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Platinum(II) complexes incorporating racemic and optically active 1-alkyl-3-phospholenes and 1-propyl-phospholane P-ligands: Synthesis, stereostructure, NMR properties and catalytic activity

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ABSTRACT

Racemic and optically active 1-propyl- and 1-butyl-3-methyl-3-phospholene oxides, as well as 1-propyl-3-methylphospholane oxides were converted after deoxygenation to the corresponding phosphine-borane and phopshine-platinum complexes. Stereostructure of the novel platinum complexes with a propyl group on the phosphorus atom was evaluated by quantum chemical calculations. The complexes displayed characteristic properties regarding their NMR spectra and showed unusual regioselectivity as catalysts in the hydroformylation of styrene derivatives. Ee-s up to 21% were obtained in the presence of optically active Pt-complex precursors.

1. Introduction

Transition metal complexes incorporating P(III)-ligands are of increasing importance due to their applicability as catalysts in homogeneous catalytic processes [1,2]. Platinum complexes, due to their high thermodynamic stability and kinetic inertness, form perhaps the best-studied field within transition metal chemistry. Regarding platinum complexes, the species with P-heterocyclic ligands represent a dynamically developing field [3–5]. Arylphospholes, 3-phospholenes, phospholanes, a 1,4-dihydrophosphinine and a 1,2,3,6-tetrahydrophosphinine were converted to the corresponding platinum complexes by Kollár and Keglevich [6–9]. Pringle et al. described the platinum complexes of a few phospholanes, phosphinines and phosphepanes [10], as well as those of 9-phosphabicyclononanes (Phobanes) [11] and 6-phospha-2,4,8-trioxaadamantanes [12]. Among the bidentate heterocyclic P-ligands, DuPhos [13], PennPhos [14] and BIPNOR [15] are to be mentioned, but only DuPhos has been applied in platinum complexes [16–18]. 3-Diphenylphosphino-1,2,3,6-tetrahydrophosphinine and 3-diphenylphosphino-1,2,3,4,5,6-hexahydrophosphinine served as bidentate P-ligands to form the corresponding *cis* chelate platinum complexes [19–22]. Recently, P-aryl, P-amino and P-alkoxy dibenzo[*c,e*][1,2]oxaphosphorines including optically active derivatives were synthesized by us and were converted to the corresponding bis(dibenzooxaphosphorino)dichloro-platinum complexes or related species [23–28]. These complexes incorporated mainly phosphinites, phosphonites and phosphonous amides as P(III)-ligands.

Recently, we were successful in resolving the racemates of aryl-, alkyl- and alkoxy-3-phopholene oxides [29–33] that are potential precursors of heterocyclic P-ligands. On the one hand, TADDOL derivatives were utilized via (diastereomeric) molecular complexes [29,30], on the other hand, the calcium salts of dibenzoyl tartaric acid derivatives were applied to form inclusive coordination complexes [31,32].

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In this paper, novel platinum complexes with racemic and optically active 1-propyl- and 1-butyl-3-phospholene and 1-propyl-phospholane P-ligands are synthesized, characterized and tested as catalysts in hydroformylation.

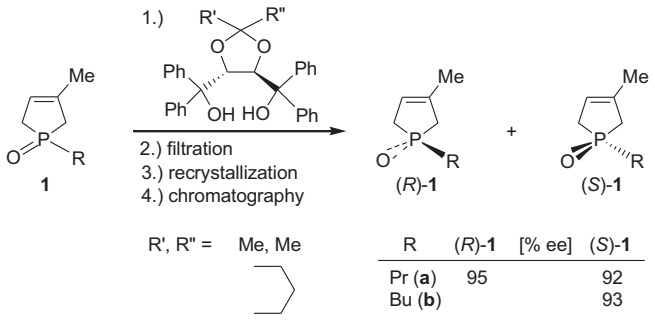
2. Results and discussion

2.1. Synthesis and structure of heterocyclic borane and platinum complexes

First, the 1-propyl- and 1-butyl-3-methyl-3-phospholene oxides (**1a** and **1b**) were synthesized [33] and the racemates were separated into the optically active forms using (*R*,*R*)-TADDOL and (*R*,*R*)-spiro-TADDOL as the resolving agent [30]. For the butyl-phospholene oxide (**1b**), this is the first case that one of the enantiomers was made available. The (*S*)-**1a** and (*R*)-**1a** enantiomers were obtained in an ee of 92% and 95%, respectively, while one of the two enantiomers of **1b** was prepared in an ee of 93%. Assuming an analogy with the case of propyl-phospholene oxide (**1a**), the negative sign of the optical rotation of the isolated enantiomer may refer to the (*S*) form of **1b** (Scheme 1).

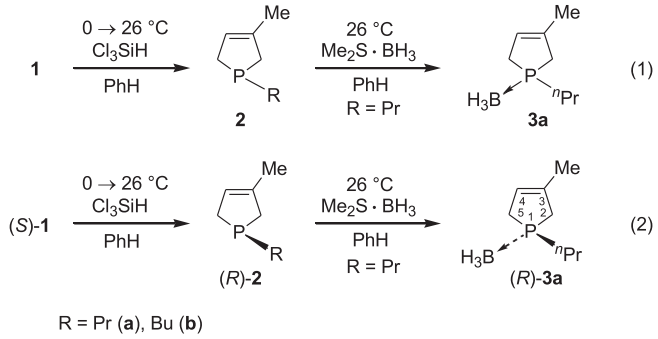
Then the racemic and optically active forms (**1a**, **b** and (*S*)-**1a**, **b**, respectively) were subjected to deoxygenation with trichlorosilane [34] to afford the phosphines (**2a**, **b** and (*R*)-**2a**, **b**, respectively). Phosphines **2a** and (*R*)-**2a** were reacted with dimethylsulfide-borane, resulting in the formation of phosphine-boranes **3a** and (*R*)-**3a**, respectively (Scheme 2). The phosphine-boranes can be regarded as protected phosphines from which the P(III) form can be liberated by reaction with a secondary amine (e.g. diethylamine) on heating in an apolar solvent [35]. 3-Phospholenes **2a**, **b** and (*R*)-**2a**, **b** were then converted to the corresponding platinum complexes **4a** and **4b** by reaction with dichlorodibenzonitrile platinum at 26 °C, using benzene as the solvent. Starting from the racemic phosphines (**2a**, **b**), complex **4a**, **b** was formed as a 1:1 mixture of the homochiral (*R*,*R*- and *S*,*S*) and the heterochiral (*R*,*S*) forms. At the same time, the complex formation of the (*R*)-**2a**, **b** phosphine with platinum provided the optically active (*S*, *S*)-**4a**, **b** product (Scheme 3).

