Novel diphosphine platinum cations: NMR and Mössbauer spectra and catalytic studies

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Abstract

The reaction of $PtCl_2$(diphosphine) with mono and bidentate phosphines has been investigated by NMR spectroscopy. [Pt(diphosphine)(PMe$_3$)$_2$]$^{2+}$, [Pt(diphosphine)$_2$]$^{2+}$ and [Pt((S,S)-bdpp)((S,S)-chiraphos)]$^{2+}$ cations have been characterized by ^{31}P NMR and conductivity measurements. The presence of tin(II) chloride promotes the formation of the complex cations. Evidence for coordination of the diphosphine in monodentate mode has been obtained by NMR spectroscopy. The platinum species possessing a platinum–tin bond and ionic complexes with an $SnCl_3^-$ counterion can easily be distinguished by ^{119}Sn Mössbauer spectroscopy. Asymmetric hydroformylation of styrene with [Pt((S,S)-bdpp)$_2$]$^{2+}$($SnCl_3^-$)$_2$ as catalyst precursor gave chemo-, regio- and enantio-selectivities different from those obtained with the covalent PtCl(SnCl$_3$)((S,S)-bdpp) as catalyst precursor.

Keywords: Platinum; Cations; Mössbauer spectra; Catalysis; Bidentate phosphine; Hydroformylation

1. Introduction

Complex cations [Pt(monophosphine)$_3$X]$^+$ (X = Cl, H) have been known for many years [1–4]. The facile formation of the cation [PtCl(diphosphine)(monophosphine)]$^+$ containing three ligating P atoms with a $SnCl_3^-$ counterion was observed in the reaction of PtCl$_2$(diphosphine) and various monophosphines [5] and some of these ionic species prepared in situ turned out to be very efficient catalysts in hydroformylation [6]. In the case of optically active chelating diphosphines moderate to high ee's were obtained in the enantioselective hydroformylation of styrene. An increase in the optical yield was observed when both mono- and optically active bidentate phosphines were used simultaneously in rhodium- and palladium-catalyzed homogeneous hydrogenation and hydroalkoxycarbonylation, respectively [7,8]. There has been no previous study of the platinum complexes formed in the presence of an excess of a diphosphine (with or without tin(II)chloride).

Although insertion of SnCl$_2$ into a transition metal–transition metal or transition metal–halide bond has been investigated thoroughly by Mössbauer spectroscopy in the case of manganese and vanadium [9–12]

for example, little is known about the related platinum complexes. The equilibria involving $SnCl_3^-$ are well-known for platinum species and have been investigated in detail by various NMR techniques [13], but no attempt has been made to use Mössbauer spectroscopy to compare platinum complexes containing covalently bonded $SnCl_3^-$ ligand with ion pairs in which $SnCl_3^-$ acts as a counterion.

We describe below the results of ^{31}P NMR and ^{119}Sn Mössbauer studies of platinum–phosphine–tin(II) chloride systems as well as their catalytic behavior.

2. Results and discussion

2.1. ^{31}P NMR investigation and conductivity measurements with PtCl$_2$(PP) + PP systems

When instead of a monophosphine one equivalent of diphosphine (chiraphos = (2S,3S)-2,3-bis(diphenylphosphino)-butane, bdpp = (2S,4S)-2,4-bis(diphenylphosphino)pentane, diop = (2S,3S)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane) was added to a solution of a PtCl$_2$(PP) complex pre-
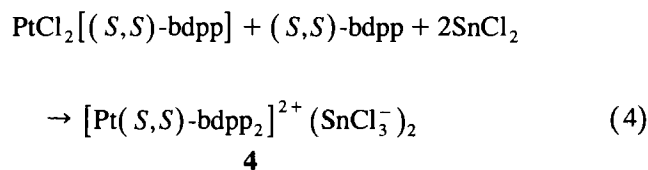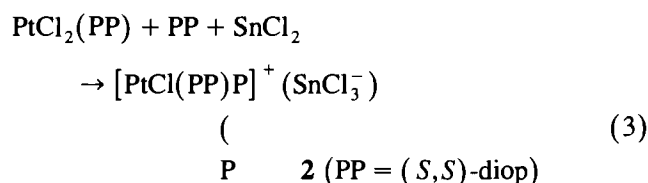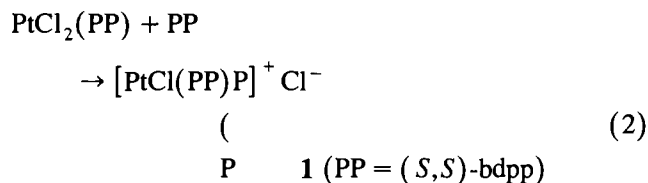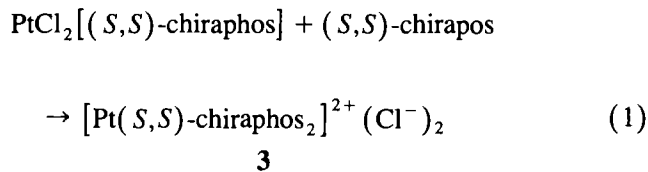
pared from the corresponding bidentate phosphine (where PP = bdpp, chiraphos, diop), products of a different type were obtained with structure depending strongly on the size of the chelate ring.

