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MAGNETIC RESONANCE IN CHEMISTRY
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^{59}Co second-order quadrupolar effects in the ^{13}C cross-polarization magic angle spinning NMR spectra of the cobaltocenium salts $[Cp^*_2Co]^+[PF_6]^-$ and $[Cp^*CpCo]^+[PF_6]^-$

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ABSTRACT: The cobaltocenium ions $[Cp^*_2Co]^+$, $[Cp^*CpCo]^+$, $[Cp_2Co]^+$ and $[(EtC_5H_4)_2Co]^+$ ($Cp^* = C_5Me_5$; $Cp = C_5H_5$) were studied by ^{13}C cross-polarization magic angle spinning NMR spectroscopy. The ring carbon signals of $[Cp^*_2Co]^+[PF_6]^-$ and $[Cp^*CpCo]^+[PF_6]^-$ showed splitting patterns which are a signature of the hitherto unknown ^{59}Co, ^{13}C dipolar coupling. In contrast, a unique signal was found for the remaining cations. The dependence of the patterns on the field, the rotor spinning rate and the temperature was investigated, and full-matrix diagonalization treatment was used to fit the spectra. The patterns were better resolved at lower fields and to some extent at lower spinning rates. Self-decoupling was observed for $[Cp^*CpCo]^+[PF_6]^-$ above 360 K. Visual fitting yielded dipolar and indirect isotropic ^{59}Co, ^{13}C coupling constants of 530 and 40 Hz, respectively. When the counter ion of $[Cp^*CpCo]^+$ was changed from $[PF_6]^-$ to Cl^- or $[TCNE]^{2-}$ the dipolar coupling pattern was not present, probably because of self-decoupling. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: NMR; solid-state magic angle spinning NMR; ^{13}C NMR; ^{59}Co, ^{13}C dipolar coupling; cobaltocenium ions

INTRODUCTION

The magic angle spinning NMR spectra of $I = 1/2$ spin nuclei interacting with quadrupolar nuclei ($S > 1/2$) often show characteristic splitting patterns.[1] The reason is that dipolar interactions between the S and the I nuclei are not completely averaged out by magic angle spinning when the quadrupolar coupling is comparable to the Zeeman splitting energy, i.e. when the S spin is no longer quantized along the magnetic field direction. This phenomenon was first discovered[2] and fully discussed[3] for the ^{13}C,^{14}N ($S = 1$) spin pair in organic compounds, where the signals of carbon atoms directly bonded to nitrogen atoms are usually split into 1 : 2 (or 2 : 1) 'doublets', with each line actually being a powder pattern. More complex splittings arise when the $I = 1/2$ nuclei are coupled to quadrupolar nuclei with higher spin values ($S > 1$), as has been observed for a large variety of spin pairs across the Periodic Table.[1,4] Furthermore, two first-order perturbation approaches for lineshape simulations have been described: The 'normal' one is valid for cases where the quadrupolar interactions are small compared with the Zeeman splitting,[5] and the 'inverse' perturbation approach holds for cases where the quadrupolar coupling dominates and the Zeeman interaction is considered a perturbation.[6] If these two interactions are comparable, lineshapes can be reproduced properly only by full theory.[7]

Recently we have discovered a residual dipolar coupling between ^{13}C and ^{59}Co when we investigated the sandwich compounds decamethylcobaltocenium hexafluorophosphate, $[Cp^*_2Co]^+[PF_6]^-$, and pentamethylcobaltocenium hexafluorophosphate, $[Cp^*CpCo]^+[PF_6]^-$, by ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectroscopy. In these compounds dipolar interactions to the ^{59}Co nucleus ($S = 7/2$) lead to an asymmetric splitting of the ring carbon signals whereas the carbon signals of the parent sandwich cobaltocenium hexafluorophosphate, $[Cp_2Co]^+[PF_6]^-$, and of 1,1′-diethylcobaltocenium hexafluorophosphate, $[(EtC_5H_4)_2Co]^+[PF_6]^-$, (Scheme 1) are not affected at room temperature, a phenomenon which we conclude is due to fast longitudinal relaxation of the ^{59}Co nucleus.[8] To the best of our knowledge, this is the first detailed report on ^{59}Co, ^{13}C dipolar coupling; previously it has been considered only for the cobalt carbonyl cluster $Co_4(CO)_{12}$, for which a substantial signal broadening has been observed in the ^{13}C CP/MAS NMR spectrum rather than a splitting.[9] In this paper we report signal splitting patterns of the ^{13}C NMR signals of the title sandwich cations, including field and temperature dependences.

