A Study of the Mechanism of Platinum(II)/Tin(II) Dichloride Mediated Hydrogenation of Alkynes and Alkenes Employing Parahydrogen-Induced Polarization

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Received August 18, 1998

Keywords: Hydrogenations / Parahydrogen / Platinum / Alkynes / Alkenes

The mechanism of hydrogenation of alkynes catalyzed by the $[(PR_3)_2PtHX]/SnX_2$ system (PR_3 = PPh_3, $PMePh_2$; X = Cl, Br) has been studied by means of parahydrogen-induced polarization of ^1H spectra (PHIP). Dihydride intermediates confirming the stepwise hydrogenation at room temperature were observed when the reaction was run in acetone. The obtained ^1H-PHIP spectra, together with NMR data for related species, are consistent with the formulation of these intermediates as *cis*-$[H_2Pt(PR_3)(SnX_3)(\sigma\text{-alkenyl})(acetone)]$, where the σ-alkenyl ligand originates from an insertion reaction of the alkyne (1-phenyl-1-propyne, 1-phenyl-1-butyne, diphenylacetylene, 3,3-dimethylbutyne). At elevated temperatures, the hydrogenation in acetone proceeds as a *cis*-synchronous transfer of the two hydrogen atoms of parahydrogen to the substrate molecule. A mechanism for this synchronous hydrogenation is suggested.

Introduction

The parahydrogen-induced polarization (PHIP) phenomenon was first observed accidentally by Bryndza and coworkers as early as 1983[1]. This NMR technique is now recognized as a valuable mechanistic probe for investigating homogeneously catalyzed hydrogenation reactions[2]. The phenomenon was proposed theoretically in 1986 by Bowers and Weitekamp[3], and soon thereafter was confirmed experimentally[4]. Furthermore, it was recognized that PHIP allows examination of the reaction mechanisms of the single-step transfer of the two parahydrogen atoms to the substrate molecule, and sometimes allows identification of the unstable dihydride intermediates participating in the catalytic cycle[5][6]. Moreover, study of the hydrogenation mechanism by traditional methods is troublesome because in many cases the reaction is accompanied by significant degrees of isomerization of the starting materials and/or products[7]. The PHIP technique offers further information, even on the stereochemistry of the fundamental step of the addition of dihydrogen to the organometallic catalyst. Quite possibly, in situ PHIP-NMR spectroscopy may provide the data relating to the structures of active intermediates that are otherwise difficult or impossible to obtain.

The physical aspects of the processes leading to PHIP-NMR spectra are discussed in a number of papers (e.g., refs.[8][9]). Using this technique, hydrogenation reactions catalyzed by rhodium[10−13], iridium[14][15], palladium[16][17], and ruthenium[18] complexes have been studied.

Although platinum complexes are well-known catalysts for hydrogenation[19−21], hydroformylation[22−25], and hydrosilylation[26] reactions, there have been only a few mechanistic studies using the PHIP technique. In a previous paper, we showed that spin-polarized products arise from the hydrogenation of alkynes in the presence of Pt^0 complexes with either coordinated alkynes or alkenes, as well as with the usual Pt^{II} phosphane hydrido chloro complexes, activated by tin(II) chloride[27].

In principal, the latter fact is contradictory to the generally accepted mechanism for $Pt^{II}/SnCl_2$ mediated hydrogenations (Scheme 1).

Since 1965, it has been accepted that the first step of the hydrogenation is the reduction of the pre-catalyst, accompanied by the formation of platinum monohydrides **2**[28][29]. These monohydrides have been shown to undergo rapid, equilibrium addition reactions to carbon−carbon multiple bonds of the substrate, with the formation of σ-C intermediates **3**[30][31]. Furthermore, the third step of the asynchronous hydrogenation, namely hydrogenolysis of the Pt^{II}−C(alkyl) bond in **3**, has been shown to proceed under relatively mild conditions[32]. The appearance of polarized products during $Pt^{II}/SnCl_2$ mediated hydrogenation using para-H_2 prompted us to engage in a more detailed study of the reaction mechanism using the PHIP technique.

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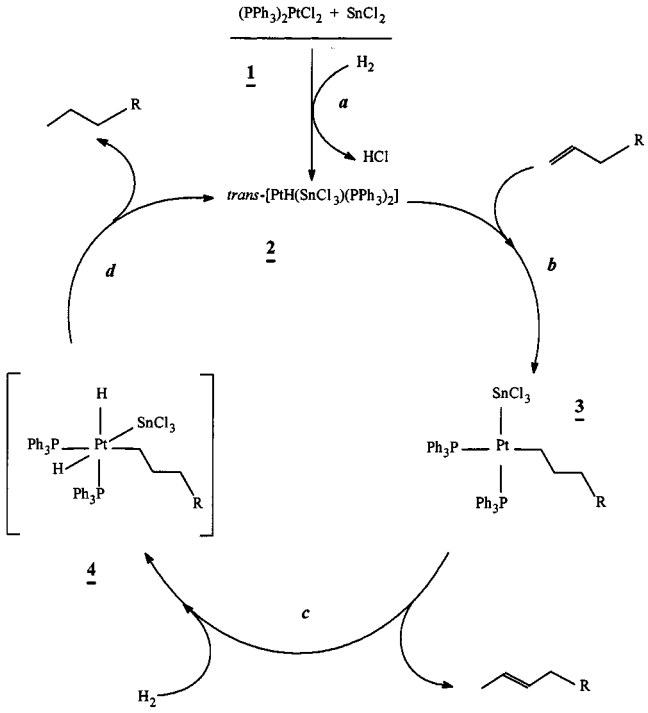
Scheme 1. Generally assumed mechanism for the Pt^{II}−tin dichloride catalyzed hydrogenation, asynchronous mechanism



It is well known that activation of Pt^{II} complexes by tin(II) halides is strongly solvent-dependent. Solvents of medium solvating ability and polarity, such as acetone, play quite a significant role in platinum-phosphane chemistry, promoting extensive phosphane redistribution reactions[33−35]. This dependence can also result in changes in catalytic activity and selectivity[22], as well as of the reaction mechanism, therefore necessitating studies in a variety of solvents.

