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Xantphos as *cis*- and *trans*-chelating ligand in square-planar platinum(II) complexes. Hydroformylation of styrene with platinum–*xantphos*–tin(II)chloride system

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Abstract

Platinum(II) complexes of a diphosphine ligand *xantphos* (4,5-bis(diphenylphosphino)-9,9-dimethyl-xanthene) have been synthesised and characterised by NMR, conductivity and catalytic investigations. In addition to the parent complex *cis*-$PtCl_2$(*xantphos*), *trans*-platinum(II) complexes of square-planar geometry containing *xantphos* as a *trans*-chelating ligand can be obtained due to the large bite angle of the ligand. The platinum–*xantphos*–tin(II)chloride system acts as active hydroformylation catalyst in the hydroformylation of styrene resulting in high chemo- and regio-selectivities of up to 99.8% and 88%, respectively.

Keywords: Platinum; Phosphine; Trigonal bipyramidal geometry; Hydroformylation

1. Introduction

The importance of carbonylation reactions has initiated many investigations [1]. Efforts have been made to exploit enantioselective carbonylation reactions, especially hydroformylation, in the synthesis of practically important derivatives [2].

Hundreds of ligands (among them chiral ligands) with different steric and electronic properties, shapes and functionalities have already been tested also in hydroformylation [3]. The fine tuning of the electronic and steric properties of the ligands [4], the understanding of their organometallic chemistry has evolved ligand (and consequently catalyst) development from trial and error into rational design.

Most of the frequently used ligands possess two chemically equivalent phosphorus donor atoms due to their C2 symmetry ('homobidentate ligands') and the minority of the bidentate ligands are mostly P, N or P, O donor ligands ('heterobidentate ligands'). The common feature of these ligands is their coordination in a *cis*-manner.

Recently, emphasis has been put on the synthesis of ligands with specific geometries. It has been found that bidentate ligands can have a preference for a specific geometry, since the bite angle, defined as donor atom(1)–metal–donor atom(2) angle, is dependent on the bridge between the two donor atoms. The majority of the ligands applicated up to now prefer the donor atom–metal–donor atom bite angle close to 90° (typically between 85° and 95°), so square-planar rather than tetrahedral geometry is favoured from sterical reasons. Van Leeuwen et al. [5] has done a seminal work on the systematic investigation of the influence of the larger bite angle ligands to complex geometry. The *xantphos* ligand family, enforcing bite angles between 100° and 120°, tends to occupy the bisequatorial position rather than an axial–equatorial position in trigonal pyramidal

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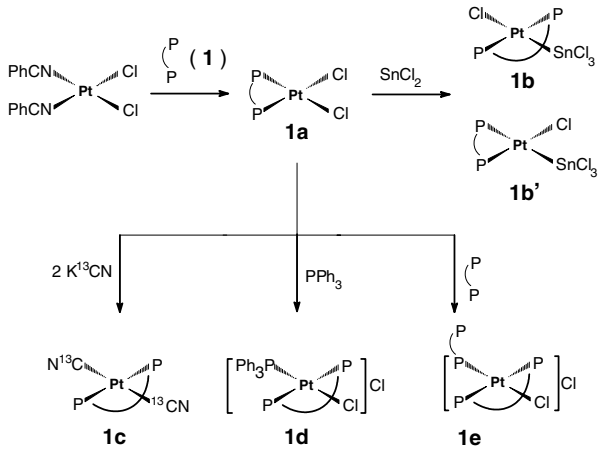
Rh(I) complexes. The first examples for the *trans*-chelating coordination of *xantphos* in Pd(*xantphos*)(Me)Cl and Pd(*xantphos*)(4-cyanophenyl)Br complexes has been published quite recently [6].

To the best of our knowledge, there is a very few examples for the use of platinum-*xantphos* hydroformylation catalyst. After the selective isomerization of methyl 3-pentenoate to methyl 4-pentenoate remarkable linear selectivity has been obtained [7]. On the basis of NMR spectroscopy study the *cis*-coordination mode for *xantphos* has been proposed in all active platinum-*xantphos* species [8].

In this paper we describe the synthesis and characterisation of some novel platinum complexes of *xantphos* (**1**), the parent ligand of the series (Scheme 1). Examples for its versatile coordination modes in platinum(II) complexes, such as *cis*- and *trans*-chelating coordination, as well as monodentate coordination in square-planar platinum(II) complexes will be shown by NMR investigations. The application of platinum–**1**–tin(II)chloride system for the hydroformylation of styrene will also be presented.



