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Platinum complexes of *P,N*- and *P,N,P*-ligands and their application in the hydroformylation of styrene

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ABSTRACT

Neutral complexes of the formula $PtCl_2(L)$ (where L = *ortho*-diphenylphosphino-*N*-(2-hydroxyethyl)-*N*-methylaniline (**1**), *ortho*-diphenylphosphino-*N*-2-(diphenylphoshinoxy)-ethyl)-*N*-methylaniline (**2**) and *N,N*-bis(2-(diphenylphoshinoxy)ethyl)aniline (**3**)) were prepared. Various binding modes, such as *P,N*- and *P,P*-bidentate and monodentate coordinations were observed with these hemilabile ligands in the parent complexes and in the triphenylphosphine-added systems. ^{31}P NMR studies on the 'in situ' systems revealed the hemilabile character of the ligands.

The platinum complexes proved to be precursors to catalysts of low activity for the hydroformylation of styrene in platinum-ligand (**1**, **2** or **3**)-tin(II) chloride system. High chemoselectivities (up to 82%) were obtained, while the two aldehyde regioisomers were formed in almost equimolar ratio with the slight preference of the branched aldehyde, 2-phenylpropanal. Remarkable increase in regioselectivity was observed in the presence of *para*-toluenesulfonic acid additive using platinum-ligand (**1**) systems.

1. Introduction

The hydroformylation reaction is a transition metal-catalysed transformation with practical industrial importance. Various cobalt- and rhodium-catalysts have been used for the highly regioselective hydroformylation of propene to the linear aldehyde regioisomer, *n*-butyraldehyde. This reaction can be considered as the largest-scale industrial application of homogeneous catalysis and has seen detailed mechanistic investigations [1]. In addition to the hydroformylation of aliphatic alkenes, that of the vinyl aromatics has also been investigated in details due to the high pharmacological importance of 2-arylpropanals, the direct precursors of 2-arylpropionic acid derivatives (such as the non-steroidal anti-inflammatory drugs ibuprofen, naproxen and suprofen [2–5]).

Although highly efficient rhodium catalysts have been explored for the enantioselective hydroformylation of styrene [6,7] and recently also for aliphatic alkenes [8], platinum–phosphine–tin(II) halide systems were used almost exclusively for this purpose at the beginning of this research. The platinum–chiral diphosphine–tin(II) chloride systems provided optical yields of practical interest [9–16] and are still in the focus of detailed mechanistic investigations [17].

The search for novel platinum-based hydroformylation catalysts has led to the application of novel achiral diphosphines [18]. In particular, xantphos [19] and its analogues [20] have proven the most successful for these transformations. The applicability of tin(II) halide-free hydroformylation catalysts based on platinum–alkyl/aryl complexes and boron additives was shown in our laboratory [21]. On the other side, monodentate ligands such as malonate-derived monodentate phosphines [22] and *P*-heterocycles (phosphole- and phospholene-based ligands) [23–27] were used as efficient ligands in the chemo- and regioselective platinum-catalysed hydroformylation of styrene.

Since *P,N*-ligands are among the most important and widely used heterodentate ligands for transition-metal homogeneous catalysis [28], as a part of our systematic investigations on platinum-catalysed hydroformylation, this paper describes the synthesis of novel platinum complexes based on heterobidentate (PN) and heteroterdentate (PNP) ligands and their application in platinum-catalysed hydroformylation of styrene. These ligands and their corresponding rhodium complexes have previously been reported as efficient hydroformylation catalysts [29–31].

2. Experimental

2.1. General

The $PtCl_2(PhCN)_2$ precursor was synthesised from $PtCl_2$ (Aldrich) according to a standard procedure [32]. Toluene was

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distilled and purified by standard methods and stored under argon. Styrene was freshly distilled immediately before use. All reactions were carried out under argon using standard Schlenk techniques.

The ^{1}H and ^{31}P NMR spectra were recorded on a Varian Inova 400 spectrometer. Chemical shifts are reported in ppm relative to TMS (downfield) or 85% H_3PO_4 (0.00 ppm) for ^{1}H and ^{31}P NMR spectroscopy, respectively.

The hemilabile *N*-containing ligands **1**–**3** were synthesised as described previously [29–31].