Whereas the addition of chiraphos (able to form five-membered chelate ring) resulted in the fast and exclusive formation of $[Pt(chiraphos)_2]^{2+}(Cl^-)_2$ (3) ionic complex (Eq. (1)), the corresponding reaction of bdpp (six-membered chelate ring), gave a 25% yield of the cation (1) (containing three ligating P atoms and bearing a single, positive charge), one diphenylphosphino center remaining uncoordinated. The formation of the cation 2 of similar structure requires the presence of tin(II) chloride in the case of diop (Eq. (3)). In the absence of added tin(II) chloride no reaction was observed.

The ionic species show ^{31}P NMR spectra characteristic of square-planar PtP_3X species. The values of the J(Pt–P) and J(P–P) coupling constants clearly indicate the presence of two phosphine ligand *trans* to each other and a third *trans* to chloride (Table 1). In addition to 1 and 2 a minor component of rather similar structure was detected in both cases. The similar spectrum, consisting of three doublets of doublets, suggests the possible formation of a five-coordinate covalent complex $PtCl_2(diphosphine)_2$, on which one of the diphosphines is in monodentate mode.

The use of one or two equivalent of $SnCl_2$ resulted in the quantitative formation of a new $[Pt(bdpp)_2]^{2+}$

complex cation (4) with Cl^-, $SnCl_3^-$ or 2 $SnCl_3^-$ counterions, respectively (Eq. (4)).

$$PtCl_2[(S,S)\text{-chiraphos}] + (S,S)\text{-chirapos}$$

$$\rightarrow \underset{\mathbf{3}}{[Pt(S,S)\text{-chiraphos}_2]^{2+}(Cl^-)_2} \qquad (1)$$

$$PtCl_2(PP) + PP$$

$$\rightarrow [PtCl(PP)P]^+Cl^-$$
$$\underset{\mathbf{P} \qquad \mathbf{1} \ (PP = (S,S)\text{-bdpp})}{(} \qquad (2)$$

$$PtCl_2(PP) + PP + SnCl_2$$

$$\rightarrow [PtCl(PP)P]^+(SnCl_3^-)$$
$$\underset{\mathbf{P} \qquad \mathbf{2} \ (PP = (S,S)\text{-diop})}{(} \qquad (3)$$

$$PtCl_2[(S,S)\text{-bdpp}] + (S,S)\text{-bdpp} + 2SnCl_2$$

$$\rightarrow \underset{\mathbf{4}}{[Pt(S,S)\text{-bdpp}_2]^{2+}(SnCl_3^-)_2} \qquad (4)$$

Probably because of steric effects only the five- and six-membered chelate rings such as chiraphos and bdpp, can give the corresponding $[PtP_4]^{2+}$ cation, diop, which

