In situ ^{1}H-PHIP-NMR studies of the stereoselective hydrogenation of alkynes to (*E*)-alkenes catalyzed by a homogeneous [Cp*Ru]$^+$ catalyst

Dana Schleyer, Heiko G. Niessen and Joachim Bargon*

Institute of Physical and Theoretical Chemistry, University of Bonn, Wegelerstrasse 12, D-53115 Bonn, Germany. E-mail: bargon@uni-bonn.de; Fax: +49 228 73 9424

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The hydrogenation of internal alkynes using a [Cp*Ru(alkene)]$^+$ complex leads to the formation of (*E*)-alkenes. This ruthenium complex represents one of the few homogeneous catalysts that *trans*-hydrogenate internal alkynes directly and stereoselectively. We have studied its stereoselectivity by *in situ* PHIP-NMR spectroscopy (PHIP = *para*-hydrogen induced polarization). With this method the initially formed products can be identified and characterized even at very low concentrations and low conversions. Furthermore, their subsequent fate can be evaluated with high sensitivity and with time resolution. Different alkyne substrates were used to demonstrate the universal applicability of this catalyst. The catalyst is not active in combination with terminal alkynes, however, possibly due to the formation of a rather stable vinylidene complex. A mechanism proceeding *via* a binuclear complex is proposed to explain the formation of the (*E*)-alkenes.

The cationic ruthenium complex [Cp*Ru(η^4-CH_3CH=CHCH=CHCOOH)][CF_3SO_3], **1**, has been shown to selectively hydrogenate sorbic acid (*trans*,*trans*-2,4-hexadienoic acid) to (*Z*)-3-hexenoic acid.[1] Mechanistic studies on that hydrogenation have been undertaken successfully before in our group.[2] Thereby, it has been found that this simple catalyst **1** is an attractive choice for the selective homogeneous (*E*)-hydrogenation of alkynes. Normally, homogeneous transition metal complexes hydrogenate alkynes mainly to (*Z*)-alkenes.[3] Traditional methods for *trans*-hydrogenation of alkynes—either homogeneous or heterogeneous—of which some yield high amounts of (*E*)-alkenes, however, frequently do not tolerate functional groups. Heterogeneous catalysis typically permits easier removal of the catalyst; by contrast homogeneous catalysis is much more product specific and stereoselective, which is desirable for easier and low-cost workup of the products. For example, totally hydrogenated and re-arranged products can usually be suppressed or limited to a certain degree through variation of the reaction conditions and through catalyst design.

In principle, the thermodynamically more stable (*E*)-alkenes—as formed here *via* homogeneous hydrogenation—could be the consequence of subsequent isomerizations of initially formed (*Z*)-alkenes, whereby the isomerizations do not occur until a high degree of conversion of the substrate is reached. The direct homogeneous hydrogenation of an alkyne to an (*E*)-alkene by a mononuclear catalyst is difficult to envision, because the hydrogen transfer would have to occur from two different sides of the substrate. Therefore, it may not proceed in one step. More likely is a pathway *via* a catalyst that contains two metal centers, since this can lead to the direct formation of an (*E*)-alkene. In this contribution, we report on the stereoselective *trans*-hydrogenation of internal alkynes to (*E*)-alkenes using **1**. The key features of this reaction are: mild reaction conditions (hydrogen pressures of only 1 bar and temperatures around 300 K), a high tolerance of other functional groups within the substrate molecule (*e.g.* hydroxyl, carbonyl, acetal), and the selective production of (*E*)-alkenes. A reaction mechanism derived from our results, which is consistent with claims published by others previously,[4] is proposed.