2.2. General method for the synthesis of $PtCl_2$(hemilabile ligand) complexes (hemilabile ligand = 1–3)

2.2.1. Preparation of cis-$PtCl_2(\kappa^1P,\kappa^1N$-**1**) (**1a**)

To a degassed solution of $PtCl_2(PhCN)_2$ (118.1 mg, 0.25 mmol) in benzene (12 mL) at reflux temperature, **1** (167.6 mg, 0.50 mmol) is added under argon. The reaction mixture is stirred at 80 °C for 3 h. A pale yellow precipitate formed which was filtered off and dried under vacuum. The target complex was obtained as pale yellow powder-like solid material. Yield: 97.7 mg (65%).

Analysis: Calculated for $C_{21}H_{22}NOPCl_2Pt$ (601.37): C: 41.94; H: 3.69; N: 2.33. Found: C: 41.76; H: 3.85; N: 2.17. For NMR data see Table 1.

2.2.2. Preparation of cis-$PtCl_2(\kappa^1P,\kappa^1N$-**2**) (**2a**)

To a degassed solution of $PtCl_2(PhCN)_2$ (45.3 mg, 0.096 mmol) in benzene (2.5 mL) at reflux temperature, a degassed solution of **2** (49.9 mg, 0.096 mmol) in 2 mL benzene was added under argon. The reaction mixture is stirred at 80 °C for 2 h. A pale yellow precipitate formed which was filtered off and dried under vacuum. The target complex was obtained as pale yellow powder-like solid material. Yield: 45.2 mg (60%).

Analysis: Calculated for $C_{33}H_{31}NOP_2Cl_2Pt$ (785.55): C: 50.46; H: 3.98; N: 1.78. Found: C: 50.26; H: 4.11; N: 1.57. For NMR data see Table 1.

2.2.3. Preparation of cis-$PtCl_2(\kappa^2P$-**3**) (**3a**)

To a degassed solution of $PtCl_2(PhCN)_2$ (130.8 mg, 0.277 mmol) in benzene (10 mL) at reflux temperature, a degassed solution of **3** (152.2 mg, 0.277 mmol) in 3 mL benzene was added under argon. The reaction mixture is stirred at 80 °C for 2 h. A pale yellow precipitate formed which was filtered off and dried under vacuum. The target complex was obtained as brown gluey solid. Yield: 108.4 mg (48%).

Analysis: Calculated for $C_{34}H_{33}NO_2P_2Cl_2Pt$ (815.58): C: 50.07; H: 4.08; N: 1.72. Found: C: 50.29; H: 4.17; N: 1.50. For NMR data see Table 1.

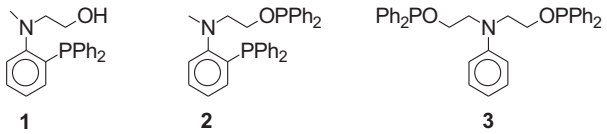


Fig. 1. The hemilabile ligands (**1**–**3**) used in this study.

2.3. Hydroformylation experiments

In a typical experiment, a solution of 0.01 mmol of $PtCl_2$(hemilabile ligand) (hemilabile ligand = **1**–**3**) and 0.02 mmol (3.8 mg) of tin(II) chloride in toluene (10 mL) containing styrene (**4**, 1.0 mmol, 0.115 mL) was transferred under argon into a 100 mL stainless steel autoclave. The reaction vessel was pressurised to 80 bar total pressure (CO/H_2 = 1:1) and placed in an oil bath (100 °C) and the mixture was stirred with a magnetic stirrer for 24 h. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed and immediately analysed by GC–MS.

