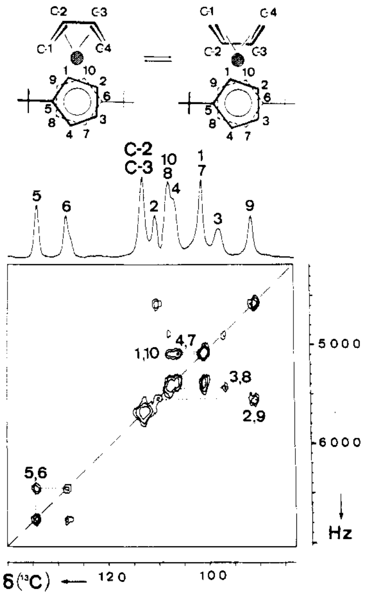

Figure 2. Two-dimensional 50.3-MHz ^{13}C CP/MAS exchange spectrum of (η^5-$^{t\text{-Bu}}$Cp)$_2$Zr(η^4-C$_4$H$_6$) (6) at T = 330 K. On the horizontal axis a one-dimensional spectrum is shown. The spectra were recorded on an AM 200 spectrometer: preparation time 2 s, spin-lock time 2 ms, mixing time 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 (η^5-Cp)$_2$ML$_2$ at T = 300 K (M = Zr, L$_2$ = η^4-C$_4$H$_6$, **2**; M = Hf, L$_2$ = η^4-C$_4$H$_6$, **3**; M = Zr, L$_2$ = η^4-C$_5$H$_8$, **4**; M = Zr, L$_2$ = η^4-C$_6$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 (η^5-$^{\text{R}}$Cp)$_2$ Zr(η^4-*s-cis*-C$_4$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 (η^5-$^{\text{R}}$Cp)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 (η^4-*s-cis*-C$_4$H$_6$) 105.0, 100.5 (2Cp); **3**, δ 115.0, 112.9, 47.3, 44.9 (η^4-*s-cis*-C$_4$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 (η^4-*s-cis*-C$_4$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.

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In spite of intensive investigation[1-4] of the different aspects of the hydroformylation reaction by cobalt and rhodium catalysts, little is known about the regioselectivity of the initial attack of cobalt and rhodium carbonyl hydrides on unsymmetrical olefins to form intermediate metal alkyl complexes during the catalytic reaction. As far as we are aware, the only studies related to this question report the addition of $HCo(CO)_4$ to propylene in the vapor phase[5] and the addition of the same hydride to different substrates,[6,7] including isobutene,[6] in solution. In the first case, in the absence of carbon monoxide, approximately 70% addition of the metal atom to the central carbon atom takes place[5] and the isomeric distribution of the aldehydic products corresponds to the regioselectivity of the addition. The addition of $HCo(CO)_4$ to isobutene under 10 psi of carbon monoxide[6] yields after decomposition of the adduct with iodine in methanol only methyl 2,2-dimethylpropionate. Furthermore, the addition of $HCo(CO)_4$ under carbon monoxide to styrene[8] and ethyl acrylate[9] has been more recently investigated. In both cases the first attack gives the branched product (alkyl or aryl), which can transform under suitable conditions into the more stable linear product.

The above results can, however, hardly be extrapolated to catalytic conditions where high carbon monoxide partial pressure and higher temperatures are normally used and where the isomeric ratio of the reaction products can be very different.[1-4,8,9] To get a deeper insight into this aspect of the hydroformylation reaction, 2,3,3-trimethyl-1-butene was deuterioformylated. The reactions were carried out in benzene as the solvent (20 mL) on 5 mL of the olefin under 200 at of an equimolar mixture of carbon monoxide and deuterium at 100 °C using either $Co_2(CO)_8$ (400 mg) or $Rh_4(CO)_{12}$ (2 mg) as the catalyst precursor. Practically complete conversion of the substrate was achieved in both cases as monitored by pressure decrease. In both cases 3,4,4-trimethylpentanal was formed almost exclusively (~99%).[12] The aldehyde was converted as described elsewhere,[13] to the corresponding methyl 3,4,4-trimethylpentanoate by oxidation with silver oxide and esterification with diazomethane. NMR analysis of the above ester, carried out in the presence of $Eu(DPM)_3$, shows complete resolution of the signals corresponding to the different types of protons. The protium content corresponding to the different signals (Chart I) is calculated from these spectra by using the signal of the carbomethoxy group as the internal standard. The intermolecular deuterium distribution was determined by mass spectroscopy, giving a total amount of label in agreement with that obtained from the NMR spectra.

