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Reactions of hydridotrihalostannato complexes of platinum {*trans*-[PtH(SnX$_3$)(PR$_3$)$_2$]} with alkenes

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An interaction of *trans*-[PtH(SnX$_3$)L$_2$] (I, L = PPh$_3$, PMePh$_2$, PEt$_3$, PBu$_3$; X = Cl, Br) with ethylene, propene and 2-methylpropene has been studied by means of ^{31}P and ^{1}H NMR spectroscopy. The reactions of platinum hydrides I with ethylene are rapid and reversible at −90°C, giving *cis*-[PtR(SnX$_3$)L$_2$] (II, R = C$_2$H$_5$). The reaction of propene with I (L = PPh$_3$, PMePh$_2$) gives II, R = C$_3$H$_7$. ^{13}C and ^{1}H NMR spectra prove the n-propyl structure for II, L = PMePh$_2$, X = Cl. Complexes II irreversibly isomerize into *trans*-[PtR(SnX$_3$)L$_2$] between −50° and 0°C. The equilibrium constants and rates are estimated for the reactions of I with alkenes. They decrease as a function of L (PMePh$_2$ > PPh$_3$ > PBu$_3$ > PEt$_3$) and X (Br > Cl). The reactivities of alkenes decrease with increase of steric hindrances at the double bond.

Keywords: Alkenes, Pt—H insertion, platinum hydrides, alkyl complexes, phosphine complexes, ^{31}P NMR

INTRODUCTION

The reactions of platinum hydride complexes with alkenes are the key stages of the catalytic cycles of alkene hydrogenation, isomerization and hydroformylation catalysed by platinum–tin systems. It is now generally accepted that an insertion of alkene into a platinum hydrogen (Pt—H) bond occurs at this stage, resulting in a platinum σ-alkyl complex, which reacts further with hydrogen or carbon monoxide. Thus these reactions, as well as the structures and properties of the alkyl derivatives formed, have been widely researched.[1]

The insertion of ethylene into the Pt—H bond in *trans*-[PtHClL$_2$] complexes occurs under forced conditions and is reversible.[2,3] Tin dichloride (SnCl$_2$) substantially accelerates attainment of the equilibrium.[4] This effect is attributed to formation of trichlorostannato complexes [PtH(SnCl$_3$)L$_2$],[5] reacting with alkenes by the associative pathway.[6] The effect of SnCl$_3$ ligands is caused apparently by their known ability to stabilize pentacoordination of platinum.[7] A promoting effect of tin dihalides in the reactions catalysed by platinum complexes is attributed to the same cause.[8–11]

Theoretical calculations for the reaction of ethylene with [PtHCl(PH$_3$)$_2$] indicate that ethylene insertion into a Pt—H bond involving a pentacoordinated intermediate [PtHCl(C$_2$H$_4$)(PH$_3$)$_2$] proceeds with a higher activation barrier than if *cis*-[PtH(C$_2$H$_4$)(PH$_3$)$_2$] is involved. The role of tin trichloride has not been elucidated by the authors.[12,13]

Recently it has been shown in our laboratory[14] that ethylene insertion into the Pt—H bond of *trans*-[PtH(SnX$_3$)(PPh$_3$)$_2$] (X = Cl, Br) proceeds rapidly at −90°C, leading to the kinetically controlled formation of *cis*-[Pt(C$_2$H$_5$)(SnX$_3$)(PPh$_3$)$_2$].

In the present work we have studied the interaction of platinum hydrides (I) with alkenes (Eqn [1]) with a view to elucidating factors affecting the rate of the insertion reaction and the stability of the alkyl complexes (II) formed.