Scheme 1. Synthesis of platinum(II)–*xantphos* complexes.

2. Results and discussion

2.1. Synthesis and NMR characterisation of the platinum–xantphos complexes

Xantphos (4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, **1**) was reacted with $PtCl_2(PhCN)_2$ in refluxing benzene resulting in *cis*-$PtCl_2$(*xantphos*) (**1a**) (Scheme 1). The ^{31}P NMR spectrum of **1a** shows characteristic 1/4/1 pattern consisting of a doublet assigned to the two equivalent phosphorus coupled with ^{195}Pt ($I = 1/2$, natural abundance 33.8%) (appearing as a 'platinum satellite') and a singlet due to those phosphorus coupled with platinum nuclei other than ^{195}Pt (appearing as a 'central line'). The $^1J(^{31}P, ^{195}Pt)$ coupling constant of about 3693 Hz clearly indicates the presence of the chloro ligands *trans* to phosphorus, i.e. the *cis*-chelation of **1** (Table 1).

In dichloromethane and chloroform one of the two Pt–Cl bonds of **1a** inserts tin(II)chloride yielding two unexpectedly broad signals at 15.5 and 5.4 ppm. Although the platinum satellites are inherently broader than the central lines, the $^1J(^{31}P, ^{195}Pt)$ coupling constants of 2410 and 3740 Hz can be determined. These diagnostic values refer to the *trans* and the *cis* arrangement of the two phosphorus [3f,3g,3j], respectively, i.e. *trans*-$PtCl(SnCl_3)$(**1**) (**1b**) and *cis*-$PtCl(SnCl_3)$ (**1**) (**1b′**) have been formed at a ratio of 60/40. The latter peak shows further broadening upon cooling down to 238 K, but unlike to the case observed with the *tert*-butyl analogue of *xantphos* [8], no separation of the two signal (P *trans* to chloro and P *trans* to trichlorostannato ligand) has been observed.

Table 1
NMR data of the platinum complexes of *xantphos* (**1**)[a]

	δP_A[b] (ppm)	δP_B[b] (ppm)	$^1J(^{195}Pt, ^{31}P_A)$ (Hz)	$^1J(^{195}Pt, ^{31}P_B)$ (Hz)	$^2J(P_A, P_B)$ (Hz)	$^2J(^{31}P, ^{117/119}Sn)$ (Hz)
1	−16.8	–	–	–	–	–
cis-$PtCl_2$(**1**) **1a**	7.1 (s)	–	3693	–	–	–
trans-$PtCl(SnCl_3)$(**1**) **1b**	15.5	–	2410 ± 10	–	–	210 ± 10[c]
cis-$PtCl(SnCl_3)$ (**1**) **1b′**	5.4[d]	5.4[d]	3740 ± 25	–	–	–[e]
trans-$Pt(^{13}CN)_2$(**1**) **1c**[f]	5.5 (t)	–	2612	–	–	
trans-[$PtCl$(**1**)(PPh_3)]Cl **1d**	11.9 (t)	13.3 (d)	4141	2593	18.5	–
trans-[$PtCl$(**1**)(η^1-**1**)]Cl **1e**[g]	15.6 (t)	12.7 (d)	4130	2641	17.8	–

[a] Spectra were measured in $CDCl_3$ (room temperature).

[b] P_A and P_B (phosphorus of double intensity) are assigned to PPh_3 (or **1** as monodentate) and **1** (bidentate), respectively (multiplicities are given for the central lines).

[c] Broad $^{117/119}Sn$ satellites.

[d] P_A and P_B as one broad central line (close to coalescence at room temperature).

[e] No detectable $^2J_{cis}(^{117/119}Sn, ^{31}P)$ and $^2J_{trans}(^{117/119}Sn, ^{31}P)$ couplings.

[f] $\delta(^{13}C) = 123.8$ ppm (t); $^1J(^{195}Pt, ^{13}C) = 1074$ Hz; $^2J(^{31}P, ^{13}C) = 14.1$ Hz.

[g] $\delta P_C = -22.1$ ppm (noncoordinated phosphorus of **1**).