EXPERIMENTAL

$[Cp^*_2Co]^+[PF_6]^-$, $[Cp^*_2Co]^+Cl^-$ and $[Cp_2Co]^+[PF_6]^-$ were prepared by literature methods.[10,11] $[Cp^*CpCo]^+$

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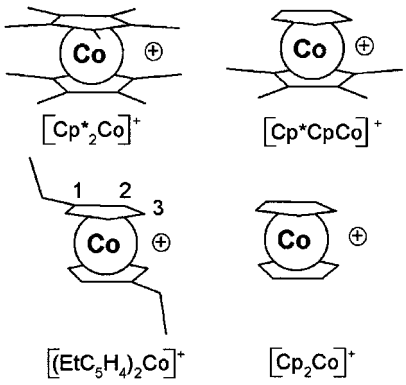

Scheme 1

$[PF_6]^-$ and $[(EtC_5H_4)_2Co]^+[PF_6]^-$ were obtained by oxidizing the corresponding neutral cobaltocenes Cp^*CpCo[12] and $(EtC_5H_4)_2Co$[13] according to Ref. 10. $[Cp^*_2Co]^+_2[TCNE]^{2-}$ was a gift from Professor J. S. Miller, University of Utah. The NMR spectra in Fig. 1 were recorded using the spectrometers and parameters listed in Table 1. All other spectra were obtained from a Bruker MSL300 spectrometer. Above room temperature a Si_3N_4 rotor with a ZrO_2 cap was used, and the temperature was measured by adding nickelocene as an internal standard in a similar way as described for vanadocene.[14] The data fit was achieved by eye using the Wsolids NMR simulation package version 1.17.8 of Eichele and Wasylishen[15] (Dalhousie University), which is based on the theory reviewed by Harris and Olivieri.[1]

RESULTS AND DISCUSSION

The ^{13}C CP/MAS NMR spectrum of $[Cp^*_2Co]^+[PF_6]^-$ displays a signal at 8.1 ppm for the methyl groups and a feature near 95 ppm for the ring carbon atoms. As shown on the left side of Fig. 1, the feature is actually an asymmetric splitting of the expected signal into a manifold of lines, and its overall width decreases when the field strength is increased from 4.7 to 17.62 T.

Table 1. Experimental parameters for recording the spectra of $[Cp^*_2Co]^+[PF_6]^-$ [a]

Parameter	Spectrometer CMX 200[b]	MSL 300[c]	DSX 500[c]	DMX 750[c]
B_0 (T)	4.7	7.05	11.74	17.62
$\nu(^{13}C)$ (MHz)	50.33	75.47	125.76	188.62
Rotor diameter (mm)	7	4	4	4
Spinning rate (kHz)	5.0	15.0	9.0	7.5
Sample weight (mg)	50	50	50	50
π-Pulse duration (μs)	3.5	4	3	1.5
Contact time (ms)	8	5	3	2
Recycle delay (s)	2.5	4	4	4
Acquisitions	24 000	1024	120	84
Digital resolution (Hz per point)	4.8	4.1	6.1	6.2
Exp. line-broadening (Hz)	2	5	10	10

[a] ZrO_2 rotor, Kel-F caps.
[b] Chemagnetics.
[c] Bruker.