The platinum complexes **4a**, **b** were characterized by ^{31}P, ^{13}C and ^{1}H NMR spectrometry, as well as by HRMS. According to expectation [5], the complexes **4a**, **b** exhibited the P-donor atoms in *cis* position. This was justified by the $J(^{31}P-^{195}Pt)$ couplings of 3421–3451 Hz obtained from the ^{31}P NMR spectra, indicating that both phosphorus atoms have chloro ligands in the *trans* position [5]. The platinum complexes **4a**, **b** exist as a mixture of isotopomers due to the different Pt isotopes in natural abundance. The isotope shifts have practically no significance in the ^{13}C NMR spectra, however, the ^{195}Pt nucleus with 1/2 nuclear spin and 33.8% natural abundance resulted in a complex signal structure, considering also that most of the signals are affected by two further and different ^{31}P



R	(*R*)-**1**	[% ee]	(*S*)-**1**
Pr (**a**)	95		92
Bu (**b**)			93

Scheme 1. [30].



Scheme 2.

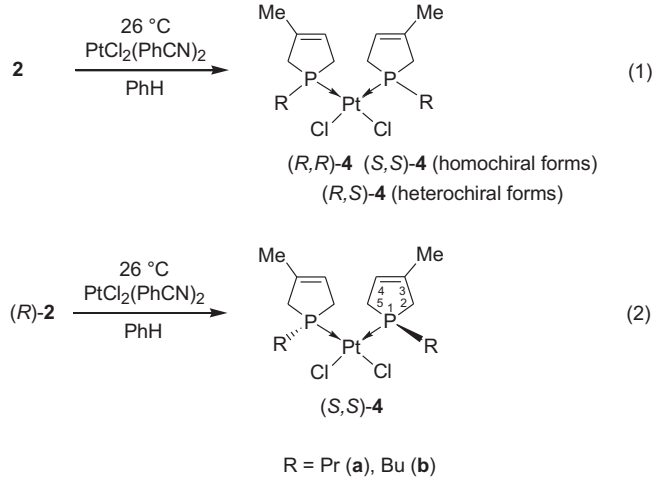
splittings. The $J(^{195}Pt-^{13}C)$ and $J(^{31}P-^{13}C)$ coupling constants were determined by first-order analysis of these splittings for complex **4a**, see (Fig. 1).

Stereostructure of the *S*,*S*-isomer of complex **4a** was calculated by the B3LYP/6-31G** + LANL2DZ methods. The most stable structure of complex (*S*,*S*)-**4a** can be seen in Fig. 2. The molecule is symmetrical. A weak interaction can be assumed between the C(3)–C(4) double bond of the heterocyclic moiety and the C(2′)H_2 group of the propyl group of the other hetero ring.

Next, the racemic and optically active ((*R*)-) forms of 3-phospholene oxide **1a** were subjected to catalytic hydrogenation to afford phospholane oxide **5** as a 1:1 mixture of two diastereomers. From racemic **1a**, product **5** was also formed as racemates, while from optically active (*R*)-**1a**, **5** was obtained as a mixture of the optically active (R_PR_C)- and (R_PS_C)- forms (Scheme 4).

The diastereomeric mixtures of the racemic and optically active ((*R*)-) phospholane oxides **5** were then reduced by trichlorosilane to give the corresponding (racemic or optically active) forms of the phospholane **6**, or after reaction with borane, the phosphine-borane **7**. Assuming retention during the reduction, the absolute configuration of the phosphorus atom in the optically active forms of the phospholane (**6**) and phospholane-borane (**7**) is *S* in both cases (Scheme 5).

Phospholanes **6** and (*S*)-**6** were then reacted with the platinum precursor at ambient temperature in benzene. Reaction of the racemic phospholane (**6**) led to an 8:22:32:13:10:15 mixture of six isomers (from among four were racemates) as shown in Scheme 6. At the same time, the complex forming reaction of the



Scheme 3.

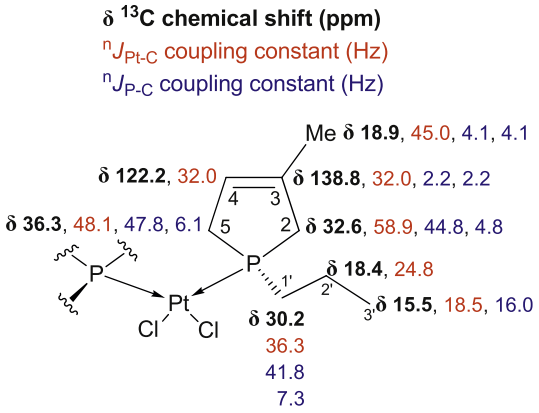
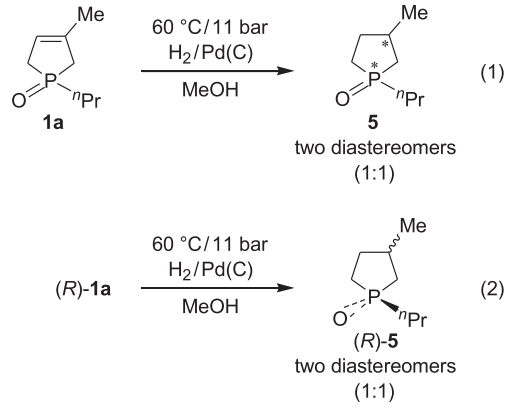


Fig. 1. The ^{13}C NMR spectral assignment for complex (*S,S*)-**4a**.



Scheme 4.

diastereomeric mixture of phospholane (*S*)-**6** afforded a 23:45:32 mixture of isomers (R_PR_C,R_PR_C)-**8**, (R_PS_C,R_PR_C)-**8** and (R_PS_C,R_PS_C)-**8** (Scheme 6).

The platinum complexes were characterized by ^{31}P and ^{13}C NMR, as well as by HRMS. ^{31}P NMR spectrum of the mixture of the phospholane–platinum complex **8** prepared from the 1:1 mixture of the (S_PR_C) and (S_PS_C) phospholanes is shown in Fig. 3. The spectrum contains two singlets, as well as an AB system. Diastereomers (R_PR_C,R_PR_C)-**8** and (R_PS_C,R_PS_C)-**8** have either a symmetry plane or an inversion center, so that their phosphorus atoms are chemically equivalent and each compound gave only one signal. At the same time, (R_PS_C,R_PR_C)-**8** does not have any symmetry element, so the two phosphorus atoms result in the appearance of two signals in the spectrum coupled with each other, forming an AB system with a $J_{P\text{-}P}$ coupling constant of *ca.* 17 Hz. In the ^{31}P NMR spectrum of the reaction mixture from the racemic phospholane (**6**), a second set of similar signals appears with quite similar intensity ratios. Each phosphorus signals shows the respective ^{195}Pt satellites with a $^1J_{Pt\text{-}P}$ coupling constant of *ca.* 3447 Hz.

Stereostructure of the (R_PS_C,R_PR_C)-isomer of *cis* complex **8** was evaluated by the B3LYP/6-31G** + LANL2DZ calculations. The best structure is shown in Fig. 4. Due to a steric interaction, the conformation of the P-propyl group is affected by the C_5-methyl group of the phospholane moiety. The P-propyl groups are against the C_5-methyl substituents of the hetero rings.

