

Synthesis and NMR Spectroscopy of Metallocenium Ions. Support for a New Ferromagnetic Coupling Mechanism in Decamethylmetallocenium Tetracyanoethenides¹

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Abstract: A strategy has been developed to prove negative unpaired electron spin density in the Cp π orbitals of ferrocenium ions which is crucial for the McConnell-Kollmar-Kahn (MCK) mechanism of ferromagnetic coupling within $[\text{Cp}^*_2\text{Fe}]^+[\text{TCNE}]^-$ stacks and—after extension to other sandwich cations—for the design of organometallic ferromagnets in general. To this end, the paramagnetic metallocenium ions $[(\text{EtMe}_4\text{Cp})_2\text{M}]^+$ ($\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Ni}$), $[(i\text{PrCp})_2\text{Fe}]^+$, and $[(t\text{BuCp})_2\text{Fe}]^+$ have been prepared as $[\text{PF}_6]^-$ salts and investigated by NMR spectroscopy. At ambient temperature the ^{13}C and ^1H signal shifts cover ranges of almost 1300 and 170 ppm, respectively, with shift signs depending on the position of the nucleus under study and on the metal. For the metallocenium ions with $\text{M} = \text{Cr}, \text{Mn}$, and Ni the signs of the signal shifts show that the spin density in the Cp π orbitals is positive for Ni and negative for Cr and Mn . By contrast, the shift sign criterion fails for Fe . The different dihedral angles between the $\alpha\text{-C}\beta$ bonds and the Cp π orbitals in $[(\text{EtMe}_4\text{Cp})_2\text{Fe}]^+$ and the two $[(\text{RCp})_2\text{Fe}]^+$ derivatives probe the sign of the π spin density selectively via hyperconjugation; it is found to be negative. The experiments support the MCK mechanism in all cases, regardless whether the intrastack coupling in $[\text{Cp}^*_2\text{M}]^+[\text{TCNE}]^-$ be ferromagnetic or anti-ferromagnetic. The NMR data determine the spin distribution within a substituted Cp ligand which should be helpful for the optimization of the magnetic interaction. The restrictions for a quantitative application of the NMR method are discussed.

Introduction

One of the challenges in the chemistry of molecular solids is the synthesis of ferromagnets because they might replace or excel metallic ferromagnets or ceramic ferrimagnets in various applications. Among the approaches that rely upon transition-metal complex ions as unpaired electron spin sources² an extensively studied example is decamethylferrocenium ion ($[\text{Cp}^*_2\text{Fe}]^+$) which, together with planar cyano-substituted π anions, crystallizes as linear stacks as shown in Figure 1. Here tetracyanoethenide ($[\text{TCNE}]^-$) has been used as an anion by Miller, Reiff, Epstein, and their co-workers^{2c} who have explained its ferromagnetism in terms of the McConnell mechanism³ suitable for alternating donor ($[\text{Cp}^*_2\text{Fe}]^+$) and acceptor ($[\text{TCNE}]^-$) radicals.⁴ This mechanism implies the excitation to $[\text{Cp}^*_2\text{Fe}]^{2+}[\text{TCNE}]^{2-}$ and the admixture of its spin triplet state with the spin states of $[\text{Cp}^*_2\text{Fe}]^+[\text{TCNE}]^-$ in such a way that the $S = 1$ rather than $S = 0$ state becomes more stable.

Very recently Kahn and Kollmar, in a series of papers,⁵ have given a thorough analysis of this mechanism and questioned its general validity.^{5a} They have estimated its contribution to the ferromagnetic coupling in $[\text{Cp}^*_2\text{Fe}]^+[\text{TCNE}]^-$ to be negligibly small, and they have shown in a detailed treatment that, instead, electron spin correlation induces unpaired spin density in the ligands of $[\text{Cp}^*_2\text{Fe}]^+$ with the sign opposite to that of the nearby

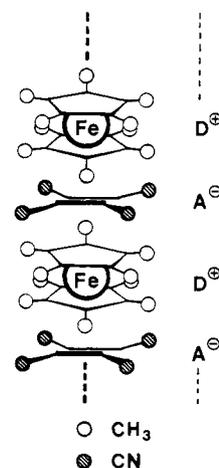


Figure 1. Structural model of $[\text{Cp}^*_2\text{Fe}]^+[\text{TCNE}]^-$: D = donor and A = acceptor.

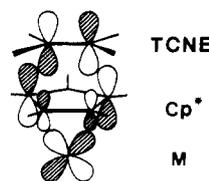


Figure 2. Orbitals relevant for the magnetic interaction in $[\text{Cp}^*_2\text{M}]^+[\text{TCNE}]^-$; only part of the chain in Figure 1 is given.

$[\text{TCNE}]^-$ radical.^{5b} The scenario which has been extended to other metallocenium ions^{5c} and which has been taken into qualitative consideration independently by Bucharenko⁶ nicely meets the requirements of a second idea put forward by McConnell⁷ which leads to ferromagnetism by Heitler-London spin exchange. For convenience we will refer to this mechanism as the McConnell-Kollmar-Kahn or MCK mechanism⁵ which competes with the McConnell-Miller-Epstein or MME mechanism.³

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The precise knowledge of the correct mechanism is of course essential for a rational design of molecular ferromagnets, in this particular case of the sandwich cation-donor/ π -anion-acceptor type. Very recently Hoffman and co-workers²⁸ have shown that the ferromagnetism of $[\text{Cp}^*_2\text{Cr}]^+[\text{TCQM}]^-$ cannot be explained by the MME mechanism. We present here an unambiguous experimental support for the MKK mechanism which is based on the sign of the spin density and which can be extended to π complexes in general. The underlying strategy is outlined in the following two sections.

1. Relating the McConnell-Kollmar-Kahn Mechanism to NMR Spectroscopy. Most of the paramagnetic sandwich compounds have a short electron spin relaxation time so that they may be studied conveniently by NMR spectroscopy. The paramagnetic (or isotropic) signal shift, $\delta^{\text{para}}(\text{X})$, is a consequence of the intramolecular interaction of the nucleus X under study and the unpaired electron(s). If the interaction is a scalar coupling (Fermi contact interaction), then $\delta^{\text{para}}(\text{X})$ is reduced to the contact shift, $\delta^{\text{con}}(\text{X})$, which is proportional to the hyperfine coupling constant of a nucleus X, $A(\text{X})$, for a given molecule and a given temperature (shifts at a standard temperature of 298 K are discussed if not stated otherwise).⁸ Since $A(\text{X})$, in turn, is related to the electron spin density at X, the NMR signal shifts reflect the amount of the spin density on the ligands and whether its magnetic moment is parallel or antiparallel to the external field (positive or negative spin density). More explicitly, signal shifts to high frequency indicate positive spin density and vice versa.

