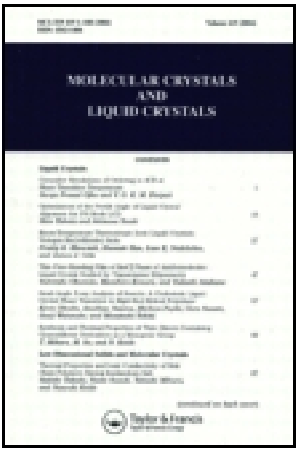

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THE FERROMAGNETIC COUPLING MECHANISM IN METALLOCENIUM/ π-ANION STACKS AS SEEN BY NMR SPECTROSCOPY

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Abstract The ^1H and ^{13}C NMR spectra of selected nickelocenium, chromocenium, and ferrocenium ions are reported. The sign of the signal shifts establishes positive or negative electron spin on the ligand for Ni or Cr sandwiches, respectively. Hyperconjugative spin transfer to β carbon atoms of substituted ferrocenium ions is used to prove negative spin on their ligands. For $(Cp^*)Cr(arene)$ derivatives negative spin on the ligand is indicated by characteristic shifts of the β-proton signals. The results meet the requirements of the mechanism of Kahn and Kollmar [5b,c] for magnetic intra-stack interactions.

A break-through in the field of molecular magnetic materials was the investigation of $[Cp^*_2Fe]^+[TCNE]^-$[1] which becomes a bulk ferromagnet at a transition temperature of $T_c = 4.74$ K [2] and which has a structure similar to that in Figure 1. The beauty of the approach is that it may be extended by changing the sandwich and/or the organic radical; examples are $[Cp^*_2Mn]^+[TCNQ]^-$($T_c = 6.2$ K [3a]), $[Cp^*_2Mn]^+[TCNE]^-$($T_c = 8.8$ K [3b]), and $[Cp^*_2Cr]^+[TCNQ]^-$($T_c = 3.1$ K [3c]). There is, however, a difficulty in the rational design of such materials and this is the understanding of the ferromagnetic coupling within the stacks.

Miller and Epstein [4] have developed a first mechanism where a triplet ground state of a pair $[Cp^*_2M]^+[Anion]$ is stabilized by the admixture of an excited state. This has been criticized as being inefficient by several groups [5], among them Kahn and Kollmar who have published a different mechanism [5b]. It implies the interaction between spin in the π orbitals of Cp^* and of the anion. The important point is that ferromagnetic interaction is only expected when the sign of the spin magnetic moment on both interacting partners is different, i.e. negative spin must be present on the ligand as shown in Figure 1. This report illustrates how the spin density can be determined by using NMR spectroscopy.