Experimental

In order to investigate the initial hydrogenation of alkynes *in situ* at low conversion rates, PHIP-NMR spectroscopy (PHIP = *para*-hydrogen induced polarization) was used in this study to obtain insight into details of the reaction mechanism. The PHIP effect gives rise to a characteristically different pattern for every alternative hydrogen transfer possibility to the substrate, consisting of characteristic emission and absorption signals in the *in situ*-recorded NMR spectrum of the hydrogenation product.[5] Both in the intermediates and in the final hydrogenation products, not only chemically, but also magnetically different protons will lead to specific and distinguishable polarization patterns *via* which alternate reaction schemes can be discriminated. Since the characteristic PHIP patterns are only observed if the two *para*-hydrogen atoms are transferred pair-wise by the catalyst, that is while maintaining the pair correlation between the two formerly *para*-hydrogen protons *via* magnetic interaction, one can obtain detailed and hence subtle information about the hydrogenation mechanism. Even if the primarily formed reaction product rearranges subsequently, its original identity manifests itself in the polarization pattern. Whether the rearranged, that is the eventually formed more thermodynamically stable product, also appears in polarization depends on the reaction conditions and the kinetics. As an additional advantage, the PHIP effect leads to a 10^4-fold increase of the NMR sensitivity, which enables us to detect small amounts of intermediates in the catalytic cycle or by-products of the reaction.

Our investigations were performed under a hydrogen pressure of 1 bar at a temperature of 298 K using an NMR spectrometer operating at a nominal proton resonance frequency of 200 MHz. For all investigations 5 mg of the catalyst were weighed into a standard 5 mm NMR tube and dissolved

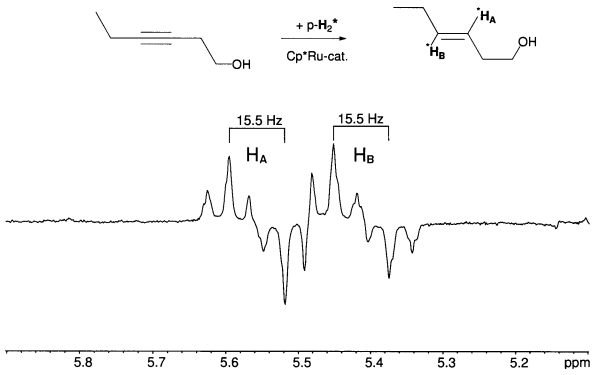


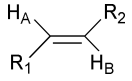
Fig. 1 Olefinic region of the 200 MHz ^{1}H-PHIP-NMR spectrum recorded during the hydrogenation of 3-hexyne-1-ol using the Cp*Ru catalyst.

in 600 µl methanol-d_4; 20 µl of the substrate were added subsequently. The whole system was purged with argon. This procedure is well established in our group and has been found to produce good results.

Results

As a typical example for the stereoselective character of this type of hydrogenation, we show the ^{1}H-PHIP-NMR spectrum of 3-hexyne-1-ol using **1** in methanol-d_4 (Fig. 1), exhibiting the characteristic PHIP polarization pattern. These polarization signals prove the pair-wise transfer of the *para*-hydrogen to the substrate. The observed antiphase coupling constant of 15.5 Hz is a typical value for an olefinic *trans* coupling constant and clearly identifies the formation of the corresponding

Table 1 Experimental ^{1}H-NMR data of the hydrogenation products at 200 MHz (in methanol-d_4, 293 K)



R_1	R_2	δ_A	δ_B	$^3J(H_AH_B)$/Hz
CH_3	CH_3	5.42	5.42	15.0
CH_3	C_2H_5	5.46	5.36	15.0
CH_3	$C{\equiv}CCH_3$	5.98	5.42	15.7
CH_3	C_6H_5	6.24	6.40	15.8
C_2H_5	C_2H_5	5.44	5.44	15.0
C_2D_5	C_2D_5	5.43	5.43	15.0
C_2H_5	C_6H_5	6.26	6.38	16.0
CH_2OH	C_3H_7	5.57	5.68	15.6
CH_2OH	C_6H_5	6.36	6.61	16.0
CH_2CH_2OH	C_2H_5	5.56	5.41	15.5
$CH(OH)CH_2CH_3$	CH_3	5.43	5.64	15.4
$CH(OH)CH_2CH_3$	C_2H_5	5.40	5.67	15.2
$CH_2CH(OH)CH_3$	C_2H_5	5.41	5.54	15.6
$C(O)CH_3$	C_2H_5	6.07	6.99	16.1
$CH(OC_2H_5)_2$	C_3H_7	5.40	5.83	15.8

