Communications

Dynamics of Organometallic Compounds in the Solid-State Studied by 2D Exchange ^{13}C CP/MAS NMR. (η^5-^RCp) Rotation and Diene Topomerization in $(\eta^5\text{-}^RCp)_2M(\eta^4\text{-}C_4H_6)$ (M = Zr, Hf)

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Summary: High-resolution 50.3-MHz ^{13}C CP/MAS spectra of various microcrystalline bent metallocenes of the type $(\eta^5\text{-}^RCp)_2ML_2$ have been obtained (M = Zr, Hf; R = alkyl; L = Cl; L_2 = alkyl-substituted η^4-C_4H_6). Variable-temperature two-dimensional ^{13}C CP/MAS exchange spectra provide evidence for ^RCp rotation and diene topomerization as two intramolecular fluxional processes occurring in the solid state. Whereas the barrier for η^5-Cp rotation is low, it is significantly enhanced upon introduction of bulky alkyl substituents at the η^5-Cp rings. The barrier for the diene topomerization is approximately 14 kcal/mol.

The study of fluxional processes in organometallic compounds is a domain of NMR spectroscopy.[2] Among the techniques used to investigate dynamic processes in solution are line-shape analysis,[3] one-[4] and two-dimensional[5] magnetization transfer, $T_{1\rho}$ measurements,[6] isotopic pertubation,[7] and metal NMR spectroscopy.[8] Variable-temperature studies for the investigation of exchange processes have also been carried out in the solid state.[9] Since here the activation barriers for such fluxional processes may be similar or even higher than those for the dissolved compounds, variable-temperature CP/MAS[9] line-shape analysis is extremely useful for the detection of fluxional processes, which occur in solution with low-energy barriers.

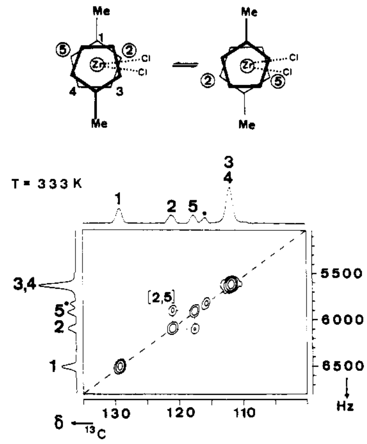

Figure 1. Two-dimensional 50.3-MHz ^{13}C CP/MAS exchange spectrum $(\eta^5\text{-}^{Me}Cp)_2ZrCl_2$ (**1a**) at T = 333 K: spinning rate 4500 Hz, preparation time 5 s, spin-lock time 3 ms, mixing time 2 s, and acquisition time 0.03 s. The size of the data matrix was 116 × 512W before zero filling. The cross peaks indicate an equivalencing of C-2 with C-5, respectively. This can be rationalized by an exchange between two enantiomeric rotamers caused by rotation of the ^{Me}Cp rings about the central Zr ring axis (any rotation of the two equivalent ^{Me}Cp rings which creates a mirror plane containing Zr and the two central Zr–^{Me}Cp axes may also account for the spectra). The asterisk denotes the impurity Cp_2ZrCl_2.

In the following, to the best of our knowledge the first two-dimensional CP/MAS exchange spectra[10] of organometallic compounds[9,11] are reported. The results indicate that many fluxional processes known to occur in solution also can occur in the solid state. Furthermore these processes can be easily monitored by 2D CP/MAS particularly if variable-temperature facilities are available.

In the ^{13}C CP/MAS spectra of $(\eta^5\text{-}^RCp)_2ZrCl_2$ (R = Me, **1a**; R = Et, **1b**; R = t-Bu, **1c**) five (equal intense) signals for the two ^RCp moieties are found, indicating that both rings are equivalent. Thus the rings possess either C_2 symmetry (staggered) or σ symmetry (ecliptic arrangement of the alkyl substituents).[12] The 50.3-MHz ^{13}C two-dimensional exchange spectrum of **1a** (cf. Figure 1) at T = 333 K reveals that in the solid state there is slow rotation of the η^5-^RCp rings around the central metal coordination axis.[13] Rotation of the ^RCp residues does not necessarily involve rotation by 180°: any process introducing a mirror plane defined by the C_2-symmetry axis of **1** and which contains the two central Zr–^RCp ring axes may account for

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(11) For two-dimensional exchange CP/MAS exchange spectroscopy of organic compounds, cf.: Szeverenyi, N. M.; Bax, A.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 2579. Meier, B. H.; Storm, C. B.; Earl, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 6072.

