# In situ NMR Detection of Dihydrides in the Systems $[RhH(SnCl_3)_5]^{3-}$/Tertiary Phosphanes/Parahydrogen

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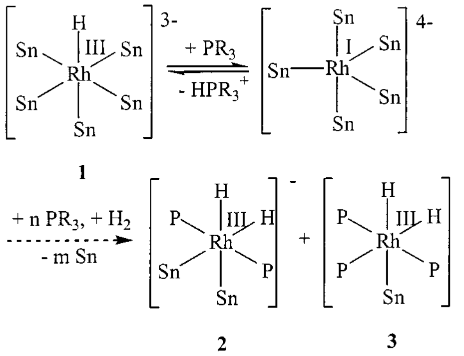
The oxidative addition of dihydrogen to the $[RhH(SnCl_3)_5]^{3-}$/$PR_3$ system ($PR_3$ = $PPh_3$, $PEtPh_2$, $PEt_3$) leads to the formation of previously unknown dihydride complexes, the $^1$H-NMR spectra of which have been studied by means of the ParaHydrogen Induced Polarization (PHIP) method. The composition of the resulting complexes crucially depends on the type of the added phosphane. With $PEt_3$ as the phosphane and acetonitrile as the solvent, a complex with a $SnCl_2L$ ligand (L = $CD_3CN$) can be detected. All systems examined catalyze the hydrogenation of phenylacetylene. During these reactions, both the $^1$H-NMR resonances of the dihydride complexes and those of styrene, the hydrogenation product of phenylacetylene, can be detected simultaneously. In the case of $SnBr_3$ ligands, hydrogen addition in the presence of phosphanes leads to similar dihydride complexes, which were also identified via $^1$H-NMR spectroscopy. Furthermore, a mixed complex of the structure $[Rh(SnBr_3)_nBr_{6-n}]^{3-}$ has been isolated.

## Introduction

The catalytic activity of rhodium complexes containing tin trichloride ligands has been the subject of many studies ever since 1970, when their activity in the dehydrogenation of 2-propanol has first been noted.[1] This reaction and, in particular, the structure of the responsible rhodium-tin complexes have been examined before using $^{119}$Sn-NMR spectroscopy.[2] Furthermore, the rhodium(III) monohydride complex **1** has previously been isolated from hydrochloric acid solutions of $RhCl_3$ and $SnCl_2$ and identified with this technique.[3] Reactions of these complexes with tertiary phosphanes have also been studied with $^{31}$P- and $^1$H-NMR spectroscopy, and upon addition of dihydrogen to these systems the formation of two dihydrido complexes **2** and **3** was detected (Scheme 1).[4]



Scheme 1. Formation of dihydrides from $[HRh(SnCl_3)_5]^{3-}$ in presence of phosphanes and hydrogen, Sn = $SnCl_3$, P = $PR_3$.

The development of an in situ NMR technique based on ParaHydrogen Induced Polarization (PHIP) allows an extensive study of rhodium dihydride complexes, both stable and transient, via their $^1$H-NMR spectra, which can be observed during homogeneous catalyzed hydrogenations.[5] Recently, the structure and reactivity of rhodium dihydrides relevant to both Wilkinson- and Schrock-type catalysts as well as their hydrogenation activity were extensively examined by use of PHIP-NMR spectroscopy. This method provides an extraordinary sensitivity for the detection of metal hydrides; therefore, it has been used to observe these typically unstable catalytic intermediates.[5–7] Due to the enhanced resonances, reliable information about the structure of species present in only minor quantities in reaction mixture can thus be obtained. This approach yields valuable insight into both the stereo- and regiochemistry of initial stages of the dihydrogen addition to the substrate.[8]

Since reports on tin-containing rhodium dihydrides and the knowledge of their role in homogeneous catalysis are scarce, we have used the PHIP technique to study the reactions of two characteristic prototypes with parahydrogen, namely of the systems $[RhH(SnCl_3)_5]^{3-}$/tertiary phosphane and $RhBr_3$/$SnBr_2$/tertiary phosphane. Recently, platinum(II)-tin hydride complexes were studied in this way,[9] providing a pool of new information about the mechanism of homogeneous, platinum-tin catalyzed hydrogenations of alkynes and alkenes thanks to the identification of previously unknown intermediates. In this study here, we were interested in identifying the consequences, in particular the intermediate products, resulting from the addition of dihydrogen to a variety of tin-containing rhodium complexes. By use of PHIP-NMR spectroscopy we wanted to detect

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previously elusive intermediates occurring during the stepwise tin-for-phosphane substitution as originally described in 1985,[4] in order to obtain more detailed information about the hydrogenation activity of this rhodium-tin system in particular.