3. Results and discussion

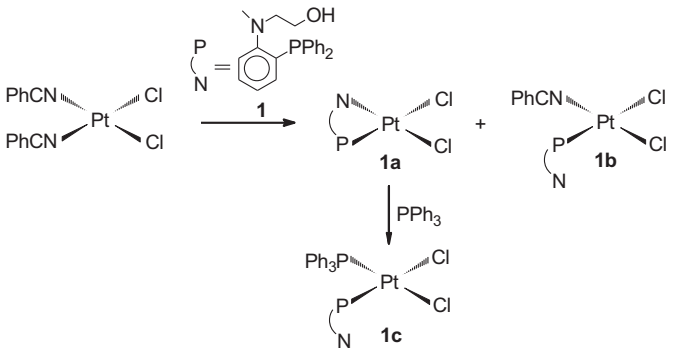
3.1. Synthesis of the complexes and their NMR investigation

Neutral complexes of general formula $PtCl_2$(hemilabile ligand) were synthesised by the reaction of $PtCl_2(PhCN)_2$ with the respective aminophosphines **1**–**3** (Fig. 1) [29–31]. The *P,N*- and *P,N,P*-ligands form different complexes. The aminophosphine with *N*-methyl- and *N*-2-hydroxyethyl-substituents (**1**) reacted with the

Table 1
NMR data of the platinum complexes containing PN and PNP ligands (**1-3**).[a]

Complex	^{31}P NMR					^{1}H NMR δ [ppm] (multiplicity, *J* [Hz], integral)		
	δP_A[b] [ppm]	$^{1}J(Pt,P_A)$ [Hz]	δP_B[b] [ppm]	$^{1}J(Pt,P_B)$ [Hz]	$^{2}J(P,P)$ [Hz]	Methyl protons	Methylene protons	Aromatic protons
cis-$PtCl_2(\kappa^1P,\kappa^1N$-**1**) (**1a**)	16.0	3899	–	–	–	3.71 (s, 3H)	4.10 (t, 5.4 Hz, 2H) 4.76 (t, 5.4 Hz, 2H)	7.12–7.71 (m, 14H)
cis-$PtCl_2(PhCN)(\kappa^1P$-**1**) (**1b**)	23.2	3510	–	–	–	2.51 (s, 3H)	3.15 (t, 5.6 Hz, 2H) 3.60 (t, 5.6 Hz, 2H)	7.12–7.89 (m, 19H)
cis-$PtCl_2(PPh_3)(\kappa^1P$-**1**) (**1c**)	27.7 7.1	3810 3376	–	–	15.5	2.51 (s, 3H)	3.15 (t, 5.6 Hz, 2H) 3.60 (t, 5.6 Hz, 2H)	7.05–7.98 (m, 29H)
cis-$PtCl_2(\kappa^1P_A,\kappa^1N$-**2**) (**2a**)	16.0	3897	22.6[c]	–	–	3.69 (s, 3H)	4.09 (t, 6.0 Hz, 2H) 4.75 (t, 6.0 Hz, 2H)	7.14–7.90 (m, 24H)
cis-$PtCl_2(\kappa^1P_A,\kappa^1P_B$-**2**) (**2b**)	28.8	3938	62.0	3883	13.8	2.48 (s, 3H)	4.04 (t, 6.5 Hz, 2H) 4.60 (t, 6.5 Hz, 2H)	7.14–7.90 (m, 24H)
cis-$PtCl_2(PPh_3)(\kappa^1P_A$-**2**) (**2c**)	7.1 27.6	3365 3813	22.6[c]	–	15.2	2.48 (s, 3H)	3.14 (t, 5.6 Hz, 2H) 3.57 (t, 5.6 Hz, 2H)	7.15–7.88 (m, 39H)
$[PtCl(PPh_3)(\kappa^1P_A,\kappa^1P_B$-**2**)]$^+$ (**2d**)	23.8 56.4	2167 3883	78.6	2927	429.0 17.9 17.6	2.48 (s, 3H)	4.04 (t, 6.5 Hz, 2H) 4.60 (t, 6.5 Hz, 2H)	7.15–7.88 (m, 39H)
cis-$PtCl_2(\kappa^2P$-**3**) (**3a**)	–	–	61.8	4034	–	–	3.57 (br s, 8H)	7.26–7.82 (m, 25H)
$[PtCl(PPh_3)(\kappa^2P$-**3**)]$^+$(**3b**)	24.6	2929	73.3 60.7	2120 3808	413.0 15.4 17.9	–	3.57 (br s, 8H)	7.15–7.82 (m, 40H)

[a] Spectra were measured in $CDCl_3$ (under Ar atmosphere at room temperature).
[b] P_A and P_B stand for 'phosphine' phosphorus (PPh_2/PPh_3) and 'phosphinite' phosphorus ($OPPh_2$), respectively.
[c] $OPPh_2$ non-coordinated.