EXPERIMENTAL

(A) Materials

The ^{31}P NMR spectra were recorded with a Varian FT-80A spectrometer operating at 32.196 MHz at −90°C with internal ^{2}D lock. Chemical shifts were calculated relative to external phosphoric acid (85% H$_3$PO$_4$, at 25°C); a positive sign corresponds to

$$trans\text{-}[PtH(SnX_3)L_2] + CH_2{=}CR^1R^2 \xrightleftharpoons{-90^\circ C} cis\text{-}[Pt(CH_2CHR^1R^2)(SnX_3)L_2] \qquad [1]$$

For **I**, **II**:
$R^1 = R^2 =$ H: X = Cl, Br, L = PPh$_3$, PMePH$_2$, PEt$_3$; X = Cl, L = PBu$_3$.
$R^1 =$ H, $R^2 =$ Me: X = Cl, Br, L = PPh$_3$, PMePh$_2$.
$R^1 = R^2 =$ Me: L = PMePh$_2$, X = Cl, Br.

downfield shift. The ^{1}H and ^{13}C NMR spectra were recorded with a Varian VXR-400 spectrometer operating at 400 and 100 MHz, respectively, at −80°C. Chemical shifts are given on the δ-scale relative to signals of ^{13}C or residual protons of deuterodichloromethane (CD$_2$Cl$_2$).

CD$_2$Cl$_2$ was purified by the standard technique,[15] dried overnight with P$_2$O$_5$ and distilled. Deuterodimethylformamide (DMF-d$_7$) was re-condensed twice from both P$_2$O$_5$ and KOH *in vacuo*.

Tin dihalides (SnX$_2$) were obtained by heating metallic tin with aqueous HX; the hydrates SnX$_2\cdot n$H$_2$O were dried *in vacuo*, recrystallized from dry acetone, and finally dried *in vacuo* (10^{-2} Torr).

Ethylene, propene, and 2-methylpropene were re-condensed several times from P$_2$O$_5$ *in vacuo*.

Trans-[PtHXL$_2$] complexes were obtained by published methods.[2,16] The purity of the complexes has been checked by ^{31}P NMR spectroscopy.

Weighed amounts of all the above reagents were placed in a vacuum before use in apparatus with appropriate breakable sealings.

(B) Solutions of *trans*-[PtH(SnX$_3$)L$_2$] and their interaction with alkenes and DMF

All manipulations were carried out in all-glass apparatus, using standard high-vacuum techniques. The reagents, *trans*-[PtHXL$_2$] (0.04 mmol) and SnX$_2$ (0.04 mmol) were allowed to react for 1 h in 1 cm^3 of CD$_2$Cl$_2$ with stirring; the yellow solution of *trans*-[PtH(SnX$_3$)L$_2$] (**I**) was transferred into a 8.5 mm tube equipped with breakable sealings containing the alkene and DMF, and then the tube was sealed. The composition and purity of the solution were checked with ^{31}P NMR (Table 1). The impurities (mainly unreacted *trans*-[PtHXL$_2$]) did not exceed 4 mol%. The reaction of an alkene was initiated by the breaking of an appropriate seal.

(C) Determination of half-life periods and equilibrium constants for the reaction [1]

The ratios of concentrations of the hydride and alkyl complexes were determined during the course of the reactions using the integrated intensities of corresponding lines in the ^{31}P NMR spectra. The relaxation times of the ^{31}P nuclei in these complexes are believed to be not much longer than 0.1 s at −90°C (as estimated for *trans*-[PtCl$_2$(PEt$_3$)$_2$]), so pulse width and pulse interval were consequently set up to 45° and 1 s to achieve a full relaxation of all the ^{31}P nuclei. Spectra were obtained as a result of at least a five-minute accumulation period. The integral intensities obtained 3—4 h after the initiation of the reaction were used to calculate the equilibrium

Table 1 ^{31}P and ^{1}H MNR spectral parameters for *trans*-[PtH(SnX$_3$)L$_2$] (CD$_2$Cl$_2$, −90°C)

