Study of Paramagnetic Chromocenes by Solid-State NMR Spectroscopy

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Summary: The application of 1H, 2H, and 13C solid-state NMR spectroscopy to polycrystalline paramagnetic sandwich compounds was tested for chromocene (Cp2Cr), deuteriated chromocene (Cp2Cr-d10), and decamethylchromocene (Cp*2Cr).

The bulk properties of paramagnetic compounds have been investigated thoroughly for a long time, and increasing effort is being observed particularly in molecular magnetism.1 The commonly employed magnetic measurements integrate all over the sample, and individual information on different species being present is difficult to obtain. This kind of information is highly desirable, however, when paramagnetic catalysts are studied2 and when molecule-based magnetic materials3 are designed from various building blocks. Our current organometallic approaches to both topics prompted us to further explore solid-state NMR spectroscopy and to select chromocenes (having two unpaired electrons) as prototypes.

Pioneering work on magic angle spinning (MAS) NMR of paramagnetic transition metal compounds has been carried out by several groups4 directed to both theory and application. But only very few studies of paramagnetic organometallic compounds are available.5 Therefore, in addition to the background mentioned above, it seemed rewarding to initiate systematic work.

Polycrystalline chromocene (Cp2Cr), its deuteriated analogue (Cp2Cr-d10), and decamethylchromocene (Cp*2Cr) were studied by 1H, 2H, and 13C NMR spectroscopy to polycrystalline paramagnetics and seemed rewarding to initiate systematic work.

Figure 1. MAS NMR spectra of polycrystalline CpCr. For details of the measurements see text. Asterisks and the circle denote rotational sidebands and a probehead background signal, respectively. A: 1H MAS NMR spectrum (300.1 MHz); rotational frequency 13 kHz. B: 13C MAS NMR spectrum (75.5 MHz); rotational frequency 10 kHz.

The spectra of Figure 1 were measured with single pulse excitation in the high-power mode of a solid-state NMR spectrometer. Idential spectra were obtained in the low-power mode (with other parameters unchanged)6 the same was true of Cp2Cr-d10 and Cp*2Cr. Hence, in general, spectra of this type can be also recorded by using conventional high-resolution NMR spectrometers equipped with a MAS probehead.

In order to assess the effect of the homo- and heteronuclear dipolar coupling on the line widths $W$ of the individual signals within the spinning sideband manifold we investigated C$_2$H$_7$-d$_{10}$. Usually, when dipolar interactions are dominant, a dramatic reduction of $W$ is expected on passing from the protonated to the deuteriated compounds for both the $^1$H$^{14}$c and $^13$C$^{11}$11 MAS NMR spectra. However, only a minor decrease of $W(^{13}$C) to 1.1 kHz was observed for C$_2$H$_7$-d$_{10}$ at MAS frequencies of 10–15 kHz, while $W(^1$H) of the residual protons did not change. This means that among the known different broadening factors$^6$, the interaction between the nuclei and the unpaired electrons determines the line widths $W$. Besides, MAS efficiently averages the internuclear dipolar interactions. $W$ should also decrease strongly upon changing from $^1$H to $^2$H NMR.$^{11,12}$ In fact, in the $^2$H MAS NMR spectrum of C$_2$H$_7$-d$_{10}$ (Figure 2) we find $W(^1$H) = 0.7 kHz for the peaks which constitute the expected Pake pattern typical of an $I = 1$ nucleus. This is seven times smaller than $W(^1$H) of C$_2$H$_7$, but the effect is less pronounced than in solution.$^{15}$

The NMR spectra of the chromocenes depend strongly on the temperature and the rotational frequency $\nu_r$. As commonly found for simple paramagnetic molecules, the magnitude of the signal shifts $\delta$ decreases on raising the temperature. By contrast, $W$ remains essentially constant so that chromocenes may serve as solid-state NMR shift thermometers whose precision hardly depends on the temperature.$^4$ Moreover, at a given bearing- and drive-gas temperature, the shift values $|\delta|$ decreased when the rotor frequency was increased. For example, raising $\nu_r$ from 3 to 15 kHz changed $\delta(^{13}$C) of C$_2$H$_7$ from $-258.4$ to $-231.3$. This would be equivalent to increasing the sample temperature by $20^\circ$C.$^3$ The data obtained in variable MAS frequency studies could be fit to the expression $\delta = a + b^{-3}$.$^{14}$ This confirms previous work$^{15}$ which attributed the effect to rotation as a result of $\nu_r^2$-dependent friction.$^{15b}$ The relation $\delta \propto \nu_r$ was also reported.$^{16}$

