Journal of Organometallic Chemistry, 429 (1992) 99–108
Elsevier Sequoia S.A., Lausanne
JOM 22281

Structure and dynamics of $[C_5H_5Fe(CO)_2(E(CH_3)_2)]BF_4$ (E = S, Se, Te) complexes studied by ^{13}C solid state NMR spectroscopy

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(Received July 19, 1991)

Abstract

The structure and dynamics of $[C_5H_5Fe(CO)_2(E(CH_3)_2)]^+$ complexes (E = S, Se, Te) have been investigated by high-resolution solid-state ^{13}C NMR spectroscopy. From the side bands in the ^{13}C CP–MAS NMR spectra the principal values of the σ-tensors of the ring carbon atoms have been determined. They are axially symmetric, pointing to mobility of the cyclopentadienyl ring. The static ^{13}C CP NMR spectra also reveal the dynamic nature of the C_5H_5 ring. From the spin lattice relaxation times of the ring carbon atoms it is concluded that the reorientation rate of the ring increases in the order S < Se < Te, probably due to the interaction of the lone pair electrons of the chalcogen with the electrons in the ring system. The observed non-equivalence of the methyl carbons for the Se and the Te compound is determined by the different local environments of the methyl groups. The merging of the methyl peaks by increase of the temperature is not caused by an exchange process, as was established by 2D exchange spectroscopy, but is probably due to subtle changes in the lattice parameters.

Introduction

During the last few years considerable interest has developed in the chemistry of ligands containing sulphur, selenium, or tellurium [1]. One of the reasons for the interest in these ligands is their coordination behaviour towards transition metals in inorganic and organometallic complexes [2]. Owing to their unpleasant nature and problems in preparation, the simplest compounds $E(CH_3)_2$ (E = S, Se and Te) have been used only occasionally as ligands in coordination and organometallic chemistry [3,4].

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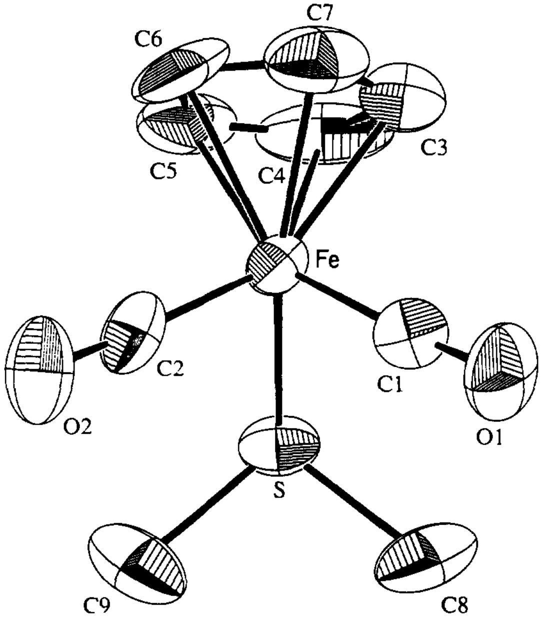
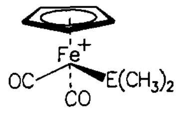


Fig. 1. ORTEP diagram of the complex cation $[C_5H_5Fe(CO)_2(S(CH_3)_2)]^+$ (I_a).

Recent investigations on $[C_5H_5Fe(CO)_2]X$ complexes indicated an unusual feature of their resistance to substitution by ligands such as phosphanes PR_3 and