## Results and Discussion

Of the two rhodium-tin-systems investigated here, the first complex, $[HRh(SnCl_3)_5]^{3-}$, has been obtained and characterized earlier as an isolated rhodium monohydride,[2,3] whereas the second system, $RhBr_3/SnBr_2/HBr$, has not been investigated before.

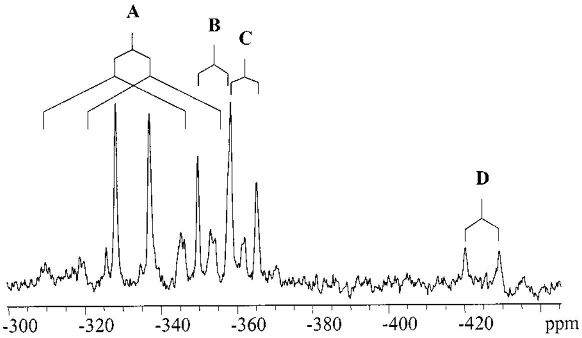


Figure 1. $^{119}$Sn-NMR spectrum of the $RhBr_3/SnBr_2/HBr$ system in $CD_3CN$ at –40° C (chemical shifts referenced to external $Me_4Sn$)

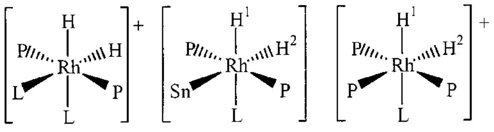
Action of $NEt_4^+$ onto the latter yields a solid, which was studied by means of NMR spectroscopy. The $^{119}$Sn-NMR spectrum (Figure 1) exhibits four main resonances A, B, C, and D, which are due to rhodium-tin-complexes of the type $[Rh(SnBr_3)_nBr_{6-n}]^{3-}$ with typical shifts and coupling values for tin coordinated to rhodium[10] (see Experimental Section). Upon addition of parahydrogen, the $^1$H-NMR spectrum in acetonitrile reveals no signals of any hydride, by contrast to the chloride analogue. The lack of formation of a monohydride upon addition of tetraethylammonium cations to the $RhBr_3/SnBr_2/HBr$ system seems to be due to the lower reductive ability of tin dibromide in comparison to tin dichloride, which would explain the lack of $Rh^I$ formation and, therefore, the lack of subsequent protonation.

### System $[RhH(SnCl_3)_5]^{3-}/PPh_3$

The action of parahydrogen on the $[RhH(SnCl_3)_5]^{3-}$ anion in acetonitrile does not give rise to any detectable dihydrides either. The addition of four equivalents of $PPh_3$ to the solution causes partial deprotonation of the hydride, since the hydride signal disappears in the $^1$H-NMR spectrum. Furthermore, the $^{31}$P-NMR spectrum reveals the presence of $HPPh_3^+$ at $\delta$ = –3 (broad), which undergoes rapid chemical exchange with $PPh_3$ on the NMR time scale. This behaviour is similar to that of the already described reaction with $PBu_3$.[4]

$$[HRh(SnCl_3)_5]^{3-} + PBu_3 \rightarrow [Rh(SnCl_3)_5]^{4-} + HPBu_3^+ \qquad (1)$$

The subsequent fate of the $Rh^I$ complex is either substitution of the tin ligands by phosphane or back-protonation to **1** as soon as a proton is liberated during the substitution. Addition of parahydrogen at room temperature gives rise to three dihydrides, two of them occurring in polarization (Figure 2).