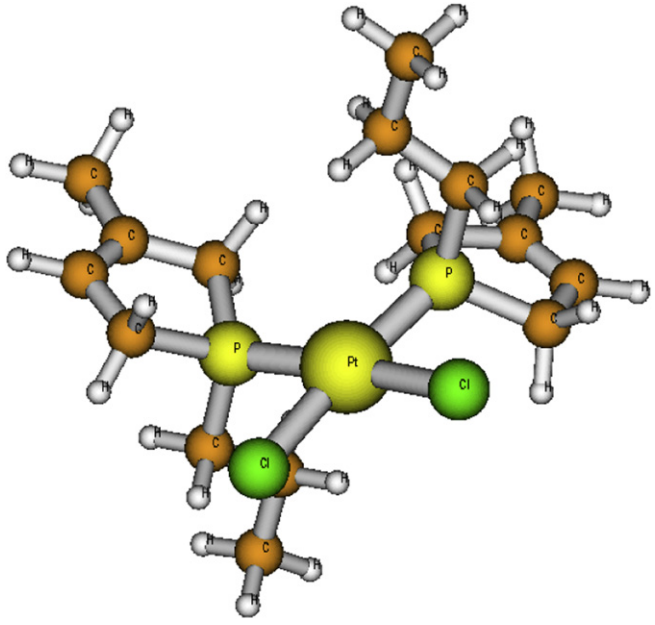


Fig. 2. Perspective view of *cis*-bis(1-propyl-3-methyl-3-phospholeno)-dichloro-platinum(II) ((*S,S*)-**4a**) calculated by the B3LYP/6-31G** and LANL2DZ (Pt) method. The optimized geometries (in Å and degree): Pt–Cl 2.425, Pt–P 2.289, P–C2 1.869, C2–C3 1.519, C3–C4 1.340, C4–C5 1.506, P–C5 1.861, P–C1′ 1.848, C1′–C2′ 1.535, C2′–C3′ 1.533; Cl–Pt–Cl 91.5, Cl–Pt–P 82.3, Pt–P–C2 123.3, Pt–P–C5 115.5, Pt–P–C1′ 112.9, P–C2–C3 105.1, C2–C3–C4 115.8, C3–C4–C5 118.5; Cl–Pt–P–C2 165.5, Pt–P–C1′–C2′ −59.7, Cl–Pt–P–C2 165.5, Pt–P–C2–C3 −138.2, P–C2–C3–C4 11.2, C2–C3–C4–C5 −0.5, P–C1′–C2′–C3′ 178.9.

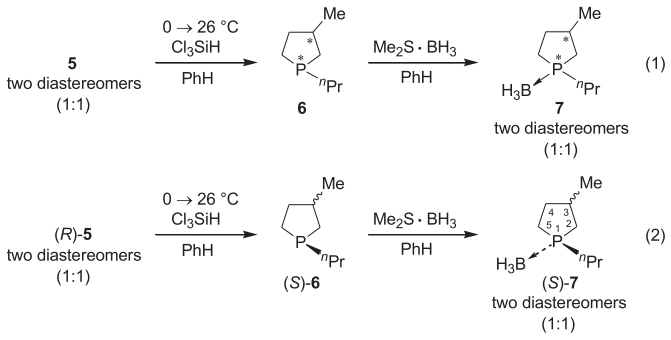
2.2. Catalytic activity of the heterocyclic platinum complexes synthesized

The $PtCl_2P_2$-type complexes, *cis*-[bis(1-alkyl-3-methyl-3-phospholeno)-dichloro-platinum(II)] **4a** and **4b**, as well as *cis*-[bis(1-*n*-propyl-3-methyl-phospholano)-dichloro-platinum(II)] **8** were tested as catalyst precursor in the hydroformylation of styrene and its 4-substituted derivatives. The catalysts formed *in situ* from **4a**, **b** or **8** and two equivalents of tin(II) chloride under standard 'oxo-conditions' [$p(CO) = p(H_2) = 40$ bar, 100 °C] were used. As generally observed, in addition to the two types of formyl regioisomers, 2-aryl-propanal derivatives (**A**) and 3-aryl-propanal derivatives (**B**), the corresponding ethylbenzenes (**C**) as hydrogenation by-products were also formed (Eq. 1).

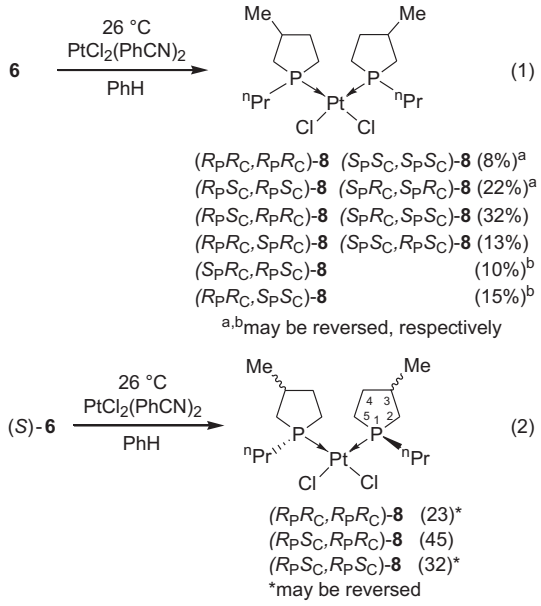
$$\mathrm{ArCH{=}CH_2} \xrightarrow{CO/H_2} \underset{\mathbf{A}}{\mathrm{ArCH(CHO)CH_3}} + \underset{\mathbf{B}}{\mathrm{ArCH_2CH_2CHO}} + \underset{\mathbf{C}}{\mathrm{ArCH_2CH_3}}$$

$$\mathrm{Ar} = \mathrm{C_6H_5},\ 4-\mathrm{CH_3}-\mathrm{C_6H_4},\ 4-\mathrm{AcO}-\mathrm{C_6H_4},\ 4-\mathrm{Cl}-\mathrm{C_6H_4} \qquad (1)$$

Based on the results obtained with similar catalysts containing *P*-phenyl-phospholenes and phospholanes [36], the pressure of 80 bar (CO/H_2 1/1) and temperature range of 60 °C to 100 °C was



Scheme 5.



Scheme 6.

chosen. It is worth noting that low catalytic activity below 50 °C and some reduction of Pt(II) to Pt(0), *i.e.*, the formation of some platinum black can be observed above 125 °C using the catalytic precursors **4a** and **4b** or **8**. Similarly, negligible conversions were obtained below 50 bar.

