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Parahydrogen induced polarization in the Pt(0)-mediated hydrogenation of alkynes and alkenes

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1. Introduction

During the past years parahydrogen induced polarization (PHIP) has been established as a valuable mechanistic probe for homogeneously catalyzed hydrogenation reactions [1]. First proposed in 1986 by Bowers and Weitekamp [2,3], this NMR technique facilitates elucidation of the reaction mechanisms of pairwise hydrogen transfer to substrate molecules. In particular it allows to identify unstable dihydride intermediates that participate in the catalytic cycles [4–7]. Using this technique, hydrogenation reactions catalyzed by rhodium [6–10], iridium [11], palladium [4,12], and ruthenium [13] complexes have been studied.

Despite the fact that platinum complexes are well known catalysts for hydrogenation [14,15], hydroformylation [16,17], and hydrosilylation [18] reactions, no PHIP studies of these reactions have yet been reported. Here, we report for the first time that the PHIP technique works successfully, when catalytic hydrogenations of alkynes with various homogeneous platinum complexes are studied. In these cases, the hydrogenations are expected to proceed similarly to the hydrogenation using Schrock's rhodium catalysts [18]. Accordingly, oxidative addition of hydrogen to the platinum complex occurs during the catalytic cycle. In addition, an exchange of ligands liberates coordination sites for unsaturated substrates. Subsequent to these steps, a reductive elimination leads to the formation of the hydrogenation product [19–28].

Since we expected only small amounts of hydrogenation products, and also very unstable dihydride com-

plexes during the hydrogenation with the platinum complexes, the use of parahydrogen was considered specifically helpful to study the mechanisms of these hydrogen transfer reactions. In particular, we investigated the hydrogenations of phenylacetylene and of *tert*-butylacetylene as model substrates with three different types of platinum complexes, namely $(PPh_3)_2Pt(\text{alkyne})$, $(PPh_3)_2Pt(C_2H_4) + \text{alkyne}$ and $(PMePh_2)_2PtHCl + SnCl_2 + \text{alkyne}$. In all of these cases we detected polarization signals, indicating pairwise transfer of hydrogen to the unsaturated substrates. This is a surprising result, especially for the hydrogenation with the tin-activated complexes.

2. Experimental

The platinum complexes $Pt(PPh_3)_2(\text{phenylacetylene})$, $Pt(PPh_3)_2(\text{diphenylacetylene})$ [22], $PtHCl(PPh_3)_2$ [29], $PtHCl(PMePh_2)_2$ [30] and $PtCl_2(PPh_3)_2$ [31] were synthesized as described in the literature. $Pt(PPh_3)_2(C_2H_4)$, tin dichloride, phenylacetylene, norbornadiene, and *tert*-butylacetylene were obtained from Aldrich, and were used without further purification. Benzene- d_6 and acetone- d_6 , also obtained from Aldrich, were dried over phosphorus pentoxide, degassed, and stored under vacuum. Parahydrogen was enriched as described in the literature [4].

2.1. Preparation of the $PtHCl(PR_3)_2-SnCl_2$ complex with $PR_3 = PPh_3$ and $PMePh_2$

Platinum hydride (25 mg, 0.04 mmol) and anhydrous tin dichloride (60 mg, 0.2 mmol) were placed into a

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1-ml Schlenk tube and positioned over a magnetic stirrer. Approx. 0.7 ml of dry and degassed benzene- d_6 or acetone- d_6 was condensed into the Schlenk tube using a vacuum line, and the mixture was stirred for 1 h under argon. Remaining connected overnight to the vacuum line, the solution was transferred under argon into an NMR tube.

2.2. Preparation of the catalytically active reaction mixtures

2.2.1. $Pt(PPh_3)_2(\text{alkyne})$ complexes

Approx. 50 mg of platinum complex was placed into a Wilmad screw-cap 5-mm NMR tube and connected to the vacuum line. Then 0.7 ml of dry and degassed deuterated solvent was condensed into the tube. The tube was flushed with argon and sealed with a silicone rubber septum.