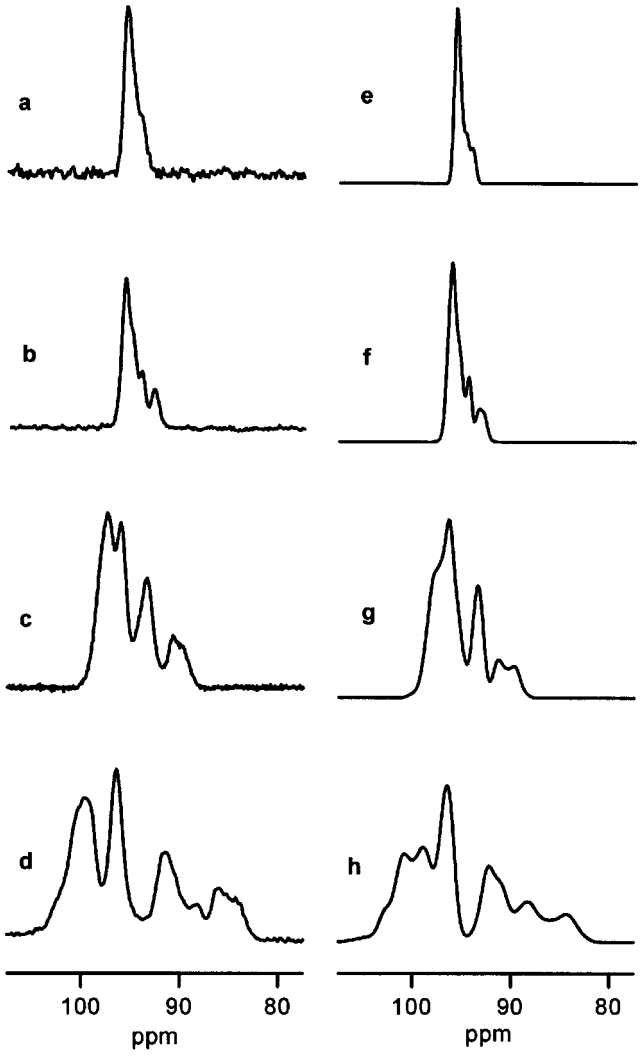

Figure 1. Left: ^{13}C CP/MAS NMR spectra of $[Cp^*_2Co]^+[PF_6]^-$ (centrebands of the ring carbons only) at different field strengths: (a) 17.62, (b) 11.74, (c) 7.05 and (d) 4.7 T. The spinning rates were (a) 7.5, (b) 9.0 (c) 15.0 and (d) 5 kHz. Right: simulated spectra; Gaussian line broadening of 100, 75, 65 and 60 Hz was used for (e), (f), (g) and (h), respectively.

The interpretation of this sort of splitting is often possible by constructing a stick pattern based on the perturbation theory approach, which is briefly summarized below from the more rigorous treatment described previously.[1] To a first-order approximation, the quadrupolar interaction at the spin S is assumed to be smaller than the Zeeman interaction such that the condition in Eqn (1) is fulfilled:

$$\left|\frac{\chi}{4S(2S-1)\nu_S}\right| \ll 1 \qquad (1)$$

where χ is the quadrupolar coupling constant (e^2Qq_{zz}/h), eq_{zz} is the largest component of the electric field gradient (EFG) at S, η is the asymmetry parameter of the EFG with $\eta = (q_{yy} - q_{xx})/q_{zz}$, (with $|q_{zz}| \geq |q_{xx}| \geq |q_{yy}|$) and ν_S is the Zeeman interaction.

The eigenstates $|\varphi_m\rangle$ of the quadrupolar nucleus can be calculated as a linear combination of Zeeman states $|n\rangle$

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according to the equation

$$|\varphi_m\rangle = \sum_{n=-S}^{S} a_{mn}|n\rangle \quad (2)$$

with the coefficients $a_{mn} = {}^0a_{mn} + {}^1a_{mn} + \cdots$. For the first-order coefficients ${}^1a_{mn}$, only those satisfying the condition $n = m \pm 1$ are needed.

The dipolar interaction between spins I and S (which transfers the quadrupolar information from the unobserved S to the observed I spin) is expressed as the dipolar coupling constant D_{IS}:

$$D_{IS} = \left(\frac{\mu_0}{4\pi}\right)\frac{\gamma_I\gamma_S h}{4\pi^2 r_{IS}^3} \quad (3)$$

where $\mathbf{r}_{IS}$ is the distance between the two spins and γ is the gyromagnetic ratio.

An additional interaction to consider is the indirect scalar coupling J_{IS}. For ease of treatment, the **J** tensor is assumed to be axial and the j_z component of the **J** tensor is collinear with the internuclear vector $\mathbf{r}_{IS}$. The dipolar interaction is then modified by J coupling, so that it is convenient to use an 'effective' dipolar interaction $D' = D - \Delta J/3$, where ΔJ is the anisotropy of the **J** tensor and with J_{IS} being the isotropic I, S indirect coupling interaction.