The formation of the aldehydes (**A**, **B**) was preferred in all cases and the chemoselectivity towards aldehydes typically varied in the range of 76 and 91% using complex **4a** as the precursor and styrene as the substrate (entries 1–4) (Table 1). The application of precursor **4b** with butyl-phospholene ligands instead of the propyl-substituted species **4a** resulted in quite similar chemoselectivities (compare entries 1 and 9 or 2 and 10/11). Considering also the substituted styrenes, the chemoselectivity fall in the range of 67–93% (entries 5–8). Using the phospholano-substituted precursor **8**, the chemoselectivity was around 90% (entries 12–14). Unexpectedly, lower aldehyde selectivity was obtained allowing a prolonged reaction time with precursor **4a** (entries 2 and 3). At the same time, the ratio of the aldehydes to the hydrogenated product was not dependent on the reaction time using **8** as the catalytic precursor (entries 12–14).

As regards the regioselectivity, the branched aldehyde predominated in all cases. In our case, regioselectivities of 66–77% towards the branched aldehyde were obtained in the presence of complex **4a** (entries 1–8). The use of the **4b** instead of **4a** resulted in similar regioselectivities (compare entries 1 and 9 or 2 and 10/11). At the same time, a slight decrease in the branched selectivity was observed with **8** (entries 12–14). Practically, no influence of the 4-substituent on the regioselectivity has been detected in the case of complex **4a** (entries 3–8). In these cases, the regioselectivities were close to 70%.

Comparing these regioselectivities with the analogous 1-phenyl-3-phospholene-based ligands [36], undoubtedly higher regioselectivities towards the branched aldehyde have been obtained with the newly tested n-alkyl analogons. It has to be

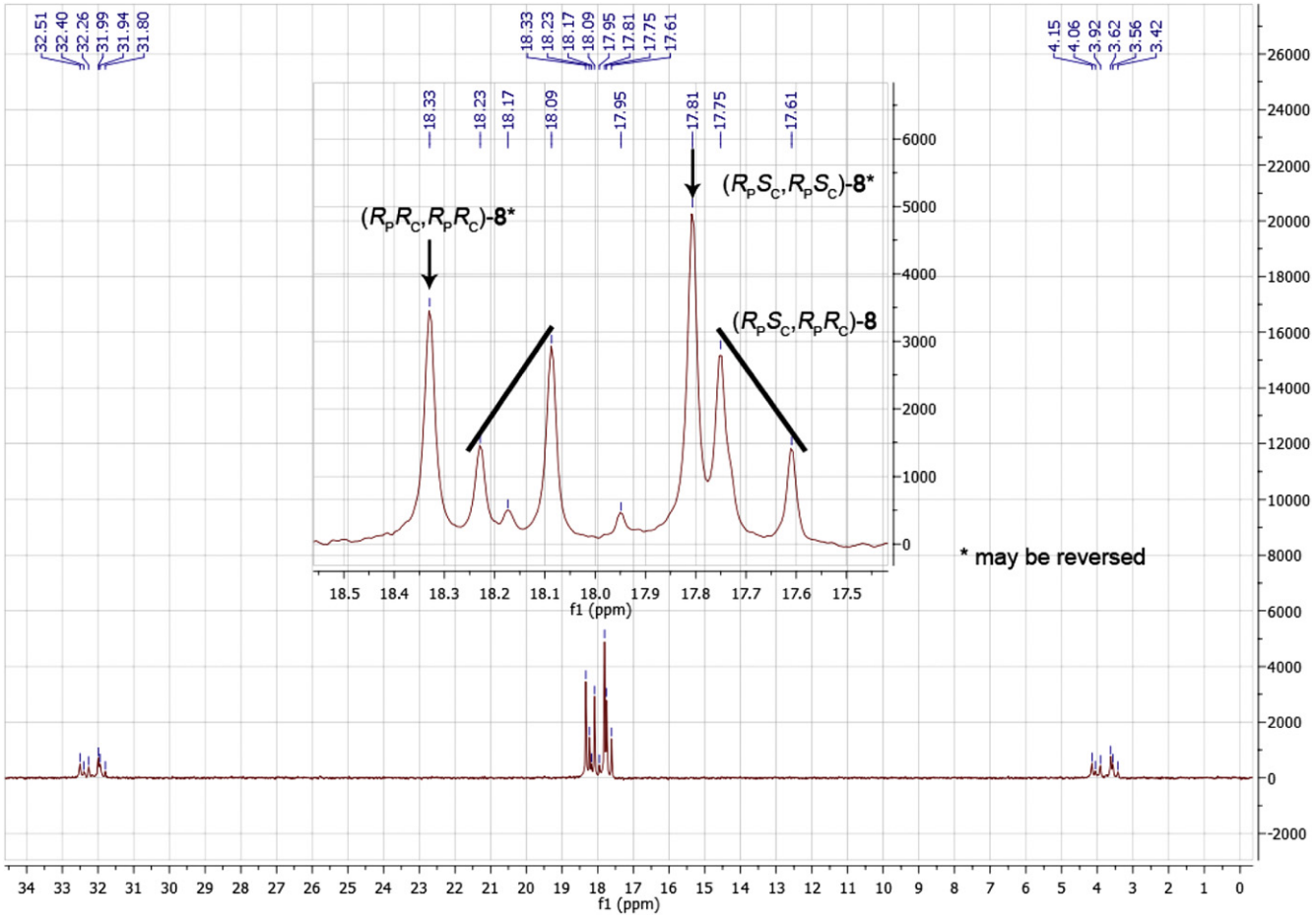


Fig. 3. Assignment for the ^{31}P NMR spectrum for the mixture of complexes (R_PR_C,R_PR_C)-, (R_PS_C,R_PR_C) and (R_PS_C,R_PS_C)-**8**.

