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In situ NMR Observation of Tin Trichloride-Activated Rhodium Dihydride Complexes Using Parahydrogen Induced Polarization

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Abstract—Starting from the binuclear complex $[RhCl(CO_2)]_2$ in the presence of the phosphines L=PMe_3, PMe_2Ph, and $PMePh_2$ various mononuclear dihydrides of the type $Rh(H)_2(SnCl_3)L_3$ have been obtained upon the addition of parahydrogen, and their ^1H NMR spectra have been investigated using **P**ara**H**ydrogen **I**nduced **P**olarization (PHIP). © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Homogeneous hydrogenation with parahydrogen yields strong **P**ara**H**ydrogen **I**nduced **P**olarization (PHIP) in the NMR spectra of the reaction products[1–7] originating from the breakdown of the initially high symmetry of parahydrogen as the consequence of a chemical reaction. The transfer of the two formerly equivalent parahydrogen protons into either chemically or magnetically inequivalent positions leads to a selective population only of those energy levels which possess some degree of singlet character. The associated deviation from the thermal equilibrium of the spin system, which is determined by the Boltzmann distribution, causes enhanced emission and absorption signals in the NMR spectra of the hydrogenation products, a phenomenon termed either PASADENA[2] (**P**arahydrogen **A**nd **S**ynthesis **A**llow **D**ramatically **E**nhanced **N**uclear **A**lignment) or PHIP.[3] The occurrence of this phenomenon requires, however, that the transfer of the two parahydrogen atoms occurs pairwise, i.e. simultaneously, whereby the transferred protons have to experience some sort of mutual interaction at any time. The associated signal enhancement is considerable and allows detection of reaction intermediates and products at lower concentrations than is feasible via conventional NMR. Therefore, this method has become a versatile tool to investigate the structure of many hydrogen-containing transition metal complexes, typically of dihydrides.[6]

The maximum signal can be detected with a flip angle of $\pi/4$ in contrast to conventional NMR using a $\pi/2$-pulse. This fact can be taken advantage of to eliminate interfering resonances stemming from unpolarized systems, i.e. from molecules which do not participate in the hydrogenation sequence. This includes the resonances stemming from the solvent, from unpolarized starting material, or from previously formed product molecules, which have since reached thermal equilibrium. For this purpose, individual scans are accumulated, whereby the flip angles are alternated between $-\pi/4$ and $3\pi/4$, consecutively. As a consequence of this change of the flip angle by 180° between two consecutive pulses, the amplitudes of thermal NMR resonances alternate in signs, whereas the signs of the PHIP signals remain the same, irrespectively. Accordingly, upon accumulating the corresponding signals the unpolarized resonances are suppressed and eliminated, whereas the polarized PHIP resonances add up and become accumulated to yield a better signal-to-noise ratio.

Results and Discussion

Previously, we have observed dihydrides of the type $Rh(H)_2(SnCl_3)L_3$ with L=PPh_3, $PEtPh_2$ and PEt_3, containing the activating tin trichloride ligands.[8–10] These dihydrides had been obtained starting from $[RhH(SnCl_3)_5]^{3-}$ in the presence of added phosphine.[11] However, this approach is not universally applicable. Therefore, in this study, we have chosen a different route, starting from the binuclear precursor $[RhCl(CO)_2]_2$ (**1**), in the presence of $SnCl_2$ (**2**), and the corresponding phosphine PMe_3 (**3a**), PMe_2Ph (**3b**), or $PMePh_2$ (**3c**) at a ratio of Rh:Sn:P=1:1:3 in acetone-d_6. Upon addition of parahydrogen to this mixture, the dihydrides $Rh(H)_2(SnCl_3)L_3$ (L=**4a–c**) are formed (Scheme 1), most likely via the complex $Rh(SnCl_3)L_3$, and their ^1H NMR resonances are detected in situ exhibiting PHIP (Fig. 1).

Fig. 1 shows polarized resonances of the dihydride protons of the complex $Rh(H)_2Cl(PMe_3)_3$ (**4a**), obtained upon

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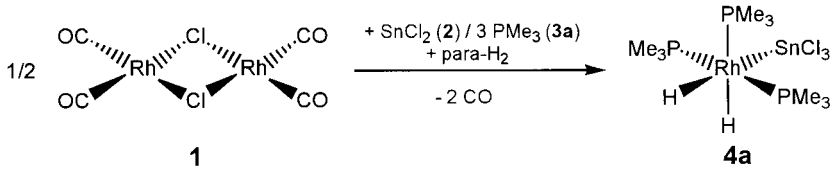

Scheme 1.