As outlined above negative spin density on the ligand is essential for the explanation of ferromagnetism by the MKK mechanism. A closer look (Figure 2) shows that the symmetry of the singly occupied TCNE orbital requires an unpaired electron in a metallocene orbital with an appreciable content of e_1'' (rather than e_2'' or a_1'') ligand π orbitals.^{5b} Indeed, the NMR signals of Cp_2M ($\text{M} = \text{V}, \text{Cr}, \text{Co}, \text{Ni}$) with $|\delta^{\text{para}}(\text{H}/^{13}\text{C})| > 250/1000^9$ reflect a considerable spin density in the ligand orbitals. The sign of the δ^{para} values may be understood qualitatively by two spin delocalization mechanisms:^{9a,10} (i) Direct delocalization of unpaired electrons within the antibonding e_g orbitals of Cp_2Co and Cp_2Ni yields positive spin density in the ligand π system,¹³ ^{13}C NMR signal shifts to high frequency, and (after spin polarization of the paired electrons of the C-H bond¹¹) ^1H NMR signal shifts to low frequency. (ii) Polarization of the paired electrons in the bonding e_g orbitals of Cp_2V and Cp_2Cr by metal-centered unpaired electrons yields negative spin density in the ligand π system and the $^{13}\text{C}/^1\text{H}$ NMR signal shifts to low/high frequency. Note that the polarization mechanism proposed by Levy and Orgel^{10b} corresponds to the spin correlation in the MKK mechanism.

So far we have seen that NMR spectroscopy should monitor the amount and the sign of unpaired electron spin density in ligand orbitals that have just the symmetry necessary for magnetic exchange in $[\text{Cp}^*_2\text{M}]^+[\text{anion}]^-$. In some cases, however, dipolar signal shifts, and direct delocalization of unpaired electrons within the σ -type orbitals must also be considered, and the NMR results are rather confusing. Ferrocenium ions are particularly affected by these modifications: The ^{13}C ¹² and ^1H ^{13,12c} signals of the

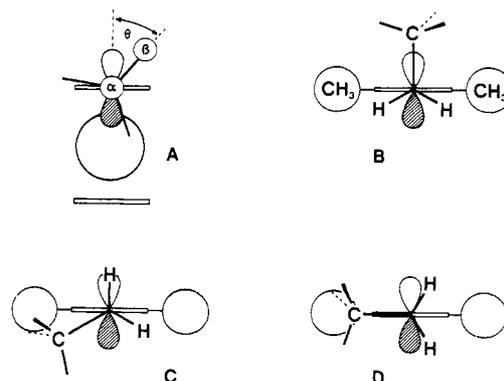


Figure 3. (A) Newman-type projection of a substituent bound to a metallocene showing the $2p_z$ orbital of the substituted C atom, the nuclei in position α and β relative to that C atom, and the dihedral angle θ . (B–D) Rotamers of one Cp ligand with additional methyl groups located next to the substituent of interest (cf. text).

five-membered rings are both shifted to high frequency, and the decision whether negative or positive spin density resides on the ligand is not straightforward. The analysis of the ^1H data alone did not allow Anderson and Rai^{13d} to give a precise answer. Later Materikova et al.,^{12c} after taking into account the metal-centered dipolar ^{13}C NMR signal shifts, argued in favor of negative spin density. However, some shifts still had the wrong sign, and additional (nevertheless inefficient¹⁴) delocalization mechanisms were proposed. In conclusion, it is difficult to determine the sign of the ligand π spin density of sandwich compounds whenever the NMR signal shifts are rather small, and dipolar shifts as well as different delocalization mechanisms can lead to a scatter of the shift signs. Besides ferrocenium ions this applies, e.g., to manganocenes.¹⁵

2. Hyperconjugation as a Window for Probing π Spin Density by NMR Spectroscopy. The NMR probe for electron spin density in a ligand π orbital is more selective when the ligand is substituted and when nuclei that are separated from the π system by two bonds (β position) are observed rather than the five-membered ring carbon atoms or nuclei in α position.¹⁶ The underlying principle is hyperconjugation. It is reflected in the angular dependence of the hyperfine coupling constants of β nuclei, it has been first derived for organic radicals,¹⁷ and it may be formulated for the signal shift of a nucleus X as

$$\delta^{\text{con}}(\text{X}) = \delta_0(\text{X}) + B(\text{X}) \cos^2 \theta \quad (1)$$

with θ being the dihedral angle shown in Figure 3. The second term of eq 1 represents the shift due to spin that is transmitted from the π system by hyperconjugation ($B(\text{X})$ is a constant for a given X in a given molecule), whereas the shift $\delta_0(\text{X})$ arises from spin that is transmitted by all other pathways.

Let us assume that the substituent at Cp in Figure 3A is an ethyl group. When the barriers to rotation about the C-C α bond are low and the energy of the various rotamers is similar, then one NMR signal is observed for H β or C β and the averaged angle $\theta \approx 45^\circ$ gives

$$\delta^{\text{con}}(\text{X}) = \delta_0(\text{X}) + 0.5B(\text{X}) \quad (2)$$

This is expected for monosubstituted Cps at ambient temperature. Substitution of the position ortho to ethyl, by, e.g., methyl, will increase the population of rotamer B (Figure 3) with

(14) (i) Direct delocalization of an unpaired electron promoted to an a_{1g} orbital. This should be negligible because the orbital is almost entirely centered at the metal. (ii) Polarization of electrons in σ orbitals. This should be inefficient because the σ orbitals are far below the singly occupied orbitals.

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$$\delta^{\text{con}}(^{13}\text{C}) = \delta_0(^{13}\text{C}) + B(^{13}\text{C}) \quad (3a)$$

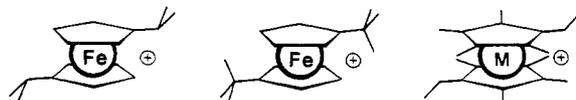
$$\delta^{\text{con}}(^1\text{H}) = \delta_0(^1\text{H}) + 0.25B(^1\text{H}) \quad (3b)$$

rather than that of rotamer C and D. It follows from the comparison of eqs 2 and 3a that on going from the monosubstituted to the bulky Cp the signal of C β moves to low frequency if the spin density in the π orbitals is negative. This is observed regardless of whether or not the signals appear at low or high frequency, depending on δ_0 .

It is conceivable to use H β instead of C β in order to probe the sign of the spin density. Comparison of eqs 2 and 3b shows that then, for the change from the monosubstituted to the bulky Cp, the signal of H β moves to high frequency. However, the maximum effect is only 0.25 B(^1H) (as compared to 0.5 B(^{13}C)) and the above mentioned dipolar shifts (and other effects discussed below) might render ^1H NMR spectroscopy less reliable.