**4a** **5a** **6a**

P = PPh₃, Sn = SnCl₃, L = CD₃CN

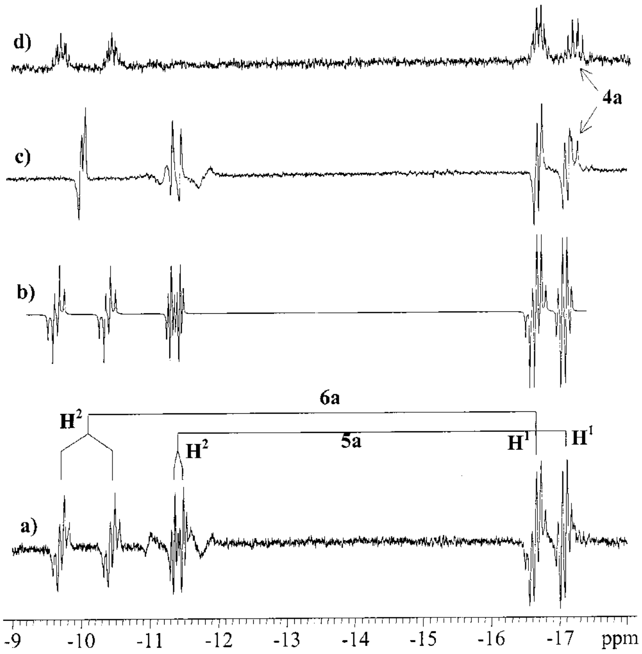


Figure 2. $^1$H-NMR spectra of the system $[RhH(SnCl_3)_5]^{3-}/PPh_3/H_2$ in $CD_3CN$; a) PHIP spectrum on heating; b) PHIP++ simulation of **6a** and **5a**; c) PHIP-$^1$H{$^{31}$P}-NMR spectrum on heating; d) product spectrum after decay of the polarization

The unpolarized hydride resonances at $\delta$ = –17.19 are assigned to the chemically equivalent protons of the symmetric complex **4a**. This complex has already been described before.[11] These hydride resonances occur with a multiplicity consisting of doublet of triplets with $^1J$(HRh) = –17.5 Hz and $^2J$(HP) = 13 Hz (Table 1). The polarized resonances, however, show coupling patterns typical for a bis-phosphane and a tris-phosphane complex, respectively. The bis-phosphane complex **5a** shows one hydride resonance $H^2$, with a chemical shift value of $\delta$ = –11.42, which is typical for a proton in *trans* position to a trichlorostannato ligand. This resonance occurs as a doublet of triplets which are further split into doublets with “antiphase” multiplicity. (In the following the designation "antiphase multiplicity" will be used as an abbreviation universally when referring to multiplets in polarization and a splitting due to $^2J$(HH′) coupling between the former two parahydrogen protons). The $^{31}$P-decoupled spectrum reveals the rhodium coupling as $^1J$(H$^2$Rh) = 25 Hz. The