Scheme 1. Synthesis of **1a** and its reaction with PPh_3.

$PtCl_2(PhCN)_2$ precursor leading exclusively to the corresponding *cis*-$PtCl_2$(**1**) complex (**1a**) in longer reaction time (more than 2 h). However, it was revealed by 'in situ' NMR investigations that **1** may coordinate to platinum also as a monodentate ligand resulting in the formation of **1b** as minor product (34%) in shorter reaction time (0.5 h) (Scheme 1).

The use of the analogous ligand possessing both phosphine and phosphinite type phosphorus donor atoms (**2**) resulted in the formation of the 25/75 mixture of *cis*-complexes with *P,N*- (**2a**) and *P,P*-coordination (**2b**) (Scheme 2). The preference of *P,P*- over *P,N*-coordination was shown by the reaction of the $PtCl_2(PhCN)_2$ with **3** containing two equivalent (phosphinite) phosphorus donors and a tertiary nitrogen. The exclusive formation of **3a** was observed (Scheme 3).

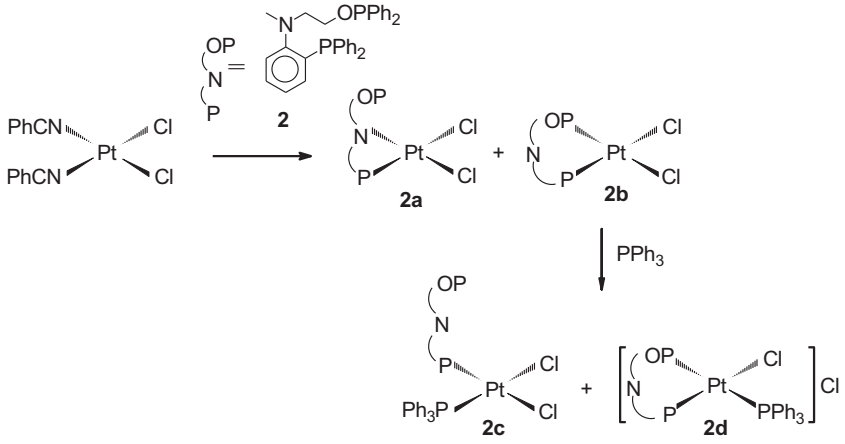
The stability of the *P,N*-type (heterobidentate) coordination of the ligands **1** and **2** was investigated by 'in situ' NMR investigations of the reaction of PPh_3 with **1a** and **2a**, respectively. Adding an equimolar amount of PPh_3 to **1a,** nearly quantitative formation of the covalent complex **1c** with monodentate type coordination of **1** was observed. However, the phosphine–phosphinite derivative **2** behaves in a different way forming both a covalent complex **2c,** coordinating **2** as a *P*-monodentate ligand, and the ionic $[PtP_3Cl]^+$ complex **2d** with P_A,P_B-heterobidentate coordination. The complex cation of square-planar geometry has a chloride counterion. In case of **3a** the bis(phosphinite) type coordination was maintained upon addition of PPh_3. The $[PtCl(PPh_3)(\kappa^2P\text{-}\mathbf{3})]^+$ cation was formed whose diphosphine analogues have been well-known fully characterised complexes [33].

As expected, each of the *cis*-$PtCl_2$(ligand)-type complexes, **1a**, **2a** containing a ligand with one phosphorus coordinated to platinum and **3a** containing **3** with two equivalent phosphorus atoms coordinated to platinum, exhibited a single central signal (flanked by platinum satellites, in a ratio of 1:4:1) in the ^{31}P NMR spectra thereof (Table 1). (Obviously, in case of **2a** the non-coordinated phosphorus appears as a singlet at 22.6 ppm) In these spectra, the $^1J(^{195}Pt,^{31}P)$ coupling constants are diagnostic, showing values of *ca*. 3900 Hz or slightly above 4000 Hz for coordinated phosphine or phosphinite moieties, respectively. The ^{31}P NMR spectra of the platinum complexes provide a sensitive probe for the structures of complexes, even in rather complicated mixtures. The magnitude of the $^1J(^{195}Pt,^{31}P)$ coupling constants is generally explained by the *trans*-influence, that is, the coupling constants are strongly dependent on whether the *P* atom has another *P* atom or a chlorine atom as ligand in the position *trans* to it on the Pt. It is known from the literature that the *trans P*–Cl arrangement features $^1J(^{195}Pt,^{31}P)$ coupling constants typically larger than 3500 Hz, while *trans-P-P* arrangement (*e.g.*, in Pt(II) square-planar complexes containing three *P*-donor atoms, see below) displays typical platinum–phosphorus coupling constants of 2500–3000 Hz [34].

