Structure and Dynamics of Zirconocene Complexes in the Solid State Studied by ^{13}C CP/MAS NMR Spectroscopy

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High-resolution one- and two-dimensional solid-state CP/MAS spectra of microcrystalline bent metallocene complexes of the type $(\eta^5\text{-}{}^R Cp)_2 ZrL_2$ have been obtained at various temperatures (L = Cl, R = H (1), Me (2), Et (3), ^{t}Bu (4); $L_2 = s\text{-}cis\text{-}\eta^4\text{-}C_4H_6$, R = H (5); $L_2 = s\text{-}cis\text{-}\eta^4\text{-}C_4H_4Me_2$, R = H (6); $L_2 = s\text{-}cis\text{-}\eta^4\text{-}C_4H_5Me$, R = H (7); $L_2 = s\text{-}cis\text{-}\eta^4\text{-}C_4H_6$, R = ^{t}Bu (8); $L_2 = s\text{-}cis\text{-}\eta^4\text{-}C_4H_6$, R = 1,1-dimethylpentyl (9); $L_2 = s\text{-}cis\text{-}\eta^4\text{-}C_4H_5Me$, R = ^{t}Bu (10)). Complexes 1-4 possess C_2 molecular symmetry, while the overall symmetry of complexes 5 and 6 is close to C_s. In 7-9 there is no element of symmetry, and 10 yields diastereoisomers (95:5). Variable-temperature MAS spectra give evidence for $^R Cp$ rotation and diene topomerization as fluxional processes occurring in the solid state. Due to steric interaction with the methyl protons in 7 the rotation of the upper η^5-bonded cyclopentadienyl ring was frozen out at T = 110 K ($\Delta G^\ddagger \approx 5.5$ kcal/mol) and the five ^{13}C chemical shifts of this species cover a range of more than 15 ppm. Due to less steric interaction the activation barrier for rotation of the lower Cp ring is smaller ($\Delta G^\ddagger \approx 4$ kcal/mol). Upon introduction of alkyl substituents at the η^5-bonded rings the rotation barrier is significantly increased: in 2 it is around 17 kcal/mol. In contrast, movement of the η^4-coordinated diene is largely independent of alkyl substituents and in 5-10 the barrier for this process is around 14 kcal/mol.

I. Introduction

Although CP/MAS NMR spectroscopy[2] is now well established, the application of this technique to air- and moisture-sensitive compounds at variable temperatures still remains a nonroutine experiment. CP/MAS spectra of organometallic compounds (many of which are very air- and moisture-sensitive) are promising since these molecules often undergo fast dynamic processes[3] and the energy barrier for exchange is generally higher in the solid state than in solution.[4]

In this work we report our approach for obtaining highly resolved ^{13}C CP/MAS spectra of organometallic compounds of the type $(\eta^5\text{-}{}^R Cp)_2 ML_2$[5-8] (L = Cl, R = H (1), Me (2), Et (3), ^{t}Bu (4); $L_2 = s\text{-}cis\text{-}\eta^4\text{-}C_4H_6$, R = H (5); $L_2 = s\text{-}cis\text{-}\eta^4\text{-}C_4H_4Me_2$, R = H (6); $L_2 = s\text{-}cis\text{-}\eta^4\text{-}C_4H_5Me$, R = H (7); $L_2 = s\text{-}cis\text{-}\eta^4\text{-}C_4H_6$, R = ^{t}Bu (8); $L_2 = s\text{-}cis\text{-}\eta^4\text{-}C_4H_6$, R = 1,1-dimethylpentyl (9); $L_2 = s\text{-}cis\text{-}\eta^4\text{-}C_4H_5Me$, R = ^{t}Bu (10)). Besides the detailed description of a home-built vessel that permits the loading of air- and temperature-sensitive organometallic samples under an inert atmosphere, we also present experimental details of some recent one- (1D) and two-dimensional (2D) NMR techniques, which are useful for signal assignment as well as the de-

termination of the structure of dynamics of 1-10 in the solid state.