2.2.2. $Pt(PPh_3)_2(C_2H_4)$ complexes + alkyne

30 mg of platinum complex and 60 mg of alkyne was placed into a Wilmad screw-cap 5-mm NMR tube and connected to the vacuum line. Then 0.7 ml of dry and degassed deuterated solvent was condensed into the tube. The tube was flushed with argon and sealed with a silicone rubber septum.

2.2.3. $PtHCl(PR_3)_2-SnCl_2$ complexes + alkyne

To the prepared solution (preparation described above) of $PtHCl(PR_3)_2-SnCl_2$, 60 mg of phenylacetylene was added. The tube was flushed with argon and sealed with a silicone rubber septum.

2.2.4. Hydrogenation

After dissolution of the solids, parahydrogen was added via a stainless steel capillary up to a pressure of 3 bar. After heating to 120°C, the tube was shaken and inserted into the probe head.

All spectra were obtained at room temperature with a Bruker AC-200 spectrometer, using a 5-mm probe operating at 200 MHz (1H) and 80,961 MHz (^{31}P). For the detection of the polarization phenomena associated with the PHIP-phenomenon, a 45-degree pulse was applied [5]. The FIDs were recorded 15–20 s after initiation of the hydrogenation reaction, stored, and processed subsequently.

3. Results and discussion

3.1. The $Pt(PPh_3)_2(\text{alkyne})$ complexes

When parahydrogen was added to a saturated solution of $Pt(PPh_3)_2(\text{phenylacetylene})$ in benzene- d_6 up to 3 bar, and the solution was heated to boiling, polarization signals in the olefinic region of the 1H -NMR

spectrum were observed. The signals at 5.1 ppm, 5.6 ppm, and 6.5 ppm are assigned to the protons of styrene. They clearly indicate 1,2-*cis*-hydrogenation, because of the strong polarization in the positions 5.1 ppm and 6.5 ppm. Furthermore, the polarization pattern of the proton at 5.6 ppm can be attributed to a strong polarization transfer due to the Nuclear Overhauser Effect (NOE) (Fig. 1a). The simulation of these patterns with the computer program PHIP 7d¹ confirms these assignments (Fig. 1b). The hydride region of the proton spectrum shows no polarization patterns, indicating a fast reaction of the intermediate dihydride after an oxidative addition of hydrogen to the Pt complex.

After prolonged heating, a broad signal at -5.46 ppm with ^{195}Pt satellites became visible ($^1J(Pt-H) = 695$ Hz) (Fig. 2). This signal also appeared when the complex $Pt(PPh_3)_2(\text{phenylacetylene})$ was heated in benzene- d_6 in the absence of any hydrogen. It can be assigned to the hydrogen-product of the oxidative addition of side-on coordinated phenylacetylene, to yield the *trans*- $PtH(CCPh)(PPh_3)_2$ complex. An analogous reaction was observed by Furlani et al. [32] of *trans*- $Pt(CCPh)_2(PPh_3)_2$ with a slight excess of phenylacetylene. The absence of the phosphoroushydride coupling is attributed to the rapid exchange of phosphines.

Similar investigations conducted with the Pt-tolene complex $[Pt(PPh_3)_2(PhCCPh)]$ revealed strong polarization signals in the olefinic region (6.6 ppm) as well. We could not obtain similar hydrogenation results with Wilkinson- or Schrock-type catalysts or with any other catalysts on the tolene complex.

After several hours the ^{31}P spectra of both complexes showed a large number of lines in the range of -10 ppm to +40 ppm, indicating decomposition of the complexes during that time.

3.2. The $Pt(PPh_3)_2(C_2H_4)$ complex and related reactions

The $Pt(PPh_3)_2(C_2H_4)$ complex is much less stable than its alkyne analogs. In the 1H spectrum it shows signals of free ethene when dissolved in benzene at room temperature. Therefore, its hydrogenation proceeds even more rapidly than the hydrogenation with the alkyne complexes. Spectra recorded from a parahydrogen saturated solution of the catalyst in benzene shows, after the solution has been heated to about 80°C, continuously decreasing signals of the coordinated ethene. No platinum dihydride complex is observed in this case.