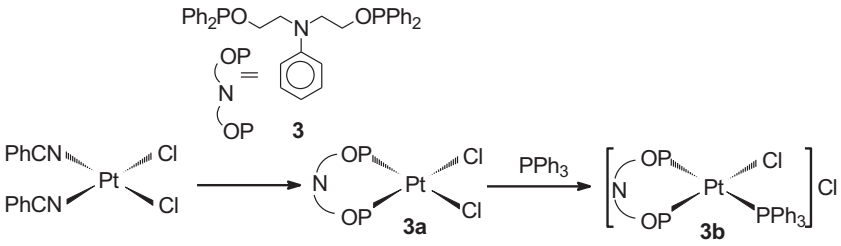
It is worth mentioning that although the ligands (**1** and **2**) used in the present study can be considered as *ortho*-substituted PPh_3 analogues possessing a methyl-(2-hydroxyethyl)amino and methyl-(2-diphenylphosphinoxyethyl)amino substituent in *ortho*-position, respectively, the $^1J(^{195}Pt,^{31}P)$ coupling constants for **1a** and **2a** are definitely higher (3899 and 3897 Hz, respectively) than that observed in the corresponding *cis*-$PtCl_2(PPh_3)_2$ (3678 Hz, 14.7 ppm) [35].

On the basis of NMR investigations, a stronger interaction between our *P*-ligands (**1** and **2**) and the platinum(II) centre can be envisaged for **1a** and **2a** than in case of the simple triarylphosphines investigated earlier [22]. Our previous investigations have shown that the *ortho*-functionalization of one of the phenyl rings of PPh_3 lead to smaller coupling constants and consequently, a weaker bond between Pt(II) centre and phosphorus donor [22]. Therefore, the opposite trend, that is, the larger $^1J(^{195}Pt,^{31}P)$ coupling constants for **1a** and **2a** cannot be considered as a consequence of steric factors. This phenomenon is probably due to *cis*-coordination of the nitrogen of the tertiary amine to the same metal centre, and therefore, the coordination of the nitrogen as a σ-donor increases Pt–*P* bond strength.

As mentioned above, the addition of PPh_3 to **1a** and **2a** resulted in the formation of *cis*-PtP_2 complexes exhibiting a characteristic J_{cis}(P,P) coupling of 15.5 Hz and *ca*. 15.2 Hz (broad satellites) for **1c** and **2c**, respectively. In the same time, the *cis* geometry is also proved by $^1J(^{195}Pt,^{31}P)$ coupling constants which refer to the chloro ligands *trans* to both phosphorus.



Scheme 2. Synthesis of **2a** and its reaction with PPh_3.



Scheme 3. Synthesis of **3a** and its reaction with PPh_3.

The *cis* and *trans* mutual arrangements of the three coordinating phosphorus atoms in **2d** are shown by the corresponding $^2J_{cis}$(P,P) and $^2J_{trans}$(P,P) coupling constants of 17.9 Hz, 17.6 Hz and 429.0 Hz, respectively. A similar set of coupling constants was determined for the ionic complex **3b** where two 'phosphinite phosphorus' and one 'phosphine phosphorus' (PPh_3) is coordinated to Pt(II) centre.

It is worth noting that the coordination of the phosphinite moiety ($OPPh_2$) to platinum(II) was manifested by significant downfield shifts. For example, free ligand **2** (and also the non-coordinated phosphinite phosphorus of the same ligand coordinated in a *P,N*-bidentate manner) exhibited a resonance as a singlet at 22.6 ppm, while the Pt complex with coordinated 'phosphinite phosphorus' thereof gave resonances at 62.0 ppm and 78.6 ppm flanked by the Pt-satellites in **2b** and **2d**, respectively. A similar phenomenon was observed in case of **3a** and **3b**.