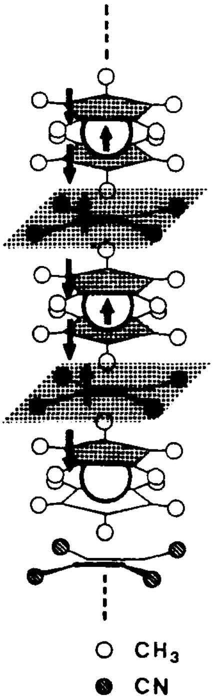

FIGURE 1

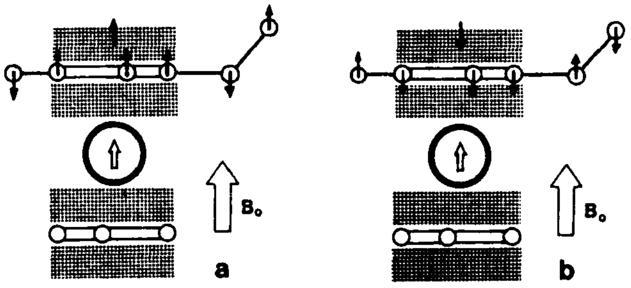

FIGURE 2

Paramagnetic metallocenes are known to yield NMR spectra. A side view of a metallocene in Figure 2 shows where the NMR-signals are expected. When the unpaired electron sits (parallel to the magnetic induction B_o) in a MO with appreciable ligand content (Fig. 2a), then spin with unchanged sign appears in the ligand π system (dashed) and the ring carbon signals will behave as if an additional field is present so that they should appear at low field. This is exactly what we find in the ^{13}C NMR spectrum of $[(EtMe_4Cp)_2Ni]^+[PF_6]^-$ [6] (1) (Fig. 3; S = CD_3NO_2, X = impurity). Note that the shifts are big, i.e. the delocalization is efficient. The spin is further delocalized by the polarization of the bonding σ electrons between C1 and any nucleus α. In fact, we find the signals of both Cα and Hα (of $[(\mathrm{EtCp})_2\mathrm{Ni}]^+[\mathrm{PF_6}]^-$[7]) at the other field side. It follows that positive spin sits in the ligand π system of nickelocenium ions and that antiferromagnetic coupling is deduced[5b,c] for corresponding stacks. This has been found for $[\mathrm{Cp^*{}_2Ni}]^+[\mathrm{TCNE}]^-$[1].

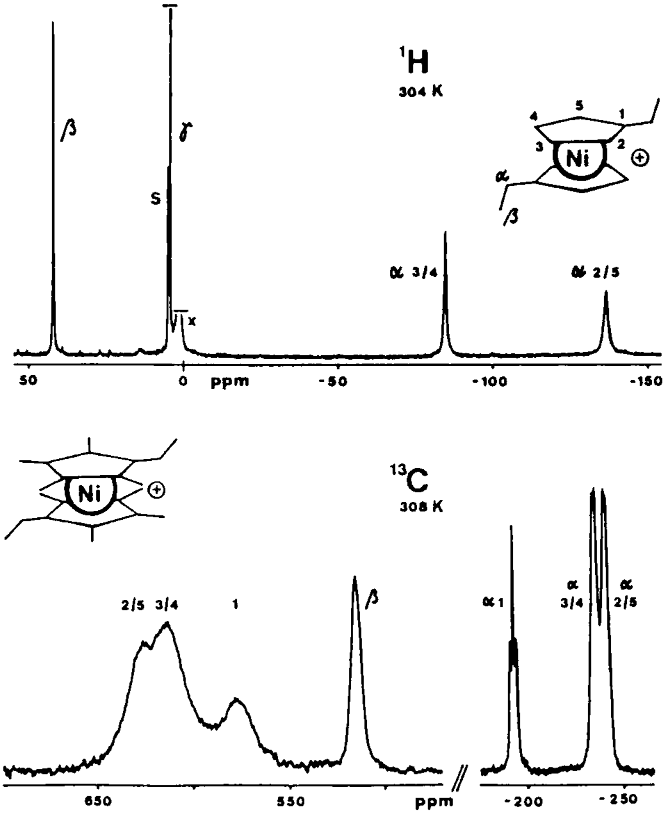

FIGURE 3

A different case are sandwiches with the unpaired electron in essentially pure metal orbitals. Here spin appears in the ligand π system through polarization of metal-ligand bonding electrons so that its sign should be negative (Fig. 2b). We have found this behaviour e.g. for chromocenium ions. Thus, the signals of C1-5 of $[(\mathrm{EtMe_4Cp})_2\mathrm{Cr}]^+[\mathrm{PF_6}]^-$[6] (Fig. 4; top/bottom: S = $\mathrm{CD_3NO_2/(CD_3)_2CO}$, X = impurity) unlike those of **1**, appear at high field. Consistently, the signals of Cα and of Hα (of $[(\mathrm{EtCp})_2\mathrm{Cr}]^+[\mathrm{PF_6}]^-$[7]) are found at low field. The spin in the ligand π system must therefore be negative and, according to the theory[5b,c], corresponding stacks should show ferromagnetism. This has been established experimentally[3c]