I

(E = S (a), Se(b), Te(c))

their homologues; namely that the $Te(CH_3)_2$ containing complex (I_c) is the most stable one and most inert towards substitution [5]. This observation is in sharp contrast to investigations on complexes of the type $[C_5H_5Fe(CO)_2(ER_3)]^+$ (E = N, P, As, Sb, Bi), for which BiR_3-containing complexes are the most labile towards substitution [6]. X-ray structure determinations for $[C_5H_5Fe(CO)_2(E(CH_3)_2)]^+$ complexes (I) (E = S, Se, Te) indicated an unusually large thermal ellipsoid for the carbon atom of the cyclopentadienyl moiety directly above the uncoordinated lone pair on E (compare Fig. 1) [7]. Investigation of solution NMR spectra in the normal temperature range (−90 to +60°C) showed no evidence for a possible interaction or freezing-out process for the rotation of the cyclopentadienyl fragment. To gain further insight in this problem, a solid state ^{13}C MAS NMR study was undertaken. During the course of this investigation Mynott *et al.* [8] reported the first direct evidence for the freezing-out of an unsubstituted C_5H_5 ring by solution ^{13}C NMR spectroscopy involving the related compounds $[C_5H_5M(P(C_6H_5)_3)_2(\eta^2\text{-}H_2C{=}CHR)]BF_4$ (M = Ru, R = H or C_6H_5; M = Os, R = C_6H_5).

Solid state MAS NMR spectroscopy has been shown to be an important tool for the characterization and investigation of dynamic processes in solids [9]. Some applications of this method to problems in organometallic chemistry have been reported in recent years [10]. In the present study we demonstrate that valuable insights into the dynamic behaviour of organometal complexes in the solid state can be obtained, complementing the information about the static structure determined by X-ray analysis.

Experimental

All spectra were recorded on a Bruker AM-500 NMR spectrometer ($B_0 = 11.7$ Tesla), equipped with an ASPECT-3000 computer for data acquisition and a double-bearing variable temperature CP–MAS probe. The electronic system of the probe can be simultaneously tuned to two frequencies so that it is possible to perform cross polarization and heteronuclear decoupling. The probe enables magic angle spinning up to 6.5 kHz. The chemical shifts were referenced to TMS by use of adamantane as a secondary reference.

The principal values of the σ-tensors are obtained by analysis of the spinning side bands by the Herzfeld and Berger method [11]. For this purpose a fitting program in Pascal was written. It optimizes the chemical shift parameters by minimizing the difference between the calculated side band intensities and the measured band intensities using a least squares fitting procedure.

Spectra were examined over a wide temperature range (173–388 K). The temperature was measured in the probe by use of a gauged thermocouple connected to a Bruker VT100 temperature control unit. Spin lattice relaxation times were determined by inversion recovery pulse sequences. Phase cycling (CYCLOPS) was always used.

The cell parameters of $[C_5H_5Fe(CO)_2(Te(CH_3)_2)]BF_4$ were determined with the aid of a Quinier-Lenné powder camera by Dr. E.J. Sonneveld (Technical University, Delft), with α-Al_2O_3 as internal standard.

The preparation and characterization of the compounds (I) have been described previously [12,13].

Results and discussion

^{13}C CP–MAS NMR

The ^{13}C cross-polarization (CP) MAS NMR spectrum at room temperature of $[C_5H_5Fe(CO)_2(Te(CH_3)_2)]BF_4$ under high power proton decoupling is shown in Fig. 2. The peaks of the three different types of carbon atoms, the ring carbon, the methyl carbon and the carbonyl carbon atom, could be easily distinguished. Owing to the large chemical shift anisotropy of the carbonyl group a large number of spinning side bands of the carbonyl carbon atom could be discerned (marked by a dot); for the ring carbon atom a smaller number is observed (indicated by a cross), and the CH_3 group owing to its small chemical shift anisotropy does not give rise to side bands. It should be noted that only one peak for the ring carbon atoms is seen and that the central band of the carbon atom of the carbonyl group has the lowest intensity. The isotropic chemical shifts for the $[C_5H_5Fe(CO)_2(E(CH_3)_2)]BF_4$ compounds (E = S, Se, Te), together with their values in acetone-d_6 [14], are listed