The existence of a direct platinum–tin bond can be proved by NMR in case of **1b**. The presence of *cis* tin satellites in the ^{31}P NMR spectra ($^2J_{cis}(^{117,119}Sn, ^{31}P) \approx$ 200 Hz) is a direct proof of the Pt–$SnCl_3$ moiety. (As it is well known, the ^{117}Sn and ^{119}Sn *cis*-satellites usually coincide [9], so the tin satellites of about 8% intensity can be determined even they are broad.) Unfortunately, since the signals are close to coalescence, neither the satellites due to $^2J_{cis}(^{117,119}Sn, ^{31}P)$ nor those of $^2J_{trans}(^{117}Sn, ^{31}P) < ^2J_{trans}(^{119}Sn, ^{31}P)$ cannot be assigned in case of **1b′**.

A complete *cis*/*trans* rearrangement occurred when chloro–cyano ligand exchange reaction was carried out by reacting **1a** with two molar equivalent of $K^{13}CN$ resulting in *trans*-Pt(^{13}CN)$_2$(**1**) (**1c**). Both the equivalency of the two phosphorus (and consequently the two cyano-carbons) and the magnitude of the coupling constants ($^1J(^{195}Pt, ^{31}P)$; $^1J(^{195}Pt, ^{13}C)$; $^2J(^{13}C, ^{31}P)$) refer to the *trans*-chelation of **1**.

Upon addition of PPh_3 to the parent complex **1a** the formation of *trans*-[PtCl(**1**)(PPh_3)]Cl ionic complex (**1d**) takes place (Scheme 1). PPh_3 occupies the position *trans* to chloro ligand. A complex with similar square-planar geometry has been obtained by reacting **1a** with an additional molar equivalent of **1**. The entering 'second' *xantphos* ligand coordinates as a monodentate resulting in [Pt(**1**)(η^1-**1**)Cl]Cl (**1e**) (Table 1).

Coupling constants of diagnostic value for 'PtP_3' species [10] can be observed also in case of **1d**. The ^{31}P NMR spectrum consists of two patterns, a doublet and a triplet ($^2J_{cis}(P,P) = 18.5$ Hz) at a ratio of 2/1 assigned to the phosphorus of *xantphos* and PPh_3, respectively. Accordingly, the doublet and the triplet are flanked by platinum satellites due to $^1J(^{31}P, ^{195}Pt)$ couplings of 2593 and 4141 Hz, respectively. On the basis of ^{31}P NMR the *xantphos* (**1**) ligand might occupy either bis-equatorial positions in a complex with trigonal bipyramidal geometry, with PPh_3 at one of the apical positions, or might coordinate as a *trans*-chelating ligand to form *trans*-[Pt(**1**)(PPh_3)Cl]$^+$ square-planar complex cation. Both geometries would lead to an AX_2 spin system in ^{31}P NMR, although no preliminary knowledge about the range of $^1J(^{195}Pt, ^{31}P)$ coupling constants in *tbp* structures is available. The two structures in solution can be distinguished by conductivity measurements.

The possible formation of the ionic species under similar conditions has been investigated with conductivity measurements. The neutral parent complex **1a** has been reacted with PPh_3 both in the absence and in the presence of tin(II)chloride in dichloromethane. On the basis of previous results, the formation of a four-coordinated complex cation [PtCl(**1**)(PPh_3)]$^+$ with chloride and trichlorostannate counterion was expected, respectively [10]. Accordingly, the addition of one equivalent of PPh_3 to the solution of **1a** resulted in equivalent conductivity of 68 $mol^{-1}\,\Omega^{-1}\,cm^2$ showing the partial dissociation of one of the two chloro ligands, i.e. the partial formation of a 1/1 electrolyte [Pt(**1**)(PPh_3)Cl]$^+$Cl$^-$ and not the neutral trigonal bipyramidal complex $PtCl_2$(**1**)(PPh_3). Upon addition of one molar equivalent of tin(II)chloride conductivity of 134.3 $mol^{-1}\,\Omega^{-1}\,cm^2$ has been measured due to the formation of [Pt(**1**)(PPh_3)Cl]$^+$[$SnCl_3$]$^-$.

By adding two molar equivalents of PPh_3 to **1a**, equivalent conductivity of 94.8 $mol^{-1}\,\Omega^{-1}\,cm^2$ has been obtained referring to a slightly higher dissociation than in case of one equivalent of PPh_3. In the presence of one equivalent of tin(II)chloride even higher conductivity ($\Lambda_0 = 154.8$ $mol^{-1}\,\Omega^{-1}\,cm^2$) was obtained due to nearly quantitative formation of [Pt(**1**)(PPh_3)Cl]$^+$[$SnCl_3$]$^-$ (as detected also by ^{31}P NMR, vide supra) by facile dissociation of the trichlorostannato leaving group.