Results

As model compounds we have selected the 1,1'-substituted ferrocenium ions [(*i*PrCp) $_2$ Fe] $^+$ and [(*t*BuCp) $_2$ Fe] $^+$ and the peralkylferrocenium ion [(EtMe $_4$ Cp) $_2$ Fe] $^+$ shown below. They were obtained as hexafluorophosphates from the corresponding ferrocenes by oxidation with AgPF $_6$ (at times as AgPF $_6$ ·(CH $_3$ CN) $_2$) or HNO $_3$ and precipitation with NH $_4$ PF $_6$. The latter seemingly cheaper method gave a lower yield and a product that was more difficult to purify. We have therefore used AgPF $_6$ for the synthesis of [(EtMe $_4$ Cp) $_2$ M] $^+$ which should provide insight



M = Cr, Mn, Fe, Co, Ni

into the spin density of metallocenium ions other than ferrocenium. [(EtMe $_4$ Cp) $_2$ Co] $^+$ which was needed as a diamagnetic isostructural reference compound was prepared by oxidation of the crude cobaltocene with NH $_4$ PF $_6$ as published by K lle 18 for [Cp $_2^*$ Co] $^+$. [(*i*PrCp) $_2$ Fe] $^+$ has been studied before only in equilibrium with its neutral precursor, 19 while [(*t*BuCp) $_2$ Fe] $^+$ has been described in preliminary form 12a,13c and in no case preparative details were given. The hexafluorophosphates of both cations are soluble in polar organic solvents; they are stable in solution when protected from air and, in particular, from reducing impurities. The metallocenium salts [(EtMe $_4$ Cp) $_2$ M] $^+$ [PF $_6$] $^-$ are deeply colored crystalline solids which are rather stable in the presence of oxygen and water; no decomposition occurs on heating up to 100 $^\circ\text{C}$ under inert gas. The salts are readily soluble in acetone, moderately soluble in THF and essentially insoluble in benzene, toluene and pentane so that organic impurities can be removed easily. Solutions in acetone are stable for months when M = Cr, Fe, Co, Ni, whereas [(EtMe $_4$ Cp) $_2$ Mn] $^+$ [PF $_6$] $^-$ decomposes slowly in acetone and reacts with CHCl $_3$ to give a dark blue solution. Therefore freshly prepared solutions of the latter compound were used for the NMR studies. In accord with the comprehensive investigations of [Cp $_2^*$ M] $^+$ by Robbins et al. 20 we were unable to isolate the vanadocenium ion [(EtMe $_4$ Cp) $_2$ V] $^+$ without an additional donor ligand.

The ^1H and ^{13}C NMR spectra could be recorded for all the metallocenium ions. Near room temperature the protons resonate at $120 > \delta > -60$ ppm, whereas the ^{13}C signals cover the range $1400 > \delta > -800$ ppm. Typical examples are the key compounds [(*i*PrCp) $_2$ Fe] $^+$ [PF $_6$] $^-$ and [(EtMe $_4$ Cp) $_2$ Fe] $^+$ [PF $_6$] $^-$ the spectra of which are shown in Figure 4. It is worth noting that the five-membered ring protons of [(*i*PrCp) $_2$ Fe] $^+$ and [(*t*BuCp) $_2$ Fe] $^+$ yield two signals. Earlier studies on [(RCp) $_2$ Fe] $^+$ 12,13 failed to confirm the expected splitting, whereas temperature dependent mea-

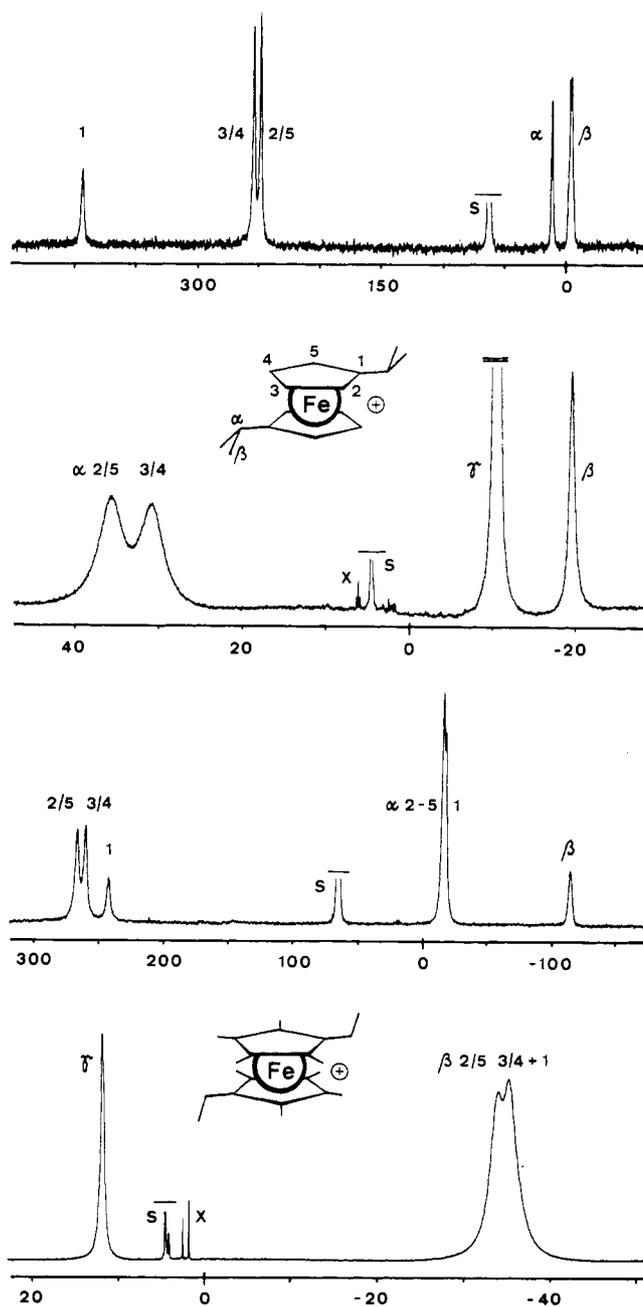


Figure 4. (Top) ^{13}C and ^1H NMR spectrum of [(*i*PrCp) $_2$ Fe] $^+$ [PF $_6$] $^-$ and (bottom) ^{13}C and ^1H NMR spectrum of [(EtMe $_4$ Cp) $_2$ Fe] $^+$ [PF $_6$] $^-$, all at 307.2 K: S = solvent (CD $_3$ NO $_2$), X = impurities, scales in ppm. The splitting of the C β signal of [(*i*PrCp) $_2$ Fe] $^+$ is due to $^1J(\text{CH})$. For the definition of α , β ... see ref 16.

surements gave evidence of two overlapping signals. 12a The ^{13}C NMR signals of the substituents of the ferrocenium ions are remarkably narrow so that the one-bond CH coupling multiplicity can be used for their assignment in some cases. Interestingly, in [(*i*PrCp) $_2$ Fe] $^+$ the CH coupling of the C α signal (half-width 120 Hz) is quenched due to the fast relaxation of the neighboring proton (^1H signal half-width 215 Hz). Further assignment is based on the signal areas which are reliable after baseline correction of the spectra and when comparison is made for signals with similar half-widths. An example is the nontrivial distinction of H β 1 and H γ of [(EtMe $_4$ Cp) $_2$ Fe] $^+$. The assignment of nuclei in the positions 2/5 and 3/4 is discussed below.

Ferrocenium ions tend to be reduced by organic impurities. One is then confronted with the rapid exchange of (R $_n$ Cp) $_2$ Fe and [(R $_n$ Cp) $_2$ Fe] $^+$ which leads to unreliable signal shifts. This can be avoided by careful purification of the salt and the solvent. Measurements of selected compounds in various solvents including

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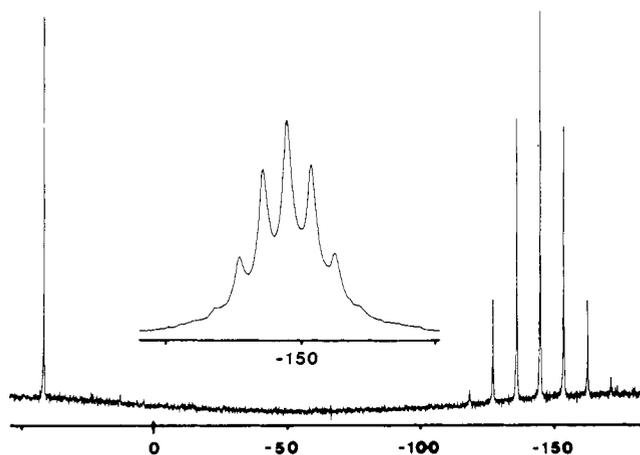


Figure 5. ^{31}P NMR spectrum of $[(\text{EtMe}_4\text{Cp})_2\text{Cr}]^+[\text{PF}_6]^-$, 0.05 mol L^{-1} in acetone at 310 K. Inset: saturated solution at 304 K. The signal at high frequency belongs to the internal standard $[\text{Et}_4\text{P}]^+[\text{PF}_6]^-$. Scales are in ppm.