Table 1. $^1$H-NMR data of the dihydride complexes

| | Formula | $^1$H δ [ppm], $J$ [Hz] |
|---|---|---|
| **6a** | $H_2Rh(PPh_3)_3L$[a] | –16.64 ($J_{HH}$ = –9.5, $J_{HRh}$ = 10, $J_{HP}$ = 13)<br>–10.08 ($J_{HRh}$ = 9.5, $J_{HP\mathit{cis}}$ = 14, $J_{HP\mathit{trans}}$ = 147) |
| **5a** | $H_2Rh(PPh_3)_2(SnCl_3)L$[a] | –17.05 ($J_{HH}$ = –4.5, $J_{HRh}$ = 13, $J_{HP}$ = 13)<br>–11.42 ($J_{HRh}$ = 25, $J_{HP}$ = 9) |
| **4a** | $H_2Rh(PPh_3)_2L_2$[a] | –17.19 ($J_{HRh}$ = 17.5, $J_{HP}$ = 13) |
| **3b** | $H_2Rh(PEtPh_2)_3(SnCl_3)$ | –12.07 ($J_{HH}$ = –6, $J_{HRh}$ = 20, $J_{HP}$ = 10)<br>–10.67 ($J_{HRh}$ = 10, $J_{HP\mathit{cis}}$ = 13, $J_{HP\mathit{trans}}$ = 130.5, $J_{HSn}$ = 1440) |
| **6b** | $H_2Rh(PEtPh_2)_3L$[a] | –17.46 ($J_{HH}$ = –8, $J_{HRh}$ = 13, $J_{HP}$ = 13)<br>–9.82 ($J_{HRh}$ = 13.5, $J_{HPcis}$ = 13.5, $J_{HP\mathit{trans}}$ = 148) |
| **2c** | $H_2Rh(PEt_3)_2(SnCl_3)_2$ | –12.52 ($J_{HRh}$ = 25, $J_{HP}$ = 11.5) |
| **3c** | $H_2Rh(PEt_3)_3(SnCl_3)$ | –12.84 ($J_{HH}$ = –5.5, $J_{HRh}$ = 25, $J_{HP}$ = 12, $J_{H119Sn}$ = 1510, $J_{H117Sn}$ = 1443)<br>–11.48 ($J_{HRh}$ = 11.5, $J_{HPcis}$ = 16, $J_{HP\mathit{trans}}$ = 131) |
| **8c** | $H_2Rh(PEt_3)_3(SnCl_2L)$[a] | –12.40 ($J_{HH}$ = –5, $J_{HRh}$ = 26, $J_{HP}$ = 13, $J_{H119Sn}$ = 1510, $J_{H117Sn}$ = 1443)<br>–10.88 ($J_{HRh}$ = 11, $J_{HP\mathit{cis}}$ = 16, $J_{HP\mathit{trans}}$ = 158) |
| **7c** | $H_2Rh(PEt_3)_2(SnCl_3)_2X$[b] | –18.77 ($J_{HH}$ = –4, $J_{HRh}$ = 16.5, $J_{HP}$ = 15)<br>–12.56 ($J_{HRh}$ = 30, $J_{HP}$ = 11) |
| **9c** | $H_2Rh(PEt_3)_3(SnBr_3)$ | –13.85 ($J_{HH}$ = –5.5, $J_{HRh}$ = –25, $J_{HP}$ = 12.5)<br>–11.16 ($J_{HRh}$ = 10.5, $J_{HPcis}$ = 15, $J_{HP\mathit{trans}}$ = 130) |
| **10c** | $H_2Rh(PEt_3)_2(SnBr_3)_2$ | –13.26 ($J_{HRh}$ = –25, $J_{HP\mathit{cis}}$ = 11.5) |
| **11c** | $H_2Rh(PEt_3)_2(SnBr_3)_2X$[b] | –18.77 ($J_{HH}$ = –6, $J_{HRh}$ = –15, $J_{HP\mathit{cis}}$ = 15)<br>–12.56 ($J_{HRh}$ = 31, $J_{HPcis}$ = 12) |

[a] L = $CD_3CN$. – [b] X = Cl, Br, $CD_3CN$.

other hydride proton, namely $H^1$ *trans* to acetonitrile, occurs as a high-field pseudo-quadruplet at δ = –17.05 with a rhodium coupling of $^1J(H^1Rh)$ = 13 Hz. The presence of acetonitrile in this complex is confirmed by the fact that the same signals are not detected in the system $RhCl(PPh_3)_3$/$SnCl_2$ (1:5) in [D$_6$]acetone as the solvent until the addition of minor quantities of acetonitrile.

In the tris-phosphane complex **6a** the large value of $^2J(H^2P)$ = 147 Hz is typical for a *trans*-alignment of the ligands. The $^{31}$P-decoupled $^1$H-NMR spectrum approves this assignment. The high-field shift of $H^1$ is also due to a *trans* acetonitrile ligand, which is concluded from the observation that the $[Rh(SnBr_3)_nBr_{6-n}]^{3-}$ system gives rise to the same signals upon addition of parahydrogen. Furthermore, these signals can also be detected in the system $RhCl(PPh_3)_3/SnCl_2/PPh_3$ (1:5:7) in $CD_3CN$.

The complexes **4a** and **6a** are stable and can, therefore, be characterized from their resonances observed in the thermal, i.e., in the regular, "unpolarized" $^1$H-NMR spectra. Complex **5a,** however, is a transient species which can only be observed in situ, i.e., enhanced by PHIP. The extensive incorporation of acetonitrile into the coordination sphere of the dihydrides can be rationalized by the relatively high π-acceptor properties of triphenylphosphane, which causes its competition with the tin ligands for the filled d-orbitals of rhodium. The tin trihalide ligands have been shown earlier to be relatively strong π-acceptors as well.[12] The instability of complex **5a** could be caused by the high *trans* effect of $H^2$; therefore, the lability of the tin ligand is enhanced, which causes its dissociation with the formation of **4a**.

### System $[RhH(SnCl_3)_5]^{3-}/PEtPh_2$

Upon addition of $PEtPh_2$ to an acetonitrile solution of **1**, deprotonation becomes evident by the appearance of $HPEtPh_2^+$ in the $^{31}$P-NMR spectrum at δ = – 8.5 (broad). In addition, several signals in the range of δ = 15 to 45 with typical $^1J$(PRh) coupling constants of 90 to 135 Hz are observed (Table 2). However, the deprotonation of the monohydride does not occur completely, since it can still be detected in the $^1$H-NMR spectrum.