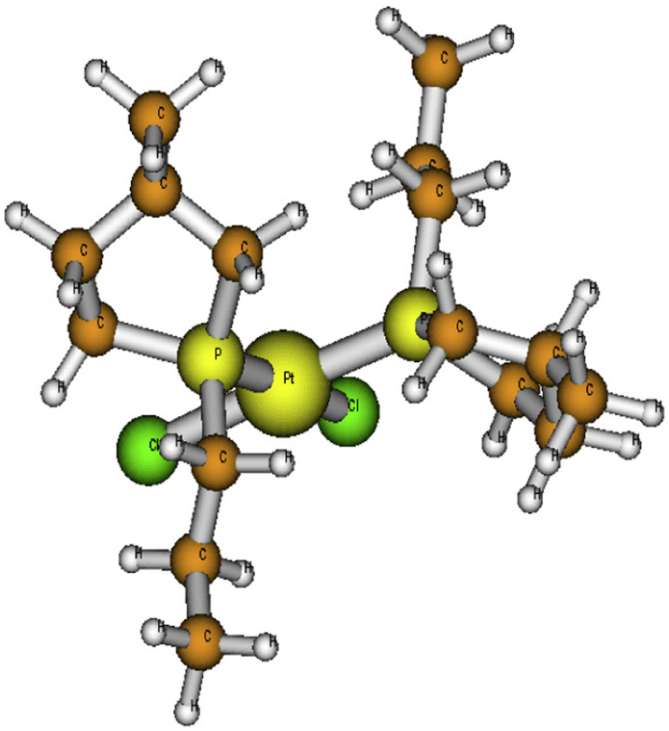


Fig. 4. Perspective view of *cis*-bis(1-propyl-3-methylphospholano)-dichloro-platinum(II) (R_PS_C,R_PR_C)-**8** calculated by the B3LYP/6-31G** and LANL2DZ method. The optimized geometries (in Å and degree): Pt–Cl 2.419, 2.419, Pt–P 2.297, 2.298, P–C2 1.874, 1.869, C2–C3 1.547, 1.545, C3–C4 1.540, 1.541, C4–C5 1.537, 1.539, P–C5 1.861, 1.867, P–C1′ 1.856, 1.856, C1′–C2′ 1.536, 1.536, C2′–C3′ 1.533, 1.533; Cl–Pt–Cl 89.6, Cl–Pt–P 85.4, 85.9, Pt–P–C2 120.2, 119.6, Pt–P–C5 117.0, 117.1, Pt–P–C1′ 113.9, 113.8, P–C2–C3 106.5, 106.3, C2–C3–C4 105.8, 106.5, C3–C4–C5 107.6, 108.4; Cl–Pt–P–C2 −147.2, −151.7, Pt–P–C1′–C2′ −47.9, −59.3, Cl–Pt–P–C2 −151.7, −147.2, Pt–P–C2–C3 114.4, 140.2, P–C2–C3–C4 34.1, −38.2, C2–C3–C4–C5 −48.6, 48.3, P-C1′-C2′-C3′ −179.5, 178.9.

Table 1
Hydroformylation of styrene and its 4-substituted derivatives (ArCH=CH_2) in the presence of *in situ* catalysts formed from $PtCl_2$(1-*n*-Pr-3-Me-3-phospholene)$_2$ (**4a**)/$PtCl_2$(1-*n*-Bu-3-Me-3-phospholene)$_2$ (**4b**)/$PtCl_2$(1-*n*Pr-3-Me-phospholane)$_2$ (**8**) and tin(II)-chloride[a].

Entry	Complex	Substrate (Ar)	Temp. [°C]	*R.* time [h]	Conv. [%]	R_c [b] [%]	R_{br} [c] [%]
1	**4a**	C_6H_5	60	110	24	85	77
2	**4a**	C_6H_5	100	24	48	86	68
3	**4a**	C_6H_5	100	48	79	76	75
4	**4a**	C_6H_5	100	48	84	91	69[d]
5	**4a**	4-CH_3-C_6H_4	100	48	65	89	72
6	**4a**	4-Cl-C_6H_4	100	48	63	93	66
7	**4a**	4-AcO-C_6H_4	100	24	58	87	70
8	**4a**	4-AcO-C_6H_4	100	48	90	67	71
9	**4b**	C_6H_5	60	72	33	87	76[e]
10	**4b**	C_6H_5	100	24	54	85	72
11	**4b**	C_6H_5	100	24	55	90	70[f]
12	**8**	C_6H_5	100	24	27	89	65
13	**8**	C_6H_5	100	48	59	90	65[g]
14	**8**	C_6H_5	100	96	87	90	65[h]

[a] Reaction conditions: Pt/$SnCl_2$/styrene = 1/2/100, p(CO) = p(H_2) = 40 bar, 1 mmol of substrate, solvent: 10 mL of toluene.
[b] Chemoselectivity towards aldehydes (**A**, **B**). [(moles of **A** + moles of **B**)/(moles of **A** + moles of **B** + moles of **C**) × 100].
[c] Regioselectivity towards branched aldehyde (**A**). [moles of **A**/(moles of **A** + moles of **B**) × 100].
[d] ee = 21 (*S*) (enantiomerically pure (*S*,*S*)-**4a** was used).
[e] ee = 4.5 (*S*) (enantiomerically pure (*S*,*S*)-**4b** was used).
[f] ee = 7.0 (*S*) (enantiomerically pure (*S*,*S*)-**4b** was used).
[g] ee = 6.5 (*S*) (a 8/22/32/13/10/15 mixture of stereoisomers of **8** was used).
[h] ee = 19 (*S*) (a 23/45/32 mixture of stereoisomers of **8** was used).

added that in general, unlike the rhodium-catalyzed hydroformylation, the proportions of the linear and branched aldehyde are comparable in the presence of platinum phosphine catalysts. The prevailing formation of the linear aldehyde was observed mostly with the most active catalysts containing bidentate ligands [4]. Our new Pt(II) complexes described in this paper may have relevance as catalyst precursors in the hydroformylation of other styrene derivatives as well (see *eg.* the synthesis of Ibuprofen and Naproxen), where the formation the branched aldehydes is required.

The catalytic precursors (**4a**, **4b** and **8**) were isolated containing the corresponding optically active 1-alkyl-phospholene-based ligand. Their application in hydroformylation resulted in optical inductions of 21%, 7% and 6.5/19% with **4a**, **4b** and **8** as the catalytic precursors, respectively (entries 4, 11 and 13/14). It is worth noting that, to the best of our knowledge, enantiomeric excesses of about 20% are unprecedented using monodentate phospholane and phospholene ligands in enantioselective hydroformylation. Furthermore, the low ee-s obtained with **8** can be substantially improved when enantiomerically pure (*e.g.* (S_PR_C,S_PR_C)-**8**) was used instead of the rather complicated mixture of stereoisomers (entries 13 and 14).

In summary, novel $PtCl_2(L)_2$ complexes with 1-alkyl-substituted 3-methyl-3-phospholene and 3-methyl-phospholane ligands were prepared and characterized. The stereostructure of the Pt(II) complex with propyl-phospholene ligands was evaluated by B3LYP/6-31G** and LANL2DZ (Pt) calculations. The Pt(II) complex precursors proved to be catalytically active in the hydroformylation of styrenes and displayed an interesting regioselectivity. With the application of the ligands in optically active form, enantioselective hydroformylation with ee-s up to 21% can be achieved that, compared to literature data, can be regarded to be significant.

3. Experimental

3.1. General (instruments)

The ^{31}P, ^{13}C, ^{1}H NMR spectra were taken on a Bruker AV-300 or DRX-500 spectrometer operating at 121.5, 75.5 and 300 or 202.4, 125.7 and 500 MHz, respectively. The couplings are given in Hz. Mass spectrometry was performed on a ZAB-2SEQ instrument.