D_2O show (Table I) that the shifts are reasonably well reproduced. The same applies for reinvestigations after months.

The ^{31}P and ^{19}F spectra of the paramagnetic salts $[(\text{EtMe}_4\text{Cp})_2\text{M}]^+[\text{PF}_6]^-$ ($\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Ni}$) and of $[(\text{EtMe}_4\text{Cp})_2\text{Co}]^+[\text{PF}_6]^-$ were also recorded in order to see whether ionic interactions influence the spin density distribution. As shown in Figure 5 the expected²¹ heptet with $^1J(^{31}\text{P}-^{19}\text{F}) = 708 \text{ Hz}$ was found for $[\text{PF}_6]^-$. When $[\text{Et}_4\text{P}]^+[\text{PF}_6]^-$ was used as an internal standard to exclude the bulk susceptibility effect on the ^{31}P signal shift, the $[\text{PF}_6]^-$ resonance at -144 ppm did not change within the error limits on passing from the diamagnetic to the paramagnetic salts nor did it change with the temperature or the concentration. By contrast, the signal half-width increased with decreasing temperature and increasing concentration; an example is given in Figure 5. The ^{19}F NMR spectra with a doublet (709 Hz) at $\delta(^{19}\text{F}) -70,7$ relative to internal CF_3Cl for $[\text{PF}_6]^-$ confirmed these results.

Discussion

From the NMR investigation of the $[\text{PF}_6]^-$ anion we conclude that if any spin density is transferred from $[(\text{EtMe}_4\text{Cp})_2\text{M}]^+$ to the anion then it must be very small. This means that the coordination of $[\text{PF}_6]^-$ to the metal of the organometallic cation (which is known in other cases²²) is unlikely and that solvent separated ions are present in solution. The line width experiments show that the paramagnetic cations are merely relaxation reagents for $[\text{PF}_6]^-$.

Sign of the π Spin Density of Ferrocenium Ions. The paramagnetic NMR signal shifts of the ferrocenium ions in Table I, except those of the β nuclei, do not allow to decide whether the spin density in the ligand π system is positive or negative. Thus, if the simple rules of section 1 are applied, the $\delta^{\text{para}}(\text{C}1-5)$ and $\delta^{\text{para}}(\text{C}\alpha)$ values point to a positive sign, whereas a negative sign is suggested by the $\delta^{\text{para}}(\text{H}\alpha)$ values (cf. also Figure 6).

One can try to improve the result by subtracting the metal-centered dipolar shifts, $\delta^{\text{dip},\text{MC}}$. The calculation of the $\delta^{\text{dip},\text{MC}}$ values for nuclei in the β and γ position of a metallocene is not straightforward because the rotation of the substituents affords an averaging and the population of the various rotamers is not known. We therefore regard the values obtained from the simplified theory⁸ as useful estimates and renounce Eicher's sophisticated alternative treatment.²³ The result is visualized in Figure 6 except for $[(t\text{BuCp})_2\text{Fe}]^+$ which is similar to the isopropyl

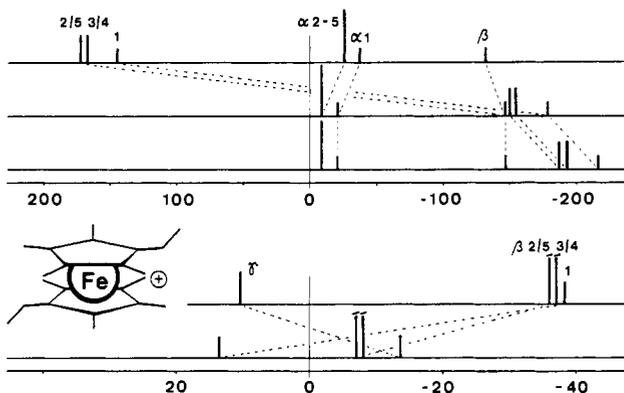
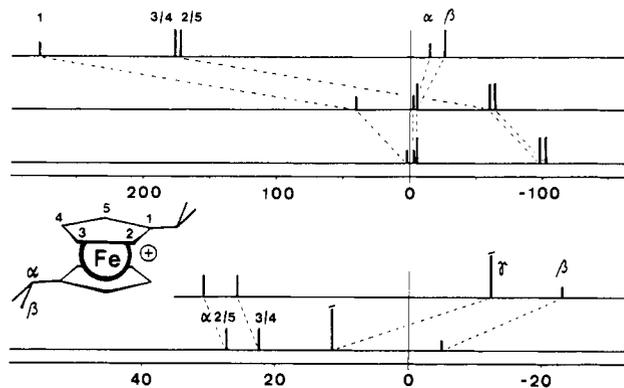


Figure 6. Evaluation of the contact shifts of $[(i\text{PrCp})_2\text{Fe}]^+$ and $[(\text{EtMe}_4\text{Cp})_2\text{Fe}]^+$. The shifts are described from top to bottom: Paramagnetic shifts $\delta^{\text{para}}(^{13}\text{C})$, shifts after correction for the metal-centered dipolar shifts $\delta^{\text{dip},\text{MC}}(^{13}\text{C})$, and contact shifts $\delta^{\text{con}}(^{13}\text{C})$ obtained after additional correction for the ligand-centered dipolar shifts $\delta^{\text{dip},\text{LC}}(^{13}\text{C})$, $\delta^{\text{para}}(^1\text{H})$, and $\delta^{\text{con}}(^1\text{H})$. Scales are in ppm.

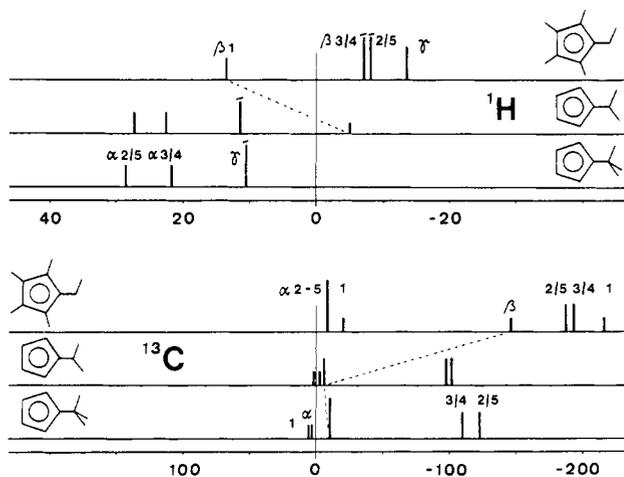


Figure 7. Comparison of the contact shifts at 298 K (top three traces, ^1H ; bottom, ^{13}C) of ferrocenium ions with indicated ligands. The hyperconjugational change of the β resonances is visualized by a broken line. Scales are in ppm.

analogue and given in the supplementary material together with the details of the calculation. After accounting for the metal-centered dipolar shifts the signals of the ring carbon atoms have changed their shift sign except for Cl of $[(i\text{PrCp})_2\text{Fe}]^+$ and $[(t\text{BuCp})_2\text{Fe}]^+$, a situation which is still unsatisfactory.

