In situ Transfer of Parahydrogen-Induced Nuclear Spin Polarization—Structural Characterization of Hydrogenation Intermediates**

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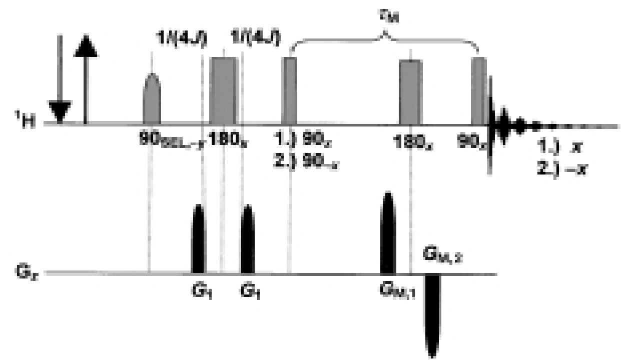
Recently, we reported the in situ detection of hydrogenation products intermediately attached to cationic Rh^I–diphosphane catalysts during the homogeneous hydrogenation of styrene derivatives.[1, 2] The detection of these hydrogenation intermediates present in very low concentrations was possible using PHIP NMR spectroscopy (PHIP = *p*ara*h*ydrogen-*i*nduced *p*olarization), which takes advantage of the large signal enhancement produced by the (pairwise) transfer of para-enriched hydrogen.[3, 4] The intermediate product–catalyst complexes have a life time of a few seconds at room temperature.[2] Several facts indirectly lead to the conclusion that the arene ring of the product molecule, for a short time, remains η^6-coordinated to the Rh^I center.[1] However, no direct proof for the intermediate bonding between the catalyst and the product molecule could so far be obtained. Based on the PHIP effect, we present the first NMR experiments that detect intra- and intermolecular cross relaxation (NOE)[5] within the life time of a hydrogenation intermediate. To that end, we used two NMR pulse sequences that, in one of many possible applications, detect a polarization transfer from the methylene proton of hydrogenated $[D_8]$styrene to the *o*-phenyl protons of the active catalyst species $[Rh(dppb)]^+$.[6] In this class of catalysts, the four phenyl groups form an "edge-face" array that, in the analogous case of chiral diphosphane ligands, represents the template for enantiorecognition of prochiral substrates.[7] In future work, polarization transfer from suitable auxiliary molecules to the surrounding will be used to investigate enantioselective hydrogenation, molecular recognition, and the structure of protein cavities with improved sensitivity.

The NOE is most frequently used for structural investigations with NMR spectroscopy,[8, 9] even though cross correlation effects recently have been exploited for this purpose.[10, 11] In contrast to conventional NMR spectroscopy, the initial density operator of PHIP is described by longitudinal two-spin order, $I_{1z}I_{2z}$ (with the two former parahydrogen nuclei numbered by 1 and 2).[4] However, bilinear operators can hardly be used to investigate intermolecular[12] interactions because the correlation of two spins is lost if the interaction is not pairwise.[13] Hence, the first step of the pulse sequences presented below is to convert two-spin order into longitudinal magnetization, I_{1z} (or into I_{1y} if an ROE[5] is used). Subsequently, the polarization is transferred to nuclei in the surrounding by cross relaxation by either an NOE or an ROE. We propose the reduction of two-dimensional to one-dimensional experiments in order to minimize the number of scans for in situ investigations under nonstationary conditions. The one-dimensional DPFGSE-NOE and GOESY[14] experiments developed by Shaka et al.[15, 16] form the basis for the development of pulse sequences for an NOE transfer in PHIP experiments. We chose the DPFGSE-NOE principle instead of GOESY because diffusion processes in low-viscosity solvents dramatically reduce the signal intensity in longer periods of spatial dephasing by pulsed-field-gradients.[15] To detect an in situ transfer of polarization, we developed the pulse sequences PH-1D-NOESY and PH-1D-ROESY outlined in Figure 1.

a) PH-1D-NOESY



b) PH-1D-ROESY

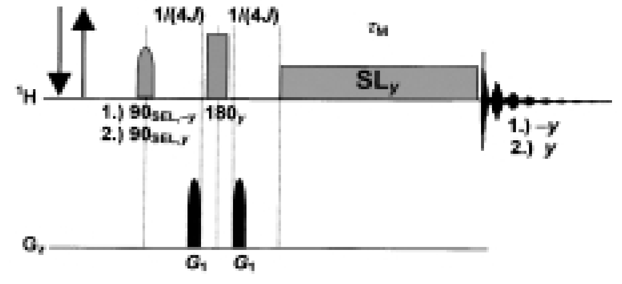


Figure 1. a) PH-1D-NOESY pulse sequence. The gray half ellipse represents the selective (SEL) pulse; the black half ellipses represent pulsed field gradients. The arrows indicate the up and down motion of the capillary providing a constant stream of parahydrogen. b) PH-1D-ROESY pulse sequence. SL_y represents a ROESY spinlock period with phase *y*.