In this paper we describe the results of PHIP studies of the Pt^{II}/Sn^{II} mediated hydrogenation of alkynes and alkenes in acetone and some other solvating media.

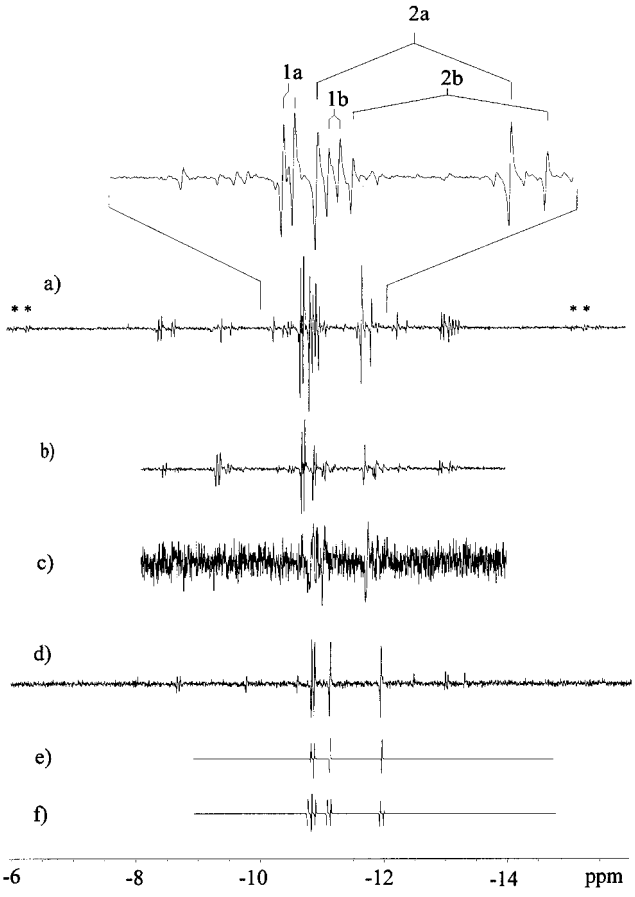
Results and Discussion

PHIP in the System $[(PPh_3)_2PtHCl]/SnCl_2$/1-Phenyl-1-propyne

Since the generally accepted catalytic cycle involves platinum hydride as an active intermediate, we avoided the activation stage (***a***, Scheme 1), as well as extensive HCl formation, by the use of pre-synthesized platinum hydride instead of the usually employed dichloro complex. The interaction of platinum monohydride with $SnCl_2$ in acetone proceeds rapidly, and the resulting clear, orange-yellow solution shows new signals in its ^{1}H-NMR spectrum attributable to *trans*-$[(PPh_3)_2PtH(SnCl_3)]$, **2**, {δ(PtH) = −9.75 [br, ^1J(PtH) = 1105 Hz]}, as well as to the products resulting from a phosphane redistribution reaction {$[(PPh_3)_3PtH]^+$, δ(PtH) = −5.75 [br, d, ^1J(PtH) = 154 Hz]; *trans*-$[(PPh_3)PtH(SnCl_3)_2]^-$, δ(PtH) = 13.355 [d, ^2J(PH) = 131 Hz, ^1J(PtH) = 412 Hz]} in accord with previously published data[34]. The spectra in ref.[34] were recorded at −90°C and thus the minor discrepancies with these data are obviously due to the different temperatures used.

Though the dihydrido-dichloro Pt^{IV} complexes were previously shown to arise as a result of an oxidative addition of HX to Pt^{II} monohydrides[36−38], our attempts to observe them using the PHIP technique during the reduction of dichloride **1** by parahydrogen were unsuccessful. Moreover, no polarization patterns were found as a consequence of the parahydrogen action on platinum−tin monohydrides. On the other hand, we observed strong, sharp polarization signals after the addition of an alkyne followed by parahydrogen to the tin-activated monohydride acetone solution (Figure 1). The relatively high field values of the chemical shift of the observed polarization patterns are consistent with Pt^{IV} species, since published data show a substantial high-field shift for Pt^{IV} dihydrides as compared to analogous Pt^{II} complexes[36][39][40][41].

Figure 1. PHIP ^{1}H-NMR spectra of the system *trans*-$[(PPh_3)_2PtHCl]/SnCl_2$/1-phenyl-1-propyne/para-H_2 in $[D_6]$acetone; **a)** at room temp. (^{119}Sn and ^{117}Sn satellite signals are marked *); **b)** the same sample after cooling; **c)** PHIP ^{1}H-NMR spectrum of the isolated insertion product **5a** in CD_2Cl_2, at 3 bar of para-H_2, room temp.; **d)** PHIP++ simulation of the monophosphane dihydride **6**; **e)** PHIP++ simulation of the diphosphane dihydride **3** (values for *cis*- and *trans*-coupling constants are taken to be as in **c)**; **f)** PHIP++ simulation of the diphosphane dihydride **3** (values for *cis* and *trans* coupling constants are taken as in **c)**)



The obtained PHIP patterns exhibit features that allow us to establish the structures of the transient platinum dihydrides. First of all, two isomers with similar couplings are

Table 1. Spectral NMR parameters of intermediate dihydrides observed in the systems $[(PPh_3)_2PtH(SnX_3)]$/alkyne/$[D_6]$acetone (δ, relative to $[D_5]$acetone; *J*, Hz). The letter **a** corresponds to the major isomer, the letter **b** to the minor isomer