Table 2. $^{31}$P-NMR data of the dihydride complexes

| Dihydride | Formula | Chemical shifts, δ [ppm], coupling constants $J$ [Hz] |
|---|---|---|
| **6a** | $H_2Rh(PPh_3)_3L$[a] | 42.8 ($J_{PP}$ = 19, $J_{PRh}$ = 111)<br>28.7 ($J_{PRh}$ = 93) |
| **6b** | $H_2Rh(PEtPh_2)_3L$[a] | 38.8 ($J_{PP}$ = 20, $J_{PRh}$ = 109)<br>24.3 ($J_{PRh}$ = 96) |
| **3c** | $H_2Rh(PEt_3)_3(SnCl_3)$ | 28.7 ($J_{PP}$ = 22, $J_{PRh}$ = 96)<br>15.6 ($J_{PRh}$ = 88) |

[a] L = $CD_3CN$

The admission of parahydrogen gives rise to polarized signals of two dihydrides, **3b** and **6b**, with coupling patterns similar to those of the $PPh_3$ analogues (Figure 3). The presence of an acetonitrile ligand in **6b** is extrapolated from the observation of the corresponding signals in the PHIP spectra of the bromide system. The signals of **6b** are also detectable in the thermal $^1$H-NMR spectrum, whereas **3b** is only visible when enhanced by PHIP. The higher stability of **3b** as compared to that of the $PPh_3$ system, can be explained by the decrease of the π-acceptor properties of $PEtPh_2$ relative to $PPh_3$; therefore, its competition with the tin ligand is less favourable. It should be mentioned that in this system only tris-phosphane dihydrides are observed.

### System $[RhH(SnCl_3)_5]^{3-}/PEt_3$

Upon addition of $PEt_3$ to an acetonitrile solution of **1**, deprotonation of the monohydride becomes evident by the appearance of $HPEt_3^+$ in the $^{31}$P-NMR spectrum at δ = –13.7 (broad). Furthermore, four main signals with $^1J$(PRh)

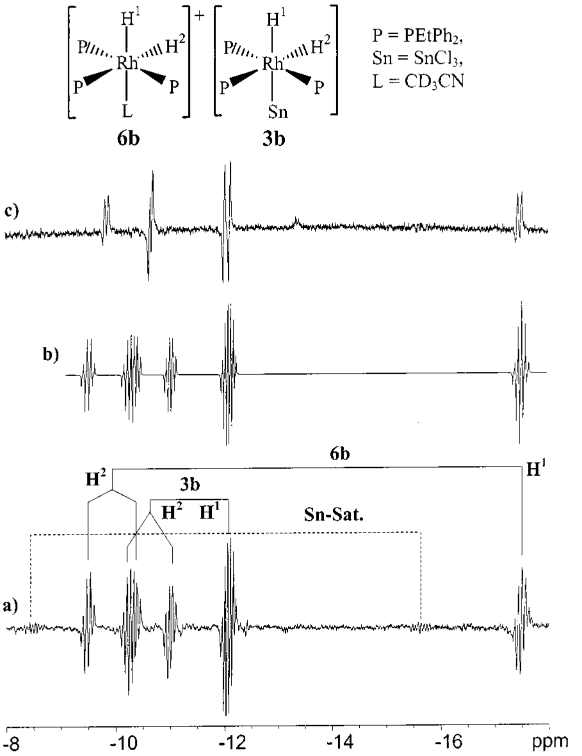
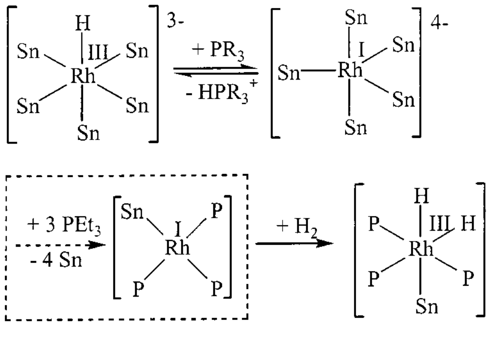


Figure 3. $^1$H-NMR spectra of the system $[RhH(SnCl_3)_5]^{3-}$/$PEtPh_2$/$H_2$ in $CD_3CN$; a) PHIP spectrum on heating; b) PHIP++ simulation of **6b** and **3b**; c) PHIP-$^1H\{^{31}P\}$-NMR spectrum on heating

couplings of 90, 90, 116, and 137 Hz occur at $\delta$ = 7.5, 20.6, 26.4, and 42.2, respectively.