In the product obtained with the cobalt catalyst, the signal of the methyl group in position 3 has an intensity corresponding to 2.52 protons and consists of three lines. The two outer lines arise from coupling to a vicinal protium atom ($^3J_{H-H}$ = ~8 Hz), whereas the center line corresponds to the same group vicinal to a deuterium atom (vide infra). The ratio between the areas of the outer lines and of the central one is approximately 2, in good agreement with the protium content on the methine carbon atom (0.67 proton). The insensity of the signals of the protons on the methylenic carbon atom (~0.90 proton) is much less significant because of the exchange with the hydrogen in the gas phase, which takes place on the α-position of the aldehydic products formed.[14]

For 3,4,4-trimethylpentanal formed in the deuterioformylation with $Rh_4(CO)_{12}$ as the catalyst precursor, the methyl group in position 3 appears as a clean singlet having intensity 3.00 (Chart I). Correspondingly there is no protium on the β-position with respect to the carbonyl group and there are 2.01 protons on the carbon atom in α-position. Considering that β-hydrogen elimination by rhodium carbonyl catalysts under "oxo condition" is accompanied by exchange with the hydrogen in the gas phase and that there is an isotope effect (k_H/k_D) of ~3 in such elimination,[17] we can assume for the rhodium-catalyzed formation of 3,4,4-trimethylpentanal path a in Scheme I.

The data from the cobalt catalyzed deuterioformylation are more difficult to interpret. Previous studies have shown that with this catalyst under the reaction conditions used (high carbon monoxide partial pressure) isomerization and dissociation of the substrate from the catalyst–substrate complex is minimized.[10,11] Furthermore, isomerization of the olefinic substrate into the catalyst–substrate complex takes place contemporaneously to a 1,2-hydrogen shift,[16] as shown by using deuteriated substrates; in such kind of substrates prevailing (but not complete) retention of the label occurs[14-18] and no isotope effect associated with the movement of deuterium was observed.[15] In the present case a small isotope effect cannot be completely excluded. However, on the basis of the previously observed not complete retention of the label and of the accuracy of the NMR results, we cannot rely on this effect.

The data show that only a relatively small part of the formed aldehyde (up to 33%) can arise according to pathway a in Scheme I, which was established for the rhodium catalysis. The remainder of the aldehyde must have passed through the tertiary alkyl intermediate (compare pathway b in Scheme I). The direction of the first addition of the cobalt carbonyl deuteride which eventually leads to this part of the aldehyde cannot be surely identified. However, it is worthy to note that under the reaction conditions used the addition to terminal olefins shows only a very limited reversibility.[14] Therefore, the formation of this aldehyde could (at least in part) form according to path b in Scheme I (in which no isotope effect has been accounted for), i.e., through the addition of the intermediate cobalt carbonyl deuteride to form first the tertiary alkyl–metal complex and then, for reasons probably connected with a high-energy barrier for CO insertion in such an intermediate, a successive formation of the primary alkyl complex, which eventually evolves to 3,4,4-trimethylpentanal.

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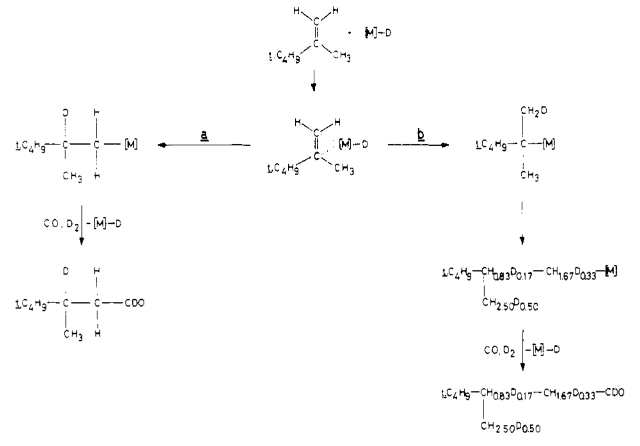
Chart I. Protium Content at the Different Carbon Atoms of 3,4,4-Trimethylpentanal Produced in the Deuterioformylation of 2,3,3-Trimethyl-1-butene by Rhodium and Cobalt Carbonyls