L	X	δ_P[a]	$^1J_{PtP}$	$^2J_{SnP}$[b]	δ_{PtH}	$^1J_{PtH}$	$^2J_{PH}$	Ref.
PPh$_3$	Cl	27.09	2649	214,207	−8.55	1268	9.3	30
	Br	28.58	2667	202,196	−10.03	1314	10.1	19, 26
PMePh$_2$	Cl	5.47	2540	221,212	−9.04	1373	9.9	
	Br	5.85	2558	—[c]	—[c]	—[c]	—[c]	
PEt$_3$	Cl	18.94	2358	219,210	−9.82	1478	11.4	
	Br	19.13	2366	207,198	−11.14	1497	10.3	
PBu$_3$	Cl	10.6	2344	213[d]				

[a] Relative to 85% H$_3$PO$_4$, positive signs for downfield shifts. [b] $^2J(^{119}$Sn—^{31}P), $^2J(^{117}$Sn—^{31}P). [c] The NMR spectral parameter is not obtained due to line broadening. [d] Mean value.

constants. The half-life periods were determined graphically, as time required for the reaction to pass one-half of the way to equilibrium.

RESULTS AND DISCUSSION

(A) Products of the reaction of platinum hydrides I with alkenes and their spectral identification

(i) The reaction of I with ethylene

Complexes formed in the course of the reaction of **I** with ethylene exhibit some characteristic patterns in their ^{31}P NMR spectra (parameters for these are given in Table 2). The spectra consist of two doublets of an AB system, assigned to nonequivalent phosphorus nuclei in a *cis* position, surrounded with corresponding satellite peaks, caused by ^{195}Pt, ^{119}Sn and ^{117}Sn isotopes. The hydride region of the ^{1}H spectrum is transparent and broad signals appearing at 0.5−1.5 ppm are ascribed to the protons of the ethyl group. No extra splittings were observed in off-resonance ^{31}P spectra, indicating the absence of large P−H couplings. Such spectral patterns for the reaction products are consistent with complexes of a square-planar geometry formulated as *cis*-[Pt(C$_2$H$_5$)(SnX$_3$)L$_2$] (II). Taking into account the large *trans* influence of an alkyl group, it is reasonable to assign the doublet with $^1J(\text{Pt–P}^1) \approx 1850$ Hz to the P^1 atom which is in a *trans* position to the ethyl group. This assignment is consistent with the values of ^2J (Sn−P) and ^2J (Sn−P^1), which are common for the *trans* and *cis* arrangement of tin and phosphorus nuclei.[17] The small decrease of ^1J(Pt−P) in the series PPh$_3$ > PMePh$_2$ > PEt$_3$ can be explained by a decrease of

Table 2 ^{31}P NMR spectral parameters for *cis*-[PtR(SnX$_3$)L$_2$] (CD$_2$Cl$_2$, −90°C)

L	X	R	δ_P[a] δ_{P^1}	$^1J_{PtP}$[a] $^1J_{PtP^1}$	$^2J_{SnP}$[a] $^2J_{SnP^1}$	$^2J_{PP^1}$[a]	Notes
PPh$_3$	Cl	C$_2$H$_5$	29.4 17.7	3989 1857	3816,3646 257[b]	17	See footnote d
	Br	C$_2$H$_5$	25.34 19.50	4017 1916	3754,3571 219[b]	15.3	See footnote d
PMePh$_2$	Cl	C$_2$H$_5$	11.80 −0.33	3879 1798	3789,3618 238[b]	17.8	
	Br	C$_2$H$_5$	8.58 0.64	3899 1822	—[c]	—[c]	
PEt$_3$	Cl	C$_2$H$_5$	20.12 9.49	3791 1816	3626,3443 258[b]	16	
	Br	C$_2$H$_5$	18.09 9.64	3811 1844	3558,3399 221[b]	15.9	
PBu$_3$	Cl	C$_2$H$_5$	11.6 2.2	3774 1803	—[c]	16	
PPh$_3$	Cl	C$_3$H$_7$	29.9 17.2	3964 1860	3783,3614 254[b]	17	
	Br	C$_3$H$_7$	25.83 19.41	3987 1911	3742,3575 257[b]	15.9	See footnote e
PMePh$_2$	Cl	C$_3$H$_7$	11.41 −0.1	3864 1807	3786,3612 244,234	18.1	See footnote f
	Br	C$_3$H$_7$	8.25 1.49	3858 1826	3705,3540 219[b]	16.7	
PMePh$_2$	Cl	CH$_2$CHMe$_2$	10.89 −0.85	3858 1789	3732,3668 278[b]	17.8	
	Br	CH$_2$CHMe$_2$	7.77 0.8	3851 1821	—[c] 201	16.7	