3.1.1. Preparation of the enantiomers of 1-propyl-3-methyl-3-phospholene-1-oxide (*1a*)

The enantiomers of 1-propyl-3-methyl-3-phospholene-1-oxide (**1**) [33] were prepared as described earlier by resolution with (*R*,*R*)-TADDOL and (*R*,*R*)-spiro-TADDOL [30]. Yield of (*S*)-**1a**: 60%; ^{31}P NMR ($CDCl_3$) δ 76.8; $[\alpha]_D^{25} = -13.3$ (c 0.6, $CHCl_3$); ee: 92%; (^{31}P NMR ($CDCl_3$) δ 76.4; $[\alpha]_D^{25} = -13.9$ [30] (*c* 1, $CHCl_3$); ee: 96%). Yield of (*R*)-**1a**: 38%; ^{31}P NMR ($CDCl_3$) *δ* 76.8; $[\alpha]_D^{25} = +13.4$ (*c* 1, $CHCl_3$); ee: 95% (^{31}P NMR ($CDCl_3$) *δ* 76.4; $[\alpha]_D^{25} = +13.4$ [30] (*c* 1, $CHCl_3$); ee: 95%).

3.1.2. Preparation of (*S*)-1-butyl-3-methyl-3-phospholene-1-oxide ((*S*)-*1b*)

(*S*)-1-butyl-3-methyl-3-phospholene-1-oxide ((*S*)-**1b**) [33] was prepared analogously, but using (*R*,*R*)-*spiro-TADDOL* as the resolving agent. (**1**). Yield: 33%; $[\alpha]_D^{25} = -15.2$ (c 2.4, $CHCl_3$); ee: 93%; ^{31}P NMR ($CDCl_3$) *δ* 69.3; ^{13}C NMR ($CDCl_3$) δ 13.6 ($C_{4'}$), 20.3 ($^3J_{P-C} = 10.4$, C_3-CH_3), 24.0 ($^2J_{P-C} = 1.2$, $C_{2'}$), 24.1 ($^3J_{P-C} = 16.7$, $C_{3'}$), 29.7 ($^1J_{P-C} = 62.9$, $C_{1'}$)*, 32.3 ($^1J_{P-C} = 62.9$, C_2)*, 35.5 ($^1J_{P-C} = 65.7$, C_5)*, 120.8 ($^2J_{P-C} = 7.5$, C_4), 136.8 ($^2J_{P-C} = 12.3$, C_3), *tentative assignment; ^{1}H NMR ($CDCl_3$) *δ* 0.94 (t, 3H, CH_2CH_3), 1.46 (m, 2H, CH_2CH_3), 1.62 (m, 2H, $CH_2CH_2CH_3$), 1.79 (bs, 3H, C_3-CH_3), 1.87 (m,

2H, PCH_2), 2.30–2.65 (m, 4H, C(2)H_2 and C(5)H_2), 5.49 (d, $J = 29.5$, 1H, CH=).

3.1.3. Preparation of 1-propyl-3-methyl-3-phospholene-borane (3)

Racemic 1-propyl-3-methyl-3-phospholene-borane **3** was prepared as described earlier [34]. Yield: 20%; ^{31}P NMR ($CDCl_3$) δ 32.6 (broad) (δ [34] (DMSO) 34.5).

The optically active 1-propyl-3-methyl-3-phospholene-borane ((*R*)-**3**) was prepared analogously from (*S*)-1-propyl-3-methyl-3-phospholene-1-oxide ((*S*)-**1**) with an ee of 92%. Yield of **3**: 18%; $[\alpha]_D^{25} = -0.5$ ($c = 1.6$, $CHCl_3$); ^{31}P NMR ($CDCl_3$) δ 30.7 (broad); ^{13}C NMR ($CDCl_3$) δ 15.7 ($^3J_{P-C} = 13.0$, $C_{3'}$), 16.8 ($^2J_{P-C} = 1.7$, $C_{2'}$), 19.1 ($^3J_{P-C} = 7.4$, C_3-CH_3), 27.7 ($^1J_{P-C} = 30.3$, $C_{1'}$),* 30.1 ($^1J_{P-C} = 34.1$, C_5),* 33.9 ($^1J_{P-C} = 35.8$, C_2),* 121.9 (C_4), 137.9 ($^2J_{P-C} = 2.5$, C_3), *tentative; FAB-MS *m*/*z*: $[M + NH_4]^+ = 174$.

3.1.4. Preparation of cis-[bis(1-propyl-3-methyl-3-phospholeno)-dichloro-platinum(II)] (4a)

The deoxygenation of 0.051 g (0.32 mmol) of racemic 1-propyl-3-methyl-3-phospholene-1-oxide (**1a**) was carried out in benzene according to the procedure described in Section 3.1.3. Then 0.076 g (0.16 mmol) of dichlorodibenzonitrileplatinum in 3 mL of degassed benzene was added to the reaction mixture under nitrogen. The mixture was stirred at 25 °C for 1 day, whereupon the complex gradually precipitated. A separation by filtration led to 0.078 g (88%) of crude product, that was dissolved in 2 mL of benzene and then 4 mL of *n*-heptane was added. The crystals precipitated were collected by filtration to give 0.052 g (58%) of **4a** as a 1:1 mixture of the homo- (*R*,*R* and *S*,*S*) and the heterochiral (*R*,*S*) forms. ^{31}P NMR (DMSO) δ 18.32 ($J_{Pt-P} = 3424$, 50%) and 18.28 ($J_{Pt-P} = 3421$, 50%); FAB-MS *m*/*z*: $[M - Cl]^+ = 513$.

The optically active *cis*-[bis(1-propyl-3-methyl-3-phospholeno)-dichloro-platinum(II)] ((*S*,*S*)-**4**) was prepared analogously from (*S*)-1-propyl-3-methyl-3-phospholene-1-oxide ((*S*)-**1a**) with an ee of 92%. Yield of (*S*,*S*)-**4a**: 53%; $[\alpha]_D^{25} = +18.7$ ($c = 1.4$, $CHCl_3$); ^{31}P NMR ($CDCl_3$) δ 18.1 ($J_{Pt-P} = 3444$); ^{13}C NMR ($CDCl_3$) δ 15.5 ($^4J_{Pt-C} = 18.5$, $^3J_{P-C} = 16.0$, $C_{3'}$), 18.4 ($^3J_{Pt-C} = 24.8$, $C_{2'}$), 18.9 ($^4J_{Pt-C} = 45.0$, $^3J_{P-C} = 4.1$, $^5J_{P-C} = 4.1$, C_3-CH_3), 30.2 ($^2J_{Pt-C} = 36.3$, $^1J_{P-C} = 41.8$, $^3J_{P-C} = 7.3$, $C_{1'}$), 32.6 ($^2J_{Pt-C} = 58.9$, $^1J_{P-C} = 44.8$, $^3J_{P-C} = 4.8$, C_2), 36.3 ($^2J_{Pt-C} = 48.1$, $^1J_{P-C} = 47.8$, $^3J_{P-C} = 6.1$, C_5), 122.2 ($^3J_{Pt-C} = 32.0$, C_4), 138.8 ($^3J_{Pt-C} = 32.0$, $^2J_{P-C} = 2.2$, $^4J_{P-C} = 2.2$, C_3); ^{1}H NMR ($CDCl_3$) δ 1.06 (t, 6H, CH_2CH_3), 1.64 (m, 4H, CH_2CH_3), 1.84 (bs, 6H, C_3-CH_3), 1.99 (m, 4H, PCH_2), 2.31 and 2.89 (AB, $J_{gem} = 18.8$, 2H, C(2)H_2), 2.32 and 3.02 (AB, $J_{gem} = 18.8$, 2H, C(5)H_2), 5.51 (d, $J = 23.2$, 2H, CH=); FAB-MS, $[M - Cl]^+_{found} = 513.1146$, $C_{16}H_{30}P_2ClPt$ requires 513.1138 for the ^{35}Cl and the ^{194}Pt isotopes.

