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[20] 7: Monoclinic, space group $P2_1/n$ (No. 14) with $a = 12.406(4)$, $b = 6.733(2)$, $c = 16.390(4)$ Å, $\beta = 95.11(2)°$, $V = 1363.6(5)$ Å^3, and $Z = 4$ ($\varrho_{calcd} = 1.685$ gcm^{-3}), $\mu(Mo_{K\alpha}) = 93.18$ cm^{-1}, 3997 unique reflections, 3777 with $F_0 \geq 0.6\sigma(F)$ were used in refinement; $R = 0.0466$, $R_w = 0.0452$; GOF = 1.22. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, GB-Cambridge CB21EW (UK), on quoting the full journal citation.

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Stepwise Stacking of Three Paramagnetic Metallocene Units: [CpNiCp(SiMe₂)₂CpCrCp(SiMe₂)₂CpNiCp]**

By Pierre Bergerat, Janet Blümel, Monika Fritz, Johann Hiermeier, Peter Hudeczek, Olivier Kahn, and Frank H. Köhler*

Molecular materials which are ferro-, ferri, or antiferromagnetic as a result of interactions between spin-carrying metal centers are currently subjects of intensive research.[1] A particularly rich chemistry is derived from chelate compounds in which like and—more promisingly—unlike metals are assembled in close proximity.[1c] Other spin sources are organometallic compounds. Thus, the reactions of polyalkylmetallocenes with tetracyanoethylene and related electron acceptors yield the salts [Cp*₂M]⁺ [π anion]⁻ which crystallize as stacks and exhibit spontaneous magnetization at low temperature when the metal is iron, manganese, or chromium.[2] In these materials the stacks are linear, that is, vertical with respect to the plane of the π ligands, and their stability is determined by ionic interactions. This organometallic/organic concept implies that different metal centers cannot be introduced in one stack by using simple sandwich molecules.

We wished to explore an alternative concept concerning pure organometallic compounds with stacking orientations other than vertical, with covalent bonding between the metallocenes, and with two different paramagnetic metal centers. We therefore synthesized biscyclopentadienyl ligands that may serve to link different metallocenes in a stereochemically well-defined manner.[3] After testing less reactive diamagnetic synthetic building blocks and their complexation behavior[4] we report here on the title compound 4, the prototype of a heteronuclear compound containing three paramagnetic metallocene units.

The synthesis (Scheme 1) is based on the stepwise metalation of two doubly bridged cyclopentadienes.[4] Thus the

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cyclopentadienide 1[3b] reacted with C₅H₅⁻ and solvated nickel(II) bromide to give the nickelocene 2 (two pairs of enantiomers syn-2a/b and anti-2a/b in the ratio 5:1).[5] Deprotonation of 2 yielded the green anion 3,[5] a key compound for further reaction with transition metal ions. The title compound 4[5] was obtained after addition of solvated chromium(II) chloride to a solution of 3 in THF. 4 is an air-sensitive compound isolated as mossy green crystals of 4 · toluene from toluene and solvent-free olive-green glittering platelets from hexane (42% yield).
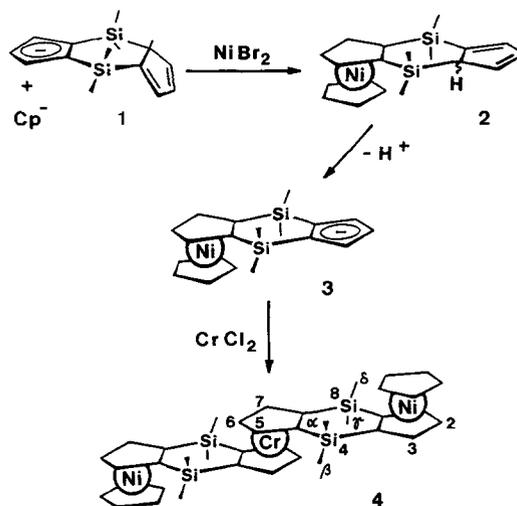
The cyclic voltammogram of 4 (Fig. 1) shows five electron transfers leading to a pentacation. An interaction between the two terminal nickelocenes is disclosed by splittings of 65 and 190 mV[6] associated with the potentials for the oxidation to the nickelocene monocations (near 1 V) and dications (near 2 V), respectively. Not surprisingly for highly charged
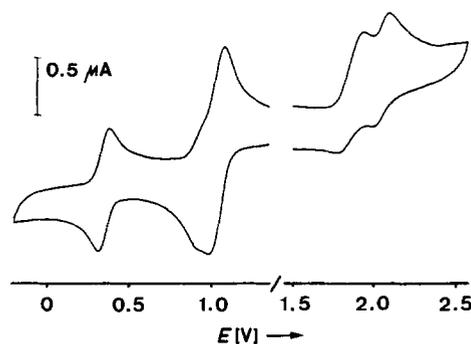
Fig. 1. Cyclic voltammogram of 4 in propionitrile, 8×10^{-4} molL^{-1}, $-20°C$, scan rate 200 mVs^{-1}, potential E vs internal Cp₂Co/Cp₂Co⁺. Electron transfers from left to right: $E_{1/2}$ (ΔE_p) 340(65), 980(80), 1045(80), 1850(170), 2040(105) mV; assignment see text.