(12) ^{13}C CP/MAS: **1a**, δ 129.2 (s), 121.5, 118.1, 112.1 (2), Me 17.1; **1b**, δ 134.3 (s), 126.9, 117.2, 111.4, 109.1, Et 22.9, 12.6; **1c**, δ 147.4 (s), 127.8, 113.8, 110.5, 109.8, t-Bu 33.9 (s), 31.5. For X-ray structures of $(^RCp)_2ML_2$ systems, cf.: Howie, R. A.; McQuillan, G. P.; Thompson, D. W.; Lock, G. A. *J. Organomet. Chem.* **1986**, *303*, 213. X-ray of $(\eta^5\text{-}^{Me}Cp)_2TiCl_2$, cf.: Peterson, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6442.

(13) In the solid state the activation barrier for Cp rotation is 2 kcal/mol in $(Cp)_2Fe$ and 8.2 kcal/mol for the substituted ring in $(\eta^5\text{-}Cp)(\eta^5\text{-}^{Et}Cp)Fe$; cf.: Makova, M. K.; Leonova, E. V.; Karimov, Y. S.; Kochetkova, N. S. *J. Organomet. Chem.* **1973**, *55*, 185.

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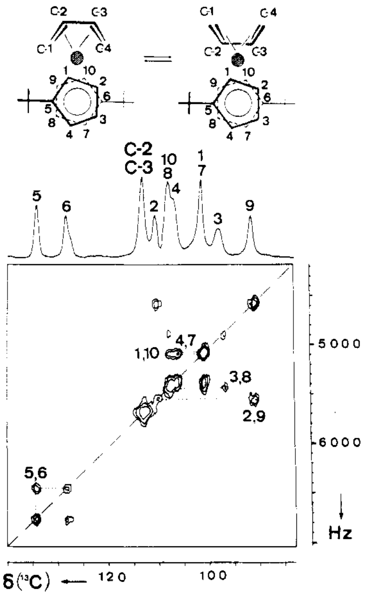

Figure 2. Two-dimensional 50.3-MHz ^{13}C CP/MAS exchange spectrum of $(\eta^5\text{-}^{t\text{-Bu}}\text{Cp})_2\text{Zr}(\eta^4\text{-C}_4\text{H}_6)$ (**6**) at T = 330 K. On the horizontal axis a one-dimensional spectrum is shown. The spectra were recorded on an AM 200 spectrometer: preparation time 2 s, spin-lock time 2 ms, mixing time 4 s, and acquisition time 0.086 s; 90° (H) pulse 5 μs. The size of 2D matrix was 64 × 512W before zero filling. The spectra were recorded with quadratur detection in both dimensions and employing 64 phase cycles (reference external TMS via absolute frequency). The spinning rate was about 4500 Hz. The cross peaks connect individual carbons within two rings indicating an equivalencing of the upper and lower $^{\text{R}}$Cp rings, which can be produced by diene topomerization.

the observed dynamic solid-state NMR spectra. This process leads to a pairwise coalescence of the methine carbons. Line-shape analysis yields ΔG = 16.9 kcal/mol as barrier for the $^{\text{Me}}$Cp rotation. The barrier increases significantly when more bulky substituents (**1b**, **1c**) are introduced. In contrast, in the solution spectra of **1a**–**1c** between 180 and 300 K there are only two signals for the methine carbons,[14] indicating that under these conditions the barrier for $^{\text{R}}$Cp rotation is less than 5 kcal/mol.

In the 50.3-MHz ^{13}C CP/MAS spectra of $(\eta^5\text{-Cp})_2\text{ML}_2$ at T = 300 K (M = Zr, $\text{L}_2 = \eta^4\text{-C}_4\text{H}_6$, **2**; M = Hf, $\text{L}_2 = \eta^4\text{-C}_4\text{H}_6$, **3**; M = Zr, $\text{L}_2 = \eta^4\text{-C}_5\text{H}_8$, **4**; M = Zr, $\text{L}_2 = \eta^4\text{-C}_6\text{H}_{10}$, **5**) all the carbons within one ring are equivalent, indicating that there is fast η^5-Cp rotation. In the solid state, distinct signals for the η^5-Cp moieties are observed at T = 300 K, whereas for the dissolved complexes this diastereotopic splitting is only observed in the low-temperature spectra.[15] However, the two-dimensional ^{13}C CP/MAS exchange spectra at T = 300 K give evidence that also in the solid state the diene topomerization process does occur with modest rate constants. Since the intensities of the cross peaks were unaffected by fast spinning or by proton decoupling during the mixing period,[16] the observed cross peaks cannot stem from spin diffusion. A very rough estimation yields for this process in **5** a barrier around 14 kcal/mol, which is only insignificantly higher than what has been found in solution.