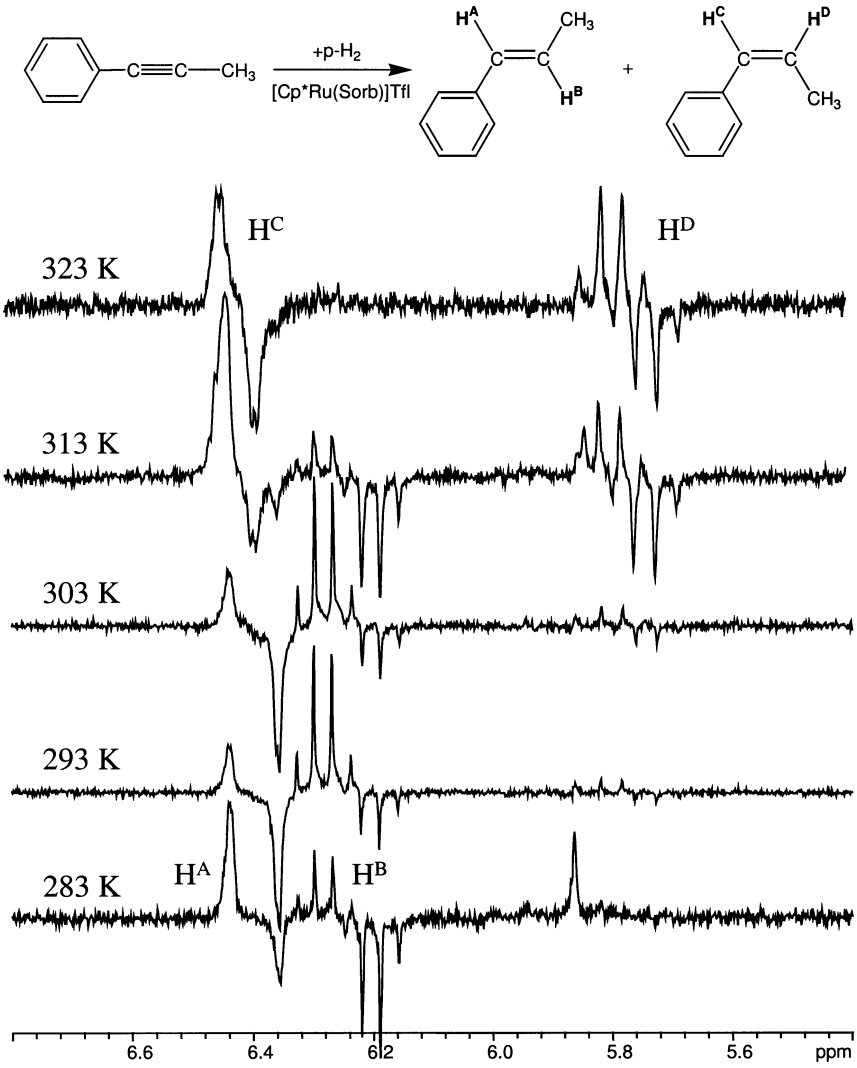


Fig. 2 Olefinic region of the 200 MHz ^{1}H-PHIP-NMR spectrum recorded during the hydrogenation of 1-phenyl-1-propyne at various temperatures using the Cp*Ru catalyst.