species, the electron transfers leading to the tetra- and pentacation are chemically not reversible. The central chromocene is oxidized more easily ($E_{1/2} = 340$ mV) in accord with what is known from the parent metallocenes.[7] In addition, a broad, unresolved wave with $E_c = -1140$ mV indicates the irreversible reduction to 4³⁻.

From the paramagnetic compound 4 we have obtained ¹³C NMR signals in the range from $\delta = -400$ to $+1600$ (Fig. 2). Their number and their approximate areas are in

Fig. 2. ^{13}C NMR spectrum of 4 in [D$_8$]THF at 298 K; the two sections have different vertical scales. S = solvent, Cp' = C1–3, C3a, and C8a.

agreement with the structure shown in Scheme 1,[8] while their shifts are characteristic of substituted nickelocenes (weighted average $\delta \approx 1400$ to $1500^{[9]}$) and chromocenes (weighted average $\delta \approx -300$ to $-400^{[9]}$). It follows that, at ambient temperature, 4 has six unpaired electrons with each metallocene unit accommodating two of them. This is confirmed by the ^1H NMR spectrum.[5] Surprisingly, however, the signals of H1–3 at $\delta = -221.6$ are shifted about 10% less than the Cp protons of mononuclear nickelocenes.[9] Since it was not clear whether this points to spin exchange between the metallocenes, we performed solid-state magnetic measurements.

The magnetic behavior is illustrated by the plot of $\chi_M T$ vs T (Fig. 3). At 250 K, $\chi_M T$ is equal to 2.94 cm^3 K mol^{-1}, which corresponds to what is expected for three uncoupled ions with $S_{Ni1} = S_{Ni2} = S_{Cr} = 1^{[10]}$ and is in agreement with the NMR results. When the temperature is lowered, $\chi_M T$ decreases more and more rapidly and reaches 0.83 cm^{3}Kmol^{-1} at 1.9 K. Such behavior may arise from the
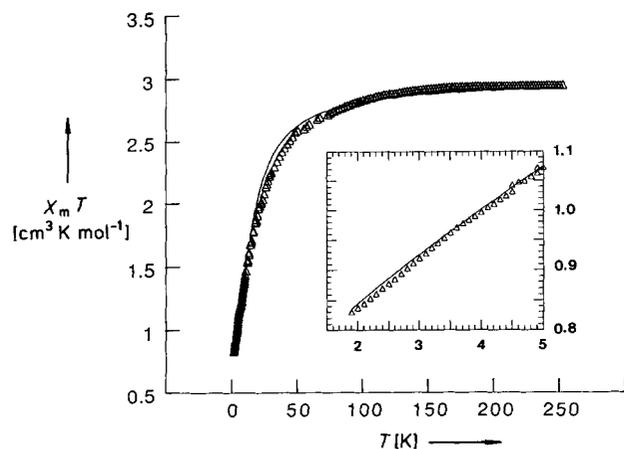
Fig. 3. Magnetic properties of 4 represented as a plot of $\chi_M T$ vs T with χ_M being the molar magnetic susceptibility and T the absolute temperature. $\triangle$: Experimental values, solid line: calculated curve. Inset: expansion of the low-temperature range.