Upon introduction of alkyl substituents at the cyclopentadienyl ring $(\eta^5\text{-}^{\text{R}}\text{Cp})_2\,\text{Zr}(\eta^4\text{-}s\text{-}cis\text{-C}_4\text{H}_6)$[17] (R = *t*-Bu, **6**; R = 1,1′-dimethylpentyl, **7**), in the 50.3-MHz CP/MAS spectra 10 signals for the two $^{\text{R}}$Cp ring carbons are observed.[18] The well-separated low-field signals (δ 133.9, 128.2, **6**; δ 131.2, 125.4, **7**) stem from the quaternary carbons as confirmed by an NQS[19] experiment. The two-dimensional 50.3-MHz CP/MAS ^{13}C spectrum of **6** at T = 330 K clearly shows one cross peak connecting the quaternary carbons and four further cross peaks belonging to the methine carbons. These findings can be rationalized by the diene topomerization, and it furthermore supports the assignment of individual carbons[17] in each ring.

From our findings we conclude that fluxional processes in solid organometallic compounds are not uncommon and that such processes can be easily monitored by variable-temperature two-dimensional ^{13}C CP/MAS exchange spectroscopy. Thereby new avenues with respect to the bridging function of solid state NMR spectroscopy between determination of the static structure in crystals by X-ray analysis and elucidation of the dynamic behavior of these molecules in solution are opened.

Registry No. **1a**, 12109-71-6; **1b**, 73364-08-6; **1c**, 32876-92-9; **2**, 75374-50-4; **3**, 80185-89-3; **4**, 75361-73-8; **5**, 75361-74-9; **6**, 95464-95-2; **7**, 109656-25-9.

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[14] For solution NMR data of $(\eta^5\text{-}^{\text{R}}\text{Cp})\text{ZrCl}_2$ compounds, cf. also: Lappert, M. E.; Pickett, C. J.; Riley, P. I.; Yarrow, P. I. W. *J. Chem. Soc., Dalton Trans.* **1981**, 805.

[15] ^{13}C CP/MAS: **2**, δ 112.8 (2), 51.9, 49.6 $(\eta^4\text{-}s\text{-}cis\text{-C}_4\text{H}_6)$ 105.0, 100.5 (2Cp); **3**, δ 115.0, 112.9, 47.3, 44.9 $(\eta^4\text{-}s\text{-}cis\text{-C}_4\text{H}_6)$ 105.2, 100.3 (2Cp); **4**, 124.2 (s) 110.7, 53.6, 47.5, 29.7 (Me) (η^4-isoprene carbons), 105.1, 102.4 (2Cp); **5**, 120.6 (s), 57.5, 25.2 (carbons of η^4-2,3-dimethylbutadiene), 105.7, 103.0 (2Cp). For solution NMR data of these compounds, cf.: Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1.

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[17] For the preparation, solution NMR data and X-ray analysis of, e.g., **6**, cf.: Erker, G.; Mühlenbernd, T.; Benn, R.; Rufińska, A.; Tsay, Y.-H.; Krüger, A. *Angew. Chem.* **1985**, *97*, 336. Erker, G.; Mühlenbernd, T.; Rufińska, A.; Benn, R. *Chem. Ber.* **1987**, *120*, 507.

[18] ^{13}C CP/MAS: **6**, δ 112.9 (2), 51.4, 50.1 $(\eta^4\text{-}s\text{-}cis\text{-C}_4\text{H}_6)$; 110.4, 107.9 (2), 106.6, 101.2 (2), 97.3, 91.1 ($^{t\text{-Bu}}$Cp methine carbons), 32.7 (4), 33.2 (4) (*t*-Bu carbons); **7**, δ 113.1, 109.0 (3), 103.7, 102.1, 96.7, 90.3 ($^{\text{R}}$Cp methine carbons), 35.9, 35.5 (C-1), 34.4, 33.06 (Me at C-1), 29.1, 25.2, (Me at C-1), 49.4, 48.0 (C-2), 27.4, 27.5 (C-3), 24.2(2) (C-4), 15.2, 14.6 (C-5) (R = 1,1′-dimethylpentyl).

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Deuterioformylation of 2,3,3-Trimethyl-1-butene by Cobalt and Rhodium Carbonyl Catalysts: Regioselectivity of the Metal Deuteride Addition

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Summary: The deuterioformylation of 2,3,3-trimethyl-1-butene leads to labeled 3,4,4-trimethylpentanal as the sole aldehyde product; protium is mostly found in the β-position with respect to the carbonyl group in the product arising from the cobalt-catalyzed reaction. In contrast, when rhodium is the catalyst, the product has only deuterium on that position. These results are interpreted in terms of different reaction pathways and possibly of opposite regioselectivities displayed by the catalysts in the formation of the metal alkyl complex intermediates.