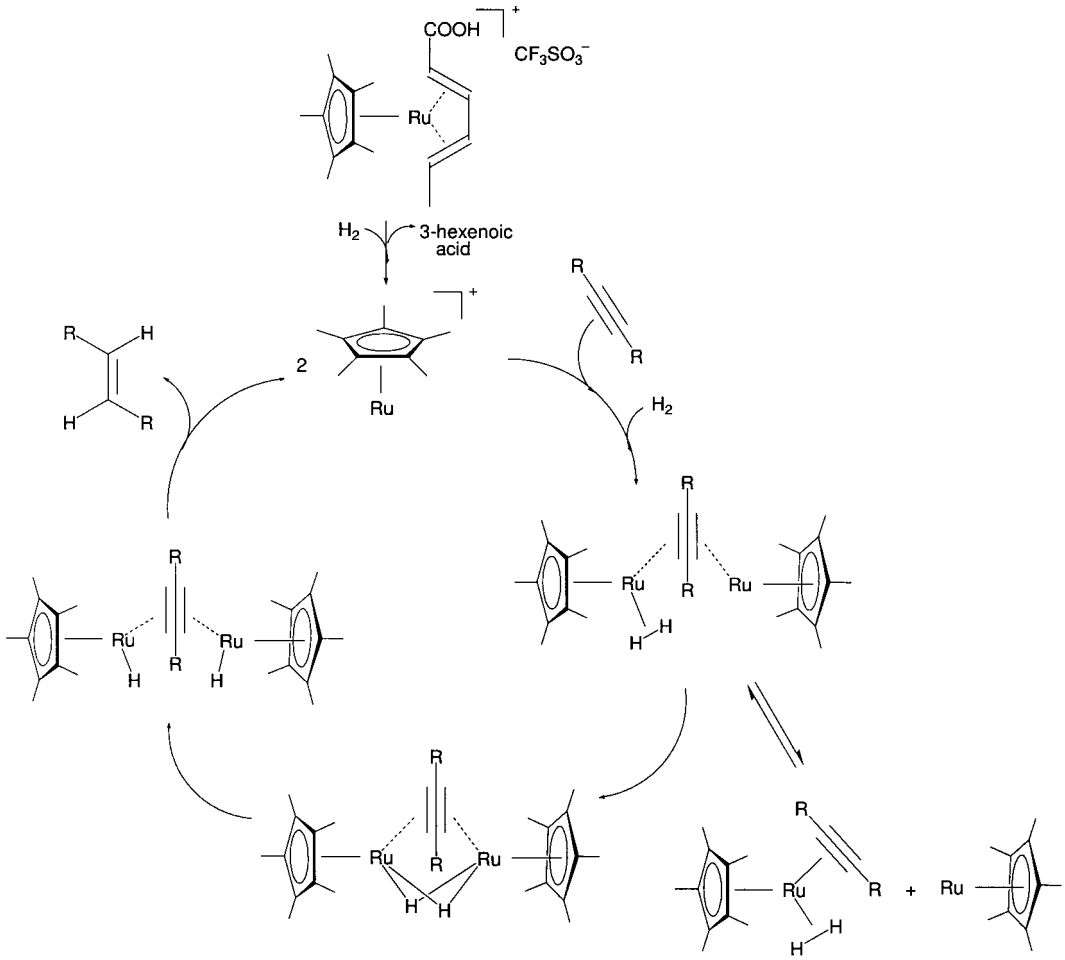


Fig. 3 Proposed dinuclear mechanism for the hydrogenation of internal alkynes with the Cp*Ru catalyst **1**.

(*E*)-alkene by *trans*-hydrogenation of the substrate. Additional ^{1}H-PHIP-NMR data of other (*E*)-alkenes obtained through hydrogenation of alkynes with **1** are presented in Table 1.

Whereas for most of the investigated substrates studied here the stereoselectivity of the formation of the (*E*)-product was found to be temperature independent, phenyl-substituted alkynes represent an exception. Accordingly, PHIP-NMR experiments revealed a change of selectivity during the hydrogenation of 1-phenyl-1-propyne depending on the temperature. At 283 K the (*E*)-alkene is the main product, whereas the formation of the (*Z*)-isomer is favored with increasing temperature. Fig. 2 shows the ^{1}H-PHIP-NMR spectra recorded during the hydrogenation of 1-phenyl-1-propyne at different temperatures.

