Study of Paramagnetic Chromocenes by Solid-State NMR Spectroscopy

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Summary: The application of ^1H, ^2H, and ^{13}C solid-state NMR spectroscopy to polycrystalline paramagnetic sandwich compounds was tested for chromocene (Cp_2Cr), deuteriated chromocene (Cp_2Cr-d_{10}), 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 studied[2] and when molecule-based magnetic materials[3] 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 groups[4] directed to both theory and application. But only very few studies of paramagnetic organometallic compounds are available.[2d,5] Therefore, in addition to the background mentioned above, it seemed rewarding to initiate systematic work.

Polycrystalline chromocene Cp_2Cr, its deuteriated analogue Cp_2Cr-d_{10}, and decamethylchromocene $Cp*_2Cr$[6] were studied by ^1H, ^2H, and ^{13}C NMR spectroscopy as MAS and static samples. The ^1H and ^{13}C MAS NMR signals of Cp_2Cr (Figure 1) cover ranges of 300 and 500 ppm, respectively; the shifts (and the half-widths) of the isotropic peaks are 315 ppm (4.9 kHz) and −258 ppm (1.2 kHz). The presence of only one ^1H and one ^{13}C NMR signal suggests that corresponding nuclei of the two molecules of the unit cell[7] are magnetically equivalent.[8]

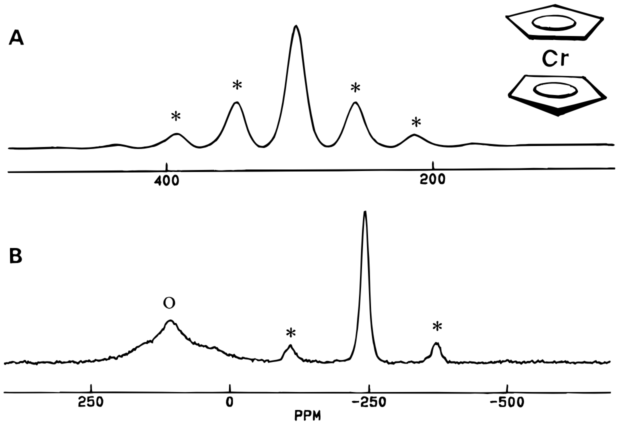

Figure 1. MAS NMR spectra of polycrystalline Cp_2Cr. For details of the measurements see text. Asterisks and the circle denote rotational sidebands and a probehead background signal, respectively. A: ^1H MAS NMR spectrum (300.1 MHz); rotational frequency 13 kHz. B: ^{13}C MAS NMR spectrum (75.5 MHz); 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. Identical spectra were obtained in the low-power mode (with other parameters unchanged);[9] the same was true of Cp_2Cr-d_{10} 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.

[†] Crystal structure analysis.

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1996.

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[9] Bruker MSL 300, 4 mm broadband double bearing MAS probehead, ca. 30 mg of polycrystalline material densely packed under N_2 and centered in ZnO_2 rotors by Teflon spacers, 90°-pulse widths for 10 μs (^2H), 6 μs (^{13}C), and 8 μs (^1H), dead time delay 10 μs, pulse spacing 100 ms. In the high-power mode the corresponding pulse widths were roughly three times smaller. Good S/N was obtained after 6000 (^2H), 4000 (^{13}C), and 100 (^1H) scans, i.e., after 10 min or less; line broadening factors of 20, 100, and 0 Hz, respectively were applied. Water and adamantane (low-frequency signal) were used as external standards.

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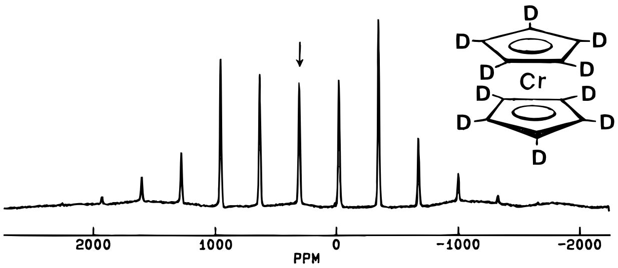

Figure 2. ^{2}H MAS NMR spectrum (46.1 MHz) of polycrystalline Cp$_2$Cr-d_{10}. The isotropic line is denoted by an arrow; rotational frequency 13 kHz.

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 Cp$_2$Cr-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[4c,10] and ^{13}C[11] MAS NMR spectra. However, only a minor decrease of $W(^{13}C)$ to 1.1 kHz was observed for Cp$_2$Cr-d_{10} at MAS frequencies of 10−15 kHz, while $W(^1H)$ of the residual protons did not change. This means that among the known different broadening factors[4c,10,11] 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 Cp$_2$Cr-d_{10} (Figure 2) we find $W(^2H) = 0.7$ kHz for the peaks which constitute the expected Pake pattern typical of an $I = 1$ nucleus. This is seven times smaller than $W(^1H)$ of Cp$_2$Cr, but the effect is less pronounced than in solution.[6c]

The NMR spectra of the chromocenes depend strongly on the temperature and the rotational frequency ν_r. As commonly found for simple paramagnetic molecules, the magnitude of the signal shifts δ 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.[4g] Moreover, at a given bearing- and drive-gas temperature, the shift values $|\delta|$ decreased when the rotor frequency was increased. For example, raising ν_r from 3 to 15 kHz changed $\delta(^{13}C)$ of Cp$_2$Cr from −258.4 to −231.3. This would be equivalent to increasing the sample temperature by 20 °C.[13] The data obtained in variable MAS frequency studies could be fit to the expression $\delta = a\nu_r^2 + b$.[14] This confirms previous work[15] which attributed the effect to rotor heating as a result of ν_r^2-dependent friction;[15b] the relation $\delta \propto \nu_r$ was also reported.[16]