The appearance of polarized dihydrides upon parahydrogen addition depends on the initial P/Rh ratio. When an excess of phosphane (Rh/P = 1:6) is used, the resonances observed correspond to the tris-phosphane *mer*-$H_2Rh(PEt_3)_3(SnCl_3)$, **3c**. This complex is also visible in the thermal spectra together with the symmetric complex **2c**, which is formed after prolonged reaction time and upon heating.



Scheme 2. Formation of a tris-phosphane rhodium dihydride at the first stage of the reaction

The dihydride **3c** is apparently the result of an oxidative addition of parahydrogen to $Rh(PEt_3)_3(SnCl_3)$ formed at the very beginning of the reaction (Scheme 2). The lack of evidence for the formation of any bis-phosphane dihydrides during the first stage of the reaction can be rationalized to be the consequence of the activating *trans* effect of the first and second $PEt_3$: If three ligands are swiftly replaced by $PEt_3$, only the tris-phosphane is available for the oxidative addition of parahydrogen.

Likewise, at lower $PEt_3$ concentrations (Rh/P = 1:4) the first PHIP spectrum reveals the formation of **3c** only (Figure 4, a). However, upon standing at room temperature, the addition of parahydrogen leads to the emergence of a complicated mixture of PHIP-active dihydrides, as can be concluded from the spectra shown in Figure 4, f.

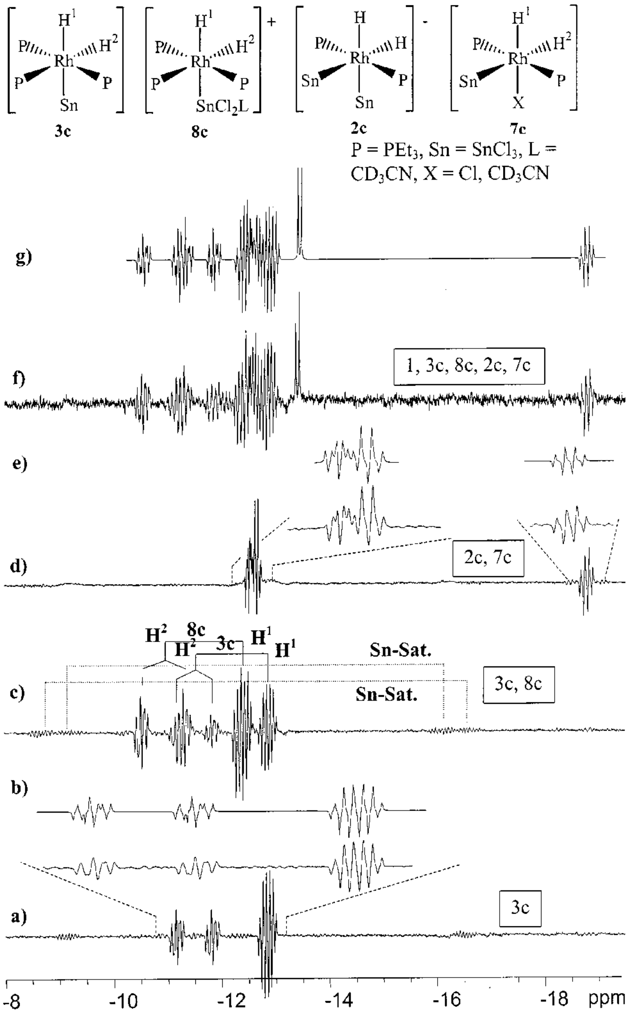
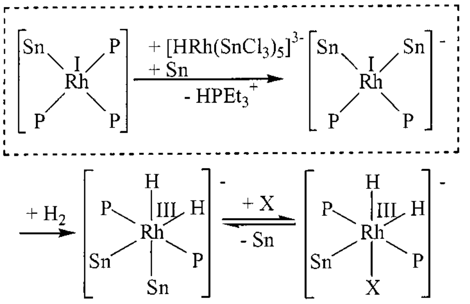