local anisotropies D_{Ni} and D_{Cr} of the metal(II) ions, and the isotropic intramolecular magnetic interaction J between the central Cr^{II} and the terminal Ni^{II} ions. Based on the pertinent spin Hamiltonian[11] the respective role of the two contributions becomes evident from the plot of $\chi_M T$ vs T when T approaches zero: neglecting J would result in $\chi_M T > 1.3$ cm^3 K mol^{-1}; neglecting D_{Ni} and D_{Cr} would result in a plateau with $\chi_M T \approx 1$ cm^3 K mol^{-1}. The latter corresponds to the temperature range in which only the triplet ground state is thermally populated. It turns out (Fig. 3) that

both contributions are operative. These contributions are not correlated below 50 K, although they are correlated above 50 K, so that the fitting of the magnetic susceptibility χ_{Mu} along the direction u by Equation (a)[12] is expected to

$$\chi_{Mu} = \frac{N\beta}{H_u} \frac{\Sigma_i(-\partial E_{i,u}/\partial H_u)\exp(-E_{i,u}/kT)}{\Sigma_i \exp(-E_{i,u}/kT)} \qquad (a)$$

provide a reliable value of J. Since both D_{Ni} and D_{Cr} contribute to the zero-field splitting within the magnetic pair state they cannot be determined separately. We therefore assumed that D_{Cr} is negligible with respect to D_{Ni}. With somewhat idealized symmetry[13] the fitting yielded a Zeeman factor of $g = 1.98$, a zero-field splitting of $D_{Ni} = 28.7$ cm^{-1} (both are close to the values for nickelocene itself[14]), and the Ni^{II}–Cr^{II} interaction parameter $J = -1.95$ cm^{-1}; the agreement factor[12] was $R = 3.8 \times 10^{-4}$. The corresponding theoretical curve is given in Figure 3. Considering that D_{Cr} is not negligible leads to the same energy spectrum for the low-lying states with a different value for D_{Ni} but the same for J.

The magnetic properties are the crucial proof that the silyl bridges in 4 function as "valves" that allow a limited electron-exchange interaction. In this particular case it is antiferromagnetic. Other metal combinations and the manipulation of the silyl bridges are conceivable so that the magnetism of trinuclear metallocenes should be adjustable.

The properties of the title compound 4 illustrate that the approach discussed at the beginning, the stepwise stacking of metallocene units, actually works. Compound 4 is a good model for analogous polymers, since here structure, redox behavior, and interactions between the metallocene units, in particular magnetic exchange, may be investigated conveniently.

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[5] The isomer ratio of syn-2a/b to anti-2a/b was determined by ^1H NMR spectroscopy. syn-2a/b: ^{13}C NMR (THF, 310 K): $\delta = 655/597$ (Cα/δ), $-15.1/56.6$ (Cβ/γ), 114.6 (C2), 139.2/132.2 (C1/3); ^{29}Si NMR (THF, 319 K): $\delta = -845/-873$ (Si4/8). anti-2a/b: ^{13}C NMR (THF, 310 K): $\delta = 220/519$ (Cα/δ), 85.7/98.4 (Cβ/γ), 191.8 (C2), 140.6/127.9 (C1/3); ^{29}Si NMR (THF, 319 K): $\delta = -832/-852$ (Si4/8). The signal-to-noise ratio did not allow the localization of the broad Cp carbon signals expected at $\delta(^{13}C) > 1000$ similar as for 4 (Fig. 2). syn/anti-2a/b gave a satisfactory elemental analysis. EI-MS (70 eV): m/z (rel. intensity) 366 (M$^+$, 100), 351

$(M^+ - CH_3, 4)$, 300 $(M^+ - C_5H_6, 2)$, 285 $(M^+ - CH_3 - C_5H_6, 3)$, 183 $(M^{2+}, 3)$; the M^+ signal shows the theoretically expected isotope pattern. — 3: ^{13}C NMR (THF, 298 K): $\delta = 1600$ (Cp, C5–7, C4a/7a), 511/34 (Cα-δ), 135.7 (C3a/8a), 125.6 (C2), 100.1 (C1/3); ^{29}Si NMR (THF, 298 K): $\delta = -842$. 4: ^1H NMR ([D$_8$]toluene, 303 K) $\delta = -239.6$ (Cp), -221.6 (H1–3), 224.0 (H5/7), 163.0 (H6), 0.6/0.3 (Hα-δ); ^{29}Si NMR (THF, 305 K): $\delta = 313$; EI-MS (70 eV): m/z (rel. intensity) 784 $(M^+, 100)$, 660 $(M^+$ -CPNi, 7) and small unassigned peaks; the M^+ signal shows the theoretically expected isotope pattern. A satisfactory elemental analysis was obtained for 4 · toluene.