¹ The computer program PHIP 7d has been developed at the University of Bonn to calculate and simulate PHIP spectra of products containing up to 7 spin. (J. Kandels, T. Greve, J. Bargon, unpublished data).

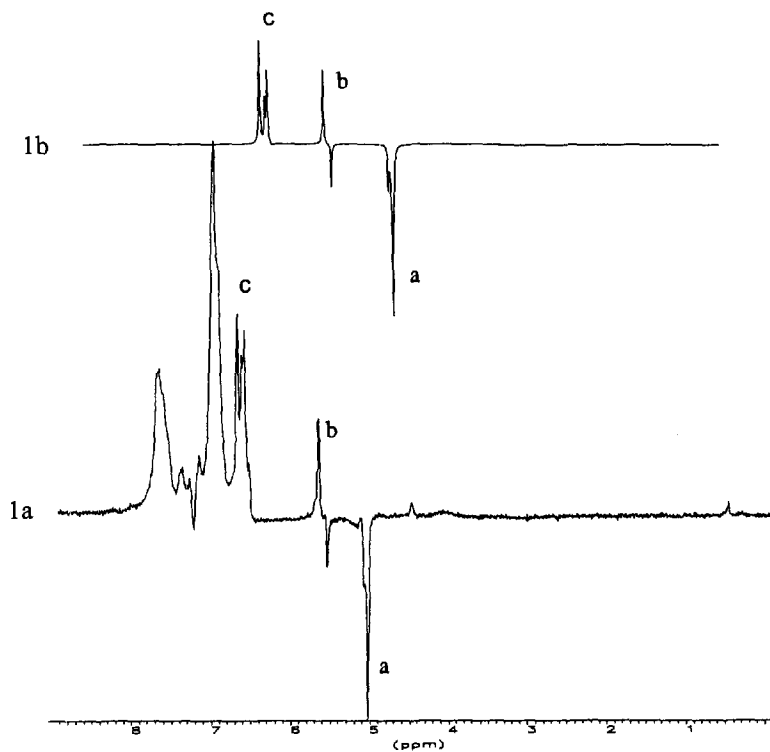


Fig. 1. 200 MHz ¹H-NMR spectra. a: spectra of the hydrogenation of phenylacetylene to styrene. b: simulation of the hydrogenation with the computer program, PHIP 7d.