Retaining the a_{mn} coefficients up to first order, the second-order quadrupolar effects on the I spin resonance can be expressed[1] under the MAS conditions (using the standard Euler angles α and β to relate the $\mathbf{r}_{IS}$ vector in the EFG frame of reference) as

$$\Delta\nu_m = -mJ + \left(\frac{3D'\chi}{20\nu_s}\right)\left[\frac{S(S+1) - 3m^2}{S(2S-1)}\right] \times (3\cos^2\beta^D - 1 + \eta\sin^2\beta^D\cos 2\alpha^D) \quad (4)$$

where $\Delta\nu_m$ is the second-order shift.

In the present case, stick patterns constructed using the three assumptions (first-order perturbation theory, axial symmetry in the **J** tensor and unique axis of the **J** tensor aligned with $\mathbf{r}_{IS}$) failed to reproduce adequately the observed experimental lineshapes. Therefore, simulations were carried out with full-matrix diagonalization, i.e. with all the values of a_{mn} from which $|\varphi_m\rangle$ are obtained.

For the fitting procedure the following starting parameters were used and varied until an acceptable visual fit was obtained. The angle $\beta = 36.36°$ was taken as a mean value from the crystal structure of $[Cp^*_2Co]^+[PF_6]^-$.[16] Quadrupole coupling constants χ in the range 166.6–172.2 MHz have been reported for methylated cobaltocenium ions.[17] In our case the axially symmetric EFG tensor ($\eta = 0$) should be aligned along the fivefold symmetry axis ($\alpha = 0$).[18] The isotropic chemical shift δ_{ISO} was determined from the high-field spectrum (where the second-order quadrupolar effects are lessened), and the ^{59}Co Larmor frequencies $\nu(^{59}Co)$ were obtained after multiplying the $\nu(^{13}C)$ values in Table 1 by 0.94. Scalar coupling constants $J(^{59}Co,^{13}C)$ or ΔJ do not seem to be available for cobaltocenium cations.[19] However, they may be estimated from $J(^{57}Fe,^{13}C) = 4.7$ Hz determined for ferrocene.[20] Multiplication by $\gamma(^{59}Co)/\gamma(^{57}Fe)$ gives $J(^{59}Co,^{13}C) \approx 34$ Hz, a value that may be modulated somewhat by different triplet excitation energies and electron densities of the molecule and the relevant nuclei, respectively. The scalar ^{103}Rh, ^{13}C coupling in a number of cyclopentadienylrhodium half-sandwich compounds has been found to be negative, but since $\gamma(^{103}Rh)$ is also negative, whereas $\gamma(^{59}Co)$ is positive, that implies $J(^{59}Co,^{13}C)$ is positive.

Although some minor discrepancies remain, a reasonable fit (Fig. 1, right-hand side) was obtained for simulated infinite spinning speed with the following parameters (with estimated errors in parentheses):

$\delta(^{13}C) = 95.3(0.5)$ ppm	$\beta = 30(2)°$
$D(^{59}Co,^{13}C) = 530(25)$ Hz	$\alpha = 0°$
$J(^{59}Co,^{13}C) = 40(4)$ Hz	$\chi = 169(5)$ MHz
$\Delta J = -50(50)$ Hz	$\eta = 0$

The spectrum displaying the greatest second-order quadrupolar effects is that collected at low field (4.7 T). An initial simulation using the geometric features from the single-crystal x-ray diffraction structure ($\beta = 36°$; $D = 850$ Hz) and with $\chi = 169$ MHz and $J = 35$ Hz gave a pattern much broader than observed. The agreement with the observed spectrum improved as D was decreased to 530 Hz and $\beta = 30°$. This may be explained in terms of fast molecular reorientation of the Cp* groups at a frequency much greater than D. Evidence for dynamic Cp* groups comes from the presence of a singlet, rather than a multiplet, for the ring methyl carbons. If the Cp* ligands were static, each crystallographically unique ring carbon atom would give rise to a corresponding unique carbon resonance. Fast Cp* molecular reorientation scales the value of the dipolar interaction determined by diffraction as $0.5(3\cos^2\beta - 1) = 0.625$.

Fine structure in the experimental lineshape at chemical shift values of ~85 and 100 ppm is very sensitive to the values of J and ΔJ. The isotropic J value fits best with small positive values, and is consistent with other estimations of J in organometallic systems. Good agreement results with the use of small, negative values for ΔJ; the spectrum is not sensitive to this parameter. We note again here our assumptions about the scalar coupling, namely that the **J** tensor is axially symmetric, and that the unique axis of the **J** tensor is aligned with $\mathbf{r}_{IS}$.