According to the NMR spectra in solution[5-7] these molecules undergo two dynamic processes. The first involves rotation of the η^5-bonded cyclopentadienyl ring. Generally, the rotational barrier for this type of process is very low,[9,10] and very recently the first example of hindered rotation of a dissolved unsubstituted η^5-bonded moiety monitored by NMR line-shape analysis was reported in some ionic Ru and Os complexes with sterically demanding ligands.[11] In 1-10, however, we deal with comparably small ligands and thus report, to the best of our knowledge, the first high-resolution CP/MAS spectra of an η^5-coordinated cyclopentadienyl ring in the slow exchange limit. Moreover, since in 5-10 each of the cyclopentadienyl rings is in a different environment, the factors which influence that barrier may be studied.

A second process, the so-called diene flip, is known to occur from the solution ^{1}H and ^{13}C NMR spectra of complexes 5-10.[6] From the analysis of the line shape in the ^{1}H NMR spectra,[12] the $^1J(^{13}C,^{13}C)$ coupling constants[13] of the dissolved zirconocene complexes, and the solid-state X-ray structural data,[6,14] a metallacyclopentene intermediate has been proposed. The crystal structure data have indicated relatively short metal–terminal diene carbon bond distances and rather long metal–central diene carbon

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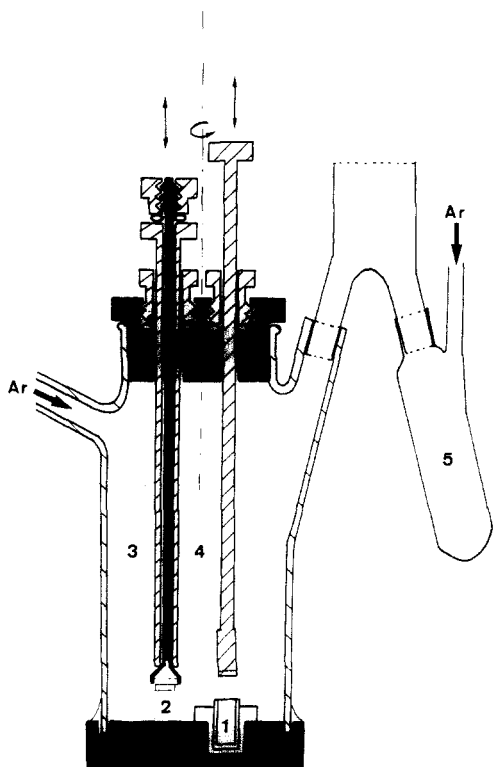
Figure 1. Glass vessel for filling of MAS rotors under an inert atmosphere: (1) rotor; (2) rotor cap; (3) gripping device for the rotor cap; (4) stamp for packing of the sample material; (5) Schlenk tube with material supply.

bond distances. In order to find out whether these structural features indicate dynamic processes in the solid state, we have examined the CP/MAS ^{13}C NMR spectra of these diene complexes.

II. Experimental Section

1. Sample Preparation. The synthesis of complexes 1–10 was reported previously.[5-7] ^{1}H and ^{13}C NMR data for the dissolved complexes are known: 1–4,[5] 5–7,[6,7] 8,[7] 9,[15] 10.[7] (For a review on the synthesis and structural characterization of this class of compounds cf. ref 14.) In addition, X-ray structures for complexes 4,[16] 6,[17] and 8[10a] have been reported. In contrast to the halogen-containing complexes 1–4, the diene complexes 5–10 decompose immediately after contact with air, and therefore for the filling of the double-bearing ceramic rotors a special vessel made of glass and aluminum was constructed (cf. Figure 1). On the right- and left-hand sides there is an inlet and outlet for the inert gas (argon). The solid sample is taken from a Schlenk tube (5) and loaded via a metal siphon into the rotor (1), which is fixed in a cylindrical cavity in the aluminum bottom of the vessel. The rotor as well as the Schlenk vessel can be cooled. When the rotor has been filled, the central cap of the vessel is rotated around its central axis such that the device (3) with the rotor cap (2) becomes located exactly above the rotor and can be mounted. Then by this special mechanical device the rotor is removed from the vessel in a vertical direction.