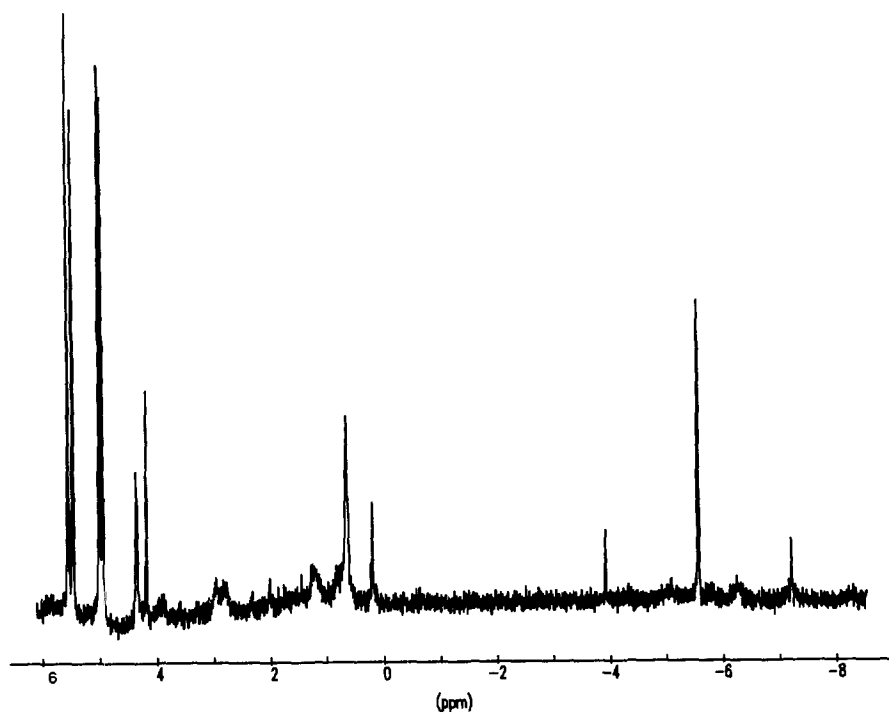


Fig. 2. 200 MHz ¹H-NMR spectra of PtH(CCPh)(PPh₃)₂.

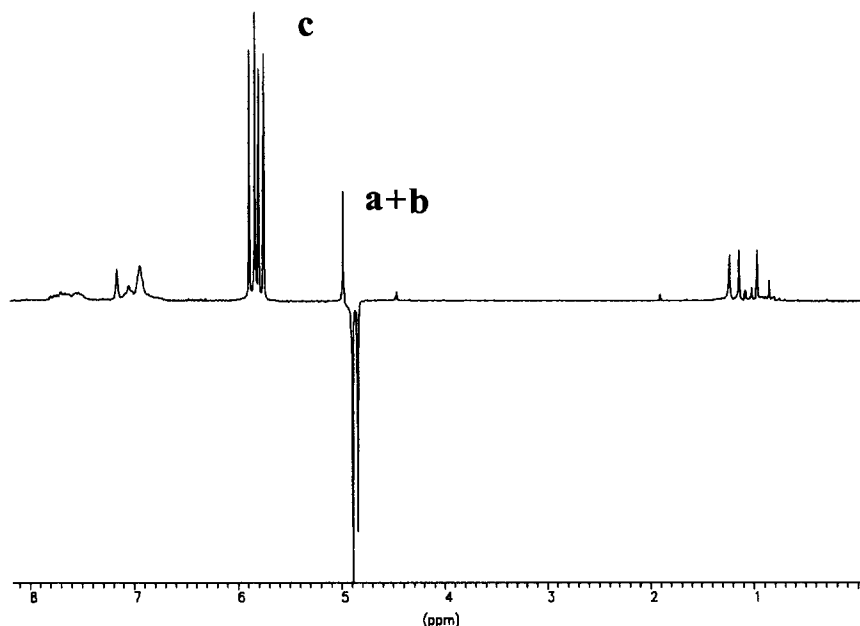


Fig. 3. 200 MHz ^1H -NMR spectra. PHIP-spectra of the hydrogenation of 3,3-dimethyl-1-butyne with the $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ complex.

The addition of free *tert*-butylacetylene (3,3-dimethyl-1-butyne) to a benzene solution of the ethene complex also causes a decrease of the coordinated ethene signal, indicating its displacement by the unsaturated substrate. This was confirmed by ^{31}P spectra where the signals of the $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ complex disappeared after the addition of the alkyne. Addition of

parahydrogen up to a pressure of 3 bar at room temperature leads to polarization signals of *tert*-butylethene (3,3-dimethyl-1-butene) (Fig. 3) and indicate a pairwise *cis* addition of hydrogen to the triple bond. Since we did not observe the dihydride complex, a reaction similar to the one reported for the side-bonded alkyne complexes described above is assumed.