By means of the excitation sequence $90_y(1)$-$1/(4J)$-G_1-180_x-G_1-$1/(4J)$-90_x, the operator $2I_{1z}I_{2z}$ is transformed into I_{1z}.[17, 18] This preparation sandwich is superior to the excitation by nonselective 45° pulses normally used,[3] because zero- (and double-) quantum coherence generated in the latter case produces artifacts in NOESY spectra. Furthermore, when using a selective excitation sandwich, the spectra represent rows of two-dimensional experiments.[19]

Imperfections of the pulses are eliminated by the pulsed field gradients. During the mixing time, τ_M, of the PH-1D-

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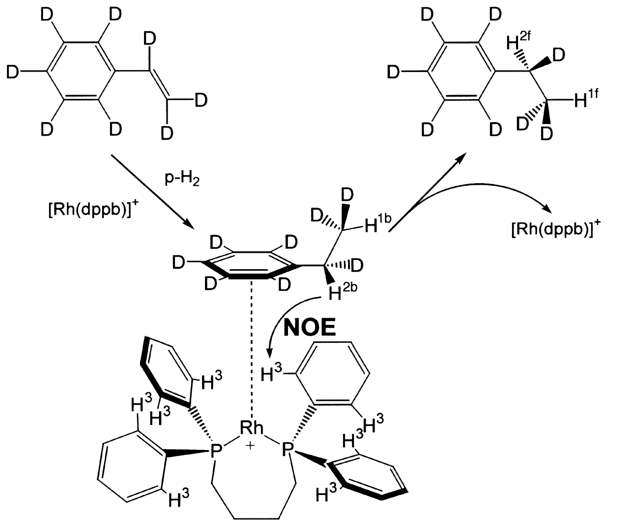
NOESY sequence (Figure 1a), I_{1z} is transferred to other nuclei by means of either cross relaxation or chemical reactions. Longitudinal magnetization produced by the thermal equilibrium and flipped by the 90_x pulse is eliminated by the pulsed field gradients during τ_M. Observable magnetization not created by means of the selective excitation is subtracted in every second scan. Additionally, T_1 recovery of thermally induced magnetization is reduced by the 180_x pulse during the mixing period τ_M. In contrast to conventional NMR experiments, $\langle I_{1z} \rangle$ and $-\langle I_{1z} \rangle$ both relax to zero because the density operator of the thermal equilibrium can be neglected. Therefore, in-phase magnetization is transferred during the entire mixing time and is accumulated by the phase cycling. Relayed production of two-spin order due to the hydrogenation is not observable.

The pulse sequence PH-1D-NOESY was applied to the reaction depicted in Scheme 1. For our experiments, we chose [D$_8$]styrene as the substrate to approximately establish the simple condition of an AX spin system in the product. To observe small effects under real catalytic conditions, we used [Rh(dppb)(cod)]BF$_4$[6] as the catalyst precursor in D$_2$O/CD$_3$OD (2:3; $c = 0.5$ mM). The resulting PH-1D-NOESY spectra are shown in Figure 2.



Scheme 1. Observable steps of the hydrogenation of [D$_8$]styrene with [Rh(dppb)]$^+$.

As can be seen in Figure 2b, in situ polarization transfer from attached [D$_8$]ethylbenzene to the o-phenyl protons H^3 of the catalyst occurs when proton H^{2b} is excited selectively. This proves that H^{2b} and H^3 are connected through a time-modulated dipolar interaction causing the cross relaxation rate σ^{NOE}.[20] According to Figure 2a, no cross relaxation occurs if the corresponding proton H^{2f} of free [D$_8$]ethylbenzene is excited. The signals between $\delta = 0.9$ and 2.7 stem from a superposition of the detachment process of [D$_8$]ethylbenzene (leading to a peak with positive intensity) and the dipolar interactions between H^{1b} and H^{2b} and H^{1f} and H^{2f} (leading to a peak with negative intensity). Compared to the excitation of H^{2b}, a smaller signal is detected at the resonance of the catalyst if the methyl proton H^{1b} is excited (Figure 2c). This corresponds to the larger (time-averaged) distance to the catalyst. The negative signal for H^{1f} in Figure 2c is a consequence of partially exciting this proton. For all experiments, Gaussian-shaped selective pulses with a duration of 35 ms were used.

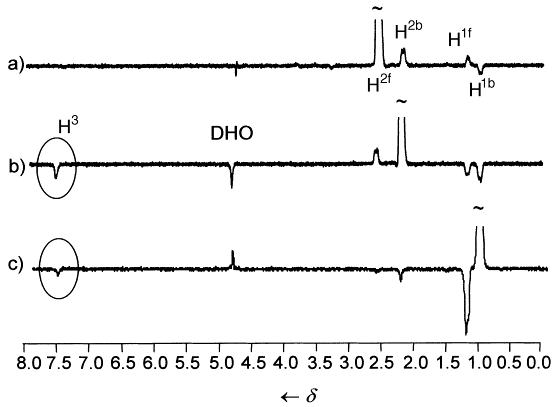


Figure 2. Experimental results of applying the PH-1D-NOESY sequence to the reaction depicted in Scheme 1. The resonance excited by the selective pulse is cut off. Each spectrum was recorded with four scans.

