

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

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Molecular materials which are ferro-, ferri, or antiferromagnetic as a result of interactions between spin-carrying metal centers are currently subjects of intensive research.\[13\] A particularly rich chemistry is derived from chelate compounds in which like—more promisingly—unlike metals are assembled in close proximity.\[13\] Other spin sources are organometallic compounds. Thus, the reactions of polyalkylmetallocenes with tetracyanoethylene and related electron acceptors yield the salts [Cp2M] + [anion]− which crystallize as stacks and exhibit spontaneous magnetization at low temperature when the metal is iron, manganese, or chromium.\[21\] 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 metallocones, and with two different paramagnetic metal centers. We therefore synthesized bisbicyclopentadienyl ligands that may serve to link different metallocones in a stereocomplexly well-defined manner.\[23\] After testing less reactive syn-2a/b and anti-2a/b in the ratio 5:1.\[25\] De- 

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 species, the electron transfers leading to the tetra- and pentacation are chemically not reversible. The central chromium is oxidized more easily (J19, 198 mV) in accord with what is known from the parent metallocones.\[51\] In addition, a broad, unresolved wave with En = −1140 mV indicates the irreversible reduction to 4−.\[52\]

From the paramagnetic compound 4 we have obtained 13C NMR signals in the range δ = −400 to +1600 (Fig. 2). Their number and their approximate areas are in
ground state is thermally populated. It turns out (Fig. 3) that their shifts are characteristic of substituted nickelocenes (weighted average $\delta \approx 1400$ to $1500$) and chromocenes (weighted average $\delta \approx 300$ to $-400$). It follows that, at ambient temperature, 4 has six unpaired electrons with each metallocene unit accommodating two of them. This is confirmed by the $^1$H NMR spectrum. Surprisingly, however, the signals of H1–3 at $\delta = -221.6$ are shifted about 10% less than the Cp protons of mononuclear nickelocenes. 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 $\chi MT$ vs $T$ (Fig. 3). At 250 K, $\chi MT$ is equal to 2.94 cm$^3$ K mol$^{-1}$, which corresponds to what is expected for three uncoupled ions with $S_{Ni} = S_{Ni} = S_{Cr} = 1$. It is in agreement with the structure shown in Scheme while (weighted average $\delta$) the agreement factor $R = 0.83$ cm$^{-1}$; the agreement factor $R = 3.8 \times 10^{-4}$. The corresponding theoretical curve is given in Figure 3. Considering that $D_{Ni}$ is not negligible leads to the same energy spectrum for the low-lying states with a different value for $D_{Ni}$ but the same value 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.

\[ J = \frac{N \beta \Sigma_{i} \left(-\Delta E_{i,j} \partial H_{j} \right) \exp \left(-\frac{E_{i,j}}{kT} \right)}{H_{s}} \]

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 the field yielding 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) and the Ni$^{II}$-Cr$^{III}$ interaction parameter $J = -1.95$ cm$^{-1}$; the agreement factor $R = 3.8 \times 10^{-4}$. The corresponding theoretical curve is given in Figure 3. Considering that $D_{Ni}$ 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 $J$.

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   c) O. Kahn, Phil. Trans. R. Soc. Lond. A 1990, 330, 195–204;


The isomer ratio of syn-2alb to anti-2alb was determined by $^1$H NMR spectroscopy. syn-2a/b = $^{1.1}$NMR (THF, 310 K): $\delta = 655/597$ (C8a/b), $-151/56.6$ (C7b/a), $114.6$ (C3), $139.2/132.2$ (C1/3); $^{13}$Si NMR (THF, 319 K): $\delta = -845/873$ (Si4/8) $^{12}$Si NMR (THF, 319 K): $\delta = -220/519$ (C8a/b), $85.7/89.8$ (C7b/a), $191.8$ (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 $\delta$ C2 > 1000 similar as for 4 (Fig. 2). syn/anti-2a/b gave a satisfactory elemental analysis: El-MS (70 eV): m/z (rel. intensity) $366$ M$^+$, 100, 351.

Fig. 2. $^{13}$C NMR spectrum of 4 in [D$_4$]THF at 298 K; the two sections have different vertical scales. S = solvent, Cp* = C1–3, C3a, and C8a.

Fig. 3. Magnetic properties of 4 represented as a plot of $\chi MT$ vs $T$ with $\chi MT$ being the molar magnetic susceptibility and $T$ the absolute temperature. $\Delta$: Experimental values, solid line: calculated curve. Inset: expansion of the low-temperature range.
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,11-31 However, only a few with selenolate and tellurolate ligands (RSe^- and RTE^-) have been structurally characterized. In all, with selenolate and tellurolate ligands (RSe^- and RTE^-), respectively, are known.4-6 They are of interest as precursors for metal chalcogenides,17-6 also and 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 ditelluridates with sodium amalgam or sodium in liquid ammonia. 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)][CpFe{C,H_3(CH_2NMe_2)Te}].14 as well as [Na(tmeda)][C_2,H_3,H_5,Te] and [K(k18crown-6)][C_2,H_3,Pr,C,H_3,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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[Fig. 1. Crystal structure of [Li(dme)][CpFe{C,H_3(CH_2NMe_2)Te}]. Selected bond distances [pm] and angles [']: T=Fe-Li 273.4(2), Li-Ni 207.9(2), N-CI1 147.8(3), C1-C2 149.3(3), C2-C1 144.6(2), C1-Te 212.2(2), Li-O1 195.3(5), O1-O2 201.0(4), C1-Fe1 206.3(2), C2-Fe1 203.9(2), C1-Te1-Li 74.2(1), T=Fe1-Li 103.7(2), Li-N1 111.0(2), N-C11-C2 112.2(2), C11-C2-C1 124.5(2), C11-C2-C3 127.1(2), C2-C1-Tel 125.5(2), C5-C1-Tel 127.9(1), C2-C5 106.6(2), T=Te1-Fe1 128.1(1), C11-Fe1-Fe1 126.6(2).


Red-brown single crystals of the composition [Li(dme)][CpFe{C,H_3(CH_2NMe_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,H_3(CH_2NMe_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 chelation (Fig. 1). The six-membered chelate ring adopts a slightly distorted boat conformation, in which Te1, C1, C2, and C11 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 [[CpFeC,H_5(CH_2NMe_2)S]_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 [[CpFeC,H_5(CH_2NMe_2)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-cryst-