The discrepancy in the NMR and diffraction determinations of the angle β is about 6°. The NMR simulation is fairly sensitive to this parameter (and there is a strong interplay with D, especially as $\beta \to 0$), and the estimated error is ±2°. It may be possible that the in-plane motion of the Cp* ligand contains a small amount of libration which is reflected only in the NMR determination, which is more sensitive to dynamic effects than is diffraction. In addition, a small contribution from non-zero α-angular dependence may give rise to a smaller value of β. We note that discrepancies in structural features between diffraction determinations and NMR measurements based on dipolar interactions are common.[22] The ^{13}C NMR spectrum

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collected at low field can be well simulated. The minor differences in the fine features of the lineshape probably arise from errors in the initial assumptions. Of course, at this field the second-order features are pronounced and discrepancies in the fitting are therefore the most likely. As the field strength increases, the agreement between experimental and simulated shapes improves as the second-order quadrupolar effects are decreased. Although a program for iterative fitting could be applied, based on the work of Ding and McDowell,[23] it would not necessarily yield significantly more accurate data. The intention of the present paper is to provide a reasonable chemical explanation, at a semi-quantitative level, for the spectra observed.

For the mixed-ligand sandwich salt $[Cp^*CpCo]^+[PF_6]^-$ the ^{13}C CP/MAS NMR spectra at 7.05 T give a methyl resonance at 10.0 ppm and two features near 87 and 98 ppm for the ring carbon atoms of Cp and Cp*, respectively. The assignment is made by comparison of the chemical shifts with those of the corresponding symmetric cobaltocenium compounds[24] and is confirmed by the shapes of the features. While the directly bound protons of Cp lead to a residual dipolar broadening which masks any fine structure of the signal near 87 ppm, the feature near 98 ppm is better resolved, because the protons of Cp* are more distant and more mobile, and an asymmetric shape together with some splitting is observed. Interestingly, the splitting is much less pronounced than in the case of $[Cp^*_2Co]^+[PF_6]^-$ [Fig. 1(c)]. However, when the spinning rate is lowered to 2 kHz, a well structured pair of centrebands accompanied by four broad pairs of sidebands can be found [Fig. 2(b)]. This phenomenon is due to the fact that each transition of the $^{59}Co,^{13}C$ dipolar coupling multiplet gives rise to a powder pattern. The chemical shift anisotropy depends on the orientation of the molecule within the rotor. Therefore, the shapes of the centreband and the spinning sidebands depend on the chemical shift anisotropy and the spinning rate. This effect which leads to a better resolution of the centreband at low spinning rates has been first demonstrated for the $^{14}N,^{13}C$ spin pair.[25] The approach can be checked by summing over the centreband and all sidebands, and, as expected, the resulting spectrum [Fig. 2(c)] is very similar to the experimental spectrum at a high spinning rate [Fig. 2(a)]. A satisfactory fit of both spectra (Figure 3) was obtained with the same parameter set as for $[Cp^*_2Co]^+[PF_6]^-$ except for $\delta(^{13}C) = 98.4(.05)$ and 86.9(.05) for the Cp* and Cp ligand, respectively. It is gratifying that the parameters do not change within the error limits when the species are rather similar, as in the case of $[Cp^*_2Co]^+$ and $[Cp^*CpCo]^+$.

Furthermore, it depends on the temperature whether the residual dipolar coupling of $[Cp^*CpCo]^+[PF_6]^-$ can be observed. Figure 4 demonstrates that on heating, the coupling patterns collapse above 360 K and that the signals are narrow at 370 K (half-width of the centrebands: 150 Hz). This phenomenon has been observed and discussed previously.[8] In general, two mechanisms can lead to the disappearance of residual dipolar coupling: either the dipolar coupling tensor is completely averaged to zero by fast isotropic motion of the molecule, or some dynamic process induces fast T_1 relaxation of the quadrupolar nucleus, leading to self-decoupling of the ^{13}C nuclei. In this context we attempted to obtain ^{59}Co NMR data, but