Further aspects of general interest were encountered when C$_2$H$_7$ was investigated. Both the $^1$H and $^{13}$C MAS NMR spectra (Figure 3A,C) showed a splitting of the expected signals. In order to explain this result, which differs from that obtained for C$_2$H$_7$, we have redetermined$^{17}$ the crystal structure. C$_2$H$_7$ crystallizes in the space group P2$_1$/2$_1$/2$_1$. Two molecules A and B out of eight in the unit cell (Figure 4) are crystallographically and magnetically nonequivalent.

It is noteworthy that cross polarization was not efficient for chromocenes, probably owing to fast proton relaxation. Apart from this, simple high-power proton decoupling led to a striking broadening of $^{13}$C MAS NMR signals which proved to be selective. Thus, irrespective of the functional group, carbon atoms that bind protons were affected, whereas quaternary carbon atoms were not. In addition, the broadening could be restricted to one of the nonequivalent molecules in the unit cell; i.e., the broadening could be made site-selective. This is demonstrated in Figure 3: Irradiation at the low-frequency $^1$H NMR signal of C$_2$H$_7$Cr (Figure 3A)$^{18}$ led to a broadening of only one of the two $^{13}$C NMR signals (again that at low frequency) of the CH$_3$ groups


$^{14}$ As derived from temperature-dependent NMR studies of C$_2$H$_7$ in toluene-d$_8$: Cao, R.; Köhler, F. H. Unpublished data.


(17) First attempt: Bottomley, F.; Chen, J.; McIntosh, S. M. Thompson, R. C. Organometallics 1991, 10, 906. These authors described the crystal structure to be in the orthorhombic C-centered space group Cmmm with disorder.
Among the origins of this effect, smearing out of the signals due to temperature drift (especially on decoupling) can be ruled out, because the broadening is selective while the temperature behavior of the signal pairs is very similar. Rather the interference between the decoupling frequency and the rotation of the Cp ligands is expected to cause the signal broadening. For diamagnetic molecules such an interference was first demonstrated by Waugh, and recent applications to the study of molecular motions were published by Günther and Griffin. In the case of Cp*₂Cr the interference should broaden the signals of CH₃ much more than that of the ring-C atoms, because the dipolar coupling is proportional to \( r^{-6} \), \( r \) being the C---H distance. This was in fact observed.

In conclusion a promising entry into solid-state NMR studies of paramagnetic metallocenes was established. It includes equivalent and nonequivalent molecules in the unit cell, the correlation of the signal shift with the square of the MAS frequency, and chemical group-selective as well as site-selective \(^{13}\)C MAS NMR signal broadening by high-power proton decoupling. The latter phenomenon is expected to be generally applicable to the assignment of MAS NMR signals of paramagnetic compounds.

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Supporting Information Available: Tables of crystal data, atomic positional parameters, and bond distances, bond angles, dihedral angles between least-squares planes, and anisotropic displacement parameters and three figures of Cp*₂Cr (12 pages). Ordering information is given on any current masthead page.

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Figure 4. Plot of the crystallographically nonequivalent molecules A and B of Cp*₂Cr. Selected averaged distances (Å) and angles (deg) for A/B: C---CH₃ 1.505(6)/1.502, C---C 1.415(6)/1.421(6), Cr---D 1.786(6)/1.779(6), D---Cr---D 179.8(2)/179.4(2). D is the center of the Cp* ligands. Bending range of the CH₃ groups out of the Cp planes: 0.5---4° (away from Cr). Average torsional angles (C---D---D---C) of the Cp* ligands of A/B: 17/---7 deg. The Cp* planes of A and those of B include an average angle of 89°.