From our PHIP-NMR studies we conclude that any pathway proceeding *via* (*Z*/*E*)-isomerization for the formation of the (*E*)-alkene product can be excluded, because no initial formation of the necessary (*Z*)-product can be detected even at low temperatures. In addition, no (*Z*/*E*)-isomerization occurred when (*Z*)-3-hexene-1-ol was exposed to catalyst **1** under the usual reaction conditions for the hydrogenation. This experiment supports the proposed reaction mechanism (Fig. 3) for the direct *trans*-hydrogenation.

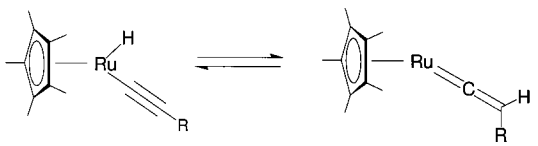


Fig. 4 Formation of a stable vinylidene complex with teminal alkynes.

Control experiments using a homogeneous rhodium catalyst, the Wilkinson catalyst, have shown that in this case the hydrogenation leads directly to the formation of the (*Z*)-alkenes with characteristically different polarization patterns. Furthermore, when using either the Wilkinson or any other of the investigated rhodium catalysts, no formation of the (*E*)-product could be observed by PHIP-NMR spectroscopy.

Discussion

We have studied the hydrogenation of various terminal or internal aliphatic alkynes, including some containing various functional groups. We found that the hydrogenation rates for these different types of alkynes are not much influenced by functional groups, but vary significantly with the position of the triple bond within the molecule. In particular, alkynes with internal triple bonds are found to be much more reactive than those with terminal ones, to the degree that no polarized products have ever been observed for the latter. Since the hydrogenation of terminal alkynes proceeds in principle readily with other transition metal catalysts, such as rhodium, the lack of activity of this ruthenium catalyst could be due to the formation of a stable catalyst–substrate complex. In contrast, using the catalyst **1** the hydrogenation of internal alkynes proceeds readily and leads to the corresponding (*E*)-alkenes with high stereoselectivity. Even if the reaction is carried out below 280 K, no signals due to the (*Z*)-alkene are detected in the *in situ* PHIP-NMR spectra. The inability of **1** to yield any PHIP polarization when hydrogenating terminal alkynes might alternatively indicate that it proceeds according to another mechanism, not "pair-wise".

Based on steric reasoning a catalyst containing only one metal center should most likely lead to the formation of

(*Z*)-alkenes as the main hydrogenation product of internal alkynes. Therefore, to explain the observed *trans*-hydrogenation, a different mechanism has to be considered.

Binuclear rhodium complexes have been reported previously to effect the homogeneous hydrogenation of alkynes to (*E*)-alkenes.[4] The intermediate is assumed to be a bridged alkyne–dihydrogen complex, which enables a different stereochemical pathway from that typical for mononuclear rhodium complexes. In the case of ruthenium, the formation of dimeric complexes with alkynes has also been reported before.[6] Since the stereoselectivity observed here—as has been pointed out before—can only be explained if the reaction takes place involving two metal centers, we propose the mechanism outlined in Fig. 3.

According to this concept, the hydrogenation has to take place rapidly and without total separation of the two *para*-hydrogen atoms. Otherwise the pair correlation of the two proton spins would be lost and no PHIP-NMR spectrum should be observed. The observation of a PHIP-NMR spectrum and steric considerations clearly favor the existence of a dimeric complex as the catalytically active species. Furthermore, our results prove that the two hydrogen atoms transferred to the alkyne stem from the same hydrogen molecule. In addition, if the (*Z*)-alkene was formed first, followed by subsequent isomerization to the (*E*)-form, this fact would manifest itself in the polarization spectrum, where signals characteristic for the (*Z*)-alkene should appear. In the event the (*Z*)-product would hypothetically exist for a very short time (a necessary requirement to be considered a product), this would manifest itself in the form of polarization signals. Furthermore, kinetic considerations would only favor the non-observability of the (*E*)-alkene if the corresponding (*Z*)-alkene was formed first but not the other way around; fast relaxation would more likely eliminate the signals for the (*E*)-alkene. Since PHIP-NMR spectroscopy provides the opportunity to investigate the reaction under initial kinetic conditions without probable isomerization at high conversions, it cannot be excluded that subsequent reactions lead to the formation of some (*Z*)-isomer. Therefore, by just looking at thermal product spectra at nearly complete conversion, no distinction between a *trans*- or *cis*-specific hydrogenation would be possible if both products were finally present.