[a] P^1 is *trans* to R; P is *cis* to R. [b] Mean value. [c] The NMR spectral parameter is not obtained due to line broadening and/or low intensity. [d] Data from Ref. 14. [e] ^{1}H NMR: 1.10 (very br., 4H), 0.44 (broadened, 3H). [f] ^{1}H NMR: 1.24 (br., 2H), 1.11 (br., 2H), 0.44 (t, br., 3H), 2.13 (d, CH$_3$–P), 1.60 (d, CH$_3$–P). ^{13}C–{^{1}H} NMR: 26.42, 18.75, 18.64, 16.47 (d, CH$_3$–P), 11.97 (d, CH$_3$–P).

phosphorus lone pair *s*-character in this series. Replacement of the SnCl$_3$ group with an SnBr$_3$ group results in an increase of both ^1J (Pt−P) and ^1J (Pt−P^1), accompanied by a decrease of ^2J(Sn−P) and ^2J(Sn−P^1). These variations in coupling constants are apparently caused by the circumstance that SnBr$_3^-$ is a poorer σ-donor than SnCl$_3^-$. This leads therefore to an increase of *s*-electron density in Pt−P bonds.[18]

As was shown recently,[14,19] addition of electron-donating solvents, such as dimethylformamide (DMF) or methanol (MeOH), caused elimination of tin dihalide from tin trihalide complexes of platinum, and formation of corresponding halogeno complexes. When an approximately two-fold excess of DMF is added at −90°C to **II** (obtained according to Eqn [1]), the formation of *cis*-[Pt(C$_2$H$_5$)HL$_2$] (**III**) occurs immediately (Scheme 1), giving rise to corresponding changes in the ^{31}P NMR spectra (Table 3). Under these reaction conditions, i.e. in the presence of SnX$_2$ and DMF, these complexes are unstable (as are also **II**, *vide infra*), and partially decompose or isomerize to *trans* alkyl complexes on warming to room temperature.

The value of ^1J(Pt−P) obtained for **III**, L = PEt$_3$, X = Cl, R = C$_2$H$_5$, is somewhat larger compared with the values for the corresponding methyl and phenyl complexes. This difference can be attributed to the greater electronegativity of methyl and phenyl groups in comparison with ethyl. Taking into account a comparatively large scattering of literature data for *cis*- and *trans*-[PtRCl(PEt$_3$)$_2$],[20–22] as well as an appreciable solvent dependence of ^1J(Pt−P) for *trans*-[Pt(C$_2$H$_5$)Cl(PEt$_3$)$_2$],[23] the spectral parameters obtained for **III** are in accord with literature data. Alternatively, complexes **III** can be formed, but much more slowly, when ethylene reacts with *trans*-[PtHXL$_2$] in the presence of catalytic amounts of SnX$_2$.

Complexes **II** isomerize in a temperature range from −50° to 0°C to *trans*-[Pt(C$_2$H$_5$)(SnX$_3$)L$_2$] (**IV**) which eliminate SnX$_2$ on the action of DMF and form *trans*-[Pt(C$_2$H$_5$)XL$_2$] (**V**, Table 4, Scheme 1).

(ii)The reaction of I with propene and 2-methylpropene

The reaction of hydrides **I** (L = PPh$_3$, PMePh$_2$) with propene at −90°C gives *cis*-[Pt(C$_3$H$_7$)(SnX$_3$)L$_2$] complexes. This has been concluded on the basis of their ^{31}P NMR spectral parameters, which are similar to those for **II**, R = C$_2$H$_5$ (Table 2).