Table 1
^{31}P NMR data for platinum–diphosphine cations

Cation	δ (ppm)	Coupling constants (Hz)	
		J(P–Pt)	Others
1 [a]	28.0 (P^A)	2348	$J(P^A–P^B) = 13.7$
	17.1 (P^B)	3493	$J(P^A–P^C) = 379$
	9.8 (P^C)	2270	$J(P^B–P^C) = 28.2$
	0.4 [b]		
2 [a]	21.7 (P^A)	2418	$J(P^A–P^B) = 17$
	4.8 (P^B)	3556	$J(P^A–P^C) = 397$
	0.9 (P^C)	2302	$J(P^B–P^C) = 18$
	−22.5 [b]		
$[Pt((S, S)\text{-chiraphos})_2]^{2+}$ (3)	48.1	2272	
$[Pt((S, S)\text{-bdpp})_2]^{2+}$ (4)	7.2	2228	
$[Pt((S, S)\text{-bdpp})(PMe_3)_2]^{2+}$ (5) [c]	12.2 (P^A)	2214	$J(AA') = 33.2$
	−22.8 (P^X)	2242	$J(XX') = 29.7$
			$J(AX) = −23$
			$J(AX') = 306$
$[Pt((S, S)\text{-chiraphos})((S, S)\text{-bdpp})]^{2+}$ (6) [c]	44.8 (P^A)	2216	$J(AA') = 36.2$
	8.5 (P^X)	2277	$J(XX') = 25.0$
			$J(AX) = −18.4$
			$J(AX') = 295.3$

[a] The three coordinated phosphorus atoms give AMX coupling system resulting in dd patterns for each phosphorus.

[b] Noncoordinated phosphorus.

[c] The chemical shifts and coupling constants are obtained from spin simulation of the AA'XX' second order coupling system.
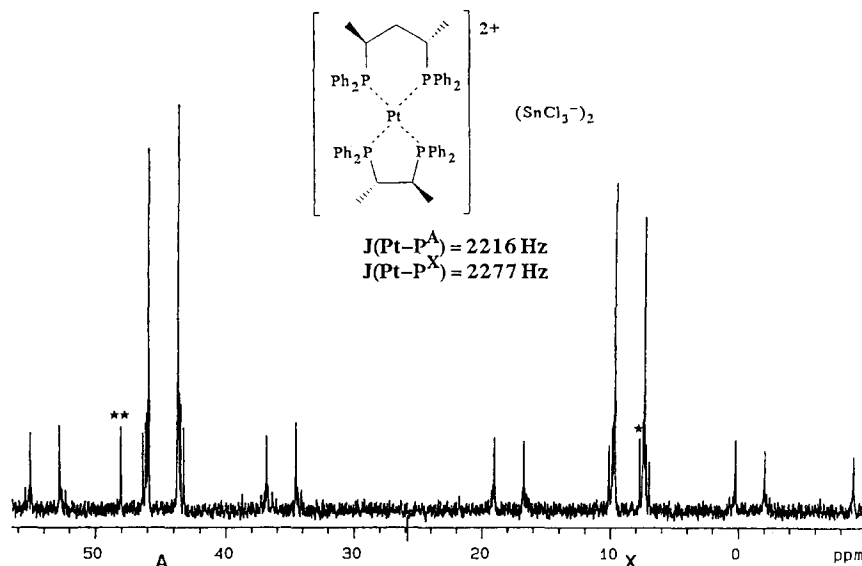
Fig. 1. ^{31}P NMR spectrum of [Pt((S,S)-bdpp)((S,S)-chiraphos)]$^{2+}$ (total spectrum; * and ** stand for [Pt((S,S)-bdpp)$_2$]$^{2+}$ and Pt((S,S)-chiraphos)$_2$]$^{2+}$ impurities, respectively).

can give seven-membered rings, cannot be attached to the platinum as a second chelating ligand, and so the complex formed in this case remains in a PtP$_3$ state. The bidentate phosphine (diop) acts as a monodentate ligand in cation 3 even in the presence of tin(II) chloride. No evidence for the formation of a [Pt(diop)$_2$]$^{2+}$ cation and an "arm-off" dissociation of one of the diop ligands has been obtained by NMR spectroscopy.

The chelate effect also plays an important role in the formation of [PtP$_4$]$^{2+}$ complexes. If one of the two chelating phosphines is replaced by two monotertiary phosphines (PPh$_3$, PBu$_3$, PMe$_3$, etc.) in the in situ system, only the small and basic trimethylphosphine can coordinate to the platinum in the presence of tin(II) chloride to give the cation [Pt(bdpp)(PMe$_3$)$_2$]$^{2+}$ (5). In the other cases the reaction stops at the PtP$_3$ state i.e. at

[Pt(diphosphine)(monophosphine)Cl]$^+$ [5]. The ^{31}P NMR spectrum of 5 is typical of a second-order AA'XX' spin system. The spin simulation parameters used for obtaining best fit to the measured spectrum are listed in Table 1.