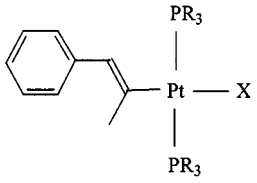
Alkyne	X	Isomer	$\delta(H^1)$	$\delta(H^2)$	^1J(Pt-H^1)	^1J(Pt-H^2)	^2J(P-H^1)	^2J(P-H^2)	$^2J(^{119}$Sn-H^1) [a]	^2J(Sn-H^2) [b]
PhC≡CMe	Cl	**a**	−10.71	−11.24	913.7	568.1	9.3	167.8	1842 (1760)	25.9
		b	−10.91	−11.34	906.7	567.8	9.3	168.5	1840	
PhC≡CMe [c]	Cl	[d]	−10.58	−11.275	869.2	542.0	9.4	165.4		
		[e]	−10.82	−11.33	918	567		167.2		
PhC≡CMe	Br	**a**	−11.46	−10.248	920.5	565.4	9.5	166.8	1850 (1768)	40.1
		b	−11.63	−10.498	918.4	566.4	9.6	167.7		
PhC≡CCH$_2$CH$_3$	Cl	**a**	−10.71	−11.181	911.2	566.1	8.9	168.5	1839 (1759)	33.5
		b	−10.893	−11.334	907.3	565.2	10.1	169.3	1837	
PhC≡CCH$_2$CH$_3$	Br	**a**	−11.443	−10.194	920.7	563.6	9.7	166.3	1853 (1779)	47.3
		b	−11.629	−10.404	919.2	563.8	9.7	166.7		46.3
Diphenylacetylene	Cl	[f]	−10.922	−11.32			9.9	169.0		
Diphenylacetylene	Br	[f]	−11.621	−10.364	913.6	558.3	9.4	165.9	1857 (1771)	44.9
3,3-Dimethylbutyne	Cl	[f]	−10.950	−11.356	940.6	588.2	9.3	172.1		

[a] Values in brackets correspond to $^2J(^{117}$Sn−H). − [b] Averaged $^2J(^{117/119}$Sn−H). − [c] Solution in CD_2Cl_2. − [d] In the absence of added acetone. − [e] 0.15 ml of $[D_6]$acetone was added. − [f] One isomer.

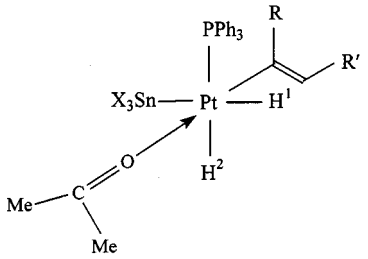
clearly discernible. This conclusion was confirmed experimentally upon cooling of the solution under parahydrogen (Figure 1, b) which resulted in a non-concerted change in the intensities and widths of the relevant resonances. Each isomer exhibits a typical ABX pattern, with large *trans*- and small *cis*-^{1}H−^{31}P couplings (Figure 1a, Table 1). The patterns for both isomers are accompanied by ^{195}Pt and $^{117/119}$Sn satellites, permitting an unambiguous assignment of the ligands in the equatorial plane of the coordination octahedron of **6a**. Only one phosphane ligand is incorporated into the coordination sphere of the transient dihydride, since the spectrum exhibits only one ^{1}H-^{31}P coupling for each proton. This was confirmed by PHIP simulations of the spectra of the mono- and diphosphane dihydrides (Figure 1, d, e, f). The assignment of the axial positions is not so clear-cut, but is supported by the observation that the presence of both an alkyne and acetone is essential for the development of polarization patterns. We suggest that the possible role of acetone lies in promoting the dissociation of one phosphane ligand, which, apparently, is followed by coordination to the platinum center. It has previously been well-documented[34][35] that the reaction of excess tin dihalides with platinum hydrides in acetone at room temperature rapidly leads to the formation of mixture of phosphane redistribution products, which contain monophosphane complexes.

Addition of 1-phenyl-1-propyne to an acetone solution of **2** leads to the disappearance of the Pt-H signals in the hydride region in the thermal spectrum and gives rise to a broadened singlet at approximately δ = 0.7. This singlet is symmetrically surrounded by broadened signals, the positions and intensities of which are consistent with the notion that they are in part ^{195}Pt and unresolved $^{119/117}$Sn satellites. The singlet was thus assigned to the methyl resonance of the σ-alkenyl ligand, resulting from an insertion of the triple bond of the substrate into the Pt−H bond (vide infra). This signal was invariably present in all cases where polarization in the Pt−H region was observed, which prompted us to ascribe the key role of a σ-bonded carbon ligand in the formation of PHIP-active Pt^{IV} dihydrides. The suggestion of the presence of this ligand was also derived from the following considerations: (a) the role of the substrate could be either to coordinate to platinum as a π-ligand or to insert into a Pt−H bond, thereby producing a σ-bonded carbon ligand; (b) the obtained PHIP corresponds to the spectrum of a dihydride, and not to a trihydride, establishing the insertion suggestion in (a); and (c) the isolated insertion product, i.e. the σ-phenylpropenyl platinum complex, shows analogous though more simple polarization patterns upon reaction with parahydrogen (Figure 1, c). The precise structure of the alkenyl radical in the transient dihydride is not clear, but it seems plausible that the existence of the two dihydrides is due to an isomerism of the alkenyl radical and, therefore, the dihydrides are in fact 2-phenyl-1-methylethenyl and 1-phenylprop-1-enyl complexes.