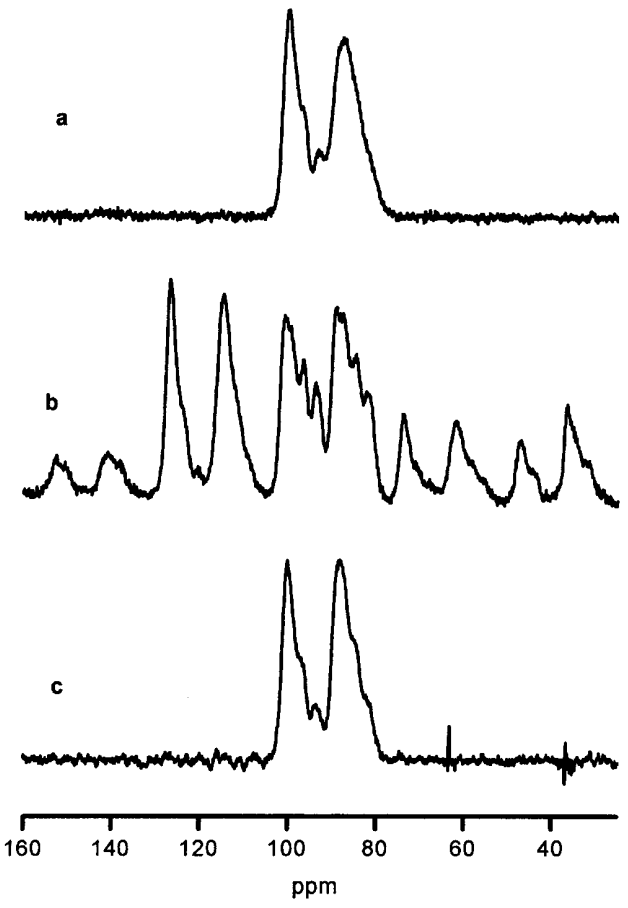

Figure 2. ^{13}C CP/MAS NMR spectra of $[Cp^*CpCo]^+[PF_6]^-$ at 7.05 T (ring carbons only, including the spinning sidebands at 2 kHz) obtained with different spinning rates: (a) 10 and (b) 2 kHz. Exponential line broadening of 5 Hz was used. In (c) the sum over all sidebands of (b) is shown (see text).

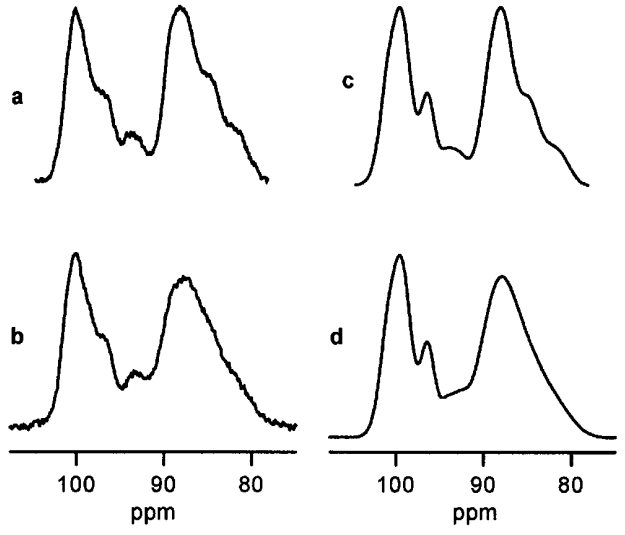

Figure 3. Left: ^{13}C CP/MAS NMR spectra of $[Cp^*CPCo]^+[PF_6]^-$ at 7.05 T (ring carbons only). (a) Summation of the spinning sidebands and the centreband at $\nu_r = 2$ kHz. (b) Signals at $\nu_r = 10$ kHz. (c), (d) Simulated spectra; Gaussian line broadenings of (c) 175 and 125 Hz and (d) 300 and 125 Hz were used.