3.1.5. Preparation of cis-[bis(1-butyl-3-methyl-3-phospholeno)-dichloro-platinum(II)] (4b)

Racemic 1-butyl-3-methyl-3-phospholene-1-oxide (**1b**) (0.059 g (0.34 mmol)) was transformed to complex **4b** analogously to the **1** → **2** → **4** conversion. Yield: 23%; ^{31}P NMR ($CDCl_3$) δ 18.3 ($J_{Pt-P} = 3451$); ^{13}C NMR ($CDCl_3$) δ 13.6 ($C_{4'}$), 19.0 ($^4J_{Pt-C} = 34.6$, $^3J_{P-C} = 7.2$, $^5J_{P-C} = 4.1$, C_3-CH_3), 24.0 ($^4J_{Pt-C} = 35.8$, $^3J_{P-C} = 7.5$, $^5J_{P-C} = 7.5$, $C_{3'}$), 26.7 ($^3J_{Pt-C} = 24.1$, $C_{2'}$), 27.8 ($^2J_{Pt-C} = 37.6$, $^1J_{P-C} = 42.2$, $^3J_{P-C} = 7.0$, $C_{1'}$), 32.6 ($^2J_{Pt-C} = 53.7$, $^1J_{P-C} = 45.0$, $^3J_{P-C} = 5.0$, C_2), 36.3 ($^2J_{Pt-C} = 51.4$, $^1J_{P-C} = 47.0$, $^3J_{P-C} = 4.4$, C_5), 122.3 ($^3J_{Pt-C} = 47.1$, $^2J_{P-C} = 14.9$, C_4), 138.8 ($^3J_{Pt-C} = 50.9$, $^2J_{P-C} = 16.0$, $^4J_{P-C} = 2.2$, C_3); ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 6H, CH_2CH_3), 1.45 (m, 4H, CH_2CH_3), 1.58 (m, 4H, $CH_2CH_2CH_3$), 1.84 (bs, 6H, C_3-CH_3), 2.00 (m, 4H, PCH_2), 2.60–3.10 (m, 8H, C(2)H_2 and C(5)H_2), 5.50 (d, $J = 23.6$, 2H, CH=); FAB-MS, $[M - Cl]^+_{found} = 541.1462$, $C_{18}H_{34}P_2ClPt$ requires 541.1451 for the ^{35}Cl and the ^{194}Pt isotopes.

The optically active *cis*-[bis(1-butyl-3-methyl-3-phospholeno)-dichloro-platinum(II)] ((*S*,*S*)-**4b**) was prepared analogously from (*S*)-1-butyl-3-methyl-3-phospholene-1-oxide ((*S*)-**1b**) with an ee of 93%. Yield: 63%; $[\alpha]_D^{25} = +7.5$ (*c* 0.7, $CHCl_3$); ^{31}P NMR ($CDCl_3$) δ 18.4 ($J_{Pt-P} = 3451$).

3.1.6. Preparation of 1-propyl-3-methylphospholane-1-oxide (5)

The hydrogenation of 0.40 g (2.6 mmol) of racemic 1-propyl-3-methyl-3-phospholene-1-oxide (**1**) was carried out in the presence of 0.20 g of Pd/C catalyst in 30 mL of methanol at 60 °C under 12 bar that led to 0.28 g (69%) of 1-propyl-3-methylphospholane-1-oxide (**5**) as a 1:1 mixture of two diastereomers. ^{31}P NMR ($CDCl_3$) δ 70.0 (50%) and 70.3 (50%).

Optically active 1-propyl-3-methylphospholane-1-oxides ((*R*P*R*C)-**5** and (*R*P*S*C)-**5**) were prepared analogously from (*R*)-1-propyl-3-methyl-3-phospholene-1-oxide ((*R*)-**1**) with an ee of 95%. Yield: 81% as a 1:1 mixture of two diastereomers; $[\alpha]_D^{25} = +5.6$ ($c = 3.2$, $CHCl_3$); ^{31}P NMR ($CDCl_3$) δ 70.5 (50%) and 70.8 (50%); ^{13}C NMR ($CDCl_3$) δ 15.7 ($^3J_{P-C} = 14.2$, $C_{3'}$), 15.8 ($^2J_{P-C} = 4.0$), 15.9 ($^2J_{P-C} = 4.1$) $C_{2'}$, 21.0 ($^3J_{P-C} = 11.3$), 21.2 ($^3J_{P-C} = 11.3$) C_3-CH_3, 27.1 ($^1J_{P-C} = 63.8$), 28.5 ($^1J_{P-C} = 62.7$) C_5,* 32.6 ($^2J_{P-C} = 5.5$), 33.0 ($^2J_{P-C} = 6.8$) C_3, 33.3 ($^1J_{P-C} = 61.4$), 33.5 ($^1J_{P-C} = 61.6$) $C_{1'}$,* 33.5 ($^2J_{P-C} = 5.7$), 33.6 ($^2J_{P-C} = 7.4$) C_4, 35.0 ($^1J_{P-C} = 65.2$), 35.7 ($^1J_{P-C} = 64.0$) C_2,* *tentative assignment; ^{1}H NMR ($CDCl_3$) δ 1.04 (t, 3H, CH_2CH_3), 1.16 (d, 3H, C_3-CH_3), 1.23–2.61 (m, 11H, CH_2CH_3, PCH_2, C(2)H_2, C(3)H, C(4)H_2, C(5)H_2); FAB-MS, $[M + H]^+_{found} = 161.1094$, $C_8H_{18}PO$ requires 161.1095.