We were fortunately also able to isolate the product of insertion of 1-phenyl-1-propyne into the Pt−H bond of the starting monohydride. Light-yellow crystals of the product were formed on leaving to stand an acetone solution of the $[(PPh_3)_2PtH(SnCl_3)]$ complex together with the alkyne in the absence of hydrogen, as well as during hydrogenation experiments. The ^{1}H-NMR spectrum of this product in CD_2Cl_2 clearly shows the signal of the CH_3 protons of the σ-alkenyl ligand with a full set of ^{195}Pt and $^{117/119}$Sn satellites, and the signal of the proton adjacent to the double bond with partially obscured satellite signals. The ^{1}H spectrum is essentially similar to published data for the analogous triethylphosphane complex[42], in spite of the large deviation of the chemical shift value for methyl protons [δ = 2.23, ^3J(PtH) = 56.5 Hz[42]], which is apparently due to the difference between an acido ligand and the phosphane. Together with the obtained ^{13}C and ^{31}P data, this spectrum allows the unambiguous assignment of the structure of this product as **5a**. The doublet splitting of the main methyl resonance (ca. 2 Hz) can be attributed to a ^4J *cis*-coupling with the olefinic proton. Large values of $^4J(^{119/117}$Sn-^{1}H) are in accord with a *trans*-position of the trichlorostannato ligand relative to the alkenyl group, and they match published values for tin−proton couplings in



5a X = $SnCl_3$
5b X = Cl



6 a R = Me, R′ = Ph, X = Cl;
6 b R = Et, R′ = Ph, X = Cl;
6 c R = R′ = Ph, X = Cl;
6 d R = H, R′ = CMe_3, X = Cl;
6 e R = R′ = Ph, X = Br

other platinum trichlorostannato complexes[43]. It is also noteworthy that addition of several equivalents of DMF results in the cleavage of the trichlorostannato ligand with formation of the corresponding chloro complex, **5b**, in accord with the reported behavior of σ-alkylplatinum complexes[31].

The polarization spectrum originating from reaction of parahydrogen with the solution of **5a** in dichloromethane indicates the presence of only one isomer. These patterns are much less intense than those obtained for catalytic mixtures in acetone, which is apparently due to the fact that acetone is present in the system only in minor amounts as an impurity or as a solvent of crystallization, as is evident from the ^{1}H and ^{13}C spectra. The low intensity of the polarization signals can be also attributed to the enhanced stability of the isolated isomer, which is hydrogenated only to a small extent. The differences between the PHIP ^{1}H-NMR spectra obtained for the isolated insertion product and those obtained from the catalytic system are due to the change of medium, since addition of 0.15 ml of [D_6]acetone to a $CDCl_3$ solution of **5a**, followed by parahydrogen, shifts the dihydride signals towards coincidence with the position observed in situ (Table 1).

Catalytic Systems with Other Substrates

Besides 1-phenyl-1-propyne, other substrates can give transient dihydrides detectable by the PHIP technique. Thus, we have attempted to hydrogenate alkynes (phenylacetylene, diphenylacetylene, 1-phenyl-1-butyne, 1,4-diphenylbutadiyne), and alkenes (norbornadiene, 3,3-dimethylbutene) under the same conditions as used for 1-phenyl-1-propyne. Our observations are summarized qualitatively in Table 2.

The interaction of the system [$(PPh_3)_2PtHCl$]/$SnCl_2$/1-phenyl-1-butyne/acetone with parahydrogen proceeds similarly to the reaction of 1-phenyl-1-propyne (Figure 2). Polarization patterns show clearly resolved ^{117}Sn and ^{119}Sn sat-

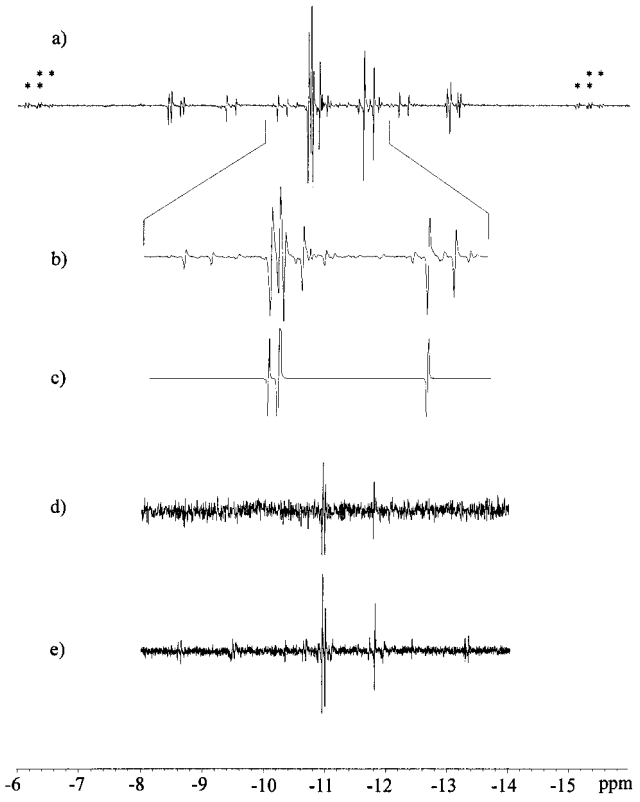
Table 2. Qualitative summary of results obtained for the studied systems [$(PR_3)_2PtHX$]/SnX_2/substrate/acetone

PR_3	X	Substrate	Pt dihydride(s), intensity, number of isomers [a]	Insertion product [b]	Synchronous/ asynchronous hydrogenation [c]
PPh_3	Br	1-Phenyl-1-propyne	+++, 2	+	++
PPh_3	Br	1-Phenyl-1-butyne	+++, 3	n.d.	+++, th.
PPh_3	Br	Diphenylacetylene	+++, 1	n.d.	th.
PPh_3	Cl	1-Phenyl-1-propyne	+++, 2	+	++, th.
PPh_3	Cl_2[d]	1-Phenyl-1-propyne	no	n.d.	th.
PPh_3	Cl	1-Phenyl-1-butyne	+++, 3	n.d.	++
PPh_3	Cl	Diphenylacetylene	+, 1	n.d.	
PPh_3	Cl	3,3-Dimetylbutyne	++, 2	n.d.	th.
PPh_3	Cl	1,4-Diphenylbutadiyne	no	n.d.	++
PPh_3	Cl	Phenylacetylene	no	n.d.	+++, th.
PPh_3	Cl	3,3-Dimetylbutene	no		no
PPh_3	Cl	Norbornadiene	no	n.d.	th.
PPh_3	Cl	1-Phenyl-1-propene	no	n.d.	no
PPh_3[e]	Cl	1-Phenyl-1-butyne	no	n.d.	no
PPh_3[f]	Cl	1-Phenyl-1-propyne	no	+, br.	+, th.
PPh_3[g]	Cl	1-Phenyl-1-propyne	no	n.d.	+, th.
$PMePh_2$	Br	1-Phenyl-1-propyne	++, 2	+	+, th.
$PMePh_2$	Cl	1-Phenyl-1-propyne	+	+	th.
PMe_2Ph	Cl	1-Phenyl-1-propyne	+	n.d.	th.