addition of parahydrogen to a solution of **1** (10 mg, 0.026 mmol), **2** (9.8 mg, 0.026 mmol) and **3a** (16 μl, 0.154 mmol) in acetone-d_6 at 315 K (**1**:**2**:**3a**=1:1:3). The hydride H^1 *trans* to a PMe_3 ligand occurs at −10.3 ppm, whereas the hydride H^2 *trans* to the tin trichloride ligand has a higher chemical shift and appears at −12.0 ppm. Since tin has two NMR-active isotopes, namely ^{117}Sn and ^{119}Sn with I=1/2 each, the hydrides *trans* to the corresponding isotopes in the tin trichloride show large couplings, i.e. $^2J_{(H119Sn)}$=1589 Hz or $^2J_{(H117Sn)}$=1520 Hz, respectively, which cause the weak tin satellites (Fig. 1; 'sat.'). The ratio of these coupling constants $^2J_{(H117Sn)}/^2J_{(H119Sn)}$ corresponds to the ratio of the gyromagnetic ratios of the tin isotopes (γ_{117Sn}=−9,578 rad T^{-1} s^{-1})/(γ_{119Sn}=−10,021 rad T^{-1} s^{-1}). The hydride resonance at lower field shows a large coupling to one *trans* ($J_{HP(trans)}$=142.2 Hz) and two equivalent *cis* phosphorus nuclei ($J_{HP(cis)}$=19.2 Hz), a coupling to the central rhodium (J_{HRh}=13.7 Hz), and a coupling to the upfield hydride proton ($J_{HH'}$=−5.8 Hz). The second hydride resonance at higher field is a complex multiplet with couplings to rhodium (J_{HRh}=28.5 Hz), the equatorial and the two axial phosphorus nuclei ($J_{HP(ax.)}$=$J_{HP(eq.)}$=14 Hz), and the lower field hydride proton ($J_{HH'}$=−5.8 Hz). Simulation of the resulting PHIP patterns using the computer program PHIP^{++} yields very good agreement confirming these data.[12] Using the phosphine

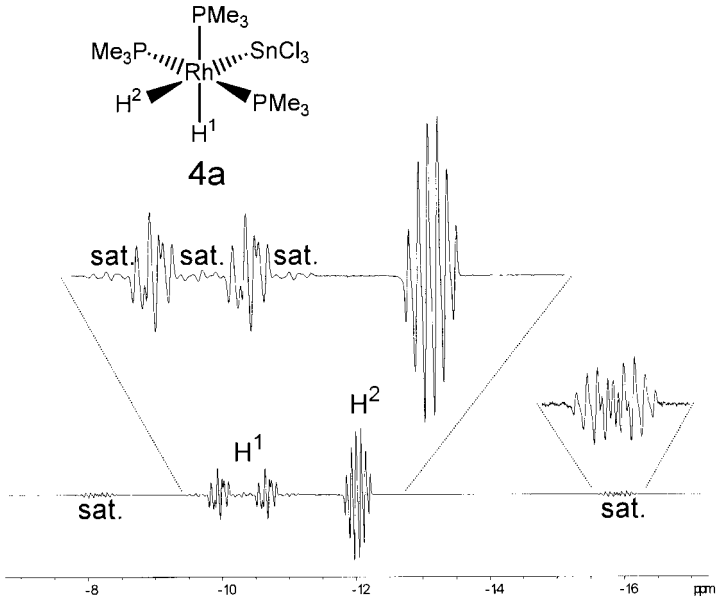

Figure 1. The hydride region of the ^{1}H NMR spectra obtained using a sample of **1**, **2** and **3a** in acetone-d_6 (**1**:**2**:**3a**=1:1:3) after bubbling parahydrogen through the solution for 5 s at 315 K. The spectrum shows the hydride resonances of the complex $Rh(H)_2(SnCl_3)(PMe_3)_3$ (**4a**) which have been recorded with 16 scans. The hydrides have been enlarged above the original spectra (sat.=$^{117/119}$Sn-satellites).