Surprisingly, when PtCl$_2$((S,S)-bdpp) was treated with chiraphos the results in the presence of one equivalent of SnCl$_2$ were completely different from those in the presence of two equivalents. In the first case an approximately equimolar mixture of [Pt((S,S)-bddp)$_2$]$^{2+}$ (4) and [Pt((S,S)-chiraphos)$_2$]$^{2+}$ (3) cations was formed (Eq. (5)), while the use of a further equivalent of tin(II) chloride resulted in a "mixed-diphosphine" platinum-containing cation [Pt((S,S)-bdpp)((S,S)-chiraphos)]$^{2+}$ (6) (Eq. (6)). This also gives an AA'XX' ^{31}P NMR spectrum similar to that of 5 and attributable to the chemi-

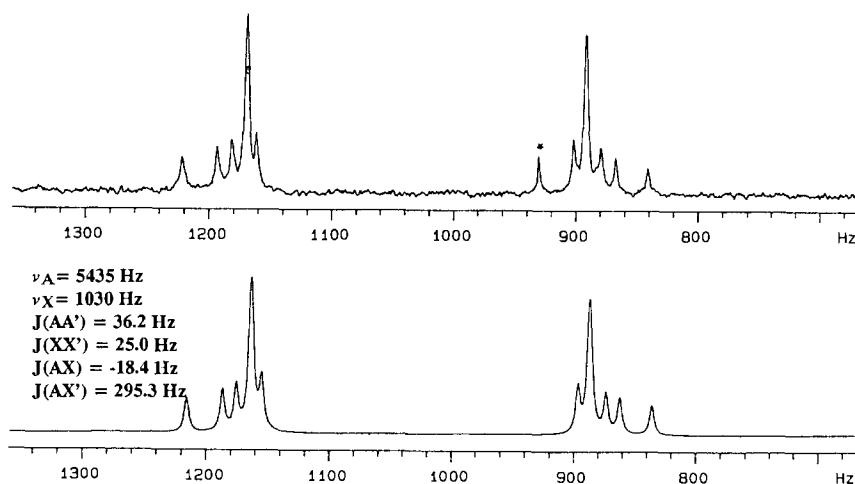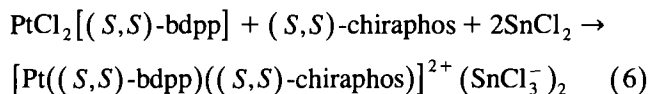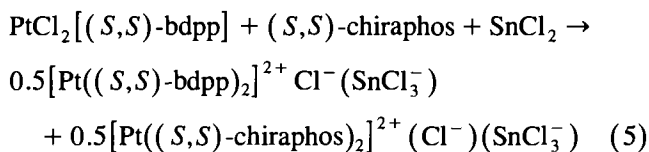Fig. 2. ^{31}P NMR spectra of [Pt((S,S)-bdpp)((S,S)-chiraphos)]$^{2+}$ (measured and simulated spectra of the central lines assigned to P^X and P$^{X'}$).

Table 2
Conductivity data for $PtCl_2[(S, S)\text{-bdpp}] + SnCl_2$ systems in CH_2Cl_2

System	Equivalent conductance, A_0 $(cm^2\ mol^{-1}\ ohm^{-1})$
$PtCl_2(bdpp)$	0.591
$PtCl_2(bdpp) + bdpp$	48.33
$PtCl_2(bdpp) + bdpp + SnCl_2$	79.7
$PtCl_2(bdpp) + bdpp + 2SnCl_2$	69.8

cally and magnetically nonequivalent phosphorous atoms of the two different phosphines (Fig. 1). The original and simulated spectra of the phosphorus atoms bonded to platinum nuclei other than ^{195}Pt ($I = 1/2$) ('central lines') are depicted in Fig. 2. These central lines are flanked by platinum satellites as a result of $^{195}Pt-^{31}P$ coupling constants in the range of 2200–2300 Hz, which indicates that each phosphine phosphorus is *trans* to a phosphorus of the other ligand and a complex of square-planar geometry. The absence of $^{119,117}Sn$-satellites in the ^{31}P NMR spectrum indicates that there is no direct platinum–tin bond.