The ^{1}H NMR spectra are less informative than ^{31}P NMR spectra both for the characterisation of the isolated complexes and for the analysis of 'in situ' systems. However, the *N*-coordination can easily be proved by the downfield shift of the *N*-methyl substituent in the ^{1}H NMR. For example, free ligand **1** (and also the non-coordinated *N*-methyl group of the same ligand coordinated in a *P*-monodentate manner) exhibited resonances at 2.51 ppm, while the Pt complex with and without coordinated tertiary amine group thereof gave resonance at 3.71 ppm (**1a**) and 2.51 ppm (**1b**), respectively.

3.2. Hydroformylation reactions

As a start of testing ligands **1**-**3**, two types of 'in situ' platinum catalysts were used for the hydroformylation of styrene (Scheme 4) under 'oxo-conditions' ($p(CO) = p(H_2) = 40$ bar, 100 °C, described in Table 2). The first type of 'in situ' catalysts were prepared from $PtCl_2(PhCN)_2$, the corresponding ligand (L) and two equivalents of tin(II) chloride per Pt (entries 1–7). For the preparation of the second type 'in situ' catalysts, "pre-formed" $PtCl_2(L)$ (where L = **1**–**3**, Fig. 1) complexes and two equivalents of additives were used (entries 8–13).

As expected, in addition to the branched and linear aldehyde regioisomers **5** and **6**, respectively, some hydrogenation product (ethylbenzene, **7**) was also formed. Although the formation of aldehydes was favoured under all conditions, the presence of **7** was not negligible even under optimal conditions (*vide infra*).

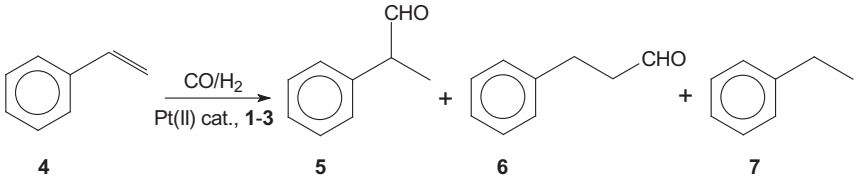
The hydroformylation activity of both 'in situ'-generated platinum–tin(II)chloride systems is rather low. Similar activities can be observed both with $PtCl_2(PhCN)_2$ (entries 1, 4 and 7) and pre-formed $PtCl_2(L)$ (L = **1**–**3**) (entries 8, 11 and 13) complexes as precursors. Nevertheless, the novel ligand-containing catalysts are of interest from several theoretical points of view.

The two types of 'in situ' catalysts resulted in very similar chemo- and regioselectivities indicating the presence of species of similar structure. For example, the $PtCl_2(PhCN)_2$ + **1** and the $PtCl_2$(**1**)-based systems containing **1** as ligand gave 79 and 80% chemoselectivity, respectively. The regioselectivities towards branched aldehyde are 56 and 53%, respectively (entries 1 and 8). The use of two equivalents of **1** to platinum resulted even lower activity. However, similar selectivities to those with Pt/**1** = 1/1 system were obtained indicating that the *P,N* coordination is probably maintained under these conditions (entry 4).

In order to protonate the tertiary nitrogen atom, and in this way, to exclude it from coordination to platinum, a further modification of the catalytic system was done. Either in addition to the tin(II) chloride or instead of it, two eq. of *p*-toluenesulfonic acid (PTSA) was added. It was revealed by a systematic study that the addition of PTSA thoroughly influenced both chemo- and regioselectivity of hydroformylation (entries 2,3; 5,6; 9,10; 12,14).

The addition of PTSA has a different influence on a system containing ligands with exclusive *P,N*-coordination (**1**) (entries 2,3,5,6,9,10) and on those systems with typical *P,P*-coordination (**2**, **3**) (entries 12, 14). The modification of the structure of the catalytically active intermediates was proved by changes in both chemo- and regioselectivities and by the favoured formation of the branched aldehyde in case of **1** and **2**,**3**, respectively.