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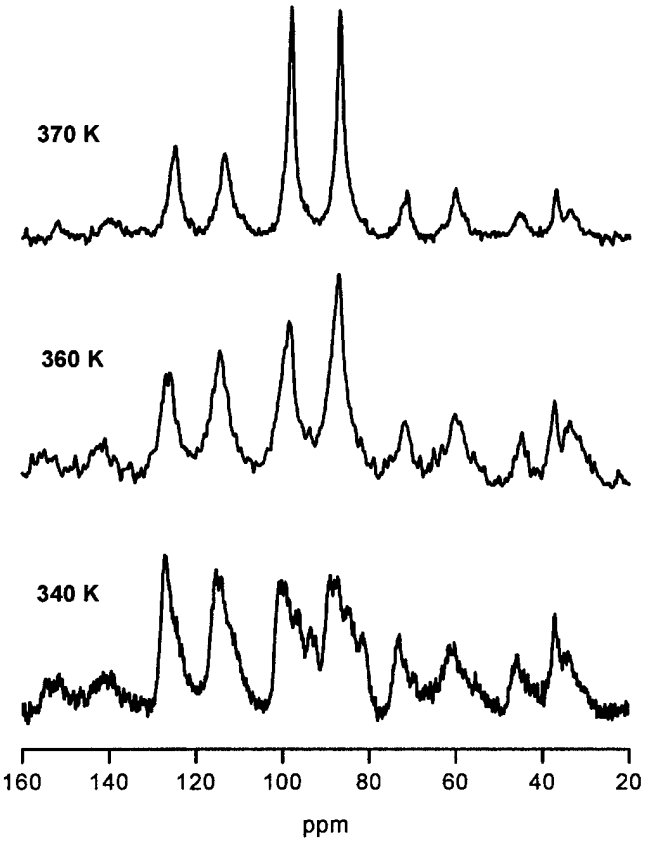

Figure 4. ^{13}C CP/MAS NMR spectra of $[Cp^*CpCo]^+[PF_6]^-$ at 7.05 T, $\nu_r = 2$ kHz.

we were not successful because of the large quadrupole interaction.

As the axially symmetric cation in $[Cp^*CpCo]^+[PF_6]^-$ is not likely to perform isotropic motions as well as the ring rotations, the observed phenomenon is more likely due to self-decoupling than to motional averaging. For $[Cp^*_2Co]^+[PF_6]^-$ the signal splitting is persistent up to 380 K, whereas self-decoupling can be observed at room temperature for the unsubstituted cobaltocenium hexafluorophosphate, $[Cp_2Co]^+[PF_6]^-$, and 1,1′-diethylcobaltocenium hexafluorophosphate, $[(EtC_5H_4)_2Co]^+[PF_6]^-$ (Fig. 5). Furthermore, the occurrence of ^{59}Co,^{13}C residual dipolar coupling in cobaltocenium compounds depends not only on the substitution pattern of the cation but also on the counter anion, which influences the mobility of the cations within the crystal lattice. Thus, the compounds $[Cp^*_2Co]^+[Cl^-$ and $[Cp^*_2Co]^+_2[TCNE]^{2-}$ (TCNE = tetracyanoethenide) are not affected by residual dipolar coupling at room temperature, in contrast to $[Cp^*_2Co]^+[PF_6]^-$.

CONCLUSIONS

Cobaltocenium ions are instructive examples for the study of ^{59}Co,^{13}C residual dipolar coupling. The observability depends on the substitution of the cyclopentadienyl ligands, the counter ions, the temperature and the rotor spinning rate. The coupling patterns, which lose structure with increasing field strength, can be simulated by applying full theory, whereas perturbation treatment is not successful.

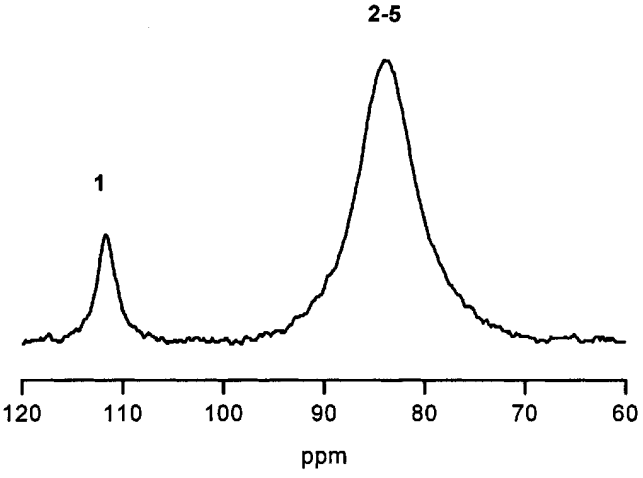

Figure 5. ^{13}C CP/MAS NMR spectra of $[(EtC_5H_4)_2Co]^+[PF_6]^-$ at 7.05 T [ring carbons only; $\delta(^{13}C) = 111.7$, 84.0, 20.2 and 12.8 for C-1, C-2–5, CH_2CH_3, and CH_2CH_3, respectively]. For signal numbering, see Scheme 1. $\nu_r = 10$ kHz. An exponential line broadening of 20 Hz was used.

Acknowledgements

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