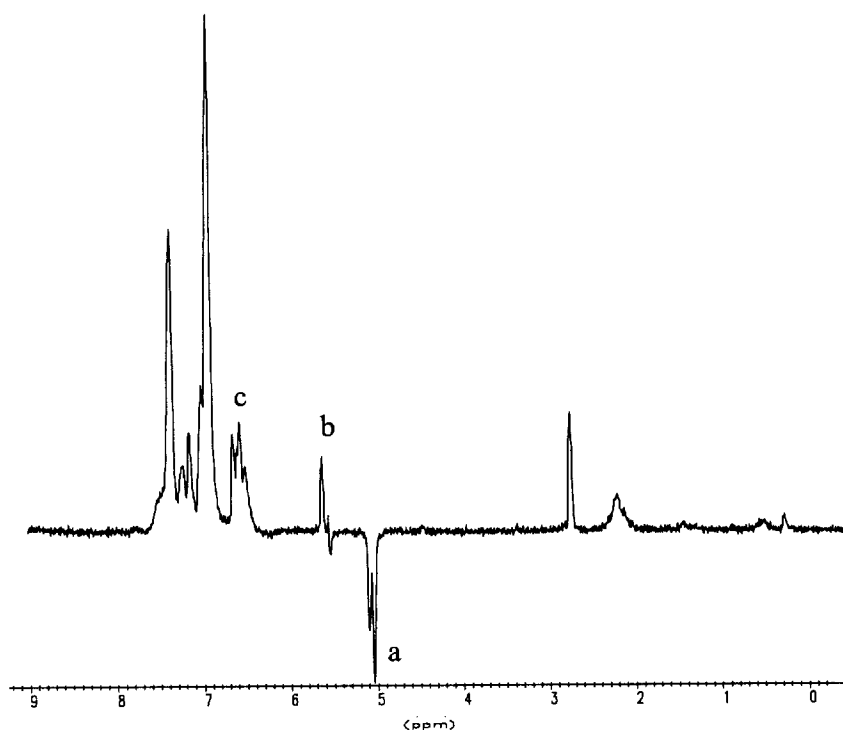


Fig. 4. 200 MHz ^1H -NMR spectra. PHIP-spectra of the hydrogenation of phenylacetylene to styrene using $\text{PtHCl}(\text{PMePh}_2)_2 + 5 \text{SnCl}_2$.

3.3. The $PtHCl(PMePh_2)_2 + SnCl_2$ system

The interaction of the platinum hydride complex $PtHCl(PMePh_2)_2$ with anhydrous $SnCl_2$ in benzene results in the formation of a clear dark-red solution. This interaction of $SnCl_2$ with Pt-complexes was shown before [33–37]. Addition of parahydrogen to this solution cause no changes in the hydride region of the proton NMR, indicating poor stability of the expected Pt(IV)–dihydride complexes. But the hydrogenation of phenylacetylene with this solution after addition of 3-bar parahydrogen and slight heating shows polarized signals of styrene (Fig. 4). This result was unexpected, since according to the generally adopted scheme, this catalytic system should follow a two-step hydrogenation mechanism [38,39], which should not yield any polarization. Pt(II)–monohydride complexes are considered to act as catalysts, thereby inserting the unsaturated substrate into the Pt–H bond. Thereafter the arising alkyl or alkenyl complexes are hydrogenolyzed via Pt(IV)–dihydride intermediates, liberating the catalyst. This mechanism would not lead to polarization, because of a loss of the ‘pairwise information’ of parahydrogen. Two principal steps of the catalytic cycle, the insertion of the alkene [40,41] and the hydrogenolysis of the alkyl complexes [20], have been reported. Nevertheless, the observation of polarization during the hydrogenation indicates that the Pt(0)-mediated route is also operative. This route can include the formation of Pt(0) species as a result of a tin dichloride or hydrogen reduction followed by oxidative addition of hydrogen to form an active dihydride. This dihydride is supposedly unstable and transfers parahydrogen to the unsaturated substrate, causing polarized signals in the proton spectra of the hydrogenation product. Another possibility is the formation of Pt(0) alkyne species and their hydrogenation in the manner as outlined in the first part of this publication.

It should be noted that the polarization effects observed during the Pt–Sn catalyzed hydrogenation has poor reproducibility. The result is dependent on the particular composition of the catalyst and the conditions of its formation. The Pt–monohydride–tin dichloride systems as studied here show complicated equilibria in solution [35,36], and further investigations will be performed on these systems in order to elucidate the particular conditions which favor either the monohydride or the dihydride route.

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