Further correction of the signal shifts by ligand-centered dipolar shifts, $\delta^{\text{dip},\text{LC}}$ is necessary owing to the spin delocalization.²⁴ For

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Table I. ^{13}C and ^1H NMR Data^a of the Hexafluorophosphates of the Paramagnetic Metallocenium Ions $[(i\text{PrCp})_2\text{Fe}]^+$ (1), $[(t\text{BuCp})_2\text{Fe}]^+$ (2), $[(\text{EtMe}_4\text{Cp})_2\text{M}]^+$ with $\text{M} = \text{Fe}$ (3), Cr (4), Mn (5), and Ni (6), and the Diamagnetic Standard $[(\text{EtMe}_4\text{Cp})_2\text{Co}]^+[\text{PF}_6]^-$ (7)

nucleus and position ^b	1 ^c	2 ^d	3 ^e	4	5	6	7
C1	275.0	279.2 281.2	143.5 142.6	-477	-166.9	521	99.12
C2/5	169.8	151.6 152.7	172.6 171.0 171.7	-414 ^f	-84.2	575	95.48
C3/4	173.9	163.8 164.4	167.3 166.2 167.5	-413 ^f	-114.3	564	94.36
C α 1	-15.1	-9.0 -11.8	-37.5 -36.7 -36.6	760	526	-185.8	16.79
C α 2/5			-26.2 -27.0 -26.6	809	570	-269.4	7.79 ^g
C α 3/4			-26.2 -27.0 -26.6	809	551	-263.6	8.03 ^g
H α 2/5	30.4	31.7 31.9					
H α 3/4	25.5	24.7 24.7					
C β 1	-26.2	-30.4 -31.4	-131.7 -133.4 -133.4	-126.5	-280.0	546.1	13.10
H β 1	-23.1		-38.5 -38.7 -39.1	-7.2	-53.7	41.9	2.27
H β 2/5			-36.3 -37.5 -37.8	6.5	-59.5	103.7	1.03
H β 3/4			-37.3 -37.5 -37.8	4.8	-54.0	102.6	1.03
H γ	-12.2	-13.4 -13.3	10.2 9.8 9.1	-0.4	5.6	8.7	1.80

^a δ^{para} values at 298 K as defined in the text for paramagnetic ions; negative sign for shifts to low frequency. Solvent $(\text{CD}_3)_2\text{CO}$ unless stated otherwise. ^b See molecular models for numbering. ^c Solvent CD_3NO_2 . ^d Upper/lower value of each entry refers to the solvents $\text{CD}_3\text{NO}_2/\text{D}_2\text{O}$. ^e Values of each entry from top to bottom refer to the solvents CD_3NO_2 , $(\text{CD}_3)_2\text{CO}$, and $(\text{CD}_3)_2\text{SO}$. ^f Signals of C2/5 and C3/4 not resolved; the splitting and assignment are a consequence of the reference procedure. ^g Interchange of C α 2/5 and C α 3/4 not excluded.

an estimate we use the formula cited by Anderson and Matwiyoff²⁵ which yields $31.1 < \delta^{\text{dip.LC}} < 45.2$ (for details cf. supplementary material). The treatment neglects slight differences of the spin density on C1-5 that are imposed by the symmetry as well as spin transfer to C β via hyperconjugation which might lead to changes of a few ppm. Protons and other carbon atoms remain essentially unaffected because only spin in the p_z orbital of the nucleus under study is concerned. The contact shifts given in Figure 6 have been obtained with the mean value $\delta^{\text{dip.LC}} 38.0$. They do not solve our spin sign problem generally. In contrast, the analysis of the C β signals yields an unequivocal result. It is illustrated in Figure 7 where the δ^{con} values are compared for all ferrocenium ions. On passing from the two monosubstituted ferrocenium ions to $[(\text{EtMe}_4\text{Cp})_2\text{Fe}]^+$ the C β signal moves to low frequency. As outlined in section 2, this is only expected if negative spin density resides in the ligand π orbitals, which in turn is crucial for the MKK mechanism to explain the ferromagnetism. Comparison

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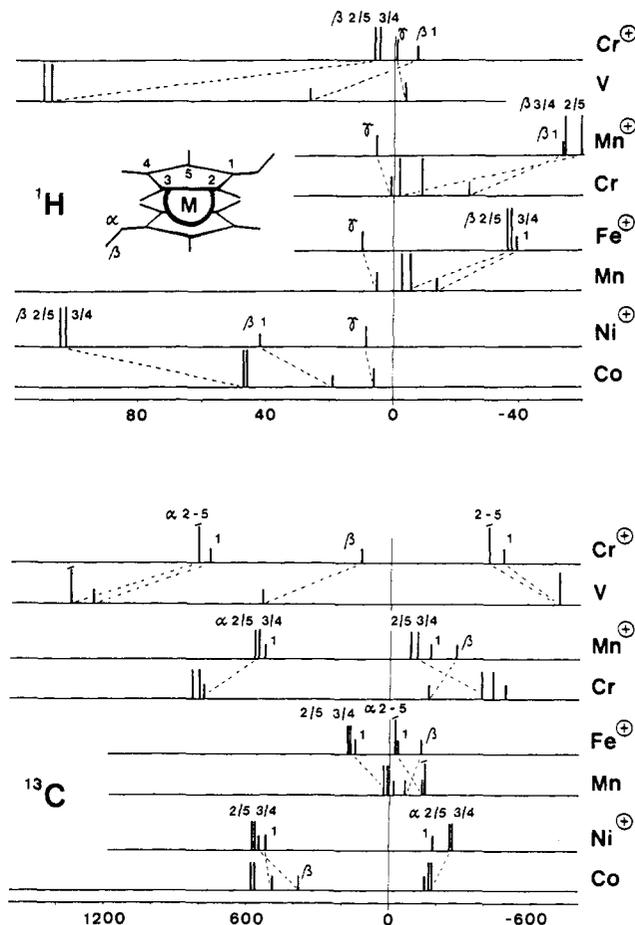


Figure 8. Comparison of the paramagnetic shifts (top eight traces, ^1H ; bottom, ^{13}C) at 298 K for isoelectronic pairs of $[(\text{EtMe}_4\text{Cp})_2\text{M}]^{+/0}$. Scales are in ppm.

with Figure 6 reveals that the same result is obtained from the easily accessible $\delta^{\text{para}}(^{13}\text{C}\beta)$ values without further correction.