2. CP/MAS Spectra. All solid-state spectra were recorded on a Bruker AM 200 spectrometer using the standard accessory. The ^{13}C spectra were performed with use of high-power proton decoupling and magic-angle spinning for line narrowing. Spinning rates were between 3000 and 4500 Hz. For a single spectrum typically between 200 and 1000 transients were collected. Due to the air-sensitive nature of the samples, nitrogen was used as

the bearing and drive gas. Cross-polarization was employed for sensitivity enhancement. The contact time was varied between 0.5 and 20 ms. Optimum signal enhancements were achieved with a contact time between 2 and 4 ms. In the experiments employing cross-polarization, the preparation time was chosen to be between 2 and 4 s, since T_1(^{1}H) was found to be around 1 s. The temperature was varied between 110 and 355 K with use of a temperature controller and a heat exchanger for the bearing gas. Calibration of the temperatures was performed via the phase transition of camphor and 1,4-diazabicyclo[2.2.2]octane (DAB-CO).[18] Referencing of the ^{13}C shifts (±0.1 ppm) was achieved by using the absolute frequencies relative to the shift of the methylene carbon of adamantane, δ_{TMS}(CH$_2$) = 38.4.

In the interrupted proton decoupling experiments[19] the dephasing time was between 40 and 80 μs. Approximate T_1(^{13}C) values were measured with use of a modified inversion recovery sequence as used by Torchia.[20] Explicit T_1 values are given only for the cyclopentadienyl carbon atoms in 6.

2D magnetization transfer experiments in the solid state were carried out at temperatures between 300 and 340 K with use of the standard pulse sequences[21,22] and absolute value mode presentation. Usually 64 FID's with different evolution times were collected. The mixing time τ was varied between 0.3 and 5 s. The experiments with τ = 0.3 s were carried out with and without proton decoupling during this time interval in order to discriminate between chemical exchange and proton-mediated spin diffusion.[23] The assignments of individual cross peaks were made from nonsymmetrized contour plots. Symmetrization was used only for the final presentation (cf. Figure 3).

The rate constants k for the chemical exchange of individual carbon atoms were obtained from the intensity of the cross peaks in the two-dimensional contour plots by using the formula[24] I_d/I_c = $(1 - k\tau)/k\tau$, where I_d and I_c denote the intensity of the diagonal peaks and cross peaks, respectively; τ is the mixing time. From the Eyring equation and the values obtained for k a lower limit for $\Delta G^{\ddagger}$ can be determined. From the low-temperature CP/MAS spectra of 2 (slow exchange limit) rate constants k were obtained by using the equation $k = \pi W_{1/2}$ in the slow exchange limit and $k = \pi 2^{1/2}$ at the coalescence temperature.[25]

III. Results and Discussion

1. Structure of Complexes 1–10 in the Solid State. In complexes 1–10, the central zirconium atom is pseudotetrahedrally coordinated and the actual number of carbon signals (cf. Table I) observed for this complex reveals information about its symmetry. At T = 300 K complex 1 exhibits only one signal at 116.1 ppm, which unequivocally can be assigned to the cyclopentadienyl carbon atoms. This signal cannot be suppressed in the dipolar dephasing experiments even with delays of 100 μs. This confirms that there is fast rotation of the Cp rings around the central coordination axis in the solid state, similar to that occurring in solution. In complexes 2–4, there are five signals in the high-field region of the ^{13}C NMR spectrum. These can be assigned to the methine and quaternary carbon atoms of the cyclopentadienyl rings. Thus, it is concluded that the rings are equivalent by symmetry (for example, C_2 with respect to the axis bisecting the Cl–Zr–Cl angle) and do not rotate relative to the NMR time scale. The arrangement in which the two