Figure 4. $^1$H-NMR spectra of the system $[RhH(SnCl_3)_5]^{3-}$/$PEt_3$(1:4)/$H_2$ in $CD_3CN$; a) PHIP spectrum immediately after mixing of the reagents; b) PHIP++ simulation of **3c**; c) PHIP spectrum in presence of $AgBF_4$; d) PHIP spectrum on heating; e) PHIP++ simulation of **2c** and **7c**; f) PHIP spectrum after prolonged reaction time; g) PHIP++ simulation of **1**, **2c**, **3c**, **7c**, and **8c**

Heating of the solution changes the patterns (Figure 4, d), apparently because of scrambling of the phosphane throughout the whole system (Scheme 3). Consequently, upon admission of parahydrogen two bis-phosphane dihydrides, **2c** and **7c**, are obtained. The spectral patterns observed correspond to overlapping signals of **2c** (in which the two former parahydrogen protons fail to appear in polarization, possibly due to their maintained symmetry) and the polarized multiplet of **7c**. This assignment has been confirmed by PHIP++ simulation.



Scheme 3. Formation of bis-phosphane rhodium dihydrides after prolonged reaction time

The complicated mixture of resonances observed in the PHIP spectra at room temperature after prolonged reaction times (Figure 4, f) could be analyzed to consist of the overlapping thermal and PHIP signals of **3c**, **2c**, **7c,** and of the starting complex **1,** respectively. This analysis was confirmed via PHIP++ simulation of the expected resonances for the components of this system and a subsequent weighted summation thereof (Figure 4, g).

However, in order to achieve a complete fitting of the observed patterns in the case above, the presence of another tris-phosphane dihydride has to be postulated, namely of **8c**. Its coupling patterns clearly display the *cis*-position alignment of three phosphorus ligands. The chemical shift of the $H^1$ proton in *cis*-position to phosphorus is characteristic for a *trans*-alignment of the tin-ligand. The difference between the two rather similar dihydrides **3c** and **8c** can only be due to variations in the structure of the tin ligand. As has already been shown before,[13,14] tin(II)chloride possesses additional coordination abilities; therefore, it can coordinate Lewis bases, leading to the formation of $SnCl_2D$ ligands (D = donor). Since this process could be strongly promoted by the abstraction of chloride, we have also recorded the spectra of this system in the presence of added $AgBF_4$ to check out the relevance of this hypothesis. The result shows a strong enhancement of the signals of **8c**, adding support to this suggestion. In addition, tin satellites are clearly visible for the resonance of $H^1$, exhibiting a value for $^2J(HSn)$, which is close to that of the related complex **3c**.

By contrast to the $PPh_3$ and $PEtPh_2$ chloride systems the addition of parahydrogen to the corresponding bromide systems gives rise to relatively stable, tin-containing dihydrides which appear in polarization in the PHIP-NMR spectra. Upon heating, the signals of **9c**, which is the bromide analogue of **3c**, are clearly visible. The complexes **10c** and **11c** can also be detected, which appear to be the tin-tribromide analogues of **2c** and **7c**, respectively. The high-field shift of the hydrogen in *trans*-position to the tin ligand indicates a lower *trans*-effect of $SnBr_3^-$ as compared to that of $SnCl_3^-$. Furthermore, the intensity of the PHIP signals observed in the bromide systems is generally lower than in the corresponding chloride system, apparently because of the lower concentration of $Rh^I$.

### Hydrogenation Experiments

Upon heating, all systems studied hydrogenate added phenylacetylene in a *cis*-manner, as can be concluded from the polarization pattern of the resulting styrene. The hydrogenation activities are rather similar for all these systems.

Characteristically, in all cases investigated, the resonances of the dihydrides are present during the hydrogenation of phenylacetylene to styrene. The apparent lack of formation of any substrate-hydride complexes – similar to those detected in the previously investigated platinum-tin systems[9] – leads us to the conclusion that the observed dihydrides may not be directly included in the catalytic cycle of the hydrogenation, but might just be the precursors for related, catalytically active species. Alternatively, the rates of the individual steps for this catalytic cycle might well be rather different from those of the previously studied platinum-tin system, with the consequence that the rate-determining steps shift with the result that such intermediates, – if they are formed at all -, occur in such minute concentrations that they cannot be detected in spite of the signal enhancement associated with PHIP.