$$PtCl_2[(S,S)\text{-bdpp}] + (S,S)\text{-chiraphos} + SnCl_2 \rightarrow$$

$$0.5[Pt((S,S)\text{-bdpp})_2]^{2+}\ Cl^-(SnCl_3^-)$$

$$+ 0.5[Pt((S,S)\text{-chiraphos})_2]^{2+}(Cl^-)(SnCl_3^-) \quad (5)$$

$$PtCl_2[(S,S)\text{-bdpp}] + (S,S)\text{-chiraphos} + 2SnCl_2 \rightarrow$$

$$[Pt((S,S)\text{-bdpp})((S,S)\text{-chiraphos})]^{2+}(SnCl_3^-)_2 \quad (6)$$

The formation of ionic complexes was also confirmed by conductivity measurements. The equivalent conductance of the "covalent" $PtCl_2[(S,S)\text{-bdpp}]$ in dichloromethane increased by two orders of magnitude upon addition of a second bdpp in keeping with Eq. (1). A further increase brought about by the addition of one equivalent of tin(II) chloride, as a consequence of the complete formation of $[Pt((S,S)\text{-bdpp})_2]^{2+}$ cation (Eq. (2)). A slight decrease upon addition of second equivalent of tin(II) chloride can be attributed to the presence of two $SnCl_3^-$ counterions (Eq. (3)) rather than Cl^- and

one $SnCl_3^-$ (Table 2), the smaller ionic mobility of $SnCl_3^-$ leading to a decrease in the anionic conductance.

2.2. ^{119}Sn Mössbauer investigation of platinum complexes possessing $SnCl_3^-$ as a ligand or counterion

Further evidence for the ionic character of the above species was gained by Mössbauer spectroscopy because in the tin-containing complexes there is a strong correlation between the Mössbauer parameters (isomeric shift and quadrupole splitting) and the electronic structure of tin. The isomeric shift of tin is proportional to the electron charge density at the nucleus. The s-electrons have a finite density at the nucleus and so an increase in the population of the s-orbitals increases the isomeric shift of tin. An increase in the population of the other orbitals (p, d) lowers the isomeric shift owing to their screening effect on the s-electrons. The quadrupole splitting measures the electric field gradient at the nucleus and so information about the symmetry of the charge distribution around the nucleus.

Since the Sn^{2+} and Sn^{4+} ions are $5s^2$ and $4d^{10}$ species, respectively, they represent the positive ($+5.6$ mm s^{-1}) and negative (-3 mm s^{-1}) ends of the isomeric shift scale for tin [14].

In four-coordinate square-planar $PtCl(PP)(SnCl_3)$ complexes containing a covalently bonded trichlorostannato ligand the phosphine ligands seem to have an almost negligible effect on the isomeric shift and the quadrupole splitting values. In all cases (five-, six- and seven-membered chelate rings) both are in the region of 2 mm s^{-1} and show a slight decrease with increase in the size of the chelate ring (Table 3, run, 1–4).

The spectra of the cationic complexes, in which three or four phosphorus atoms are bonded to platinum, reveal the presence of two components in each case except the one for that the frozen liquid-phase experiment, where a precipitate, formed as a minor component was separated. This minor component (isomeric shift 0.41 mm s^{-1}, quadrupolar splitting 0.35 mm s^{-1}) is thought to be $SnOCl_3^-$ anion, formed by oxidation of

Table 3
^{119}Sn Mössbauer data for platinum–phosphine–tin(II) chloride systems

Run	Complex [a]	Isomeric shift (mm s^{-1})	Q splitting (mm s^{-1})
1	$PtCl(SnCl_3)[(S, S)\text{-chiraphos}]$	2.024	2.079
2	$PtCl(SnCl_3)(dppp)$	1.954	1.971
3	$PtCl(SnCl_3)[(S, S)\text{-bdpp}]$	2.007	2.010
4	$PtCl(SnCl_3)(dppb)$	1.979	1.962
5	$[Pt((S, S)\text{-chiraphos})_2]^{2+}(SnCl_3^-)_2$	3.32	1.38
6	$[PtCl(dppp)(PPh_3)]^+(SnCl_3^-)$	3.25	1.43
7	$[Pt((S, S)\text{-bdpp})_2]^{2+}(SnCl_3^-)_2$	3.331	1.400
8	$[Pt((S, S)\text{-bdpp})_2]^{2+}(SnCl_3^-)_2$ [b]	3.450	1.183

[a] dppp = 1,3-bis(diphenylphosphino)propane; dppb = 1,4-bis(diphenylphosphino)butane
[b] Frozen from a 0.025 mmol cm^{-3} CH_2Cl_2 solution.