Complementary to the C β signal shift, the H β signal should be shifted to high frequency, but this is only observed for the contact shifts. Here we have an example where the change of the dipolar shift overrides the change of the spin transfer by hyperconjugation. The comparison of eqs 2 and 3b has shown that this is expected for H β with a small effect of the hyperconjugation rather than for C β . Actually, the change of the $\delta^{\text{para}}(\text{C}\beta)$ values is only slightly smaller than that of the $\delta^{\text{con}}(\text{C}\beta)$ values (Figure 7), and no sign inversion occurs. It follows that the C β signal of suitable model compounds is the most reliable probe for the sign of the spin density in the ligand π orbitals when the overall pattern of the ring carbon, the α proton, and the α carbon signals is ambiguous.

Sign of the π Spin Density of Other Metallocenium Ions. For the metallocenium ions with metals other than iron it is sufficient to analyze the ^{13}C NMR results of $[(\text{EtMe}_4\text{Cp})_2\text{M}]^+$, in particular when they are compared to those of the isoelectronic neutral congeners^{15,16} (Figure 8). We have used δ^{para} rather than δ^{con} values in Figure 8 because no g factors are available for the calculation of the metal-centered dipolar shifts of manganocenium ions.²⁰ Except for ferrocenium ions, however, the dipolar shifts should be smaller than the contact shifts (verified for vanadocene and cobaltocenes²⁷ which are isoelectronic with chromocenium and nickelocenium ion, respectively) so that our qualitative arguments are still valid. In the case of chromocenium and manganocenium ions the signals of C1-5 and C α 1-5 appear at low and high frequency, respectively. In analogy to C α , the H α signals of chromocenium ions²⁸ are also found at high frequency, whereas

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manganocenium ions having α protons do not seem to have been synthesized yet. The shift signs clearly indicate that the spin density in the Cp π orbitals of chromocenium and manganocenium ions is negative. Hence the MKK model for ferromagnetism is supported experimentally also in the case of the 7,7,8,8-tetracyano-*p*-quinodimethanides of decamethylmanganocenium^{2f} and decamethylchromocenium²⁸ ion.

It is gratifying that the opposite behavior can be established as well. When passing to [(EtMe₄Cp)₂Ni]⁺ the signal shifts of C1-5 and C α 1-5 have opposite signs as compared to [(EtMe₄Cp)₂Cr]⁺ and [(EtMe₄Cp)₂Mn]⁺. The high frequency signals of H α of other nickelocenium ions²⁹ also fit into a pattern that implies positive spin density in the Cp π orbitals. Within the MKK model our experimental spin density should result in antiferromagnetism for charge transfer complexes of the decamethylnickelocenium ion. This has been actually found and explained alternatively in terms of the MME model by Miller's group.³⁰

Beyond that, Figure 8 requires some comments on the electronic analogy of the pairs [(EtMe₄Cp)₂M]^{0/+} having the same electronic ground state. Generally, the signals have pairwise similar pattern and shift ranges. There are, however, remarkable differences which are only partly due to the differences in the metal-centered dipolar shift because the *g* factors^{12c,20,31} and the geometry³² are rather similar. For instance the ¹H signal shifts of [(EtMe₄Cp)₂Ni]⁺ are much larger than those of (EtMe₄Cp)₂Co, thus pointing to an increase of spin on the Cp ring of the nickelocenium ion. This has been also deduced from X α MO calculations³³ and EPR spectroscopy.³⁴ The ¹³C shifts are less suitable for similar conclusions because the effect of increased spin density on the shift of a Cp ring carbon atom is partly compensated by the ligand-centered dipolar shift and the increased spin density residing on the neighboring carbon atoms.³⁵ In fact, the signal shifts of C1-5 of the d⁷ sandwiches are almost equal, whereas those of C α 1-5 show the expected behavior (Figure 8).

Since the contact shifts are proportional to the spin density on the ligand⁸ and since the magnetic interaction within, e.g., [(R₅Cp)₂M]⁺[TCNE]⁻, increases with that spin density,⁵ one can, in principle, sort out the best cation by NMR spectroscopy. The quantitative analysis is, however, hampered by the evaluation of the dipolar shifts and the contribution of the σ -delocalization to the contact shifts. On the other hand, the difference of the ¹³C NMR data of the Fe⁺ and the Cr⁺ derivative in Figure 8 is so pronounced that the latter should be the better cation. This is in accord with the work of Broderick and Hoffman.²⁸ As for a series with a given metal the ¹³C NMR data in Figure 7 show that (if the redox potential of all neutral sandwiches is sufficient to reduce TCNE and the like) [(EtMe₄Cp)₂Fe]⁺ is a better candidate than [(RCp)₂Fe]⁺.

Ligand Orbitals Dominating the Spin Distribution. In a stack made up from a metallocenium ion [(R₅Cp)₂M]⁺ and, e.g., TCNE⁻, the symmetry is lower than for [(R₅Cp)₂M]⁺ itself. Therefore, in an arrangement like in Figure 2 and for the one-

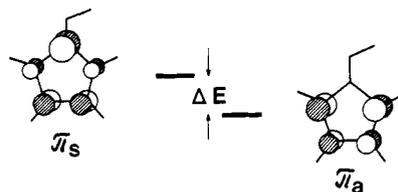


Figure 9. Energy splitting of the e₁-type π orbitals of the ligand EtMe₄Cp⁻.

electron part of the interaction, only one of the e_{1g}-type³⁶ orbitals of the metallocenium ion contributes to the ferromagnetic interaction as has been pointed out by Kollmar, Couty, and Kahn.^{5b} This offers the possibility to tune the intrachain ferromagnetic coupling by lowering the symmetry of the Cp ligands as, for example, in [(R'R₄Cp)₂M]⁺. If R' is big enough (and if the oxidation potential of the parent metallocene is still sufficiently low) a stack is expected where the donor and the acceptor are locked in the relative orientation shown in Figure 2 thereby selecting the MO that contains the antisymmetric ligand orbital π_a (cf. Figure 9) for the interaction with the π^* orbital of TCNE. Another consequence is that in addition to the "lattice-induced" splitting of the metallocenium e_{1g}-type orbitals there is a substituent induced splitting. For the ligand [EtMe₄Cp]⁻ this is illustrated in Figure 9. Obviously, both orbitals will interact with the π^* orbital of TCNE to a different extent, and the effect will be most pronounced when only one unpaired electron resides in the e-type orbitals. More details concerning this reasoning have been given in a previous publication.³⁷ From the foregoing it is clear that it is of interest to know which orbital has the biggest spin density.

As long as no reliable MO calculation for the specific sandwich is available the NMR data is a source of information. Thus, when the spin sits predominantly in a MO with π_a ligand orbital content, then the amount of the NMR contact shifts should have the order C1 < C3/4 < C2/5 (cf. Figure 9). The same trend should be visible for C α (if present), whereas the signal shifts of C β and H β are less suitable because their signal shifts may be dominated by preferred conformations of the substituents (vide supra). An example is [(EtMe₄Cp)₂Ni]⁺ for which Figure 8 shows unequivocally that the unpaired electron prefers the MO with a π_a ligand content. Difficulties arise (i) when the substitution pattern induces only a small perturbation (which should have little effect on the ferromagnetic interaction anyway), (ii) when σ delocalization operates as well, and (iii) when the dipolar shifts are neglected as in Figure 8. This is why for M = Cr, Mn, and Fe inconsistent conclusions result from the signal shifts of C1-5 and C α 1-5. Nevertheless, in these cases, the signal sequence of the nuclei in the positions 1-5 and their splitting is very useful: (i) It shows how much π_a (Figure 9) is favored energetically and whether π_a and π_s are interchanged or not. For instance, we have shown that the signal sequence of C1-5 is reversed on going from (EtMe₄Cp)₂Cr²⁶ to (Me₄Cp)₂Cr³⁸ and that for the latter the signal splitting (as a measure for ΔE in Figure 9) is bigger. (ii) By comparison with the orbital coefficients in Figure 9 the signal sequence allows to identify the nuclei in the positions 3/4 and 2/5 which are difficult to distinguish otherwise. The assignment given in Table I and Figures 6, 7, and 8 is based on this principle. As for H β it is assumed that the shifts of H β 3/4 and H β 2/5 behave like those of C3/4 and C2/5 (due to hyperconjugation) rather than those of C α 3/4 and C α 2/5.

