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In situ NMR Study of the Rhodium(I)-Catalyzed Hydrogenation of the Allene 1-Methoxy-propa-1,2-diene Using Parahydrogen

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Abstract: **1.** The homogeneous hydrogenation of 1-methoxy-propa-1,2-diene was investigated via in situ ^{1}H-NMR spectroscopy using different rhodium(I) catalysts and parahydrogen (p-H_2). **2.** The detected polarization signals allow the determination of the hydrogenation products due to their characteristic patterns.

The homogeneous hydrogenation of allenes has been investigated only in very few cases [1-3]. In this communication we report results of the homogeneous rhodium(I)-catalyzed hydrogenation of the mono-substituted allene 1-methoxy-propa-1,2-diene using para-enriched hydrogen. It has been reported earlier [4] that NMR signal enhancement of several orders of magnitude can be observed with in situ ^{1}H-NMR spectroscopy, if the two hydrogen atoms of parahydrogen are transferred into magnetically inequivalent positions [5] under retention of their singlet spin correlation. This phenomenon is the result of a selective population of individual nuclear spin levels, which deviates from the Boltzmann distribution. Polarization patterns of enhanced emission and absorption signals are observed, which allow to characterize the positions of the transferred hydrogens [6]. The method is capable to distinguish between different hydrogenation products, even in cases of minor product formation.

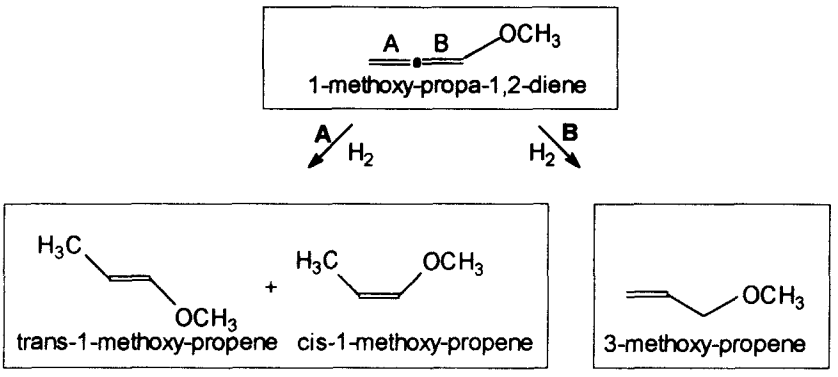

Figure 1: Possible primary hydrogenation products of 1-methoxy-propa-1,2-diene.

Allenes contain cumulated double bonds with π orbitals that are orthogonal to each other. Therefore, in one catalytic cycle only one of the two double bonds can be hydrogenated. In order to differentiate between the two alternatives, a mono-methoxy-substituted allene was used. Figure 1 shows the possible primary hydrogenation products as a result of the reduction of the individual double bonds A or B.

Three different catalysts, namely Wilkinson's catalyst $RhCl(PPh_3)_3$ [7] and the cationic catalysts $[Rh(NBD)(PPh_3)_2]PF_6$ [8] as well as $[Rh(COD)(Ph\text{-}\beta\text{-}glup\text{-}OH)]BF_4$ [9] were used for the reaction of the allene with a hydrogen mixture that was enriched to 50 % p-H_2 [13]. The experimental spectra observed during the hydrogenations are shown in Figure 2a,c,d.