## Conclusions

In comparison to $PPh_3$, the $PEt_3$ ligand has profound electron donor properties, which causes an extensive incorporation of tin ligands into the resulting dihydrides. Accordingly, when using $PPh_3$ as the tertiary phosphane, the formation of only one tin-containing dihydride is observed, which is thermally unstable. By contrast, in the system $[RhH(SnCl_3)_5]^{3-}/PEt_3/CD_3CN$/parahydrogen four dihydrides are detectable, which all contain tin ligands. Two of them, namely **3c** and **2c**, are rather stable species. The low stability of the tin-containing complexes with $PPh_3$ as the ligand is apparently due to the competition of the tin and phosphane ligands. Furthermore, this process is accompanied by more extensive incorporation of acetonitrile into the dihydrides.

In particular, the system $[RhH(SnCl_3)_5]^{3-}/PEtPh_2/CD_3CN$/parahydrogen is remarkable in the sense that it gives rise to tris-phosphane complexes only. This fact can be explained when assuming that there exists a fine balance of σ-donating and π-accepting properties of the phosphane which is apparently optimal for rhodium-phosphorus-binding here.

## Experimental Section

**General Remarks:** All $^1H$, $^1H$ PHIP-, $^{31}P$ and $^{119}Sn$ NMR spectra were recorded using a Bruker AC 200 spectrometer; the $^1H\{^{31}P\}$-PHIP NMR spectra were obtained with a Bruker DRX 200 spectrometer. Chemical shifts are referenced to either external TMS ($^1H$), 85% $H_3PO_4$ ($^{31}P$), or $Sn(CH_3)_4$ ($^{119}Sn$), respectively. For recording the $^{119}Sn$ spectrum a repetition time of 0.5 s was used, and the accumulation of 28000 scans was necessary to obtain a spectrum with a satisfactory signal-to-noise ratio. In order to obtain the PHIP spectra, excitation pulses corresponding to a flip angle of 45° were used. To record the conventional or "thermal" $^1H$ NMR spectra, however, the pulse width was set such that it corresponded to the conventional flip angle of 90°. The solvent $CD_3CN$

was purchased from Aldrich, dried and degassed prior to use, and stored under vacuum. – The simulations of the PHIP-$^1$H NMR spectra were performed using the OS/2-based PHIP++ program, developed by Greve.[15] – The complex $[RhH(SnCl_3)_5][NEt_4]_3$ was prepared as reported in the literature.[3] All starting materials were commercial products (Aldrich) which were used without additional purification.

**Typical Preparation of Solutions for Hydrogenation Studies:** The $Rh^{III}$ complex, as well as $PPh_3$, were placed into a screw-capped NMR tube attached to a vacuum line. Then 0.7 mL of dry degassed $CD_3CN$ was condensed into the tube. The weighted amounts of $PEt_3$ were vacuum-transferred to the sample. After thawing and filling with dry argon, the sample tube was disconnected from the vacuum line and fitted with a septum stopper. The necessary volumes of $PEtPh_2$ were added to the solution of the starting $Rh^{III}$ complex using an Eppendorf micropipette. Parahydrogen was subsequently introduced into the NMR tube through a stainless steel needle through the septum at a pressure of 3 bar. After shaking of the solution in the parahydrogen atmosphere, the tube was inserted into the probe, and the $^1$H-PHIP spectrum was recorded immediately thereafter.

**Tetraethylammonium (Bromo(tribromostannato)rhodium(III) Complexes:** 2 g of $SnBr_2$ (7.2 mmol) was added to a stirred solution of 0.3 g $RhBr_3$ (1 mmol) in 10 mL of 3 M HBr under argon. The mixture was heated for 1 h. After the solution had cooled down to room temperature, 0.2 M of $NEt_4Br$ in 3 M HBr was added dropwise. A red precipitate formed which was filtered, washed three times with 3 M HBr, and dried in vacuo. The $^{119}$Sn-NMR analysis revealed that the product contained several rhodium-tin complexes of the composition $[Rh(SnBr_3)_nBr_{6-n}][NEt_4]_3$. – $^{119}$Sn-NMR ($CD_3CN$): $\delta = -332$ (d, $J_{Rh,Sn} = 669$ Hz), –354 (d, $J_{Rh,Sn} =$ 603 Hz), –361 (d, $J_{Rh,Sn} = 520$ Hz), –425 (d, $J_{Rh,Sn} = 674$ Hz).

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