For structural theory reasons and from the viewpoint of the interpretation of the results of homogeneous catalytic reactions involving the participation of the Pt−Sn system, it is important to obtain information about the direction of platinum hydride addition to alkenes. According to the ^{31}P NMR spectra, the *cis*-[PtR(SnX$_3$)L$_2$] complexes are the only products in the reactions of **I** with propene. In order to ascertain the structure of the propyl groups in these complexes, we have studied ^{13}C and ^{1}H NMR spectra (at 100 and 400 MHz respectively), of *cis*-[Pt(C$_3$H$_7$)(SnCl$_3$)(PMePh$_2$)$_2$], formed nearly quantitatively at a Pt:C$_3$H$_6$ ratio equal to one. The ^{1}H NMR spectra showed broad signals with unresolved patterns in the alkyl region with relative intensities of 2:2:3. This fact, together with the ^{13}C NMR spectrum (Table 2), proves a linear or unbranched structure of the propyl group. Our ^{1}H NMR data are in accord with published data for *trans*-[Pt(C$_2$H$_5$)Cl(PEt$_3$)$_2$] (Table 4). Similarly, the n-propyl complex is the result of the reaction of propene with *trans*-[PtH(acetone)(PMePh$_2$)$_2$]$^+$PF$_6^-$.[24] Complexes obtained by the interaction of a large excess of 2-methylpropene with **I** (L = PMePh$_2$) are suggested to be *cis*-[Pt(2-methylpropyl)(SnX$_3$) (PMePh$_2$)$_2$] (Table 4). Singlets in the ^{31}P NMR spectra of *trans*-[PtR(SnX$_3$)L$_2$] (Table 4) appeared upon standing of solutions of **II** (R = propyl, 2-methylpropyl) at room temperature for several hours.

(iii) The rates and equilibrium constants for the reactions of alkenes with I

We have estimated the half conversion periods for several reactions of some platinum hydrides **I** with

$$\begin{tikzcd}
\underset{\textbf{I}}{trans\text{-}[PtH(SnX_3)L_2] + \text{alkene}} \arrow[r, shift left, "-90^\circ C"] & \underset{\textbf{II}}{cis\text{-}[PtR(SnX_3)L_2]} \arrow[l, shift left] \arrow[r, "-50^\circ C"] \arrow[d, "\text{DMF}"', "-90^\circ C"] & \underset{\textbf{IV}}{trans\text{-}[PtR(SnX_3)L_2]} \arrow[d, "\text{DMF}"'] \\
 & \underset{\textbf{III}}{cis\text{-}[PtRXL_2]} \arrow[r] & \underset{\textbf{V}}{trans\text{-}[PtRXL_2]}
\end{tikzcd}$$

Scheme 1

Table 3 ^{31}P NMR spectral parameters for *cis*-[PtRXL$_2$] (CD$_2$Cl$_2$, −90°C)

L	X	R	δ_P^{a} δ_{P^1}	$^1J_{PtP}$^{a} $^1J_{PtP^1}$	$^2J_{PP^1}$^{a}	Ref.
PPh$_3$	Cl	C$_2$H$_5$	22.7	4778	13.0	14
			25.9	1542		
	Br	C$_2$H$_5$	21.46	4730	14.4	14
			21.11	1558		
PMePh$_2$	Cl	C$_2$H$_5$	2.48	4574	12.9	
			9.04	1598		
	Br	C$_2$H$_5$	3.77	4574	13.4	
			6.22	1618		
PEt$_3$	Cl	C$_2$H$_5$	8.93	4396	13.4	
			13.98	1582		
	Br	C$_2$H$_5$	9.20	4415	13.4	
			11.49	1588		
PEt$_3$	Cl	CH$_3$	8.7	4179		20
			14.6	1719		
	Br	CH$_3$	10.9	4179		20
			12.9	1743		
PEtPh$_2$	Cl	C$_6$H$_5$		4365	14.9	31
				1630		

[a] P^1 is *trans* to R, P is *cis* to R.