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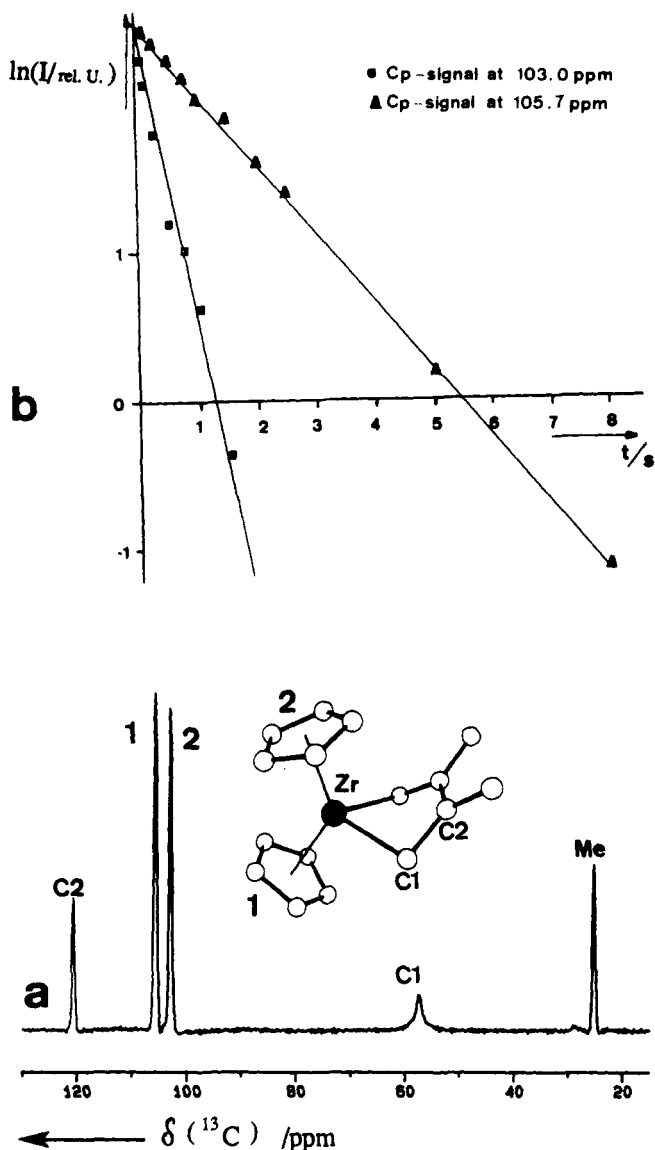(17) Erker, G.; Engel, K.; Krüger, C.; Chiang, A. *Chem. Ber.* **1982**, *115*, 3311.

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Figure 2. (a) ^{13}C CP/MAS spectrum of 6 (50.3 MHz) at $T = 300$ K. The assignment of the Cp signals is based on a $T_1(^{13}C)$ measurement. (b) Intensity of the Cp signals versus the delay time τ.

alkyl groups are eclipsed and bisect the Cl–Zr–Cl angle, as has been found in the case of $(^{Me}Cp)_2TiCl_2$,[26] can be excluded since this should produce a set of signals for the cyclopentadienyl carbons with the intensity ratio 4:4:2. In line with these suggestions, the X-ray analysis of 4[16] indicates that the R groups point away from each other.