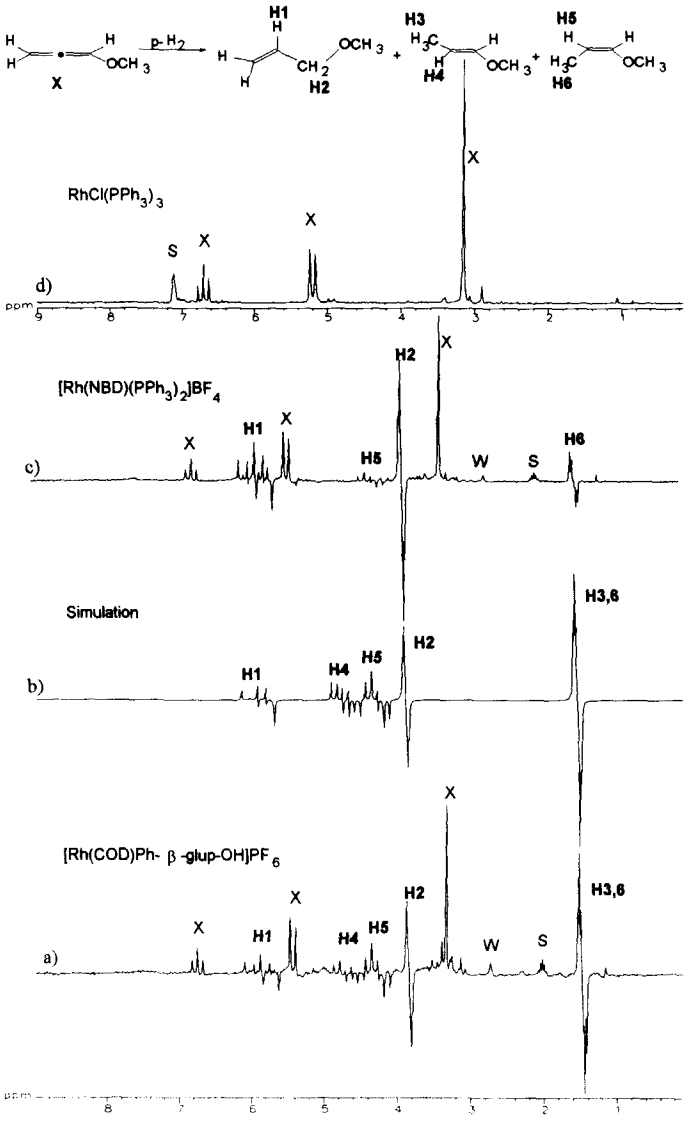

Figure 2:
a) Experimental ^{1}H-NMR spectrum of $[Rh(COD)(Ph\text{-}\beta\text{-}glup\text{-}OH)]BF_4$ (10 mg) and 35 µl substrate dissolved in 1.5 ml acetone-d_6 (S = solvent; W = water signal) after hydrogenation with p-H_2 for 13 s (20 accumulations);
b) Simulated polarization spectrum; all possible hydrogenation products weighted equally.
c) Experimental ^{1}H-NMR spectrum of $[Rh(NBD)(PPh_3)_2]PF_6$ (10 mg) and 60 µl substrate dissolved in 1.5 ml acetone-d_6 (S = solvent; W = water signal) after hydrogenation with p-H_2 for 13 s (20 accumulations);
d) Experimental ^{1}H-NMR spectrum of $RhCl(PPh_3)_3$ (10 mg) and 60 µl substrate dissolved in 1.5 ml benzene-d_6 (S = solvent signal) after hydrogenation with p-H_2 for 13 s (20 accumulations).

The polarization patterns of the experimental spectra were analyzed by comparison with computer simulated ones. Simulations were obtained using the computer program PHIP7 [10]. A simulated spectrum containing all possible primary hydrogenation products, i.e., 3-methoxy-propene, trans-1-methoxy-propene, and cis-1-methoxy-propene, in a ratio of 1:1:1, is shown in Figure 2b. The NMR parameters for the simulation of the product spectra are listed in the experimental section [14].

The observed polarization patterns of the experimental ^{1}H-NMR spectra were analyzed as follows: the bidentate catalyst [Rh(COD)(Ph-β-glup-OH)]BF_4 reveals no selectivity toward either double bond (Fig. 2a) as is evident from the polarization patterns obtained by computer simulations depicted in Figure 2b. In contrast, the polarization patterns shown in Figure 2c indicate that [Rh(NBD)(PPh_3)$_2$]PF_6 is directing the hydrogenation predominantly toward the double bond adjacent to the methoxy substituent. A simulation that assumes a formation of seven parts 3-methoxy-propene and one part cis-1-methoxy-propene yields good agreement with the experimental spectrum. Our result confirms a previous study of Brown et al. [3], who hydrogenated 3,5-dimethyl-hexa-3,4-diene-2-ol to 3,5-dimethyl-hex-4-ene-2-ol using the cationic catalyst [Rh(DIPHOS)(NBD)]BF_4. They found 95 % regioselectivity and suggested a directing influence of the OH-sustituent of the substrate.