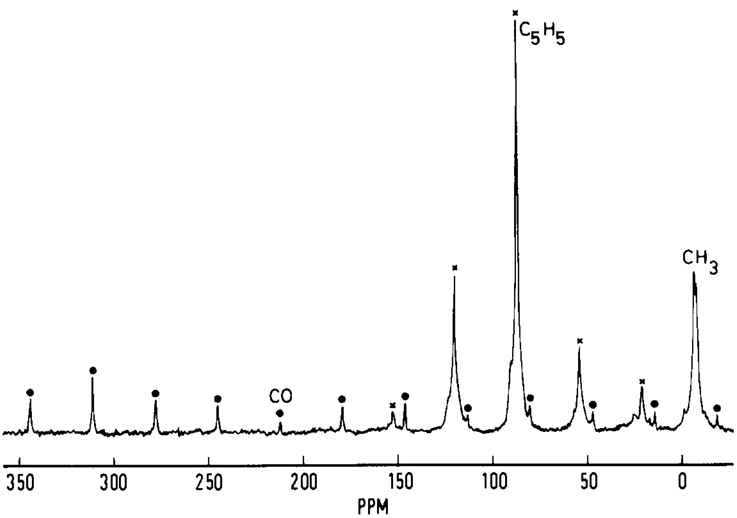


Fig. 2. ^{13}C CP–MAS NMR spectrum of $[C_5H_5Fe(CO)_2(Te(CH_3)_2)]BF_4$ (I_c) at $T = 298$ K. ●, Side band pattern of CO (the CO label marks the centre band); ×, *idem* for C_5H_5.

in Table 1. The differences between the chemical shift values in the solid state and in solution are small. On going from Te to S all the signals move to lower field in solution and in the solid state. The spectra do not show any indication of a possible interaction between the lone pair of the chalcogen and the cyclopentadienyl ring. A single resonance is observed for all five ring carbon atoms, although it is somewhat broadened.

In Table 2 are listed the principal values of the σ-tensor of the ring carbon atoms as obtained by side band analysis. Axially symmetrical σ tensors were obtained, which means that the cyclopentadienyl rings are reorienting probably with jumps over angles of $2\pi/5$ [15]. No significant differences between the principal σ values were found among the series of $[C_5H_5Fe(CO)_2(E(CH_3)_2)]^+$ cations, so that we can conclude that the difference in donor strengths of the various $E(CH_3)_2$ ligands is small. It is interesting to compare the σ values with those for ferrocene ($(C_5H_5)_2Fe$), namely $\sigma_\perp = 94$ ppm and $\sigma_\parallel = 18$ ppm [16]. The $\sigma_\perp$ tensor element of the cyclopentadienyl ring is found at lower field than the

Table 1

Isotropic chemical shifts for $[C_5H_5Fe(CO)_2(E(CH_3)_2)]^+$

Compound	Isotropic chemical shift (ppm)					
	C_5H_5 solid	 solution	CH_3 solid	 solution	CO solid	 solution
	a	b	a	b	a	b
I_a	87.7	88.50	26.5	27.46	210.4	210.04
I_b	87.3	87.83	15.9	16.98	211.7	210.87
I_c	86.6	87.12	−7.8	−6.85	211.9	211.70

a, Accuracy = ±0.5 ppm. b, Solution values obtained at 75.5 MHz (accuracy = 0.01 ppm) in acetone-d_6.

Table 2

Principal values for the σ-tensor of the ring carbon atoms in $[C_5H_5Fe(CO)_2(E(CH_3)_2)]^+$ at 298 K (accuracy = ±5 ppm)

Compound	σ_{11} (ppm)	σ_{22} (ppm)	σ_{33} (ppm)
I_a	19	122	122
I_b	19	122	122
I_c	20	120	120

corresponding tensor element of ferrocene, indicating that the ring–metal bond in the $[C_5H_5Fe(CO)_2(E(CH_3)_2]^+$ cations is more ionic than in ferrocene.

Finally we draw attention to the doublet splitting of the peak due to the methyl carbons. We return to this point later below.