If the two chlorine ligands are replaced by a η^4-bonded diene moiety in the s-cis conformation, the C_2 symmetry element is lost and consequently the upper and lower cyclopentadienyl rings are always inequivalent. In complexes 5–7 the unsubstituted cyclopentadienyl rings rotate quickly around the central coordination axis and thus yield two ^{13}C NMR signals at $T = 300$ K. X-ray crystallographic studies on $(\eta^5\text{-}Cp)_2Zr(\eta^4\text{-}s\text{-}cis\text{-}diene)$ complexes show[14] that their overall symmetry is close to m (C_s). Actually this molecular symmetry is even imposed crystallographically on 6.[17] In line with these results, in the ^{13}C CP/MAS spectrum of 6 there are two sharp signals for the four diene carbon atoms and one singlet for the methyl group. The assignment of the two signals of the ring carbons was

performed with the help of a $T_1(^{13}C)$ measurement (cf. Figure 2). The Cp signal at $\delta = 103.0$ ppm has a significantly shorter $T_1(^{13}C)$ value (0.4 s) than the signal at $\delta = 105.7$ ($T_1(^{13}C)$ = 2.2 s). Since the methyl substituents at the C-2 and C-3 positions of the diene still rotate in the solid state at $T = 300$ K, an additional fluctuating field is generated for the upper cyclopentadienyl carbon atoms. Thus, the Cp signal with the shorter $T_1(^{13}C)$ value is assigned to the upper ring.

The ^{13}C CP/MAS spectrum of complex 5 exhibits two signals for the terminal diene carbon atoms (cf. Table I). Since the shift difference between C-1 and C-4 is relatively large, this effect is interpreted as arising from different bond lengths to the diene termini. In fact the X-ray analysis of $(\eta^5\text{-}Cp)_2Zr(\eta^4\text{-}s\text{-}cis\text{-}2,3\text{-}diphenylbutadiene)$ and $(\eta^5\text{-}Cp)_2Zr(\eta^4\text{-}tetramethylbis(methylene)tricyclo-[3.1.0.0^{2,6}]hexane)$ yielded differences of 0.43 and 0.23 Å for these distances.[14] Since the isoprene ligand is η^4-bonded in an s-cis conformation to zirconium, in 7 there is no longer an element of symmetry and all the diene carbons possess different chemical shifts.

In the CP/MAS spectra of complexes 8 and 9, there are 10 signals belong to the 10 ring carbon atoms. This indicates that these molecules do not possess an element of symmetry and that already at $T = 300$ K there is restricted rotation of the substituted cyclopentadienyl rings. The X-ray analysis of 8[10a] shows that the alkyl substituents are trans to each other and are located in the lateral sectors of the bent metallocene. Since complexes 8 and 9 are also chiral, the four η^4-bonded carbon atoms are inequivalent. (The degeneracy of C-2 and C-3 in 8 and C-1 and C-4 in 9, respectively, is accidental.) Upon replacement of butadiene by isoprene (10), it is possible that diastereomers are formed. For 10 in the region between 140 and 90 ppm there are 12 signals (10 ring and two central diene carbon atoms) for the major isomer (95%) and seven signals of low intensity. The latter have been assigned to the minor diasteromer (5%), and it is assumed that the remaining five lines are hidden under the major signals. In the preceding section, evidence has been presented that there is a repulsive steric interaction between the alkyl substituents R at the Cp ring and the methyl groups at the central carbon atoms of the η^4-bonded s-cis diene moiety; thus, it seems reasonable to assume that in 10 the major diastereoisomer has the substituent R of the upper Cp ring in a position trans to the methyl group of the coordinated isoprene.

Although an unambiguous assignment of the chemical shifts in 1–10 was not possible in every case, the chemical shift values of the solution and solid-state spectra coincide within a few ppm. Such differences are quite usual and frequently arise from different weighting of certain conformations in the solid state or crystal-packing effects. The most remarkable aspect is the different chemical shift of the terminal diene carbons in 5. In principle, an individual site may exhibit several signals if the symmetry of the molecule within the crystal is lower than that of an isolated single molecule. Usually in ^{13}C CP/MAS spectra these splittings are small. In 5 the shift difference for the terminal carbon atoms is relatively large (5.3 ppm),[27] and moreover, the solution shift of the terminal diene carbon atoms is close to the average of the solid-state shifts. This is best rationalized by the assumption that in solution a

