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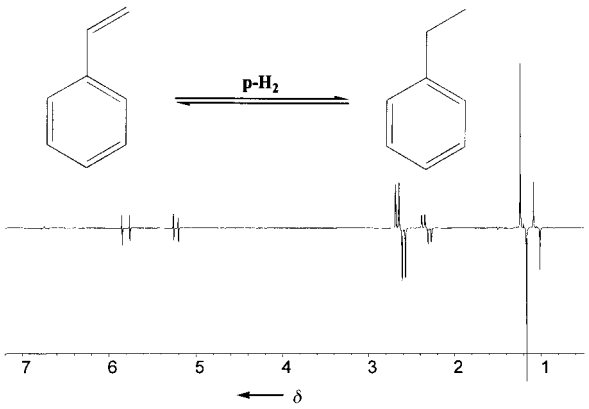


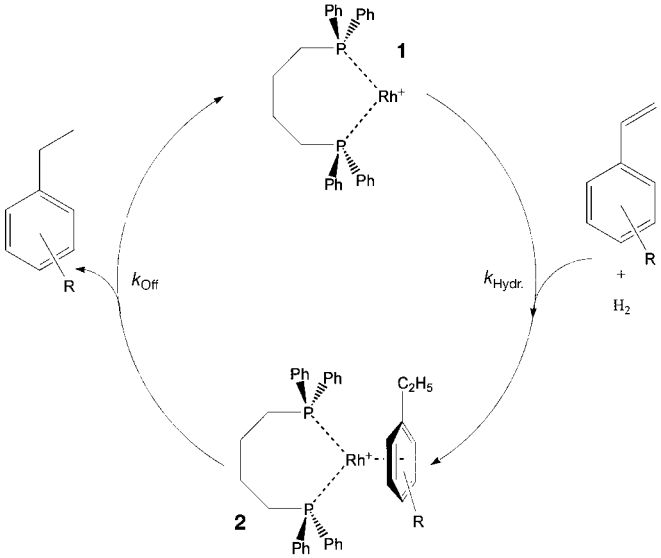
Figure 1. PHIP-NMR spectrum recorded 2 s after the end of the para-hydrogen addition to styrene and $[Rh(cod)(dppb)]BF_4$ in $[D_6]$acetone.

Intermediate Product – Catalyst Complexes in the Homogeneous Hydrogenation of Styrene Derivatives with Parahydrogen and Cationic Rh^I Catalysts

Ralf Giernoth, Patrick Huebler, and Joachim Bargon*

PHIP-NMR spectroscopy (PHIP = *p*ara*h*ydrogen *i*nduced *p*olarization) is an analytical method that provides profound insight into the mechanisms of homogeneously catalyzed hydrogenations, presupposed that the two parahydrogen nuclei remain *J*-coupled in the product molecule.[1–3] Recently, we have shown that PHIP-NMR spectroscopy is a suitable tool for the investigation of a pairwise hydrogen transfer into styrene, catalyzed by cationic Rh^I complexes.[4] In contrast to former assumptions,[5, 6] the corresponding catalytic cycle turned out to be partially reversible.[4] Herein, we report the PHIP-NMR spectroscopic detection of hydrogenation intermediates, which remain initially coordinated to the catalyst through their arene ring and then detach from the catalyst in a slow subsequent reaction step that influences the rate of the hydrogenation.

Addition of parahydrogen to a solution of styrene and the Rh^I precatalyst $[Rh(cod)(dppb)]BF_4$[7] in $[D_6]$acetone gave the PHIP-NMR spectrum shown in Figure 1. The product signals of ethylbenzene appear in the range of $\delta = 1-3$ (i.e., as an antiphase quartet at $\delta = 2.65$ and an antiphase triplet at $\delta = 1.20$).[8] In addition, high-field-shifted signals occur that show the same coupling constants as the signals of the free ethylbenzene. Evidently, they originate from product molecules just generated and still coordinated to the catalyst complex through their arene ring (Scheme 1). Their high signal intensities strongly suggest that the formation of the final hydrogenation product proceeds exclusively or predominantly via the intermediate product – catalyst complex.