[6] The poorly resolved splitting near 1 V was estimated as described in: H. Atzkern, J. Hiermeier, F. H. Köhler, A. Steck, J. Organomet. Chem. 1991, 408, 281–296.

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[8] The study of the tris-iron analogues excludes the all-cis arrangement[6].

[9] F. H. Köhler, W. A. Geike, J. Organomet.Chem. 1987, 328, 35–37 and earlier contributions in the series. Note that we have changed the sign convention since.

[10] Calculated from $\chi_M T = (N\beta^2/3k)$ $(4g_{Ni}^2 + 2g_{Cr}^2)$ where g_{Ni} and g_{Cr} are the local Zeeman factors and the other symbols have their usual meaning.

[11] $H = -J$ $(S_{Ni1} + S_{Ni2})$ $S_{Cr} + S_{Ni1}$ D_{Ni} $S_{Ni1} + S_{Ni2}$ D_{Ni} $S_{Ni2} + S_{Cr}$ D_{Cr} $S_{Cr} + \beta(S_{Ni1} + S_{Ni2})$ $g_{Ni} + S_{Cr} \cdot g_{Cr} \cdot H$, where D_{Ni} and D_{Cr} are the local anisotropy tensors and g_{Ni} and g_{Cr} are the local Zeeman tensors.

[12] In Equation (a) the summation runs over the 27 levels $E_{i,u}$ in the presence of the magnetic field H_u. The powder magnetic susceptibility was calculated by averaging over 15 directions of the magnetic field. The energies $E_{i,u}$ were obtained by diagonalizing the spin Hamiltonian of ref. [11] using the $|M_s(Ni1), M_s(Cr), M_s(Ni2) >$ functions as a basis set. Then the parameters J, D_{Ni}, and g were determined by minimizing the agreement factor $R = \Sigma[(\chi_M T)^{cal} - (\chi_M T)^{obs}]^2/\Sigma[(\chi_M T)^{obs}]^2$.

[13] D_{Ni} and the zero-field splitting parameter D_{Ni} $(= 3D_{Ni,zz}/2)$ were assumed to be axial, and g_{Ni} and g_{Cr} to be isotropic with the same principal g value.

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Chelate Stabilization of a Monomeric Lithium Tellurolate**

By Heinz Gornitzka, Susanne Besser, Regine Herbst-Irmer, Ulrike Kilimann, and Frank T. Edelmann*

Metal complexes with alkoxide (RO^-) and thiolate ligands (RS^-) have been well studied.[1–3] However, only a few with selenolate and tellurolate ligands (RSe^- and RTe^-, respectively) are known.[4–6] They are of interest as precursors for metal chalcogenides,[7, 8] and also play an ever increasing role as reagents in organic synthesis.[4–6,9–11] In both cases alkali metal chalcogenolates act as intermediates. Sodium tellurolates are for example accessible by the reduction of the corresponding ditellurides with sodium amalgam or sodium in liquid ammonia.[12] They can undergo reactions to give transition metal tellurolates[13] as well as compounds with Te–C bonds.[9–11] Very little is known about the structural chemistry of alkali metal tellurolates: only [Li(thf)$_3$][2,4,6-tBu$_3$C$_6$H$_2$Te][14] as well as [Na(tmeda)][2,4,6-Me$_3$C$_6$H$_2$Te] and [K([18]crown-6)][2,4,6-iPr$_3$C$_6$H$_2$Te][15] have been structurally characterized. In all three cases bulky substituents led to a kinetic stabilization of the alkali metal tellurolate. We have now found that the stability of alkali metal chalcogenolates can also be increased dramatically by chelation. Crystalline lithium chalcogenolates are readily accessible also in the case of the higher homologues by incorporation of a Li–E unit (E = S, Se, Te) into a six-membered chelate system.