^{13}C CP NMR

As a spinning side band analysis is rather insensitive in revealing whether or not a chemical shift tensor is exactly axially symmetric, static ^{13}C NMR spectra of the C_5H_5-ring at room temperature were recorded for the Se and Te compounds under high power proton decoupling. Normally the powder spectrum of the compounds under investigation would consist of three overlapping powder line shapes, one for each ^{13}C spin species. It is, however, possible to remove the unwanted ^{13}C signals from CH_3 and CO. The latter signal can be suppressed by choosing a very short cross polarization mixing time (0.5 ms), since the carbon atoms in CO have a relatively long cross relaxation time due to the weak dipolar interaction with the protons in the sample. The carbon signal of the CH_3 group can be removed by employing the large T_1 difference between the carbons of the C_5H_5 ring and the methyl carbons. By choosing time τ in Fig. 3 as the zero passage time of the methyl carbons their signal can be suppressed. Fig. 4 shows the spectrum of the Se compound together with a simulation. The powder spectrum is clearly a spectrum of an axially symmetrical σ-tensor. However, it is not a normal powder spectrum; compared with the simulation, intensity is lost in the middle of the spectrum. The explanation for this has been given by Pines *et al.* [17] in a

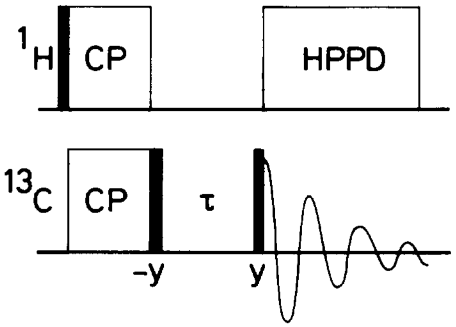


Fig. 3. Pulse sequence used for recording the powder line shape of the C_5H_5 ring. The CO resonance is suppressed by using a short CP mixing time. The methyl resonance is eliminated by a T_1 selection after cross-polarization. τ is chosen to be the point where the methyl magnetization passes zero.

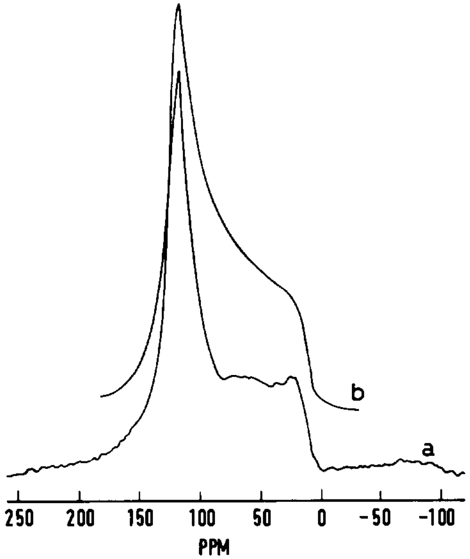


Fig. 4. (a) Static ^{13}C CP NMR spectrum of $[C_5H_5Fe(CO)_2(Se(CH_3)_2)]BF_4$ (I_b) using the pulse sequence of Fig. 3. (b) Powder simulation.

report of their study of the cross polarization NMR spectrum of solid benzene. Rapid intramolecular reorientations in a polycrystalline sample distorts the powder line shape in a static CP experiment, because for those molecules for which the rotation axis makes the magic angle with the external magnetic field the cross polarization rate is slow. This is manifested clearly in NMR spectra of reorienting axially symmetrical molecules. For those molecules with the symmetry axis at the magic angle with respect to the external field the intensity loss is at maximum. For this angle σ is equal to

$$\sigma = \sigma_{\perp} + \tfrac{1}{3}(\sigma_{\parallel} - \sigma_{\perp})$$

For our compounds the minimum in intensity should lie at $\sigma = 88$ ppm. The loss in intensity is additional evidence that the cyclopentadienyl ring is reorienting. Since the chemical shift anisotropy in the plane of the ring is of the order of 40–90 ppm [16,18], the rotation frequency is > 6–10 kHz. From the powder spectra the σ components could also be determined, and were in good agreement with the values reported in Table 2.