Using Wilkinson's catalyst, no hydrogenation was observed under the chosen reaction conditions (Fig. 2d). This result agrees with a study of Osborn et al. [1], who found that $RhCl(PPh_3)_3$ is not active for hydrogenating the unsubstituted allene but forms a stable complex with the catalyst instead.
From the identification of the polarization patterns, we are able to classify the hydrogenation products that have been obtained by using the different rhodium(I)-catalysts as shown in Table 1:

Table 1: Comparison of the observed hydrogenation products in presence of different rhodium(I) catalysts (• = very weak polarization pattern detected; + = weak polarization pattern detected; ++ = medium polarization pattern detected; +++ = strong polarization pattern detected; - = no polarization pattern detected).

	3-methoxy-propene	trans-1-methoxy-propene	cis-1-methoxy-propene
$RhCl(PPh_3)_3$	-	-	-
[Rh(NBD)(PPh_3)$_2$]PF_6	+++	•	+
[Rh(COD)(Ph-β-glup-OH)]BF_4	++	++	++

From a comparison of the experimental polarization spectra with appropriate simulations, we draw the conclusion that the three catalysts hydrogenate 1-methoxy-propa-1,2-diene in rather different ways even under comparable reaction conditions. The results demonstrate that this method is well suited to detect hydrogenation products, even if different products are formed simultaneously. A distinctive advantage of this analytical in situ method is its high sensitivity for hydrogenation products, which requires no work up and yields pertinent information about homogeneous hydrogenation reactions precisely and instantaneously.

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[13] All ^{1}H-NMR spectra were recorded using a modified 80 MHz spectrometer (Varian CFT20). All hydrogenations were carried out in situ in open NMR tubes within the NMR probe at room temperature. Para-enriched hydrogen containing about 50 % p-H_2 was prepared by passing H_2 through activated charcoal at 77 K and bubbled in an interrupted mode through a capillary into the spinning NMR tube containing the reaction solution [11].
Prior to their use, the deuterated solvents were degassed with argon for about 5 min to remove traces of oxygen.
1-Methoxy-propa-1,2-diene was prepared as described in the literature [12], and purified by freezing and selective melting.
[14] NMR simulation parameters of the primary hydrogenation products:
cis-1-methoxy-propene: ^{1}H-NMR (acetone-d_6): δ = 1,49 (**d**; **d**, J = 6,8; 1,47 Hz, 3H, CH_3); 3,53 (**s**, 3H, OCH_3); 4,24 (**d**; **d**, J = 6,8; 6,1 Hz, 1H, H_3C-CH=); 5,89 ppm (**d**; **d**, J = 6,8; 1,47 Hz, 1H, =CH-OCH_3)
trans-1-methoxy-propene: ^{1}H-NMR (acetone-d_6): δ = 1,51 (**d**; **d**, J = 6,8; 1,47 Hz, 3H, CH_3); 3,43 (**s**, 3H, OCH_3); 4,68 (**d**; **d**, J = 12,2; 6,8 Hz, 1H, H_3C-CH=); 5,89 ppm (**d**; **d**, J =12,2; 1,47 Hz, 1H, =CH-OCH_3)
3-methoxy-propene: ^{1}H-NMR (acetone-d_6): δ = 3,35 (**s**, 3H, OCH_3); 3,85 (**d**; **d**; **d**, J = 4,88; 1,42; 1,42 Hz, 2H, CH_2-OCH_3); 5,07 (**d**; **d**; **t**, J = 9,75; 2,2; 1,42 Hz, 1H, HCH=CH); 5,17 (**d**; **d**; **t**, J = 17,58; 2,2; 1,42 Hz, 1H, HCH=CH); 5,87 ppm (**d**; **d**; **t**, J = 17,58; 9,75; 4,88 Hz, 1H, =CH-).

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