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2-(Dimethylaminomethyl)ferrocenyllithium (1) served as the starting material, which is readily accessible by metalation of (dimethylaminomethyl)ferrocene[16] with n-butyllithium.[17] In THF solution 1 rapidly reacts with elemental sulfur, selenium, or tellurium under insertion of a chalcogen atom into the lithium–carbon bond. The crystalline lithium chalcogenolates 2–4 can be isolated in high yield from the resulting solution. The yellow-brown solids are readily soluble in THF, but almost insoluble in diethyl ether and hydrocarbon solvents.

2, E = S (73%)
3, E = Se (84%)
4, E = Te (100%)
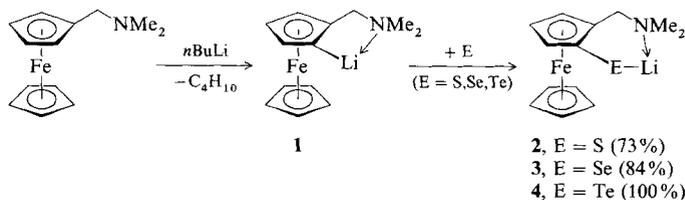
Red-brown single crystals of the composition [Li(dme)]-[CpFe{C$_5$H$_3$(CH$_2$NMe$_2$)Te}] were obtained by recrystallization of 4 from dimethoxyethane (DME). In contrast to other alkali metal tellurolates, which are very sensitive to oxidation, crystalline [Li(dme)][CpFe{C$_5$H$_3$(CH$_2$NMe$_2$)Te}] can be handled in air for a short period of time without noticeable decomposition. The X-ray structure analysis[18] reveals that the Li–Te unit is stabilized by intramolecular chelate formation (Fig. 1). The six-membered chelate ring
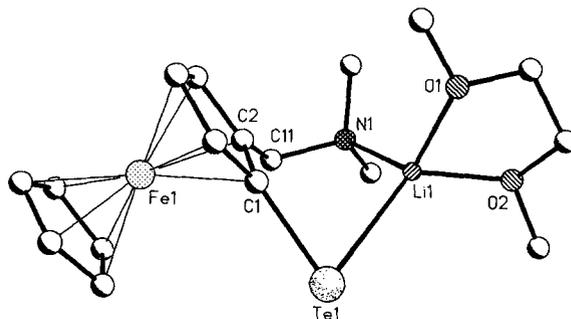
Fig. 1. Crystal structure of [Li(dme)][CpFe{C$_5$H$_3$(CH$_2$NMe$_2$)Te}]. Selected bond distances [pm] and angles [°]: Te1-Li1 273.4(4), Li1-N1 207.9(4), N1-C11 147.8(3), C11-C2 149.0(3), C2-C1 144.0(3), C1-Te1 212.2(2), Li1-O1 195.3(5), Li1-O2 201.0(4), C1-Fe1 206.3(2), C2-Fe1 203.9(2); C1-Te1-Li1 74.2(1), Te1-Li1-N1 103.7(2), Li1-N1-C11 111.0(2), N1-C11-C2 111.2(2), C11-C2-C1 124.5(2), C11-C2-C3 127.1(2), C2-C1-Te1 125.5(2), C5-C1-Te1 127.9(1), C2-C1-C5 106.6(2), Te1-C1-Fe1 128.1(1), C11-C2-Fe1 126.6(2).

adopts a slightly distorted boat conformation, in which Te 1, C 1, C 2, and C 11 are found almost in a plane. Noteworthy is the relatively small angle at the tellurium atom (74.2(1)°). The Te–C bond length (212.2(2) pm) lies in the normal range.

Their easy accessibility and unusual stability render the lithium chalcogenolates 2–4 of interest for subsequent reactions. Air oxidation of THF solutions leads to the corresponding dichalcogenides [{CpFe[C$_5$H$_3$(CH$_2$NMe$_2$)E]}$_2$] (E = S, Se, Te) as yellow crystalline solids.[19] Initial experiments show that the new ferrocenyl chalcogenolate ions are suitable ligands for transition metals and rare-earth elements. Thus, the ytterbium(III) thiolate [{CpFe[C$_5$H$_3$-(CH$_2$NMe$_3$)S]}$_2$Yb] is accessible from 2 and YbCl$_3$.[20] As a typical example the reaction of 4 with HgCl$_2$ is outlined, which leads to the mercury(II) tellurolate 5. The orange crys-