An intramolecular NOE transfer from dihydride ligands to o-phenyl protons based on the PHIP effect has already been observed in the case of a steady-state formation of stable Ir^I di- and trihydride complexes.[21, 22] The spectra in Figures 2 and 3, however, represent the first direct proof of a dipolar interaction between a hydrogenated molecule and a catalyst within an intermediate state. PH-1D-NOESY experiments are restricted to cases where this intermediate lives for a period of time (at least half a second) that is long enough for an in situ detection.

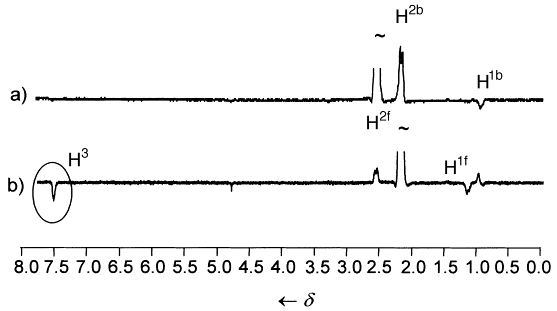


Figure 3. Experimental results of applying the PH-1D-ROESY sequence to the reaction depicted in Scheme 1. Each spectrum was recorded with four scans.

In medium-sized molecules where the spectral density function for cross relaxation is small or even zero, the ROESY technique usually is applied which detects cross relaxation in the rotating frame.[23] During a spinlock-period, (in-phase) y-magnetization is transferred to the neighboring protons. The corresponding pulse sequence PH-1D-ROESY is outlined in Figure 1b. Again, phase cycling is used to eliminate all magnetization that has not been produced by the selective excitation sequence. Under the same experimental conditions as chosen for the experiments in Figure 2 but using the pulse sequence PH-1D-ROESY, very similar spectra are obtained

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(Figure 3). Again, excitation of the proton H^{2b} yields a cross relaxation signal at the resonance of the catalyst proton H^3, whereas excitation of the proton H^{2f} does not.

Experimental Section

All NMR experiments were conducted at 298 K using a Bruker DRX200 spectrometer. The chemicals were used as obtained by Aldrich. The enrichment of parahydrogen was performed at 77 K catalyzed by activated charcoal. For the PHIP experiments, the resulting 50:50 mixture of ortho- and parahydrogen was bubbled through the reactive solution inside of the magnetic field for 3 s.

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[5] NOE = nuclear Overhauser effect; ROE = rotating frame nuclear Overhauser effect.

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Hexaaryltetragermabuta-1,3-diene: A Molecule with Conjugated Ge=Ge Double Bonds[**]

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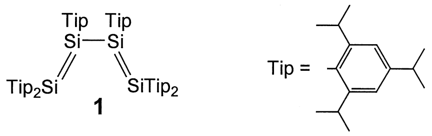
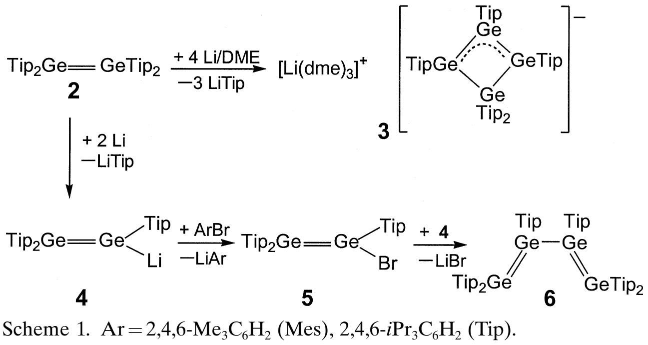
With the recent isolation of the first diplumbenes,[1, 2] molecules containing a short lead–lead double bond, homonuclear double bonds of the type $R_2E{=}ER_2$ (E = C, Si, Ge, Sn, Pb) are now known between all elements of Group 14.[3] The strong decrease in bond dissociation energies of these double bonds from silicon to lead is reflected in the distinctly different behavior in the crystalline state and in solution. Under exclusion of air and moisture all compounds are stable in the solid state. This is also true for solutions of most disilenes, whereas digermenes tend to dissociate partly into germylenes R_2Ge:. Distannenes and diplumbenes, on the other hand, exist almost exclusively as stannylenes R_2Sn: and plumbylenes R_2Pb: in solution.[3]

Recently, we obtained the tetrasilabuta-1,3-diene **1**, the first and to date only molecule containing conjugated Si=Si double bonds. The most remarkable feature of this brownish-red substance **1** is that it adopts the s-*cis* conformation in the solid state,[4] which is also the favored form in solution. We have now examined if the germanium compound **6** analogous to **1** is accessible by following a similar synthetic approach (Scheme 1).



As a starting compound we chose the tetraaryldigermene **2** whose structural integrity, according to previous investiga-



Scheme 1. Ar = 2,4,6-$Me_3C_6H_2$ (Mes), 2,4,6-$iPr_3C_6H_2$ (Tip).

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