It has to be added, that the natural bite angle of 111° given for *xantphos* makes the *cis*-chelate coordination in a square-planar geometry (ideal P–Pt–P bond: 90°) very strained. On the other side, the two examples for *trans*-chelation of *xantphos* known to date shows that the bite angles of 153° [6a] and 150.7° [6b] are rather far from (i.e. significantly smaller than) the ideal *trans*-coordination angle.

2.2. Hydroformylations

Styrene (**2**) as the model substrate was reacted in the presence of the platinum containing precursor **1a** and anhydrous tin(II)chloride with CO/H_2 (1/1) at 25–100 °C and at a pressure of 120 bar (Table 2).

$$\underset{\mathbf{2}}{PhCH{=}CH_2} \xrightarrow{CO/H_2} \underset{\mathbf{3}}{PhCH(CHO)CH_3} + \underset{\mathbf{4}}{PhCH_2CH_2CHO} + \underset{\mathbf{5}}{PhCH_2CH_3} \quad (1)$$

In addition to the formyl regio-isomers **3** and **4** also the hydrogenation product **5** is expected to be formed as usual under 'oxo-conditions'.

The tested platinum catalysts show catalytic activities comparable to those published up till now. The platinum–*xantphos* system proved to be active in the above temperature range. At lower temperatures (below 40 °C) the activity is negligible and lower than usually observed. The low activity of the system at room temperature probably cannot be explained by the extremely long induction period, since slightly increasing conversions have been obtained in 50 and 116 h reaction time at 25 °C. The conversions at higher temperature are in the same range as usually expected. However, strikingly different features related to the previous platinum-based systems has been observed.

1. The platinum–*xantphos* catalyst differs from all the previous ones in providing complete chemoselectivity toward aldehyde regioisomers. The hydrogenated

Table 2
Hydroformylation of styrene (**2**) with $PtCl_2$(**1**) + $2SnCl_2$ catalytic system[a]

Entry	Temperature (°C)	Reaction time (h)	Conversion (%)	R_C[b] (%)	R_{lin}[c] (%)
1	25	50	2	>99.8	79
2	40	50	25	>99.8	84
3	60	28	76	>99.8	87
4	80	24	70	>99.8	87
5[d]	80	24	89	>99.5	88
6	100	24	91	99	87

[a] Reaction conditions (unless otherwise stated): 30 ml toluene, 0.1 mol styrene (**2**); $p(CO) = p(H_2) = 40$ bar; Pt/**2** = 1/4000.
[b] Selectivity towards formyl products [(mol **3** + mol **4**)/(mol **3** + mol **4** + mol **5**) × 100].
[c] Selectivity towards linear regioisomer [(mol **4**/(mol **3** + mol **4**) × 100].
[d] $p(CO) = 40$ bar; $p(H_2) = 80$ bar.

side-product, **5** has not been detected even in traces at low temperatures. (The reaction can be considered as chemospecific except for the data obtained at around 100 °C.) This high chemoselectivity is exceptional even in rhodium-catalysed hydroformylations. It is worth noting that aldehydes were formed exclusively even at higher hydrogen partial pressure ($p(CO) = 40$ bar; $p(H_2) = 80$ bar).

2. The regio-selectivity towards linear aldehyde (**4**) is much higher than in any other cases by using platinum–phosphine–tin(II)halide systems for styrene hydroformylation. The regio-selectivity of hydroformylation is sensitive to the variation of the temperature. While at room temperature branched selectivity of about 20% has been obtained, it is dropped to almost 10% at 100 °C. (The tendency of forming linear aldehyde (**4**) rather than branched one (**3**) at higher temperatures is what expected.) It has to be noted, that the predominant formation of the linear aldehyde has been observed in the platinum-catalysed hydroformylation of 1-octene using *xantphos*-type ligands [11]. In a related carbonylation reaction, in palladium-catalysed hydroxycarbonylation, branched to linear ratio of 19/81 for the two carboxylic acid regioisomers (2-phenylpropionic acid vs. 3-phenylpropionic acid) was found [5b]. This regioselectivity is very close to those obtained in our hydroformylation experiments (Table 2).