Table 4 ^{31}P NMR spectral parameters for *trans*-[PtRXL$_2$] (CD$_2$Cl$_2$, −90°C)

L	X	R	δ_P	$^1J_{PtP}$	$^2J_{SnP}$^{a}	Ref.
PPh$_3$	SnCl$_3$	C$_2$H$_5$	25.8	3002	241^b	14
	SnBr$_3$	C$_2$H$_5$	26.68	3026	227^b	14
PMePh$_2$	SnCl$_3$	C$_2$H$_5$	7.87	2877	—^{c}	
	SnBr$_3$	C$_2$H$_5$	9.10	2897	—^{c}	
PEt$_3$	SnCl$_3$	C$_2$H$_5$	9.73	2637	—^{c}	
	SnBr$_3$	C$_2$H$_5$	9.48	2650	217,208	
PPh$_3$	SnCl$_3$	C$_3$H$_7$	25.4	2986	—^{c}	
	SnBr$_3$	C$_3$H$_7$	27.4	3003	—^{c}	
PMePh$_2$	SnCl$_3$	C$_3$H$_7$	8.7	2854	—^{c}	
PEt$_3$	SnCl$_3$	C$_3$H$_7$	9.76	2619	247,234	
	SnBr$_3$	C$_3$H$_7$	9.60	2636	—^{c}	
PPh$_3$	Cl	C$_2$H$_5$	27.2	3340	—	14
	Br	C$_2$H$_5$	28.38	3293	—	
PMePh$_2$	Cl	C$_2$H$_5$	15.2	3173	—	
	Br	C$_2$H$_5$	9.10	—^{c}		
PEt$_3$	Cl	C$_2$H$_5$	15.57	2911	—	
			15.08	2979	—	23^d
			15.5	3013	—	23^e
	Br	C$_2$H$_5$	13.41	2885	—	
		C$_2$D$_5$	13.51	2991	—	23^e
	Cl	C$_3$H$_7$	15.2	2959	—	31^f
		C$_4$H$_9$	15.0	2961	—	31^f

[a] $^2J(^{119}Sn-^{31}P)$, $^2J(^{117}Sn-^{31}P)$. [b] Mean value. [c] The value was not determined due to overlapping of lines or their low intensities. [d] In C$_6$D$_6$. ^{1}H NMR: 1.32 (m). [e] In C$_6$H$_{12}$. [f] In C$_6$D$_6$.

alkenes as well as the equilibrium constants for the formation of alkyl complexes, using the integrated intensities of the ^{31}P NMR spectral lines. Data (Table 5) show that both rates and equilibrium constants for the reactions studied vary, depending on the phosphine, halogen and alkene, according to the following series:

PMePh$_2$ > PPh$_3$ > PBu$_3$ > PEt$_3$
Br > Cl
C$_2$H$_4$ > C$_3$H$_6$ > 2-CH$_3$C$_3$H$_5$

In some cases, the equilibrium constants appear to be too large to be measured under these conditions, since at a platinum:alkene ratio equal to one, the complete conversion of hydride **I** into a *cis*-alkyl complex was observed. Complexes **I**, containing PMePh$_2$ ligands, as well as **I** (L = PPh$_3$, X = Br) react rapidly with alkenes at −90°C, i.e. the equilibrium is accomplished during the course of the mixing of the reagents and before acquiring the first ^{31}P NMR spectrum (*ca* 5 min) and the quantities of the reagents do not change upon further storage of the solution at −90°C.