Table 1. ^{1}H NMR data of the reported dihydrides **4a**–**c**

No.	Complex	^{1}H Chemical shifts δ [ppm] in acetone-d_6 and coupling constants J [Hz]
4a	$Rh(H)_2(SnCl_3)(PMe_3)_3$	−10.3 ($^1J_{RhH}$=13.7, $^2J_{PH(trans)}$=142.2, $^2J_{PH(cis)}$=19.2, $^2J_{HH}$=−5.8 $^2J_{(H119Sn)}/^2J_{(H117Sn)}$=144 −12.0 ($^1J_{RhH}$=28.5, $^2J_{PH(ax.)}$=14, $^2J_{PH(äq.)}$=14, $^2J_{HH}$=−5.8), $^2J_{(H119Sn)}$=1589, $^2J_{(H117Sn)}$=1520
4b	$Rh(H)_2(SnCl_3)(PMe_2Ph)_3$	−10.2 ($^1J_{RhH}$=13.4, $^2J_{PH(trans)}$=141.8, $^2J_{PH(cis)}$=18.5, $^2J_{HH}$=−5.5 $^2J_{(H119Sn)}/^2J_{(H117Sn)}$=142 −11.3 ($^1J_{RhH}$=27, $^2J_{PH(ax.)}$=11.5, $^2J_{PH(äq.)}$=11.5, $^2J_{HH}$=−5.5), $^2J_{(H119Sn)}$=1540, $^2J_{(H117Sn)}$=1470
4c	$Rh(H)_2(SnCl_3)(PMePh_2)_3$	−9.8 ($^1J_{RhH}$=13.2, $^2J_{PH(trans)}$=141.8, $^2J_{PH(cis)}$=12.4, $^2J_{HH}$=−4.8 $^2J_{(H119Sn)}/^2J_{(H117Sn)}$=129 −11.2 ($^1J_{RhH}$=22.2, $^2J_{PH(ax.)}$=9.5, $^2J_{PH(aq.)}$=9.5, $^2J_{HH}$=−4.8), $^2J_{(H119Sn)}$=1460, $^2J_{(H117Sn)}$=1413

ligands **3b** and **3c** the related complexes **4b** and **4c** have also been observed and analyzed with ^{1}H NMR spectroscopy (Table 1).

Upon the addition of phosphine to the solvated complex **1**, the replacement of CO becomes evident via gas bubbles escaping from the solution. No dihydrides containing residual CO as a ligand have been detected.

At higher temperatures, the intensities of the polarized hydride resonances increase significantly at the expense of resolution, apparently due to efficient exchange of the phosphine ligands. In acetone-d_6, experiments in open systems can be carried out up to about 330 K, since above this value boiling and evaporation of the solvent becomes so significant that this deteriorates the resolution of the spectra even further. Decreasing the temperature sharpens the resonances, since then the rate of phosphine dissociation slows down. The spectrum shown in Fig. 1 has been recorded at 315 K. This study demonstrates the high sensitivity of the PHIP NMR method to identify intermediate dihydrides at correspondingly low concentrations.

Experimental

The complex $[RhCl(CO)_2]_2$, $SnCl_2$, and the phosphines PMe_3, PMe_2Ph, and $PMePh_2$ were all purchased from Aldrich and used as obtained. The solvent acetone-d_6 (Eurisotop) was dried using standard methods and stored under argon prior to use. The spectra were recorded using a Bruker AC 200 FT-NMR spectrometer. Chemical shift values are given in ppm using acetone-d_6 at 2.05 ppm as internal reference.

In situ hydrogenation using parahydrogen

Para-enriched hydrogen containing about 50% para-H_2 was prepared by passing H_2 through activated charcoal at 77 K at a pressure of 3 bar as described in literature.[13]

The hydrogenation with parahydrogen is carried out in situ. For this purpose, a glass capillary connected to the parahydrogen source can be lowered into the NMR probe actuated by an electromagnet, i.e. by a solenoid, which is electrically controlled by the computer of the NMR spectrometer. In this fashion, parahydrogen can be bubbled through the reaction mixture for a defined period of time followed by the detection pulse of the NMR experiment. In most cases, a hydrogenation time of 3 s has turned out to be sufficient. About 2 s after the hydrogen addition has stopped, the NMR detection can start. This procedure can be repeated to afford a subsequent accumulation of several scans, which yields a good signal-to-noise ratio of the PHIP resonances and allows suppression of signals of components, which are uninvolved in the hydrogenation as outlined above. The spectrum in Fig. 1 is the result of the accumulation of 16 scans, thereby alternating the flip angles between $-\pi/4$ and $+3\pi/4$, respectively, to suppress any thermal signals.

General procedure for the in situ generation of the complexes 4a–c

Typically, the rhodium complex **1** (10 mg, 0.026 mmol), **2** (9.8 mg, 0.026 mmol) and the corresponding amount of phosphine ligand **3a–c** (0.154 mmol) are placed into a 5 mm NMR tube (**1**:**2**:**3a–c**=1:1:3) together with 750 μl degassed acetone-d_6. The NMR tube is placed in the magnetic field of the spectrometer and heated up to 315 K. Parahydrogen is added in situ according to the above described procedure.

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