2.3. Mechanistic considerations

The generally accepted mechanism of platinum-catalysed hydroformylation is based on the square-planar catalytic intermediates [9,12]. The role of tin(II)halide (in most cases tin(II)chloride) is crucial, but not fully cleared up considering all steps of the catalytic cycle. It can act as a $SnCl_3^-$ counter-ion, a Lewis acid and a trichlorostannato-ligand bonded to platinum by forming a Pt–Sn bond [9,12,13]. In case of generally used bidentate ligands, coordinated in *cis*-manner exclusively, ionic mechanism has been postulated for the CO activation step, its insertion into the Pt-alkyl bond forming Pt-acyl complexes and that of the product forming step. The good leaving $SnCl_3$ ligand forms a counter-ion providing a vacant coordination site in four-coordinated species [12].

For *cis*-chelating ligands an optimum of natural bite angle has been obtained concerning catalytic activity: the hydroformylation activity increases with increasing natural bite angle, however for larger bite angles it drops [14]. It has been shown, that the larger the bite angle of the ligand, the higher the ratio of complexes containing the ligand as a *trans*-chelating one. The activity of the catalyst decreases accordingly [8]. The explanation is based on the facts, that both carbon monoxide insertion and hydrogenolysis is slowed down in case of square-planar platinum complexes with *trans*-chelating ligands, since *trans*/*cis* isomerization has to occur. The *cis*-coordination of the phosphorus donors is considered as a prerequisite of migratory insertions [15].

In our case however, *neither the decrease in catalytic activity*, *nor that of the chemoselectivity has been observed*. In contrary, unexpectedly high hydroformylation selectivity and regio-selectivity towards linear aldehyde have been obtained. If **1** is coordinated as a *trans*-chelating ligand in square-planar catalytic species, the drop in activity would be expected as a consequence of the *trans* disposition of alkene and hydrido ligand (platinum-alkyl intermediate formation step) or carbonyl and alkyl ligand (platinum-acyl intermediate formation step).

On the basis of the catalytic results, we suppose that **1** occupies diequatorial positions of the *tbp* geometry in catalytically highly active species of low concentrations. Assuming the apical coordination of the chloro(trichlorostannato) ligand, the *cis* position of the hydrido-ligand and the coordinated olefin, as well as the alkyl-ligand and the coordinated CO necessary for insertions is ensured, and facile insertion providing platinum-alkyl and platinum-acyl species could take place, respectively. The importance of the formation of five-coordinated catalytic species has been shown by a recent theoretical study [16]. In case of a ligand like **1** with natural bite angle close to the optimum of 120° in trigonal geometry, the coordination in diequatorial positions of a *tbp* structure is supposed (Fig. 1).

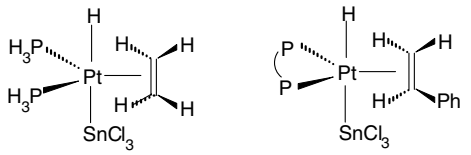


Fig. 1. Pentacoordinated platinum(II) species (Pt–PH_3 complex [16] and the suggested structure for Pt–**1**–$SnCl_2$ (P–P = **1**) complex).

The trend of increasing regio-selectivity towards linear aldehydes is also explained by the increasing natural bite angle of the ligand, which leads to an increase of the steric congestion and to the formation of less hindered linear rhodium-alkyl (and acyl) intermediate [8,17].

It can be concluded that the high activity of platinum–**1**–tin(II)chloride systems and the unexpectedly high chemoselectivity of the hydroformylation reaction could be explained by two reasons: (1) A square-planar complex precursor containing **1** can extend its coordination number to five in case of platinum-hydrido and platinum-alkyl complexes and might easily activate carbon monoxide without the dissociation of any ligand (including *trans* activating $SnCl_3^-$). (2) The *xantphos* ligand (**1**) due to its large bite angle occupies diequatorial and trichlorostannato ligand one of the apical positions. Consequently, the *cis* arrangement of hydrido and alkene ligands, as well as that of the alkyl and carbon monoxide ligands in axial–equatorial disposition is assured.

3. Experimental

3.1. General procedures

All reactions were carried out under Ar using standard Schlenk techniques. Toluene was distilled from sodium in the presence of benzophenone. Diethylether and benzene were distilled from $LiAlH_4$. Styrene was freshly distilled before use.