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(27) In the 50.3-MHz CP/MAS spectrum of the homologous $(\eta^5\text{-}Cp)_2Hf(s\text{-}cis\text{-}\eta^4\text{-}butadiene)$ complex the shifts of the terminal and central diene carbon atoms are 47.5, 44.9, 115.0, and 112.9 ppm, respectively. Here also the solution ^{13}C spectra yield only two signals for the corresponding diene carbon atoms at 45.0 and 114.5 ppm.

Table I. Isotropic ^{13}C Shifts of 1–10 at $T = 300$ K unless Otherwise Noted

compd	δ(Cp)					δ(s-cis diene)				δ(Me)	δ(R)	
1			116.1									
2	129.2 (s)	121.5	118.1	112.1	112.1						17.1	
3	134.3 (s)	126.9	117.2	117.2	111.4						22.9	31.5
4	147.4 (s)	127.8	113.8	110.5	109.8						33.9 (s)	31.5
5			105.0			115.0	112.9	47.5	44.9			
			100.5									
6			105.7			120.6	120.6	57.5	57.5	25.2		
			103.0									
7			105.1			124.2	110.7	53.6	47.3	29.7		
			102.4[a]									
8	133.9 (s)	110.4	107.9	101.2	97.3	112.9	112.9	51.4	50.1		32.7	33.2
	128.2 (s)	107.9	106.6	101.2	91.1							
9	131.2 (s)	113.1	109.0	103.7	96.7	114.7	111.3	51.2	51.2		35.9, 34.4 (C-1)	
	125.7 (s)	109.0	109.0	102.1	90.3						34.4, 33.1 (Me)	
											29.1, 25.2 (Me)	
											49.4, 48.0 (C-2)	
											27.4, 27.5 (C-3)	
											24.2, 24.2 (C-4)	
											15.2, 14.6 (C-5)	
10	133.1	112.3	105.5	101.6	91.4	123.2	110.6	53.5	48.8	30.0	33.6 (s)	32.7
	130.0	106.3	105.5	103.5	95.5							

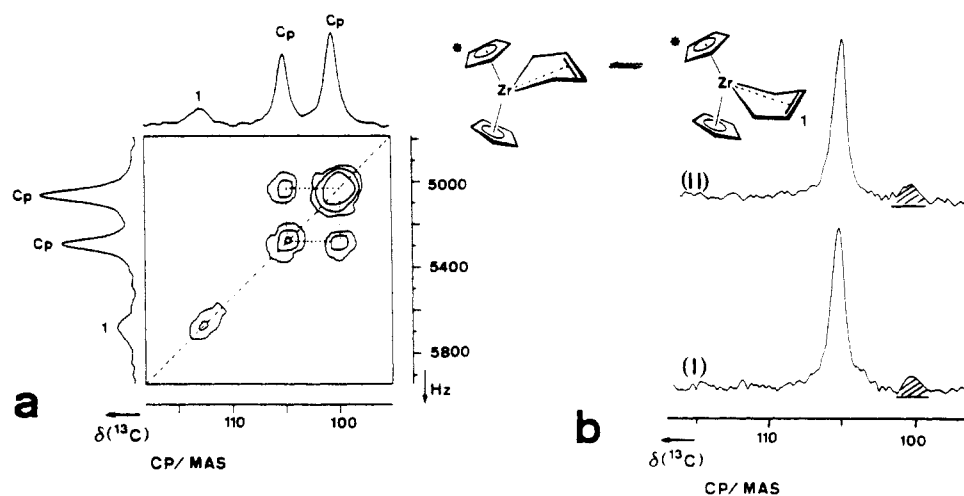[a] At $T = 110$ K Cp signals at δ 107.3, 103.8, 99.6, 96.7, and 92.8.