[a] +++, strong polarization signals, with ^{195}Pt and $^{117/119}Sn$ satellites visible in spectrum; ++, medium polarization, $^{117/119}Sn$ satellites are not visible due to low signal/noise ratio; +, low polarization, only central part of the patterns is clearly visible. – [b] +, the signal(s) attributable to the insertion product are present; **n.d.**, not detected, the signals of the insertion product are presumably obscured. – [c] +++, ++, and +, strong, medium, and weak polarization of product signals, respectively; **th.**, continuous rise of the thermal product signals without polarization. – [d] The corresponding dichloro complex was used instead of [$(PR_3)_2PtHX$]. – [e] In acetonitrile as solvent; 1 mol equivalent of $SnCl_2$. – [f] In $CDCl_3$/[D_8]THF mixture, 7:1 (*v/v*). – [g] In $CDCl_3$.

ellites for both isomers, confirming the general assignment of the transient dihydrides to the structures **6b**. Upon heating, extensive isomerization of the alkenyl part of the σ-ligand occurs, complicating the spectrum and leading to the appearance of a third isomer. This isomer could be due to an isomerization of the side-chain of the alkyne into an allenic structure. With 1-phenyl-1-butyne as the substrate, the insertion product was not discernible in the ^{1}H spectrum owing to the low intensity and complicated patterns due to its ethyl group, but it was readily observable in the ^{31}P spectrum of the reaction mixture [δ_P = 17.75, ^1J(Pt−P) = 2995 Hz].

Figure 2. PHIP ^{1}H-NMR spectra of the systems *trans*-[$(PPh_3)_2$PtHCl]/$SnCl_2$/alkyne/para-H_2 ([D_6]acetone, room temp.); **a)** alkyne = 1-phenyl-1-butyne; **b)** central lines of the spectrum (a) in the range δ = −10 to −12; **c)** PHIP++ simulation of the central part of the spectrum (a); **d)** alkyne = diphenylacetylene; **e)** alkyne = 3,3-dimethylbutyne

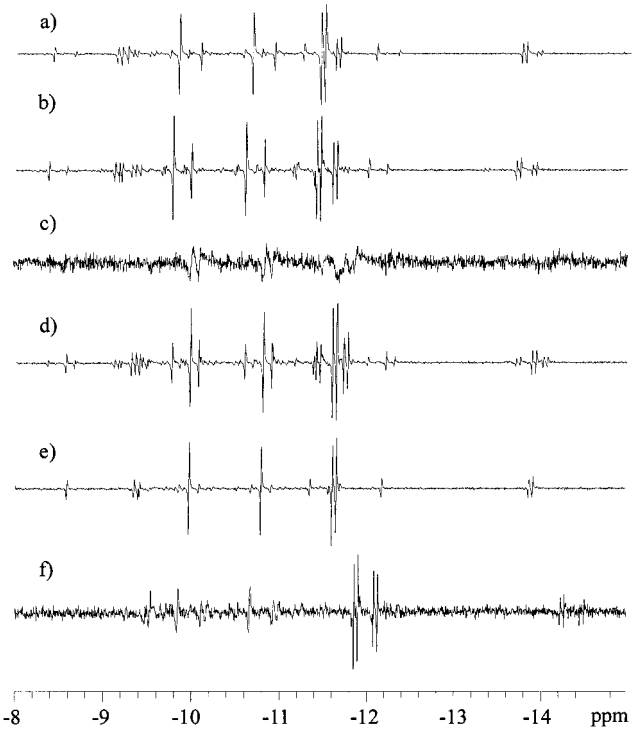


As expected, the system [$(PPh_3)_2$PtHCl]/$SnCl_2$/diphenylacetylene produced simple polarization patterns upon reaction with parahydrogen in acetone (Figure 2, d) due to the symmetry of the substrate and, therefore, resulted in the presence of only one dihydride, **6c**. The intensity of the signals was much lower than in the case of the 1-phenyl-1-propyne system. The reaction with 3,3-dimethylbutyne (Figure 2, e) also gave a simple polarization spectrum, despite the lack of symmetry of the substrate. This simplicity is apparently due to the fact that one alkenyl isomer strongly predominates in this case. The major isomer is suggested to be the 3,3-dimethylbutenyl-1 complex (**6d**), in view of the considerable steric requirements of the *tert*-butyl group. When the PHIP spectrum is recorded at elevated temperatures, a reversible formation of the second isomer is observable. Since in this case no changes in the alkenyl ligand can readily occur without undergoing skeletal rearrangements, we suggest these two reversible isomers to be the 3,3-dimethylbutenyl-1-platinum complex as the major component, and the corresponding -2-platinum complex as the minor component. Phenylacetylene and 1,4-diphenylbutadiyne gave no detectable dihydrides, but polarized signals of styrene and 1,4-diphenyl-3-en-1-butyne, respectively, were seen on heating (vide infra).