Fig. 3. ^{119}Sn Mössbauer spectra of [Pt((S,S)-bdpp)$_2$]$^{2+}$ (SnCl$_3^-$)$_2$ and PtCl(SnCl$_3$)((S,S)-bdpp) ($\ll$ stands for Pt(IV) derivative of unknown structure).

SnCl$_3^-$ in the dichloromethane solvent. The major component was identified as the well-known trichlorostannate anion (isomeric shift 3.2–3.4 mm s^{-1}, quadrupolar splitting 1.38–1.43 mm s^{-1}). No significant effect of the phosphines on the Mössbauer data was observed, indicating that the phosphines have no influence on the electronic structure of tin.

The Mössbauer spectrum of an easily distinguishable covalent–ionic complex pair (bdpp as chelating ligand) is depicted in Fig. 3.

2.3. Asymmetric hydroformylation in the presence of [Pt((S,S)-bdpp)$_2$]$^{2+}$(SnCl$_3^-$)$_2$ precursor

The title complexes were used for the enantioselective hydroformylation of styrene.

$$PhCH=CH_2 + CO + H_2$$

$$\rightarrow PhCH^*(CHO)CH_3 + Ph(CH_2)_2CHO + PhC_2H_5$$
$$\quad\quad\quad\quad B \quad\quad\quad\quad\quad\quad L$$

The [Pt((2S,4S)-bdpp)$_2$]$^{2+}$ (SnCl$_3^-$)$_2$ complex is a suitable catalyst for hydroformylation, although at low temperature, at which good optical yields are expected, the relatively strong Pt–P bonds probably inhibit dissociation and so the complex is too stable for carbon monoxide and olefin coordination. Although even at higher temperatures the presence of an excess of phosphine (relative to the amount of PtCl$_2$(PP) and SnCl$_2$) causes inhibition the complex proved to be an active hydroformylation catalyst. (It should be noted that the use of basic monophosphines (e.g. PBu$_3$ or PMe$_3$) in a two-fold (or larger) excess in a PtCl$_2$(diphosphine) + monophosphine + tin(II) chloride in situ system results in a practically inactive system.)

The presence of novel catalytic intermediates can be deduced from the following observations. The selectivities are different from those with PtCl(SnCl$_3$)[(2S,4S)-bdpp] a precursor; while the chemoselectivity towards aldehydes is higher the regioselectivity toward branched aldehyde is lower (Table 4). The most interesting feature of this system, the strong temperature dependence of the optical yield, is also different from that discussed earlier. Whereas when PtCl(SnCl$_3$)[(2S,4S)-bdpp] is used as a precursor the change of the absolute configuration occurs at 88°C, in the presence of an excess of chiral diphosphine (S)-2-phenylpropanal is predominate even at 100°C. The R enantiomer becomes dominant only above 105°C.

The dissociation of one of the phosphorus atoms could result in a "PtP$_3$" species coordinating with one

Table 4
Hydroformylation of styrene with [Pt((2S, 4S)-bdpp)$_2$]$^{2+}$(SnCl$_3^-$)$_2$ as catalytic precursor

Temperature (°C)	Reaction time (h)	Conversion (%)	R_C [b] (%)	R_{RB} [c] (%)	ee (%)
40	72	—	—	—	—
40 [d]	55	76	96	42	64.5(S)
60	72	58.6	96.1	31.9	49.8(S)
100	15	66.4	90.7	31.7	3.6(S)
100 [d]	4.5	76	86	27	17.1(R)
120	15	89.1	84.6	26.2	11.7(R)

[a] Reaction conditions: 35 ml toluene; 0.1 mol substrate; Pt/substrate = 1/2000; p(CO) = p(H$_2$) = 40 bar.
[b] chemoselectivity (mol aldehyde/mol reacted substrate × 100).
[c] regioselectivity towards branched aldehyde (mol B/(mol B + mol L) × 100.
[d] results obtained with PtCl(SnCl$_3$)((2S, 4S)-bdpp) precursor (See Ref. [15]).

of the diphosphines in monodentate mode under "oxo-conditions". If it is assumed that these species are responsible for the observed differences in selectivities, the activation of the olefin, its insertion into a Pt–H bond and the further steps of the hydroformylation mechanism might involve a five-coordinate catalytic species.