Scheme 1. Simplified scheme for the hydrogenation turnover. The kinetic parameters k_{Off} and k_{Hydr} determine the degree of enrichment of the intermediate complex **2**. Saturation of free coordination sites at the Rh center with solvent or substrate molecules is not considered in this scheme.

A η^6 coordination of arenes to cationic Rh^I complexes has been extensively described before in the literature.[9a–f] For example, a slightly distorted η^6 coordination was found in the X-ray structure of $[Rh(P(OMe)_3)_2]BPh_4$.[9f] Likewise, the ^1H NMR spectrum of $[Rh(nbd)(C_6Me_6)]BF_4$[7] showed a singlet for the methyl protons over a wide range in temperature. The latter signal can, however, also be explained by a rapidly fluctuating η^4 coordination.[9a]

In the PHIP-NMR spectrum, the ratio of the catalyst attached to the free ethylbenzene (deduced from Figure 1) does not correspond to the thermodynamic equilibrium. If the delay between the end of the hydrogen addition and the detection pulse is extended to more than 30 s, this ratio

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strongly diminishes. Apparently, the production of attached species has decelerated and the detachment has now become the dominant reaction.

Consequently, conventional ^{1}H NMR spectroscopy of ethylbenzene and **1** (Scheme 1) in the thermodynamical equilibrium yields a much smaller ratio of intensity. Furthermore, the detection of separate and unbroadened signals leads to the conclusion that the detachment reaction is slow relative to the NMR time scale. Previous investigations of the homogeneously catalyzed hydrogenations of styrene derivatives did not take into account the consequences of an intermediate product attachment through the arene ring and the slow kinetics of the detachment process. Furthermore, the enrichment of the intermediate **2** (in contrast to the concentration in thermal equilibrium) a few seconds after the hydrogen addition is stopped suggests an important conclusion: under the assumption of the reaction scheme shown in Scheme 1, the enrichment of species **2** can only be explained, if the rate constant of its formation is at least of the same order of magnitude as the rate constant of its decomposition (or faster).

Likewise, the slow kinetics of the detachment process can be convincingly documented if the hydrogenation of [D_8]styrene is investigated with the PHIP method (Figure 2). Here,

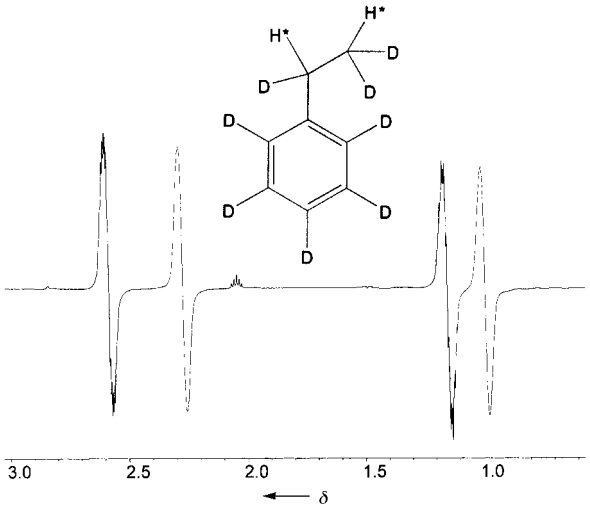

Figure 2. PHIP-NMR spectrum recorded after the parahydrogen addition to [D_8]styrene and [Rh(cod)(dppb)]BF_4 in [D_6]acetone.

the polarization signals of the free hydrogenation product show a fine-structure originating from the H – D couplings, whereas the corresponding signals of the bound species do not. This is due to the fact that the nonequilibrium concentration of the ethylbenzene still attached to the catalyst is diminished by the detachment process from the catalyst. Therefore, the lifetime of the bound species is shortened and the corresponding signals are broadened.[10]