The most pronounced effect was observed in all catalytic systems containing ligand **1**. In this case protonation of the *N* resulted in completely different coordination mode of **1**, that is, bidentate *P,N*-coordination was changed to monodentate *P*-coordination. The unexpectedly high regioselectivities of up to 92% obtained with Pt/**1** ratio of 1/1 and 1/2, indicate that ligand **1** cannot be considered as a simple monodentate *ortho*-substituted triphenylphosphine. It has to be noted that the application of the obviously analogous catalytic precursor, *cis*-$PtCl_2(PPh_3)_2$ resulted in much lower regioselectivity of 45% towards branched aldehyde [22]. Similar results have been obtained also by using the corresponding Pt–PPh_3–$SnCl_2$ 'in situ' system for the hydroformylation of styrene [36]. As for the platinum



Scheme 4. Hydroformylation of styrene.

Table 2
Hydroformylation of styrene in the presence of 'in situ' platinum catalysts.[a]

Entry	Ligand (or preformed complex)	$SnCl_2$/Pt	PTSA[b]/Pt	Time (h)	Conv. (%)	R_c[c] (%)	R_{br}[d] (%)
1	**1**	2	–	48	12	79	56
2	**1**	–	2	48	8	90	92
3	**1**	2	2	48	5	72	72
4[e]	**1**	2	–	48	8	82	62
5[e]	**1**	–	2	48	5	77	86
6[e]	**1**	2	2	48	5	81	77
7	**2**	2	–	48	7	68	72
8	**1a**	2	–	72	16	80	53
9	**1a**	–	2	48	9	91	91
10	**1a**	2	2	48	5	84	75
11	**2a**/**2b**[f]	2	–	96	5	71	50
12	**2a**/**2b**[f]	–	2	48	28	95	51
13	**3a**	2	–	72	33	63	44
14	**3a**	–	2	48	18	84	34

[a] Reaction conditions (unless otherwise stated): 0.01 mmol of $PtCl_2(PhCN)_2$ and 0.01 mmol of ligand (entries 1–7) or 0.01 mmol of $PtCl_2(L)$ preformed catalyst (entries 8–14); Pt/styrene = 1/100; $p(CO) = p(H_2) = 40$ bar; 100 °C; solvent: 10 mL of toluene.
[b] PTSA = *p*-toluenesulfonic acid.
[c] Chemoselectivity towards aldehydes (**5**, **6**). [(moles of **5** + moles of **6**)/(moles of **5** + moles of **6** + moles of **7**) × 100].
[d] Regioselectivity towards branched aldehyde (**5**). [moles of **5**/(moles of **5** + moles of **6**) × 100].
[e] Two eq. of **1** was used.
[f] An inseparable mixture of **2a**/**2b** (25/75).

complexes of PN and PNP ligands, *cis*-[(benzyl-bis(diphenylphosphinomethyl)amine)-dichloro-platinum(II)] and *cis*-[(aryl-bis(diphenylphosphinomethyl)amine)-dichloro-platinum(II)] were tested recently in the hydroformylation of styrene. In general, lower chemo- and regioselectivities ranging from 56 to 71% and from 63 to 70 % were obtained using these complexes under similar conditions, respectively [37]. However, they pretended much higher activities than those ones in the present study.

One of the possible explanations for the unexpectedly large difference in regioselectivities is the coordination of the hydroxyl group of ligand **1** to platinum in the key-intermediates. A less likely possibility is the coordination of the *para*-toluenesulfonate ion to platinum. It could be stated that the activation of the alkene (styrene) by the hydrido–platinum complex and its insertion into Pt–H bond, leading to platinum-alkyl intermediate, is strongly affected by the geometry of the Pt complex.

In summary, the chemoselectivity of hydroformylation was rather high (up to 91%), accompanied by low rates of reaction. The regioselectivity of the hydroformylation reaction is significantly influenced both by the phosphorus ligands and *para*-toluenesulfonic acid additive employed in this study. While the two aldehyde regioisomers are formed in nearly equimolar ratios in the presence of the ligands containing phosphinite moiety(ies), a high preference of branched regioisomer was observed with the aminophosphine ligand under all conditions investigated. It is also pointed out that all Pt complexes with the presented hemilabile ligands were displayed considerably lower reaction rates and regioselectivities towards the branched aldehyde compared to the Rh analogues, reported previously [29–31].

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