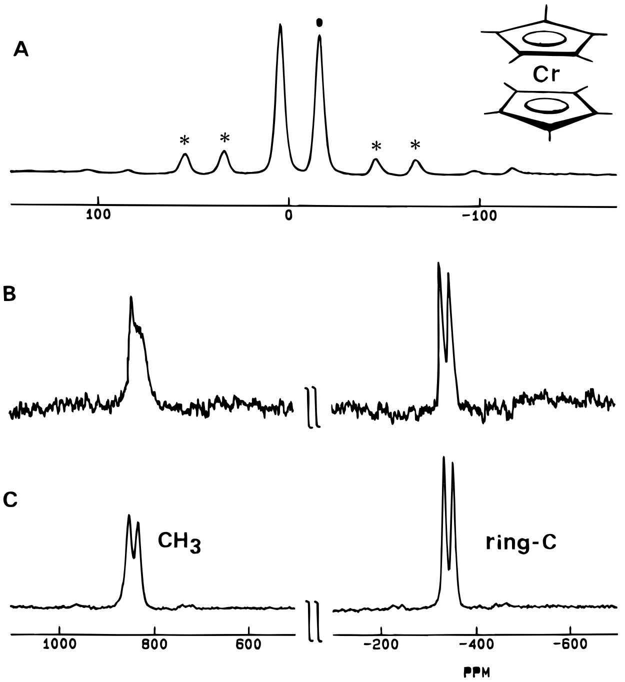

Figure 3. Solid-state NMR spectra of polycrystalline Cp*$_2$Cr. Asterisks denote rotational sidebands. A: ^{1}H MAS NMR spectrum (300.1 MHz); rotational frequency 15 kHz. B: ^{13}C MAS NMR spectrum (75.5 MHz) recorded with irradiation[9] at the low-frequency ^{1}H NMR resonance of spectrum A (denoted by the dot) during acquisition; rotational frequency 15 kHz. C: ^{13}C MAS NMR spectrum (75.5 MHz) recorded with a simple one-pulse sequence; rotational frequency 8 kHz.

Further aspects of general interest were encountered when Cp*$_2$Cr 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 Cp$_2$Cr, we have redetermined[17] the crystal structure. Cp*$_2$Cr crystallizes in the space group $P2_12_12_1$. 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 quarternary 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 Cp*$_2$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

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(13) As derived from temperature-dependent NMR studies of Cp$_2$Cr in toluene-d_8: Cao, R.; Köhler, F. H. Unpublished data.

(14) Cp$_2$Cr: $\delta(^{13}C) = 0.144\nu_r^2 - 263.9$ for $\nu_r \geq 6$ kHz, $\delta(^1H) = -0.111\nu_r^2 + 332.3$ for $\nu_r \geq 8$ kHz. Cp*$_2$Cr, ring-C atoms: $\delta(^{13}C) = 0.160\nu_r^2 - 346.2$ and $\delta(^{13}C) = 0.166\nu_r^2 - 364.9$ for $\nu_r \geq 2$ kHz. Cp*$_2$Cr, CH$_3$: $\delta(^{13}C) = -0.298\nu_r^2 + 870.4$ and $\delta(^{13}C) = -0.292\nu_r^2 + 851.2$ for $\nu_r \geq 3$ kHz; ν_r^2 in kHz^2. ν_r was incremented in 1 kHz steps up to 15 kHz. The correlation was good in all cases ($r^2 > 0.995$), the bearing- and drive-gas temperature was 298 K. Below the indicated MAS frequencies the signal shifts in the same order as given above were −258.4, 315.2, −345.2, −363.5, 867.9, and 847.5 ppm. Cp*$_2$Cr: $\delta(^1H) = 5.0$ and −16.1.

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(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 *Ccmm* with disorder.

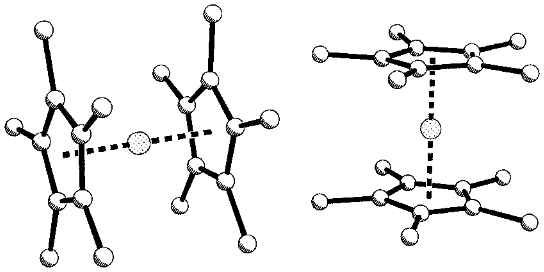

Figure 4. Plot of the crystallographically nonequivalent molecules A and B of Cp*$_2$Cr. Selected averaged distances (Å) and angles (deg) for A/B: C−CH$_3$ 1.505(6)/1.502, C−C 1.415(6)/1.421(6), Cr−D 1.786(6)/1.779(6), D−Cr−D 179.8(2)/179.4(2). D is the center of the Cp* ligands. Bending range of the CH$_3$ 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°.

(Figure 3B). Note that the signals of the ring carbon atoms did not change.

Among the origins of this effect, smearing out of the signals due to a temperature drift (especially on decoupling) can be ruled out, because the broadening is selective while the temperature behavior[14] 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.[19] For diamagnetic molecules such an interference was first demonstrated by Waugh,[20a] and recent applications to the study of molecular motions were published by Günther[20b] and Griffin.[20c] In the case of Cp*$_2$Cr the interference should broaden the signals of CH$_3$ 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*$_2$Cr (12 pages). Ordering information is given on any current masthead page.

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(18) A high MAS frequency was necessary in order to minimize the overlap of the proton signals due to rotational sidebands, and reduced decoupling power[9] was applied.

(19) A reviewer suggested that off-resonance proton irradiation (Mehring, M. *Principles of High Resolution NMR in Solids*, 2nd ed.; Springer-Verlag: Berlin, 1983; Chapter 4.4) might be another reason.

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