Limitations to Probing the Ligand π Spin Density by C β Signal Shifts. With the optimum ferromagnetic interaction in view it is, of course, desirable to determine the spin density in the ligand π orbitals quantitatively. However, even if it is possible to eliminate the dipolar shifts, problems arise for the use of eq 1 because

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$\delta_0(X)$ and $B(X)$ are not perfectly constant when passing from one ligand to another unless we reformulate eq 1 as follows:

$$\delta^{\text{con}}(X) = L_0\delta_0(X) + LB(X) \cos^2 \theta \quad (1a)$$

L_0 and L are parameters that are specific for a given substituted ligand and that contain various contributions. The first contribution is the ligand content in the relevant metallocene orbitals. For instance, on going from Cp to Cp* the ligand content increases as has been shown by PE spectroscopy³⁹ and cyclovoltammetry.^{20,40} This in turn leads to an increase of L_0 and L . The second contribution is due to the fact that the orbital splitting ΔE shown in Figure 9 changes with the substitution pattern of the ligand. Hence the interaction of π_a and π_s with the appropriate metal orbitals also changes, and this will be reflected in L_0 and L . A third contribution to L_0 and L is effective when one rather than two unpaired electrons sit in the e_{1g} -type orbitals. Then ΔE strongly influences the population of π_a and π_s , and hence the spin distribution within the five-membered ring which in turn is transmitted to $X\beta$. A fourth contribution must be considered when there is a variation of the angles by which the substituents are bent out of the Cp plane. Experimentally, these contributions are most probably reflected in the slightly different $C\beta$ contact shift of the two monoalkylated ferrocenium ions in Figure 7.

Since $L_0 \neq L$ the change of the $\delta^{\text{con}}(C\beta)$ value on passing from, e.g., $[(EtCp)_2M]^+$ to $[(EtMe_4Cp)_2M]^+$ will not only depend on the dihedral angle θ as shown in section 2 but also on changes in the overall spin delocalization. A quantitative analysis must take these contributions into account.

Conclusions

In order to determine the sign of the unpaired electron spin density in the ligand π orbitals of sandwich cations—the crucial point within the McConnell–Kollmar–Kahn mechanism of the intrastack magnetic interaction—the signs of the NMR signal shifts may be unreliable. The best criterion is the hyperconjugative spin transfer from the ligand π orbitals to at least two different β carbon atoms; the dihedral angle between the π orbitals and the $C\alpha$ – $C\beta$ bond should be as different as possible. Protons in β position are useful only when the dipolar shifts have been removed.

As for the signs of the π spin density, which we have determined in this work, they confirm what has been postulated by the MKK mechanism⁵ for both ferromagnetic and antiferromagnetic coupling.

With some effort it should be possible to approach the metallocenium ion (or any sandwich cation) which is best suited for a molecular ferromagnet by NMR spectroscopy. The “tuning screws” are the number and the type of the substituents as well as the metal.

Experimental Section

All compounds except for the starting ferrocenes and the cobaltocenium ion were handled under dry and oxygen-free argon or nitrogen by using Schlenk techniques and solvents that were dried by standard methods and saturated with inert gas. The elemental analyses were carried out by the microanalytical laboratory of this institute. Literature procedures were followed to prepare the neutral metallocenes $(iPrCp)_2Fe$,⁴¹ $(tBuCp)_2Fe$,⁴¹ $(EtMe_4Cp)_2Fe$,⁴² $(EtMe_4Cp)_2M$ ($M = V, Cr, Co, Ni$),²⁶ and $(EtMe_4Cp)_2Mn$.¹⁵

Bis(1-ethyl-2,3,4,5-tetramethyl- η^5 -cyclopentadienyl)metal Hexafluorophosphates (Cr, Mn, Fe, Co, Ni). Approximately 1 g (1.3 mmol) of $(EtMe_4Cp)_2M$ ($M = Cr, Mn, Fe, Ni$) was dissolved in 25 mL of THF

Table II. Experimental Details of the Preparation of the Metallocenium Hexafluorophosphates

cation	yield, ^a g (%)	color	analysis ^b		
			C	H	metal
$[(EtMe_4Cp)_2Ni]^+$	0.50 (64)	yellow brown	52.62	6.82	11.69
			52.62	6.84	11.28
$[(EtMe_4Cp)_2Co]^+$	3.16 (53)	yellow brown	52.92	6.86	
			53.01	7.22	
$[(EtMe_4Cp)_2Fe]^+$	1.15 (72)	green	46.29	5.34	13.45
			46.02	5.41	14.1
$[(iPrCp)_2Fe]^+{}^c$	0.77 (75)	blue green	48.78	5.91	
			49.06	5.89	
$[(tBuCp)_2Fe]^+$	2.40 (55)	blue green	53.01	6.88	11.03
			53.13	7.04	11.22
$[(EtMe_4Cp)_2Mn]^+$	1.20 (86)	red brown	53.33	6.92	10.49
			53.35	6.88	10.43

^a Relative to the starting metallocene. ^b Experimental below calculated value. ^c Analysis of F: Calcd 27.46, Found 27.61.

and cooled to 0 °C. To the solution was added dropwise under stirring 0.75 g (3 mmol) of $AgPF_6$ in 20 mL of THF. The mixture which became dark from elemental silver was stirred for 1 h at ambient temperature. After filtration the solid was washed with 20-mL portions of THF until the filtrate was colorless. The combined solutions were concentrated to 40 mL and cooled to –25 °C. The colors of the crystals formed after prolonged standing and their analytical data are given in Table II. From the mother liquors additional product could be precipitated by adding pentane. The combined yield is also given in Table II. The cobaltocenium ion was prepared following the procedure published for $[Cp^*_2Co]^+$.¹⁸

Bis(isopropyl- η^5 -cyclopentadienyl)iron hexafluorophosphate was prepared by adding 0.80 g (2.39 mmol) of $AgPF_6(CH_3CN)_2$ to a solution of 0.67 g (2.48 mmol) of $(iPrCp)_2Fe$ dissolved in 15 mL of acetone at ambient temperature. A blue solution and a dark highly dispersed precipitate was obtained after stirring for 1 h. The solid was removed by filtering over Na_2SO_4 , and acetone was evaporated until 2–3 mL were left. After addition of 50 mL of Et_2O and cooling to 0 °C a microcrystalline precipitate formed. The solid was collected on a frit, washed 3× with 50 mL of hexane, and dried in vacuo. The product was then dissolved in 5 mL of CH_3NO_2 , filtered over Na_2SO_4 , and cooled to 0 °C. Addition of 100 mL of Et_2O gave a microcrystalline precipitate that was washed with little Et_2O and dried in vacuo (cf. Table II).