PHIP in Related Catalytic Systems

Bromide Systems: The interactions of the systems [$(PPh_3)_2$PtHBr]/$SnBr_2$/alkyne (alkyne = 1-phenyl-1-propyne, 1-phenyl-1-butyne, diphenylacetylene) in acetone with parahydrogen also give rise to polarization in the Pt−H spectral region (Figure 3). The difference in chemical shifts of the two hydride resonances provides clear evidence for first-order patterns of an AMX spin system in these cases. In general, bromide systems give more intense and sharp signals compared to the corresponding hydrido chloro complexes. The resulting Pt^{IV} dihydrides possess an enhanced thermal stability compared with the chloro analogues, and are readily observable even upon heating. Furthermore, the initial patterns are fully restored on cooling once more (al-

Figure 3. PHIP ^{1}H-NMR spectra of the systems [L_2PtHBr]/$SnBr_2$/alkyne/para-H_2 in [D_6]acetone; **a)** L = PPh_3, alkyne = 1-phenyl-1-propyne, room temp.; **b)** L = PPh_3, alkyne = 1-phenyl-1-butyne, room temp., before heating; **c)** L = PPh_3, alkyne = 1-phenyl-1-butyne, on heating; **d)** L = PPh_3, alkyne = 1-phenyl-1-butyne, at room temp. after heating; **e)** L = PPh_3, alkyne = diphenylacetylene, room temp.; **f)** L = $PMePh_2$, alkyne = 1-phenyl-1-propyne, room temp.



kyne = 1-phenyl-1-propyne, Figure 3, a). With 1-phenyl-1-butyne, the additional third isomer of the dihydride is formed only after heating (Figure 3, b−d). With diphenylacetylene, the bromide system gives strong and well-resolved polarization patterns with a full set of satellite signals (Figure 3, e).

Variation of the Phosphane Ligands: Generally speaking, electron-donating phosphanes show less intense and poorly resolved polarization patterns in the Pt−H region under the conditions employed. The results obtained for the $[(PR_3)_2PtHX]/SnX_2$/alkyne/acetone systems are summarized in Tables 2 and 3. The triethylphosphane monohydride system did not give rise to PHIP. The system $[(PMePh_2)_2PtHCl]/SnCl_2$/1-phenyl-1-propyne/acetone produces only weak polarization in the Pt−H region (Figure 3, f). diphenylacetylene in the presence of $[(PPh_3)_2PtHCl]/SnCl_2$. Nevertheless, in addition to these signals, in some cases relatively strong polarization patterns are observed on heating (Figure 4). In general, hydrogenation of 1-phenyl-1-butyne and 1-phenyl-1-propyne gives moderately intense polarization signals of the corresponding *cis*-alkenes (Figure 4, a, b). Phenylacetylene is hydrogenated readily, giving rise to strongly polarized styrene signals as a result of *cis*-addition of parahydrogen (Figure 4 c). The *cis*-addition of para-H_2 was confirmed by means of the PHIP++ program simulation. Due to the ALTADENA conditions of the hydrogenation (i.e. the addition of parahydrogen proceeds in the Earth's magnetic field, and the subsequent transfer to the strong B_0 field for the NMR measurement is adiabatic), extensive polarization transfer to the methyl and phenyl

Table 3. Spectral NMR parameters of intermediate dihydrides observed in systems with other phosphanes, $[(PR_3)_2PtH(SnX_3)]$/1-phenyl-1-propyne/$[D_6]$acetone (δ, relative to $[D_5]$acetone; *J*, Hz). The letter **a** corresponds to the major isomer, the letter **b** to the minor isomer.

PR_3	X	Isomer	$\delta(H^1)$	$\delta(H^2)$	$^1J(Pt\text{-}H^1)$	$^1J(Pt\text{-}H^2)$	$^2J(P\text{-}H^1)$	$^2J(P\text{-}H^2)$
$PMePh_2$	Cl	**a**	−11.17	–	–	–	9.5	–
		b	−11.392					
$PMePh_2$	Br	**a**	−11.875	−10.25	951.3	563?	9.3	163.2
		b	−12.102		948.6		9.2	
PMe_2Ph	Cl	[a]	−11.869	−11.487	9.5	–	–	164.5

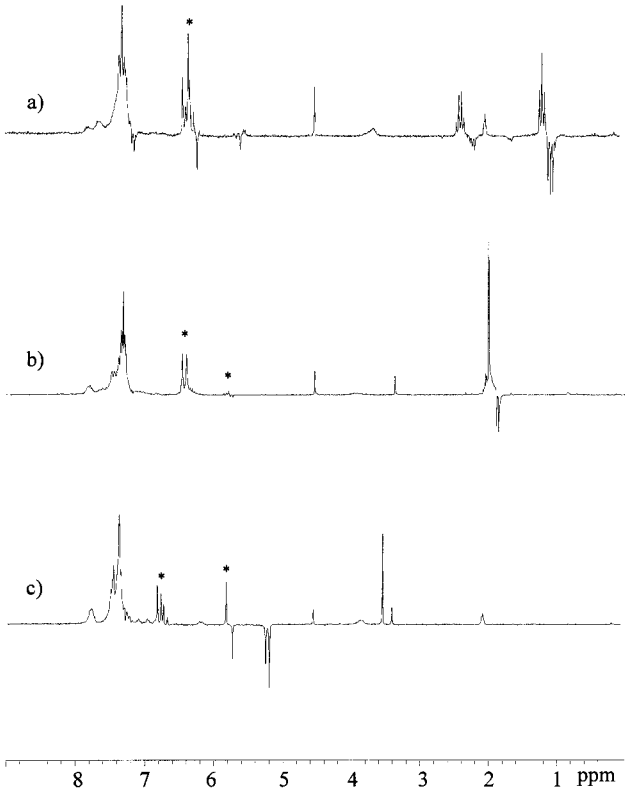
[a] One isomer.

The methyl resonance attributable to the insertion product, analogous to **5**, is also observable in this system [$\delta(CH_3)$ = 1.24, $^3J(^{195}Pt-H)$ = 53.4 Hz]. Due to the low intensity and broadness of the signals, the exact composition of the insertion product remains unclear.

Using the $[(PMePh_2)_2PtHBr]/SnBr_2$ system, the hydrogenation of 1-phenyl-1-propyne proceeds rapidly at room temperature, mainly via an asynchronous mechanism, i.e. not pairwise. This is reflected in the low polarization signals of the hydrogenation product, as opposed to rapidly arising thermal ones, and furthermore, the polarization in the Pt−H region is low. These Pt-H PHIP signals become stronger upon heating. It should be noted, however, that the signals attributable to the insertion product are clearly visible even at elevated temperature.