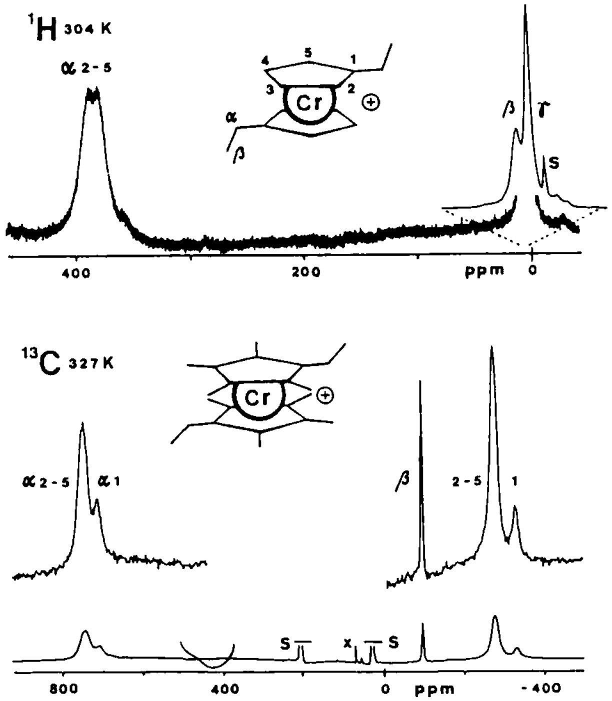

FIGURE 4

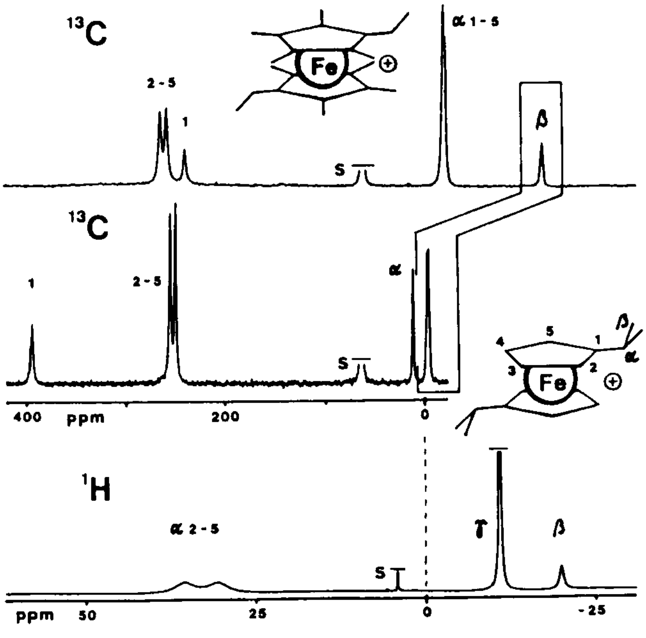

FIGURE 5

The NMR spectra of ferrocenium ions lead to contradictory conclusions. An example is $[({}^{i}PrCp)_2Fe]^+$ $[PF_6]^-$ [8] (2) (Fig. 5; S = CD_3NO_2, all spectra at 307 K) with the signals of C1-5 and Hα at the same field side. This problem is due to σ delocalization and dipolar contributions to the signal shifts. It can be overcome by probing the ligand π spin density through hyperconjugation as shown in Figure 6. Looking down the Cα-C1 bond of a substituted metallocene (Fig. 6a) gives Figure 6b. Here the dihedral