Bis(tert-butyl- η^5 -cyclopentadienyl)ion Hexafluorophosphate. To a solution of 4.40 g (9.93 mmol) of $(tBuCp)_2Fe$ in 10 mL of benzene was added 20 mL of 5 M HNO_3 , the mixture was stirred until the organic layer was almost colorless and filtered. From the separated blue aqueous layer a precipitate was obtained after addition of 0.8 g (3.66 mmol) of NH_4PF_6 in 10 mL of H_2O and standing over night. The solid was collected by filtration, washed 5× with H_2O , 2× with benzene, and again 5× with H_2O and dried in vacuo. A sample recrystallized from acetone/ H_2O was used for the elemental analysis (cf. Table II).

The NMR spectra were measured with a Bruker CXP 200 or MSL 300 and a Jeol GX 270 spectrometer; the temperature which was close to room temperature was measured with a Lauda R42 resistance thermometer. The experimental shifts at the given temperature, $\delta_{\text{exp}}^{\text{pl}}$, were determined relative to the internal solvent signals (acetone- d_6 , $\delta(CD_2)$ 28.9, $\delta(CHD_2)$ 2.04; nitromethane- d_3 , $\delta(CD_3)$ 62.8 $\delta(CHD_2)$ 4.33; dimethyl sulfoxide- d_6 , $\delta(CD_3)$ 39.5, $\delta(CHD_2)$ 2.49; H_2O , δ 4.80). $(C-H_3)_3Si(CH_2)_3SO_3Na$ with $\delta(CH_3)$ 1.7 was used as internal standard for ^{13}C measurements in H_2O . The $\delta_{\text{exp}}^{\text{pl}}$ values were transformed to $\delta_{\text{ref}}^{\text{pl}}$ values by calculation relative to the corresponding signals of the homologous cobaltocenium ions: $[(tBuCp)_2Co]^+$, $\delta(^{13}C)^{43,44}$ 121.3, 81.0, 83.3, 28.8, 29.3 (C1, C2/5, C3/4, $C\alpha$, $C\beta$); $\delta(^1H)^{45}$ 5.66, 1.28 (H2-5, H γ); $[(iPrCp)_2Co]^+$, $\delta(^{13}C)^{43,44}$ 116.1, 82.2, 83.7, 26.3, 21.8, (C1, C2/5, C3/4, $C\alpha$, $C\beta$); $\delta(^1H)^{45}$ 5.60, 3.10, 1.30 (H2-5, H β , H γ); $[(EtMe_4Cp)_2Co]^+$ see Table I. For the latter compound the assignment

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(45) Hebenanz, N.; Köhler, F. H., unpublished results.

of $C\alpha 2/5$ and $C\alpha 3/4$ is unclear. Therefore the mean value δ 7.91 has been used as reference shift. The $\delta_{\text{para}}^{\text{para}}$ values were converted to the final standard values $\delta_{\text{para}}^{\text{para}}$ following the Curie law.

Acknowledgment. We thank Profs. O. Kahn and B. M. Hoffman for preprints of their publications cited in refs 5 and 2g. Our work has been supported by the Fonds der Chemischen

Industrie and a scholarship (W.S.) of the Technische Universität München.

Supplementary Material Available: Calculation of the metal-centered and the ligand-centered dipolar ^1H and ^{13}C NMR shifts (6 pages). Ordering information is given on any current masthead page.

Self-Assembly of Dinuclear Helical and Nonhelical Complexes with Copper(I)

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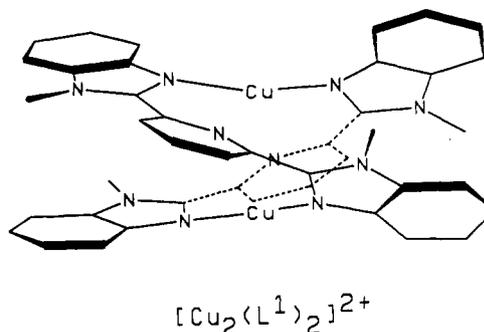
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Abstract: The ligand 1,3-bis(1-methylbenzimidazol-2-yl)benzene (mbzimbe, L^3) reacts with copper(I) to give $[\text{Cu}_2(L^3)_2](\text{ClO}_4)_2$. The crystal structure of this compound ($\text{Cu}_2\text{C}_{44}\text{H}_{56}\text{N}_8\text{Cl}_2\text{O}_8$, $a = 13.661$ (1) Å, $b = 19.829$ (3) Å, $c = 15.413$ (2) Å, orthorhombic, $Pbca$, $Z = 4$) shows a dinuclear centrosymmetrical nonhelical structure in which each copper is linearly coordinated by a benzimidazole group of each ligand. The complex displays a weak intramolecular stacking interaction between the benzene groups. This complex can be considered as a stereoconformer of the double-helical complex $[\text{Cu}_2(L^1)_2](\text{ClO}_4)_2$ (L^1 : 2,6-bis(1-methylbenzimidazol-2-yl)pyridine). Conductivity measurements and UV-visible spectra show that the dimeric structures are maintained in solution in polar aprotic solvents. ^1H NMR measurements show that $[\text{Cu}_2(L^1)_2]^{2+}$ retains its helical structure in solution. Comparison of helical and nonhelical structures with those formed by Cu(I) with related ligands allows discussion of the factors favoring the formation of self-assembled dinuclear complexes.

Introduction

The design of complex three-dimensional supramolecular architectures requires the use of selective and efficient self-assembling processes.¹ A feature of self-assembly is the use of elementary modular building blocks which contain sufficient structural information to guide the self-assembly reaction.² These reactions may be driven by the formation of specific intra- and intermolecular interactions between units, as is well-known in biological systems, or by the complexation of the modules to a metal ion. The development of new polydentate ligands which give organized supermolecules upon complexation to two or more metal ions is thus a theme of considerable interest in supramolecular chemistry.^{1,3} Particular interest has been shown in double-helical structures which may be generated by the complexation of two ligands twisted around metal ions lying on the helical axis. Many such systems have been reported for dimetallic complexes containing cadmium(II),⁴ copper(I),⁵ copper(II),⁶ iron(II),⁵ manganese(II),⁵ and nickel(II).⁷ Planned syntheses of double-helical complexes containing up to five Cu(I) ions have been developed by Lehn and his collaborators,⁸ while Dietrich-Buchecker and Sauvage⁹ used double-helical complexes with Cu(I) for the synthesis of the first molecular knot. Although most helical complexes with Cu(I) display tetrahedral coordination around the metal ion,^{5,8,9} we recently reported¹⁰ a double-helical complex of Cu(I) in which the ligand 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (L^1 , mbzimpy) acts essentially as a bis(monodentate) ligand, giving a quasi-linear coordination of the two copper ions which show, however, a weak interaction with the bridging pyridines. If this interaction is included, the coordination of the copper ions may be considered as a highly distorted tetrahedron.

As an aspect of our general interest in self-assembly reactions, this system offers possibilities for investigating the factors which



favor the self-assembly of polynuclear metal complexes. In particular, we were interested to know if the weak bridging pyridines were essential for the helical twist, and if the double-

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