	$t\text{-}C_4H_9$—	CH—	CH_3	CH_2—CDO
$Co_2(CO)_8$	9.00	0.67	2.52	0.90
$Rh_4(CO)_{12}$	8.98	0.00	3.00	2.01

Scheme I



It follows, therefore, that in spite of practically exclusive formylation at the terminal carbon atom in 2,3,3-trimethyl-1-butene both by cobalt and rhodium carbonyls as the catalyst precursor, different pathways probably caused by different regioselectivities can be displayed by either catalyst in the first step of the reaction. A similar phenomenon could also be responsible for the extensive formylation (32%) of the methyl group in [1-^{14}C]-propene,[19,20] in the presence of $Co_2(CO)_8$. These results had previously been interpreted in terms of a rapid interconversion with considerable isomerization of π-olefin complexes. Alternatively, insertion of propylene into the H–Co bond could prevail with the addition of the metal atom to the internal carbon atom; equally probable β-elimination[21] from the two methyl groups should then bring about the high extent of formylation in position 3 of propylene.[19,20,22] A tentative rationalization has been proposed for such kind of attack, which has been called "anti-Markownikoff insertion".[23] However, the different reaction pathways observed using either rhodium or cobalt carbonyls as the catalyst precursors point out either that too much is still unknown for such rationalization or that the nature of the catalytic species formed from both metals is rather different.

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Synthesis and Structures of Titanaoxacyclobutanes

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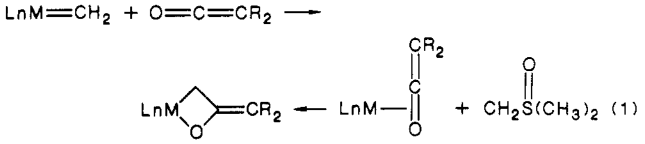
Summary: Titanaoxacyclobutanes can be prepared by the addition of a ketene to a titanium methylene complex or by the addition of a methylene fragment to a titanium ketene complex. For example, the addition of 2 equiv of dimethylsulfoxonium methylide to titanocene chloro–acyl complexes yields titanaoxacyclobutanes. The first equivalent deprotonates the acyl to form the titanocene ketene complex which is trapped by the second equivalent of the methylide to yield the metallaoxacyclobutane. Both routes yield complexes that are stable to temperatures above 60 °C. Variable-temperature NMR studies show that the metallaoxacyclobutane ring is puckered with a barrier to inversion of 13–19 kcal/mol.

Metallaoxacyclobutanes have long been considered as intermediates in transition-metal-catalyzed olefin epoxidations and conversions of carbonyls to alkenes by metal alkylidenes.[1] To date, the major route to metallaoxacyclobutanes has been the reactions of high-valent, electron-rich, late transition metals with electron-deficient tetracyanooxiranes.[2] The analogous organic heteroatom complexes have also been observed in the olefin oxidation by SO_3 as well as in "Wittig" transformations.[4] We report here two independent routes to early-transition-metal metallaoxacyclobutanes: (1) reaction of a metal methylidene complex with an organic ketene and (2) coupling of a metal ketene complex with dimethylsulfoxonium methylide (eq 1).



$$LnM{=}CH_2 + O{=}C{=}CR_2 \longrightarrow \quad (1)$$

Treatment of a yellow suspension of titanocene chloro–acyl complex 1[4] with an excess of dimethylsulfoxonium methylide[5] resulted in the instantaneous formation of a dark solution from which a red solid, 2, was isolated in 77% yield[6] (eq 2). The product is moderately air-sensitive and

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[†] Contribution No. 7664.

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(6) To a cooled suspension of the chloro–acyl complex 1 (1.0 g, 3.9 mmol) in 20 mL of benzene was added 0.79 g (8.6 mmol) of neat dimethylsulfoxonium methylide by syringe. The resulting red solution was filtered through a medium frit packed with Celite (2 cm). The solvent was evaporated under vacuum to yield a brick-red solid that was washed with pentane and cold ether and then dried under vacuum overnight to yield 0.66 g (77%) of product 2. Protonolysis of 2 with anhydrous HCl yielded titanocene dichloride and acetone.

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