The finding that no intermediates as outlined in the scheme depicted in Fig. 3 have been observed in our PHIP studies is attributed to the fact that in all proposed intermediates *the two transferred hydrogen atoms are chemically and magnetically equivalent*, which makes the detection of these complexes impossible. We are aware that the reaction mechanism is not yet fully established and is partly based on chemical reasoning; however, we find the mechanism consistent with the literature and our results. Therefore, we consider it at least a good working hypothesis and a starting point for further investigations and discussions. At this point, kinetic investigations to prove and substantiate the mechanism further are under the way.

Accordingly, **1** represents the first homogeneous ruthenium catalyst that is capable of a direct *trans*-hydrogenation of internal alkynes. We assume that the relatively small demand for space and the open structure of the resulting activated complex are important features that characterize and enable this binuclear mechanism. Sterically hindered substrates may obstruct the double-sided coordination of the catalyst. This may apply to phenyl-substituted alkynes as well, but it is also possible that some other form of specific coordination occurs between the phenyl group and the active center of the catalyst.

With increasing temperature, the reaction pathway changes to a mononuclear mechanism that gives rise to the formation of (*Z*)-alkenes. Further investigations of phenyl-substituted alkynes are warranted. As shown in previous studies, the rate of addition of the dihydrogen to a metal center, not that of the transfer of the hydrogen to the substrate molecule, is the rate-determining step at room temperature and 1 bar of hydrogen.[2]

As mentioned before, **1** does not exhibit any hydrogenation activity towards 1-alkynes. Therefore, we propose that a terminal alkyne complex isomerizes into a vinylidene complex *via* a 1,2-hydrogen shift. The corresponding mechanism is outlined in Fig. 4. Such an acetylene–vinylidene rearrangement is well known and has been described in the literature previously.[7]

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References

1 S. Steines, U. Englert and B. Drießen-Hölscher, *Chem. Commun.*, 2000, 217.
2 H. G. Niessen, D. Schleyer, S. Wiemann, J. Bargon, S. Steines and B. Drießen-Hölscher, *Magn. Reson. Chem.*, 2000, **38**, 747.
3 (*a*) R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, 1976, **98**, 2143; (*b*) M. W. van Laren and C. J. Elsevier, *Angew. Chem.*, 1999, **111**, 3926; M. W. van Laren and C. J. Elsevier, *Angew. Chem., Int. Ed.*, 1999, **38**, 3715.
4 (*a*) R. R. Burch, E. L. Muetterties, R. G. Teller and J. M. Williams, *J. Am. Chem. Soc.*, 1982, **104**, 4257; (*b*) R. R. Burch, A. J. Shusterman, E. L. Muetterties, R. G. Teller and J. M. Williams, *J. Am. Chem. Soc.*, 1983, **105**, 3546.
5 (*a*) T. C. Eisenschmidt, R. U. Kirss, P. P. Deutsch, S. I. Hommeltoft, R. Eisenberg, J. Bargon, R. G. Lawler and A. L. Balch, *J. Am. Chem. Soc.*, 1987, **109**, 8091; (*b*) J. Bargon, in *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, VCH, Weinheim, 1996, vol. II, p. 672.
6 (*a*) H. Suzuki, H. Omori, D. H. Lee, Y. Yoshida, M. Fukushima, M. Tanaka and Y. Moro-oka, *Organometallics*, 1994, **13**, 1129; (*b*) H. Omori, H. Suzuki, T. Kakigano and Y. Moro-oka, *Organometallics*, 1992, **11**, 989.
7 J. Silvestre and R. Hoffmann, *Helv. Chim. Acta*, 1985, **68**, 1461.