Figure 3. (a) 2D exchange spectra of 5 (50.3 MHz) at $T = 300$ K with a mixing time of $\tau = 3$ s. (b) Individual traces of a 2D matrix recorded with a mixing time $\tau = 0.3$ s (I) with and (II) without high-power proton decoupling during the mixing time.

low-energy fluxional process hides the deviations from C_s symmetry in 5.

2. Dynamics of 1–10 in the Solid State. The most prominent feature in the NMR spectra of the dissolved metallocene complexes with η^4-coordinated dienes in the s-cis conformation is the so-called diene flip[6,12] (cf. Figure 3). In solution substituents on either the diene or the Cp rings do not influence the barrier ($E_a \approx 13$ kcal/mol) significantly.[7] 2D magnetization transfer experiments confirm that in the solid state the ring flip also takes place. For example, in 5 2D magnetization transfer experiments exhibit cross peaks connecting to the two inequivalent Cp rings. They thus give direct evidence for chemical exchange between the two rings. In principle, proton-mediated spin diffusion[22] also can produce cross peaks. However, this was excluded for the following reasons. First, decoupling in the mixing time ($\tau = 0.3$ s) did not affect the intensity of the cross peaks.[23] Second, the intensity of the cross peaks increased by raising the temperature. From the intensity of the cross peaks, E_a was estimated to be around 14 kcal/mol.

The s-cis-butadiene complexes 8 and 9 are chiral, and

the diene flip therefore leads to an equivalencing of the terminal and the central diene carbons, as well as the upper and lower cyclopentadienyl rings. Neglecting the alkyl substituents R, this process should produce seven cross peaks in the 2D exchange matrix. In fact all these peaks were identified, and furthermore, these experiments substantiate the assignments given in Table I. The activation barrier for the diene topomerization was estimated to be around 14 kcal/mol. This estimate was made by using the peak intensities as discussed before.

It is interesting to note that in the solid state the activation barrier for the diene flip is insignificantly higher than in solution. Apparently, in the solid state, the metallacyclopentene structural elements contribute to the actual bonding situation to a significant extent, such that there is little steric hindrance for the diene flip.

As mentioned earlier, there is fast rotation of the unsubstituted cyclopentadienyl rings in 1, 5, 6, and 7 at $T = 300$ K. This was ascertained on the basis of symmetry considerations and experiments with interrupted proton decoupling. In line with this suggestion, the chemical shift anisotropy pattern of that signal has axial symmetry. Also,
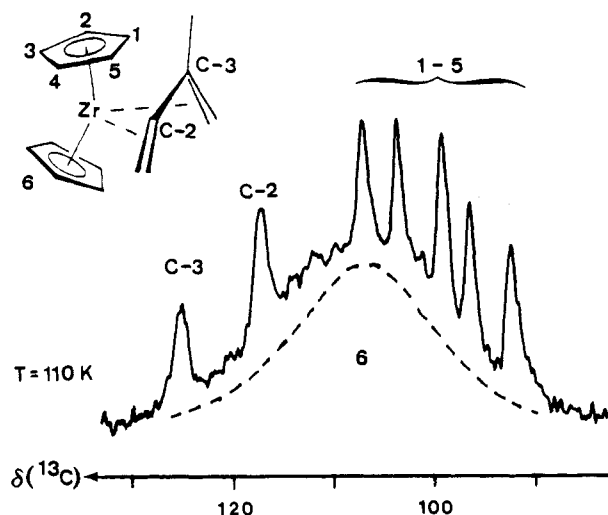
Figure 4. ^{13}C CP/MAS spectrum of **7** (50.3 MHz) at T = 110 K in the region of the cyclopentadienyl and the central diene carbon atoms.