3. Experimental details

3.1. Reagents and measurements

The $PtCl_2P_2$-type complexes were prepared by the standard methods [15]. The anhydrous $SnCl_2$ was made by dehydrating $SnCl_2 \cdot 2H_2O$ with a stoichiometric amount of acetic anhydride followed by washing with ether.

The ionic complexes were isolated as bright transparent crystals or as white powders by adding cold pentane dropwise to their dichloromethane solutions.

The ^{31}P NMR spectra were recorded in CD_2Cl_2 and $CDCl_3$ solutions on a Varian Unity 300 spectrometer operating at 121.42 MHz. The signals were referenced to the external 85% H_3PO_4. (A positive sign indicates a shift to lower field.) The measurements were carried out under argon.

The ^{119}Sn Mössbauer spectra were recorded on a conventional RANGER spectrometer in constant accelerating mode with a source of activity of 1 GBq. Computer analysis was used to determine isomeric shifts (IS) and quadrupole splitting (QS) values. The reproducibility of the Mössbauer parameters was found to be ± 0.02 mm s^{-1} (IS) and ± 0.04 mm s^{-1} (QS), respectively. The IS values are relative to that for $CaSnO_3$.

The conductivity measurements were carried out under argon in freshly distilled CH_2Cl_2.

3.2. Hydroformylation experiments

In a typical experiment a solution of 0.025 mmol of $[Pt(bdpp)_2]^{2+}(SnCl_3^-)_2$ in 30 ml of toluene containing

0.1 mmol (11.5 ml) of styrene was transferred under argon into a 150 ml stainless steel autoclave. The vessel was pressurized to 80 bar total pressure $(CO/H_2 = 1/1)$ and placed in an oil bath and the mixture stirred with a magnetic stirrer. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed and immediately analyzed by GLC then fractionally distilled, and the optical rotation of the 2-phenylpropanal fraction was measured.

References

[1] M.J. Church and M.J. Mays, *J. Chem. Soc. A*, (1968) 3074.
[2] J.P. Collmann, *Accounts Chem. Res.*, *1* (1968) 136.
[3] F. Cariati, R. Ugo and F. Bonati, *Inorg. Chem.*, *5* (1966) 1128.
[4] H.C. Clark and K.R. Dixon, *J. Am. Chem. Soc.*, 91 (1969) 596.
[5] L. Kollár and G. Szalontai, *J. Organomet. Chem.*, 421 (1991) 341.
[6] L. Kollár, J. Bakos, I. Tóth and B. Heil, *J. Organomet. Chem.*, *370* (1989) 257.
[7] S. Törös, B. Heil and L. Markó, *J. Organomet. Chem.*, *159* (1978) 401.
[8] G. Consiglio, *J. Organomet. Chem.*, *132* (1977) C26.
[9] M.S. Holt, W.L. Wilson and J.H. Nelson, *Chem. Rev.*, *89* (1989) 11.
[10] B. Mahieu, D. Apers, I. Vanden Eynde and M. Gielen, *J. Organomet. Chem.*, *246* (1983) 49.
[11] D.E. Fenton and J.J. Zuckermann, *Inorg. Chem.*, *8* (1969) 1771.
[12] R.V. Parish and P.J. Rowbotham, *J. Chem. Soc., Dalton Trans.*, (1973) 37.
[13] I. Tóth, T. Kégl, C.J. Elsevier and L. Kollár, *Inorg. Chem.*, *33* (1994) 5708, and references therein.
[14] A. Vértes, L. Korecz and K. Burger, *Mössbauer Spectroscopy*, Elsevier, New York, Amsterdam, 1979, p. 245.
[15] L. Kollár, J. Bakos, I. Tóth and B. Heil, *J. Organomet. Chem.*, *350* (1988) 277.