Only weak and poorly-resolved polarization patterns in the Pt^{IV} dihydride region are observed in the course of hydrogenation of PhC≡CMe in the presence of $[(PMe_2Ph)_2PtHCl] + SnCl_2$ in acetone. This hydrogenation proceeds without polarization of the product signals.

Figure 4. Polarization of product signals during hydrogenation with para-H_2 of alkynes in the presence of $[(PPh_3)_2PtHX]/SnX_2$ catalytic systems in $[D_6]$acetone on heating; **a)** X = Br, alkyne = 1-phenyl-1-butyne; **b)** X = Br, alkyne = 1-phenyl-1-propyne; **c)** X = Cl, alkyne = phenylacetylene. The absorption signals of the products, i.e. of the *cis*-alkenes, are marked *.



The Relationship between Synchronous (Pairwise) and Asynchronous Hydrogenation Mechanisms

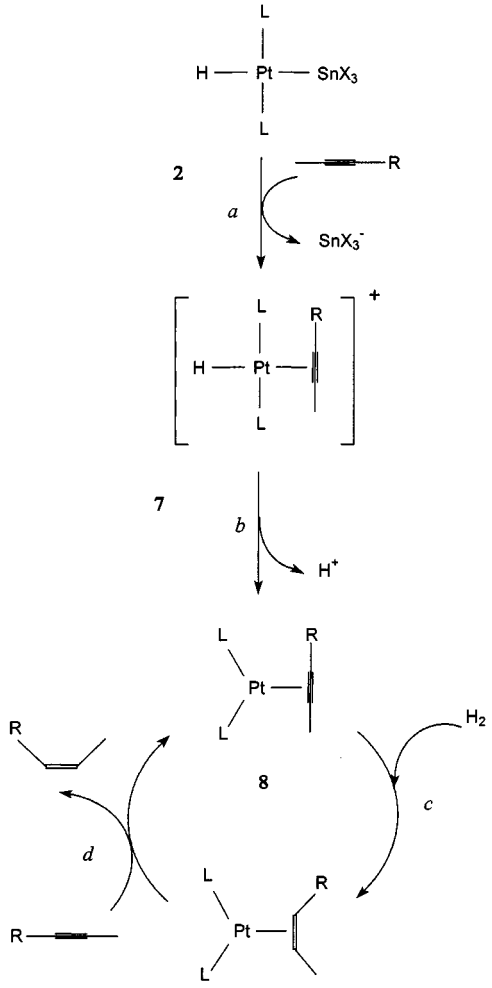
The observed Pt^{IV} dihydrides are assumed to be the intermediates in the stepwise hydrogenation of an alkyne. Decomposition of these dihydrides leads via reductive elimination to an alkene and a platinum monohydride. Consequently, only thermal signals are observed from the product, as is the case during the hydrogenation of

groups of the substrate is also observed. The efficient polarization transfer under these conditions is due to strong isotropic mixing of the proton spin functions in the whole molecule at low magnetic field[44], as was previously shown for the hydrogenation of the diphenylacetylene-Pt^0 complex, $[(PPh_3)_2Pt(PhC{\equiv}CPh)]$[27]. Alternatively, for the hydrogenation of 1-phenyl-1-propyne, the polarized signals of the methyl group of the product can be accounted for by assuming a 1,3-dihydrogen addition to the intermediate platinacyclobutene, formed by methyl C−H activation, although the geometry of such an addition should favor the *trans*-alkene as a primary product, rather than the *cis*-isomer, which is in fact obtained. Furthermore, the same effect is also operative for the methyl group of 1-phenyl-1-butyne, and seems to have the same origin.

The mechanism of the synchronous dihydrogen addition observed in the SnX_2-activated systems described here is suggested to be related to the Pt^0-mediated hydrogenation.

This mechanism could involve the η^2-coordination of an alkyne, and the reductive elimination of HX together with SnX_2, followed by oxidative addition of dihydrogen to the resulting Pt^0 complex with subsequent formation of an alkene (Scheme 2). The formation of the Pt^0 intermediate

Scheme 2. The proposed mechanism for the synchronous hydrogenation of alkynes catalyzed with the $[(PR_3)_2PtHX]-SnX_2$ system in acetone



should be favored at higher temperatures, as well as by an increased electronegativity of the π ligand. This process is of little significance for alkenes, where asynchronous hydrogenation is observed, giving rise to thermal signals of the products. It is also noteworthy that the Pt^{IV} dihydrides (**6a**) are not usually observable in the spectrum at elevated temperatures in cases where the polarized signals of the products appear instead.

The Role of Structural Factors and Reaction Conditions for the Appearance of PHIP in the Pt^{II}/Sn^{II} Catalytic Systems

Solvent Effects: The described polarization patterns of the Pt^{IV} dihydrides were observed only with acetone as the solvent. The sole exception was the interaction of isolated **5a** with parahydrogen in dichloromethane solution, as discussed above. The synchronous hydrogenation of alkynes proceeded well in acetone, but was hardly reproducible in benzene or in other non-solvating media. Experiments in acetonitrile, which is a much poorer solvent for $SnCl_2$, did not lead to any PHIP effects either. Strongly solvating additives, such as DMF and THF, can easily destroy the catalytic system, facilitating the cleavage of solvated SnX_2 molecules from the active platinum hydride and/or from a σ-carbon intermediate (**3** in Scheme 1[31][45]). Since Pt^{IV} dihydride contains only one phosphane ligand, the promotion of phosphane dissociation by the attached trihalotin ligand and acetone as the solvent seems to be necessary for the generation of PHIP-detectable dihydrides. It is noteworthy that phosphane redistribution proceeds only for platinum monohydrides with PPh_3 and $PMePh_2$[46], and correspondingly, polarized Pt^{IV} dihydrides are observable mainly with these ligands. Furthermore, the processes suggested to be essential for synchronous hydrogenation, the formation of cationic intermediates **7** (Scheme 2), as well as their deprotonation with formation of Pt^0 intermediates **8**, are strongly favored with polar, solvating acetone as the solvent.