With the chiral catalyst [((*R*)-(*S*)-JOSIPHOS)Rh(cod)]BF_4 (**3**) and 3-methylstyrene as the substrate, hydrogenation with parahydrogen leads to a mixture of products, as shown in the PHIP-NMR spectrum (Figure 3). In this case, *two* high-field-shifted antiphase triplets (at $\delta = 0.93$ and 1.09) appear. They originate from two possible diastereomeric product – catalyst

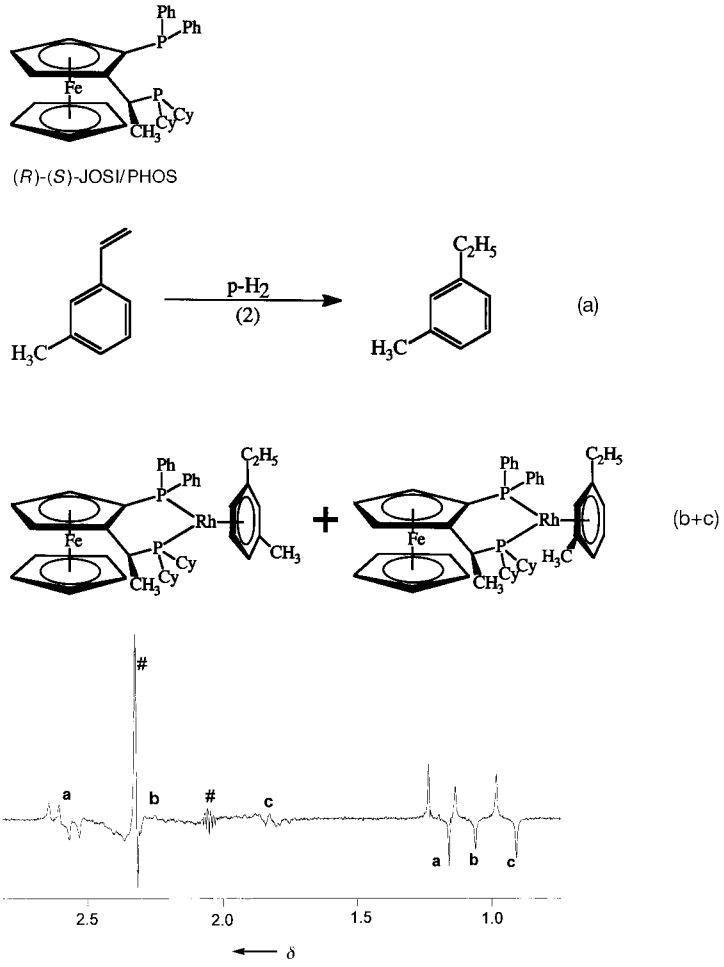

Figure 3. PHIP NMR spectrum recorded after the parahydrogen addition to 3-methylstyrene and **3** in [D_6]acetone. Structural proposals are given to explain the occurrence of the signals. NMR signals marked with # result from equilibrium magnetization incompletely supressed by the phase cycling (see Experimental Section). Cy = cyclohexyl.

complexes. The antiphase quartets corresponding to the two bound species additionally split up into two quartets as a consequence of the diastereotopy of the methylene protons. The experiment strongly indicates that, for symmetry reasons, the substrate is bound to the catalyst through the arene ring in two different fashions. Analogous to the major/minor theory of Halpern,[11] it is possible to distinguish between two stereochemically different reaction routes for the whole time of the hydrogenation turnover. Remarkably, both routes generate identical products, whereas two stereochemically different complexes only exist as the intermediates. The corresponding intensities depend both on the rates of their formation and on the rates of their decomposition.

Experimental Section

The ^{1}H NMR spectra were recorded at 298 K on a Bruker AC-200 NMR spectrometer with a proton resonance frequency of 200 MHz. Hydrogen was added within 5 s. To this end, a spectrometer-controlled capillary was lowered into the probe and hydrogen was bubbled through the solution. The detection pulse was set 2 – 5 s after the hydrogen addition had been stopped. NMR signals originating from the magnetization in the thermo-

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dynamical equilibrium[12] were eliminated by using alternating 45° and 135° detection pulses and accumulating eight consecutive FIDs.