Spin–lattice relaxation time measurements

To investigate further the possible interaction of the lone pair electrons of the chalcogenide atom with the C_5H_5 ring we determined the spin–lattice relaxation times of all the ^{13}C signals. To eliminate non-cross polarized signals spin temperature alternation was applied [19]. The results of the T_1 measurements are given in Table 3 together with the data for solutions. The T_1 values of the ring carbon atoms increase in the series S < Se < Te. To explain this in terms of mobility of the ring system we must know which branch of the T_1 versus τ_c (correlation time) curve applies to our measurements. Therefore we examined for the S compound the variation in T_1 as a function of the temperature. From $T = 298$ K to $T = 216$ K

Table 3

Spin lattice relaxation times at $T = 298$ K for complexes I_{a-c}

	T_1 (s)					
	I_a		I_b		I_c	
	solid	solution	solid	solution	solid	solution
C_5H_5	21	5.4	35	7.2	40	9.8
CH_3	0.23	2.5	0.60	4.4	1.50	5.5
CO	≈ 50	8.3	-	11.5	≈ 40	16.3

the T_1 dropped from 21 s to 12 s. Thus the fast branch of the T_1–τ_c curve applies. This means that the jumping rate of the C_5H_5 ring is at least of the order of 10^9 Hz ($2\pi\nu\tau_c < 1$, $\nu = 125$ MHz). This high rate of reorientation is consistent with the low energy barriers found for ferrocene and derivatives thereof (2–4 kcal/mol) [15]. The increase in T_1 going from S to Te indicates increasing mobility of the ring in the same order. In order to establish whether this effect is caused by the lone pair electrons of the chalcogenide atom we determined T_1 for the compound $[C_5H_5Fe(CO)_2P(CH_3)_3]^+$. We found for the ring carbon atoms $T_1 = 11$ s and for the methyl carbon atoms $T_1 = 0.41$ s. Since the phosphorus atom has no lone pair electrons and the C_5H_5 ring in the phosphorus compound, according to the T_1 value, has the lowest mobility, it is tempting to attribute the increased mobility of the ring in the compounds under investigation (S < Se < Te) to the interaction of the lone pair electrons of the chalcogenide atom with the ring system. The increasing mobility of the ring in the series S < Se < Te can be rationalized in terms of the decreasing strength of the (η^5-C_5H_5)–metal bond. This runs parallel with an increasing ionic character of the Fe–chalcogenide bond on going from S to Te [13].

The inequivalence of the methyl carbon atoms

We mentioned earlier the doublet splitting of the methyl peak of the Te compound. The crystallographic structure shows that the two methyl groups have different local environments with respect to their position relative to the cyclopentadienyl ring of a neighbouring molecule in the unit cell, which renders them magnetically non-equivalent. In order to gain more insight into this phenomenon we examined the NMR spectra of the $[C_5H_5Fe(CO)_2E(CH_3)_2]^+$ cations over the temperature range 170–388 K. The results for the Se and Te compounds are shown in Fig. 5. The splitting for the methyl peaks in the Te compound decreased from 138 Hz at 298 K to 64 Hz at 388 K, the highest attainable temperature. For the Se compound a splitting was observed below 228 K, but for the S compound no splitting was found in the investigated temperature range. This temperature-dependent behaviour suggests an exchange of the two methyl groups. Such an interchange of methyl groups can be effected by a rotation around the Fe–E bond of 180°, accompanied or followed by a pyramidal inversion with respect to the E centre. In solution such a process can take place [2,20]. Whether or not such an exchange takes place in the solid state can be decided by a two-dimensional exchange experiment, at a temperature at which the supposed exchange process should be fast enough to be observable at the chosen mixing time. When this