NMR spectra were recorded in $CDCl_3$ (if not otherwise noted) on a Varian Inova 400 spectrometer at 400.13 MHz (^1H), 100.62 MHz (^{13}C) and 161.89 MHz (^{31}P). Chemical shifts δ are reported in ppm relative to $CHCl_3$ (7.26 and 77.00 ppm for ^1H and ^{13}C, respectively) or relative to H_3PO_4 (^{31}P). In case of in situ NMR experiments a similar procedure was followed as described in 3.3–3.6 (at 10 μmol scale), but $CDCl_3$ was used as solvent).

Elemental analyses were measured on a 1108 Carlo Erba apparatus.

The catalytic precursor $PtCl_2(PhCN)_2$ was prepared as described previously [18]. Samples of the catalytic reactions were analysed with a Hewlett–Packard 5830A gas chromatograph fitted with a capillary column coated with OV-1.

3.2. Synthesis of $PtCl_2$(**1**) (**1a**)

A degassed solution of 46.7 mg (0.099 mmol) dibenzonitrilo platinum(II)chloride in 6 ml benzene is heated to 80 °C for about 5 min and a degassed solution of 57.9 mg (0.1 mmol) *xantphos* is added under argon. The reaction mixture is refluxed for 1 h and then stirred at room temperature for another 16 h. The precipitated product is washed with benzene and hexane and dried in vacuum. Yield: 92%. Anal. Calc. for $C_{39}H_{32}Cl_2OP_2Pt$: C: 55.51; H: 3.83. Found: C: 55.76 H: 3.95. For NMR see Table 1.

3.3. Synthesis of $PtCl(SnCl_3)$(**1**) (mixture of cis and trans isomers)

To the stirred solution of 186 mg of **1a** (0.22 mmol) in 20 ml chloroform 41.8 mg of anhydrous $SnCl_2$ (0.22 mmol) was added at room temperature. After 2 h stirring a few drops of pentane was added to the cooled solution (0 °C) and the pale yellow solid was filtered. Yield: 78%. Anal. Calc. for $C_{39}H_{32}Cl_4$ OP_2PtSn: C: 45.31; H: 3.12. Found: C: 45.54 H: 3.30. For NMR see Table 1.

3.4. Synthesis of trans-Pt(**1**)(^{13}CN)$_2$ (**1c**)

The $PtCl_2$(**1**) complex (**1a**) (84.5 mg; 0.1 mmol) was added to the solution of potassium cyanide (13.2 mg; 0.2 mmol) dissolved in 15 ml methanol. The powder did not dissolved but was kept in suspension at 50 °C with constant stirring for 10 h. The white powder-like crystals were filtered, washed with water, methanol and ether then dried. Yield: 85%. Anal. Calc. for $C_{39}(^{13}C)_2H_{32}N_2OP_2Pt$: C: 59.72; H: 3.90; N: 3.39; Found: C: 59.92; H: 4.11; N: 3.27. For NMR see Table 1.

3.5. Synthesis of [PtCl(**1**)(PPh_3)]Cl (**1d**)

To the stirred solution of 148 mg (0.175 mmol) of **1a** in 10 ml chloroform 45.9 mg (0.175 mmol) of PPh_3 was added. After 2 h stirring the solvent was evaporated and the residue crystallised from benzene/methanol (1/1) mixture. Yield: 67%. Anal. Calc. for $C_{57}H_{47}Cl_2OP_3Pt$: C: 61.89, H: 4.29; Found: C: 62.08; H: 4.43. For NMR see Table 1.

3.6. Synthesis of [PtCl(**1**)(η^1-**1**)]Cl (**1e**)

To the stirred solution of 125 mg of **1a** (0.15 mmol) in 10 ml chloroform 85.6 mg (0.15 mmol) of **1** was added. After 2 h stirring the solvent was evaporated and the residue crystallised from benzene/methanol (1/1) mixture. Yield: 72%. Anal. Calc. for $C_{78}H_{64}Cl_2O_2P_4Pt$: C: 65.86; H: 4.54; Found: C: 65.97; H: 4.76. For NMR see Table 1.

3.7. Hydroformylation experiments with **1a**

In a typical experiment a solution of 21.3 mg (0.025 mmol) of $PtCl(SnCl_3)$(**1**) and 9.5 mg (0.05 mmol) of $SnCl_2$ in 30 ml toluene containing 0.1 mol of styrene is transferred under argon into a 150 ml stainless steel autoclave. The reaction vessel is pressurised to 80 bar total pressure ($CO/H_2 = 1/1$) and the magnetically stirred mixture is heated in an oil bath. The pressure is monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution is immediately analysed by GC.

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