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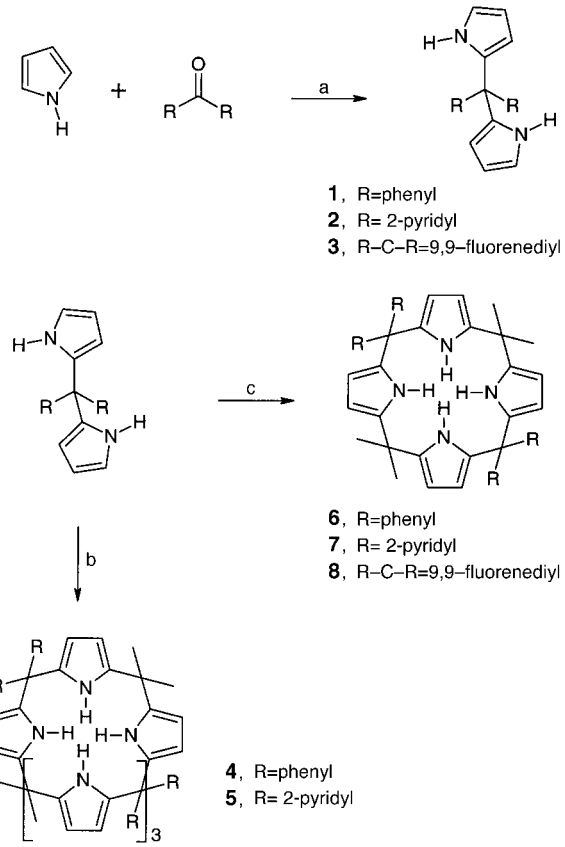
Extended Calixpyrroles: *meso*-Substituted Calix[6]pyrroles**

Boaz Turner, Mark Botoshansky, and Yoav Eichen*

Calix[*n*]pyrroles derived from pyrrole and simple ketones have recently become the subject of intensive research aimed at the development of novel ligands,[1] molecular hosts for anionic species[2–4] and for uncharged species such as simple alcohols, amines, and amides.[5] Octaalkylcalix[4]pyrroles, which are readily accessible, are hosts for fluoride and chloride ions both in solution and in the solid state. Some of these hosts exhibit a remarkable selectivity for binding fluorides rather than other halides even though the guest anion is bound outside the cavity.[3]

It is anticipated that larger calix[*n*]pyrroles with larger cavities will enable selective and effective complexation of other anionic as well as uncharged species. Nevertheless, despite the rather simple synthesis of *meso*-alkylcalix[4]pyrroles, the only extended calix[*n*]pyrrole reported to date is the calix[5]pyrrole – calix[5]arene, the product of condensation of pyrrole with *p-tert*-butyl calix[5]arene pentamethyl ketone derivatives.[4] Furthermore, the only calix[4]pyrroles reported to date are products of condensation between pyrrole and simple aliphatic ketones containing acidic protons at the C_α atom. Here we report on a new, two-step synthesis for the preparation of *meso*-substituted calix[6]pyrroles and some new, dissymmetric, *meso*-substituted calix[4]pyrroles.

Acid-catalyzed condensation of pyrrole with aromatic ketones such as benzophenone, di-(2-pyridyl) ketone and 9-fluorenone results in formation of the corresponding diaryldi-(2-pyrrolyl)methanes **1** – **3** in moderate to good yields (reaction a in Scheme 1). The diaryldi-(2-pyrrolyl)methane products failed to react further with the corresponding aromatic ketones to form linear polymers or cyclic products even after prolonged reaction times or at elevated temper-



Scheme 1. Synthesis of the *meso*-substituted calix[4]- and calix[6]pyrroles. a) Ketone/pyrrole = 1:2, $BF_3 \cdot OEt_2$, ethanol, room temperature, 7 days; b) pyrrole derivatives from reaction a) in ethanol/acetone (1/1), trifluoroacetic acid, room temperature, 7 days; c) pyrrole derivatives from reaction a) in ethanol/acetone (1/1), $BF_3 \cdot OEt_2$, room temperature, 7 days.

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