Substrate and Halide Ligands: The appearance of polarized Pt^{IV} dihydrides depends principally on the hydrogenation substrate. The intensity of the polarization pattern reflects the suggested stability of the insertion product, while the number of isomers corresponds to the possible number of isomeric alkenyl radicals. For symmetrical alkynes, only one isomer is observed; for 1-phenyl-1-propyne two main insertion products are possible, giving rise initially to two dihydrides. Accordingly, 1-phenyl-1-butyne, being able to form more isomers, gives a complicated mixture of polarized dihydrides after heating. Alkenes, especially internal ones, generally adopt a quite unfavorable equilibrium position for insertion into Pt−H bond[31]. This factor is believed to be the reason for the failure to observe intermediates of type **6** in the course of the hydrogenation of alkenes such as NBD and 3,3-dimethylbutene. Furthermore, steric bulkiness of an alkyne (e.g. diphenylacetylene) can prevent extensive formation of the alkenyl complex, thereby decreasing the intensity of the signals of the Pt^{IV} dihydrides.

Tribromostannato hydrides give insertion products with higher equilibrium constants, and the resulting σ-insertion products are less fluxional compared to the chloro analogues. This feature is reflected in the higher intensity and sharpness of the corresponding polarization patterns.

We thank the *Russian Foundation for Basic Research (RFBR)*, and the *Deutsche Forschungsgemeinschaft (DFG)* for financial support, and Dr. *S. Klages* for many helpful discussions.

Experimental Section

General Remarks: The ^{1}H-, ^{1}H-PHIP-, and ^{31}P-NMR spectra were recorded with a Bruker AMD 200 MHz spectrometer with an Aspect 2000 operating system. In order to obtain the PHIP spectra, one 8K FID signal was acquired using 45° excitation pulses covering the spectral range between δ = −30 and δ = +10. To record the conventional or "thermal" ^{1}H-NMR spectra, the same parameters were used, except for the pulse width, which was set at 90°. The ^{13}C spectra were recorded with a Varian VXR-400 spectrometer operating at 100.6 MHz. The ^{1}H- and ^{13}C-NMR spectra were referenced to residual protons of known chemical shift and the ^{13}C signals of the solvent, respectively, while ^{31}P spectra were referenced to external 85% H_3PO_4.

The simulation of the PHIP ^{1}H-NMR spectra was performed with the OS/2-based PHIP++ program, developed by Greve[47].

Deuterated solvents for NMR spectroscopy were purchased from Aldrich, dried ($CDCl_3$) and degassed prior to use, and stored under vacuum.

Tin dichloride and tin dibromide (anhydrous) were both obtained from Aldrich, and used without additional purification.

The platinum complexes, *trans*-[$(PR_3)_2$PtHCl] (PR_3 = PPh_3,[37]; $PMePh_2$, PMe_2Ph[48]) were synthesized as described previously. The corresponding hydrido bromo complexes were obtained according to ref.[49], by reaction of the hydrido chloro complex with excess NaBr in acetone.

Typical Preparation of Solutions for Hydrogenation Studies: Weighed amounts of *trans*-[$(PPh_3)_2$PtHCl] (10 mg, 13 μmol) and $SnCl_2$ (7.5 mg, 40 μmol) were placed in a screw-capped NMR tube attached to a vacuum line, and 0.7 ml of dry degassed [D_6]acetone was condensed into the tube. After thawing and filling the tube with dry argon, it was disconnected from the vacuum line and fitted with a septum stopper. About 15 μl of the substrate was then added to the sample by means of 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 probehead, and the ^{1}H-PHIP spectrum was recorded immediately thereafter.

(σ-1-Phenylpropen-2-yl)(trichlorostannato)bis(triphenylphosphane)platinum (**5a**): [$(PPh_3)_2$PtHCl] (100 mg, 0.132 mmol) and $SnCl_2$ (100 mg, 0.53 mmol) were taken up in 2 ml of dry degassed acetone. Upon formation of a clear, orange solution, an excess of 1-phenyl-1-propyne (0.2 ml) was added under argon. The solution was degassed and sealed in a tube. After 5 min at +100°C, the tube was stored at 0°C for 48 h. Light-yellow crystals were deposited, which were collected, washed with acetone, and dried in vacuo (72 mg, 52%); m.p. 165−166°C. − ^{1}H NMR: δ = 0.69 [d, CH_3, ^3J(PtH) = 51.2, ^4J(HH) = 1.3, $^4J(^{117/119}$SnH) = 76.4 Hz], 6.45 [br, =C*H*Ph, ^3J(PtH) = 82.2, $^4J(^{117/119}$SnH) = 119.5 Hz]. − ^{13}C NMR: δ = 150.67 [t, Pt*C*, ^1J(PtC) = 772, ^2J(PC) = 9.2 Hz], 139.35 [s, *C*Ph, ^2J(PtC) = 94.8 Hz], 23.50 [s, CH_3, ^2J(PtC) = 28.9 Hz]. − ^{31}P NMR: δ = 18.85 [s, ^1J(PtP) = 3007, $^2J(^{119}$SnP) = 240.4, $^2J(^{117}$SnP) = 230.7 Hz].

Reaction of **5a** *with Dimethylformamide:* To a solution of isolated **5a** (46 mg, 43 μmol) in 0.7 ml of CD_2Cl_2, 10 μl of dimethylformamide was added. ^{1}H NMR of **5b**: δ = 1.131 [s, ^3J(PtH) = 48.8 Hz]. − ^{31}P NMR: δ = 24.607 [s, ^1J(PtP) = 3306 Hz].

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