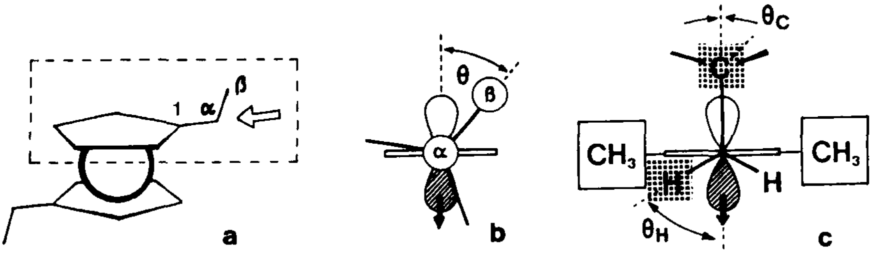

FIGURE 6

angle θ determines the spin transfer from the π orbital to Cβ so that its signal shift is proportional to $\cos^2\Theta$. For freely rotating groups like ethyl (or ^{i}Pr in Fig. 5) θ is 45° for any nucleus. When CH_3 is introduced next to ethyl the rotamer in Figure 6c will be favoured. For Cβ we then have $\Theta_C = 0°$. Thus, on going from Figure 6b to 6c the spin transfer to Cβ should increase and its signal should move to high field when the spin density is negative. Ferrocenium ions behave exactly in this way as is evident from the striking change of the signal shift of Cβ (Fig. 5) on passing from 2 to $[(EtMe_4Cp)_2Fe]^+$-$[PF_6]^-$ 6. In accord with the mechanism of Kahn and Kollmar 5b negative spin on Cp* leads to ferromagnetism as found for 1 1.

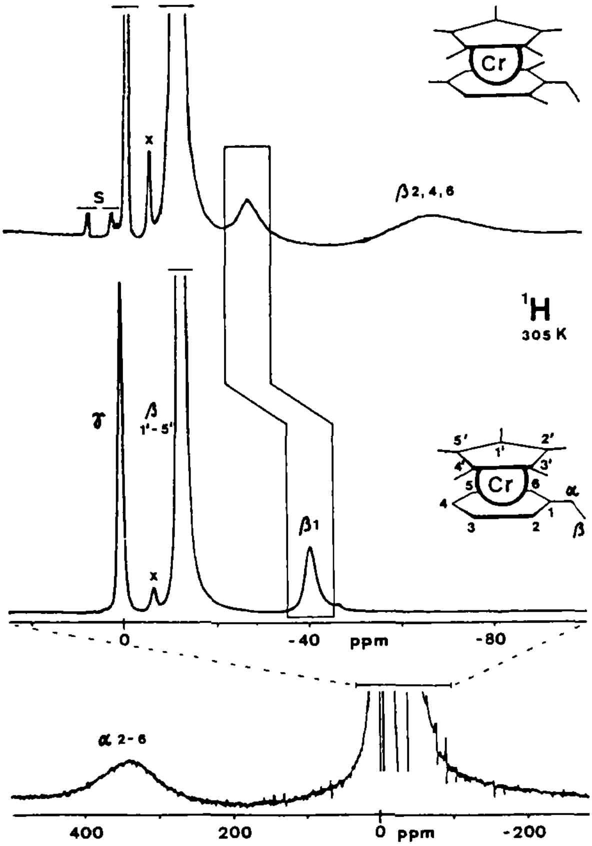

FIGURE 7

^1H NMR signals which, of course, are much easier to detect, may also be used as hyperconjugative probe. We have tested this for the Cp^*Cr(arene) derivatives [9] in Figure 7. Again the freely rotating ethyl group of $Cp^*Cr(EtC_6H_5)$ (**3**) leads to $\theta = 45^o$ (cf. Fig. 6b) whereas for $Cp^*Cr(EtMe_3C_6H_2)$ (**4**) the rotamer in Figure 6c with $\theta_H = 60^o$ and hence with less efficient hyperconjugation is most stable. It follows that the signal of Hβ should move to low field when we go from **3** to **4** and when the spin on the ligand is negative. This behaviour is found experimentally as shown in Figure 7 ($S = CD_3C_6D_5$, $X = Cp^*{}_2Cr$). CpCr(arene) derivatives have a $^2A_1$ ground state [10] and therefore the dipolar shifts are small [11]. In other cases problems may arise because, due to the $\cos^2\theta$ dependence and smaller overall contact shifts, ^1H is less efficient than ^{13}C NMR spectroscopy.

In conclusion, hyperconjugation detected by ^{13}C NMR spectroscopy is the most reliable probe for the sign of the ligand spin density in these and other compounds. Our investigations do not prove that the ferromagnetic coupling mechanism of Kahn and Kollmar is the only correct one, but we have found no example which is at variance with its predictions.

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