Figure 5. ^{13}C CP/MAS spectrum of **2** (50.3 MHz) as a function of the temperature. The chemical shifts of C-3 and C-4 are degenerate, and an asterisk denotes the impurity (η^5-Cp)$_2$ZrCl$_2$.

various experiments[9,28] and calculations[29] have shown that even in the solid state the rotation of a five-membered ring that is η^5-bonded to a metal is fast.

Further evidence of the fluxional behavior of the Cp rings is obtained by lowering the temperature in the CP/MAS spectrum of complex **7** down to 110 K. The signal of the upper ring at δ = 103 ppm broadens significantly and finally splits into five lines (cf. Figure 4). This process is reversible, and the average chemical shift of these five lines exactly corresponds to the high-temperature chemical shift, as is expected for a restricted rotation of the cyclopentadienyl ring. A remarkable feature is that the chemical shifts cover a range of nearly 20 ppm. This indicates that the chemical environment for each carbon is surprisingly quite different. The signal of the second Cp ring also broadens, but no splitting into sharp signals was observed. These findings are interpreted as a minor restriction to the Cp rotation, such that the slow-exchange limit was not reached. Thus, the two Cp rings are postulated to have different $\Delta G^{\ddagger}$ values. The steric interaction with the butadiene methyl groups can cause the higher rotational barrier for the upper ring. Further evidence that this ring interacts sterically with the methyl group arises from the $T_1(^{13}\text{C})$ values in complex **6**.

Upon introduction of alkyl substituents at the cyclopentadienyl rings, the barrier for ring rotation increases drastically. At T = 300 K in the 50.3-MHz ^{13}C CP/MAS spectrum of **2** there are four methine signals, two of which are degenerate. When the temperature is raised to 385 K,
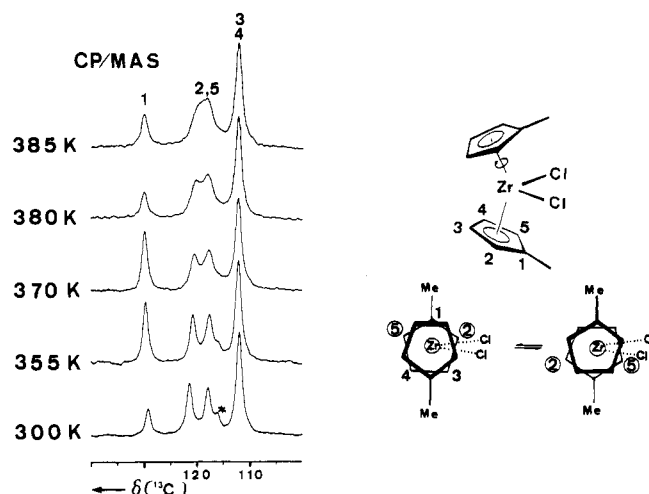
the signals of C-2 and C-5 coalescence. These line-shape changes are fully reversible and are interpreted as ring rotation. This process does not necessarily require ring rotation by 360°: any process that creates a plane of symmetry containing the metal and both central ring coordination axes may account for the observed spectral changes. A rough calculation yielded $\Delta G^{\ddagger}$ = 17 kcal/mol. Upon introduction of bulkier alkyl substituents, this barrier becomes higher, and for **3** and **4** even with 2D magnetization transfer experiments at T = 360 K, there are no indications for chemical exchange. 2D experiments have also been carried out on complexes **8** and **9**. If we focus on the Cp and diene carbon atoms, ring rotation generates the above-mentioned σ symmetry plane and thus should lead to four cross peaks, connecting the methine carbon atoms. In contrast, the diene flip would make the Cp rings equivalent and thus produce five cross peaks. In the 2D experiment there are clearly five cross peaks with equal intensity. Note also that the diene flip leads to exchange at different sites and thus produces the cross peaks at different positions. In particular, the cross peak belonging to the quaternary ring carbon atoms cannot be produced via ring rotation. Consequently we conclude that in zirconocenes which have substituents larger than methyl groups, the Cp rotation in the solid state is a high-energy process.

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