The variation in reactivities of platinum hydrides towards the alkenes as a function of the phosphine ligand were attributed to specific combinations of σ-donor and π-acceptor properties of phosphine ligands affecting the ability of the formation of the key five-coordinate intermediate for the alkene insertion reaction, in which the coordinated alkene competes with the phosphine ligands for the same platinum orbitals. Low thermodynamic stabilities of *cis*-alkyl complexes **II** (L = PEt$_3$) were apparently caused by the fact that two strong σ-donors (PEt$_3$ and the alkyl group) were *trans*-situated and competed for the unoccupied platinum orbitals. This is why complexes **II** with the less basic PBu$_3$ are more stable.

The series of alkene reactivities, being independent of the phosphine, are caused rather by steric interactions of the substituents at alkene double bonds with the relatively bulky phosphine ligands, rather than by electronic factors.

Complexes **I** with SnBr$_3$ ligands react more rapidly and completely in comparison with the corresponding SnCl$_3$ complexes. This observation is in agreement with facts obtained for catalytical reactions,[10] but it is hardly understandable on the basis of the known properties of trihalotin ligands, since the SnBr$_3$ ligand exhibits poorer *trans* and *cis* influences in comparison with SnCl$_3$.[19,26] Apparently, poorer σ-donating and π-

Table 5 Half-conversion periods for reactions of platinum hydride complexes with alkenes ($\tau_{1/2}$) and equilibrium constants for formation of *cis*-[$PtR(SnX_3)L_2$] (K_{eq}) at −90°C in CD_2Cl_2 (c_{Pt} = 0.04 mol dm^{-3})

L	X	R	Pt:alkene	*cis*-Pt−C[a](%)	$K_{eq} \times 10^{-2}$ (dm^3 mol^{-1})	$\tau_{1/2}$ (min)
PPh_3	Cl	C_2H_5	1:1	89	18	46
	Br	C_2H_5	1:1	100	—[b]	—[c]
$PMePh_2$	Cl	C_2H_5	1:1	100	—[b]	—[c]
	Br	C_2H_5	1:1	100	—[b]	—[c]
PEt_3	Cl	C_2H_5	1:10	80	0.11	—[d]
	Br	C_2H_5	1:10	100	—[b]	—[c]
PBu_3	Cl	C_2H_5	1:1	82	6.3	165
PPh_3	Cl	C_3H_7	1:50	94	0.08	60
	Br	C_3H_7	1:1	69.6	1.9	—[d]
$PMePh_2$	Cl	C_3H_7	1:1	97.7	461	—[c]
	Br	C_3H_7	1:1	100	—[b]	—[c]
	Cl	CH_2CHMe_2	1:100	72	0.006	—[d]
	Br	CH_2CHMe_2	1:100	82.5	0.011	—[d]

[a] Mole fraction of *cis*-alkyl complex **II** (%). [b] The value is too large to be measured, > 5 × 10^4 dm^3 mol^{-1}. [c] Rapid, $\tau_{1/2}$ < 5 min. [d] The kinetics were not studied.

accepting properties of the $SnBr_3$ relative to the $SnCl_3$ ligand[18] lead to lower Pt−Sn bond strengths and therefore, on the one hand stabilize the five-coordinate intermediate of the insertion, and on the other hand facilitate the formation of *cis*-alkyl complexes.

Due to the fact that the equilibrium [1] is achieved easily even at low temperature, the compounds **II** can be regarded as somewhat resembling hydrido−π−alkene complexes. However, the ^{1}H NMR parameters for *trans*-[$Pt(C_2H_4)H(PEt_3)_2$] [$\delta(C_2H_4)$ = 7.2 ppm[27]) differ significantly from those we have obtained. This means that complexes **II** contain usual σ-bonded alkyl groups. The NMR data for ethylpalladium complexes[28] give evidence for rapid averaging and equivalence of CH_3 and CH_2 signals, caused apparently by β-hydrogen coordination to the palladium atom. For complexes **II** the possibility for such coordination can be considered, although X-ray data for the related chloro complex, *cis*-[$Pt(C_2H_5)Cl(PEt_3)_2$],[29] are not consistent with β-H coordination, since the Pt−C−C angle (110.6°) has the normal tetrahedral value.

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