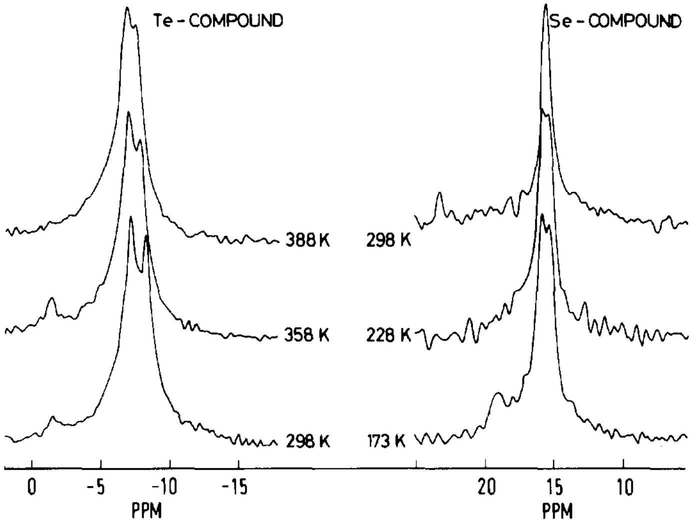


Fig. 5. Temperature dependence of the methyl resonance of the Te (left) and the Se compound (right).

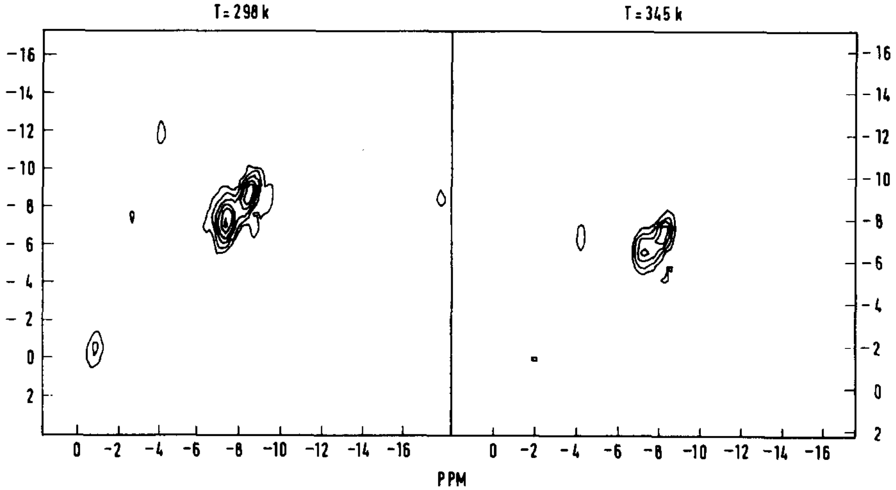


Fig. 6. 2D exchange spectra of the Te compound at a temperature of 298 K (left) and at 345 K (right). In both cases a mixing time of 250 ms was used. There are no signs of exchange at a rate expected from the 1D spectra of Fig. 5.

Table 4

Cell parameters of $[C_5H_5Fe(CO)_2(Te(CH_3)_2)]BF_4$ (I_c) at three temperatures

	T (K)		
	293	358	388
a (Å)	8.386(2)	8.419(2)	8.428(3)
b (Å)	12.886(3)	12.961(3)	12.999(4)
c (Å)	13.399(3)	13.491(3)	13.528(4)
α (deg)	90	90	90
β (deg)	109.47 (2)	109.26 (2)	109.07 (3)
γ (deg)	90	90	90

experiment was carried out no cross peaks were found (see Fig. 6), neither for the Te compound nor the Se compound. Therefore the temperature dependence of the doublet splitting cannot be ascribed to an exchange process of the type described above.

An alternative source of the effect might be subtle changes in the lattice parameters as a function of the temperature. To verify this the lattice parameters of $[C_5H_5Fe(CO)_2(Te(CH_3)_2)]BF_4$ were determined at three relevant temperatures 293 K, 358 K and 388 K. The results are given in Table 4. A slight increase of the cell dimensions can be noticed, but the question remains whether or not this is sufficient to account for the experimental results.

Acknowledgements

The authors are grateful to Dr. E.J. Sonneveld, Technical University, Delft for determining the lattice parameters, and to Mrs. G. Nachtegaal of the SON HF NMR facility for her help with the recording of the NMR spectra. One of the authors (H.S.) is grateful to Prof. R.W. Parry and Prof. T.G. Richmond, University of Utah, for their kind interest and support, and appreciates the tenure of a scholarship of Studienstiftung des Deutschen Volkes, Bonn (Germany) during his stay at the University of Utah 1987–1988.

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