, for a series of CT salts with fixed anion, $T_C \propto S(D^+)$ when D^+-A^- couplings dominate (and vice versa), other things being equal.

The 1:1 CT salt **3** was prepared by combining equimolar acetonitrile solutions of $[Cr(C_5(CH_3)_5)_2]$[8] and TCNQ. Crystals suitable for X-ray analysis were obtained by recrystallization from acetonitrile. A unit cell analysis[14] demonstrated that **3** is isomorphous to the ferromagnetic ...$D^+A^-D^+A^-$... CT salt, **2**.

The magnetization, M, of polycrystalline **3** was measured with a superconducting quantum interference device (SQUID) magnetometer.[15] Field cooled magnetization data recorded from 300 to 1.9 K at 250 G are shown in Figure 1, plotted as $\chi_m T$ and χ_m^{-1} vs T. The room temperature value, $\chi_m T$ = 2.32 cm³ K mol⁻¹, corresponds to $\mu_{eff} = (3k/N\mu_B)^{1/2}(\chi_m T)^{1/2}$ = 4.31 μ_B, which is consistent with the spin-only value (4.24 μ_B) calculated for an uncorrelated two-spin system with $S(D^+) = {}^3/_2$ and $S(A^-) = {}^1/_2$, and g = 2 for both spins. $\chi_m T$ for **3** is constant from ambient temperature to ~50 K, and a plot of χ_m^{-1} vs T is linear (Figure 1). Together these show that the susceptibility of **3** follows the Curie–Weiss law, $\chi_m = C/(T - \Theta)$ for $T >$ ~50 K, with a positive Weiss constant, Θ = +11.6 K, which indicates that ferromagnetic interactions dominate. As the sample is cooled below 10 K, an abrupt increase in $\chi_m T$ confirms this dominance and signals the possible approach of a ferromagnetic phase transition.

The occurrence of a ferromagnetic phase transition was established by measuring the magnetization of **3** as a function of temperature and field in the ranges of 1.9–10 K and 0–50 000 G. As **3** is cooled in a low field (15 G), its magnetization (Figure 2) shows a sharp transition, increasing abruptly between 3.5 and 3 K; below 3 K the magnetization approaches saturation as expected for a bulk ferromagnet. The critical temperature for this transition, T_c, is taken here as the maximum of the slope, dM/dT: T_c = 3.1 K. The field dependence of the magnetization at 2 K

(inset, Figure 2) is also characteristic of a polycrystalline 3-D ferromagnet, showing a steep rise to a value of ~1.5 × 10⁴ cm³ G mol⁻¹ by 1000 G, followed by a gradual increase to a maximum of 2.25 × 10⁴ cm³ G mol⁻¹ at the highest field attainable, 50 000 G. This saturation magnetization value, M_{sat}, agrees with that expected for a ferromagnet, $M_{sat} = N\beta[g_D S(D^+) + g_A S(A^-)]$ = 22 333 cm³ G mol⁻¹ (g = 2 for both spins). This demonstrates that **3** is *not* a ferrimagnet,[13] as it might have been if the $D^+(S={}^3/_2)$-$A^-(S={}^1/_2)$ coupling were antiferromagnetic, for in such a case one would have $M_{sat} = N\beta[g_D S(D^+) - g_A S(A^-)]$ = 1.12 × 10⁴ cm³ G mol⁻¹. Indeed, even the plot of $\chi_m T$ vs T (Figure 1) does not show the minimum characteristic of one-dimensional ferrimagnetism.[16]

These results clearly demonstrate that **3** exhibits ferromagnetic coupling; indeed, **3** even is a 3-D bulk ferromagnet. Therefore, spin coupling in **3** is not introduced by configuration mixing of a virtual CT state, and by extension this conclusion can be generalized to other metallocenium-based CT salts that display the mixed-stack $D^+A^-D^+A^-$ arrangement, such as **1** and **2**.

Why then do the metallocenium CT salts routinely display ferromagnetic interactions? Soos and McWilliams,[10] in a critique of the CT mechanism, also concluded that Heisenberg exchange of electrons in orthogonal orbitals would lead to values of J/k much smaller than observed. The most likely mechanism[12] is that proposed by Kahn and co-workers and by Buchachenko and is based on another idea of McConnell.[2b] It recognizes that spin correlation in metallocenium cations such as $[M(C_5(CH_3)_5)_2]^+$, M = Fe, Mn, Cr, causes the positive spin density on the metal ion to induce negative spin density on the pentamethylcyclopentadiene rings.[17] According to this mechanism, antiferromagnetic coupling between negative spin density on the ring and the spin of the radical anion results in the overall ferromagnetic alignment of the metal-centered and anion-radical spins.

Interestingly, the TCNQ salt of the $S = {}^1/_2$ $[Fe(C_5(CH_3)_5)_2]^+$ cation (**4**) is not a bulk ferromagnet as are **2** and **3**; **4** displays significant intrachain ferromagnetic (FM) interactions but weak antiferromagnetic (AF) interchain couplings, as evidenced by its metamagnetic behavior with T_c = 2.55 K.[18] One may understand the differing magnetic properties of **2–4** as follows. In the highly anisotropic crystals **2–4** one expects[19] that $T_c \propto |E_{intra} \times E_{inter}|^{1/2}$, where the strong intrachain near-neighbor D^+-A^- interaction energy has the form $E_{intra} \propto -S(D^+)S(A^-)J^{ra}_{DA}$, and one may schematically write the much weaker interchain interaction as $E_{inter} \propto -[S(D^+)S(A^-)J^{er}_{DA} - (S(D^+)^2 J^{er}_{DD} + S(A^-)^2 J^{er}_{AA})]$. Thus, in the classical limit a series of CT salts where D^+-A^- couplings dominate E_{inter} should be FM and should have $T_c \propto S(D^+)$, if other factors remain constant. The form of T_c further shows how increasing $S(D^+)$ can change a metamagnet to a ferromagnet and that, with a series of metamagnets, $T_c(T_N)$ could appear to depend on $S(D^+)^n$, with ${}^1/_2 \le n \le {}^3/_2$. The fact that $[M(C_5(CH_3)_5)_2]^+$ salts with M = Mn ($S(D^+)$ = 1) and Cr ($S(D^+) = {}^3/_2$) now appear to order more frequently than their Fe counterparts supports this analysis. However, the result $T_c(3) < T_c(2)$ shows that the dependence of the degree of spin polarization, zero-field splitting, etc. on the cation cannot be ignored.

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(14) **2** crystallizes[4a] in the monoclinic space group $P2_1/n$ with a = 10.829 (2) Å, b = 31.014 (4) Å, c = 8.544 (1) Å, β = 103.39 (2)°, and V = 2792 (1) Å³. For **3**: a = 10.972 (3) Å, b = 30.941 (5) Å, c = 8.511 (2) Å, β = 102.96 (2)°, V = 2815 (1) Å³. A complete structural analysis of **3** is currently underway and will be discussed later.

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