3.1.7. Preparation of 1-propyl-3-methylphospholane-borane complex (7)

Racemic 1-propyl-3-methylphospholane-1-oxide (**5**) was transformed to phosphine-borane **7** analogously to the **1** → **3** conversion. Yield: 19%; ^{31}P NMR ($CDCl_3$) δ 32.1 (broad); ^{13}C NMR ($CDCl_3$) δ 15.8 ($^3J_{P-C} = 13.0$, $C_{3'}$), 17.2 ($^2J_{P-C} = 1.1$), 17.3 ($^2J_{P-C} = 1.1$) $C_{2'}$, 20.3 ($^3J_{P-C} = 8.9$), 20.5 ($^3J_{P-C} = 10.7$) C_3-CH_3, 24.0 ($^1J_{P-C} = 35.1$), 24.1 ($^1J_{P-C} = 36.0$) C_5,* 28.4 ($^1J_{P-C} = 29.7$), 28.6 ($^1J_{P-C} = 29.6$) $C_{1'}$,* 32.0 ($^1J_{P-C} = 36.1$), 32.3 ($^1J_{P-C} = 35.7$) C_2,* 34.7, 36.1 (C_4), 35.2, 35.8 (C_3), *tentative assignment; ^{1}H NMR ($CDCl_3$) δ 1.02 (t, 3H, CH_2CH_3), 1.09 (d, 3H, C_3-CH_3), 1.17–2.63 (m, 11H, CH_2CH_3, PCH_2, C(2)H_2, C(3)H, C(4)H_2, C(5)H_2); FAB-MS, $[M + Na]^+_{found} = 181.1298$, $C_8H_{20}PBNa$ requires 181.1293 for the ^{11}B isotope.

Optically active 1-propyl-3-methylphospholane-boranes ((*S*P*R*C)-**7**, (*S*P*S*C)-**7**) were prepared analogously from the 1:1 mixture of (*R*,*R*)-, (*R*,*S*)-1-propyl-3-methylphospholane-1-oxides ((*R*P*R*C)-**5**, (*R*P*S*C)-**5**). Yield: 19% (1:1 mixture of two diastereomers); $[\alpha]_D^{25} = +74.4$ (c = 0.5, $CHCl_3$); ^{31}P NMR ($CDCl_3$) δ 32.1 (broad); FAB-MS, $[M + Na]^+_{found} = 181.1297$, $C_8H_{20}PBNa$ requires 181.1293 for the ^{11}B isotope.

3.1.8. Preparation of cis-[bis(1-propyl-3-methylphospholano)-dichloro-platinum(II)] (8)

Racemic 1-propyl-3-methylphospholane-1-oxide (**5**) (0.054 g (0.34 mmol)) was transformed to complex **8** analogously to the **1** → **2** → **4** conversion. Yield: 39% as a 8[a]:22[a]:32:13:10[b]:15[b] mixture of (*R*P*R*C,*R*P*R*C)-**8**/(*S*P*S*C,*S*P*S*C)-8, (*R*P*S*C,*R*P*S*C)-8/(*S*P*R*C,*S*P*R*C)-**8**, (*R*P*S*C,*R*P*R*C)-**8**/(*S*P*R*C,*S*P*S*C)-**8**, (*R*P*R*C,*S*P*R*C)-**8**/(*S*P*S*C,*R*P*S*C)-**8**, (*S*P*R*C,*R*P*S*C)-**8**, (*R*P*R*C,*S*P*S*C)-**8** isomers, respectively, [a,b] may be reversed; ^{31}P NMR ($CDCl_3$) δ 18.47 ($^1J_{Pt-P} = 3445$, 8%) for (*R*P*R*C,*R*P*R*C)-**8** and (*S*P*S*C,*S*P*S*C)-**8**[a], 17.93 ($^1J_{Pt-P} = 3446$, 22%) for (*R*P*S*C,*R*P*S*C)-**8** and (*S*P*R*C,*S*P*R*C)-**8**[a], 17.84 ($^1J_{Pt-P} = 3448$, $^2J_{P-P} = 17$), 18.27 ($^1J_{Pt-P} = 3444$, $^2J_{P-P} = 17$) (32%) for (*R*P*S*C,*R*P*R*C)-**8** and (*S*P*R*C,*S*P*S*C)-**8**, 18.05 ($^1J_{Pt-P} = 3444$, $^2J_{P,P} = 18$) and 18.36 ($^1J_{Pt-P} = 3446$, $^2J_{P-P} = 18$) (13%) for (*R*P*R*C,*S*P*R*C)-**8** and (*S*P*S*C,*R*P*S*C)-**8**, 18.22 ($^1J_{Pt-P} = 3447$, 10%) for (*S*P*R*C,*R*P*S*C)-**8**[b], 17.86 ($^1J_{Pt-P} = 3447$, 15%) for (*R*P*R*C,*S*P*S*C)-**8**[b], [a,b] may be reversed; ^{13}C NMR ($CDCl_3$) δ 15.6 ($^4J_{Pt-C} = 18.7$, $^3J_{P-C} = 15.6$, $C_{3'}$), 19.4 ($^3J_{Pt-C} = 23.8$, $C_{2'}$), 20.1–20.6 (m, C_3-CH_3); FAB-MS, $[M - Cl]^+_{found} = 517.1476$, $C_{16}H_{34}P_2ClPt$ requires 517.1451 for the ^{35}Cl and the ^{194}Pt isotopes.

The optically active *cis*-[bis(1-propyl-3-methylphospholano)-dichloro-platinum(II)] ((R_PR_C,R_PR_C)-, (R_PS_C,R_PR_C) and (R_PS_C,R_PS_C)-**8**) was prepared analogously from the 1:1 mixture of 1-propyl-3-methylphospholanes ((S_P,R_C)-**6**, (S_P,S_C)-**6**). Yield: 22% as a 23*:45:32* mixture of the (R_PR_C,R_PR_C)-**8***:(R_PS_C,R_PR_C)-**8**:(R_PS_C,R_PS_C)-**8*** isomers, *may be reversed; $[\alpha]_D^{25} = -17.3$ ($c = 0{,}1$, $CHCl_3$); ^{31}P NMR ($CDCl_3$) δ 18.34 ($^1J_{Pt-P} = 3445$, 23%) for (R_PR_C,R_PR_C)-**8***, 17.69 ($^1J_{Pt-P} = 3448$, $^2J_{P-P} = 17$), 18.17 ($^1J_{Pt-P} = 3443$, $^2J_{P-P} = 17$, 45%) for (R_PS_C,R_PR_C)-**8**, 17.81 ($^1J_{Pt,P} = 3447$, 32%) for (R_PS_C,R_PS_C)-**8***,*, *may be reversed, ^{13}C NMR ($CDCl_3$) δ 15.6 ($^3J_{P-C} = 15.8$, $C_{3'}$), 19.3 ($^3J_{Pt-C} = 24.9$, $C_{2'}$), 20.1–20.5 (m, C_3-CH_3); FAB-MS, $[M - Cl]^+_{found} = 517.1458$, $C_{16}H_{34}P_2ClPt$ requires 517.1451 for the ^{35}Cl and the ^{194}Pt isotopes.

3.2. Hydroformylation experiments

A solution of 0.01 mmol of $PtCl_2$(ligand)$_2$ and 3.8 mg (0.02 mmol) of tin(II) chloride in 10 mL of toluene containing 0.115 mL (1 mmol) of styrene was transferred under argon into a 100 mL stainless steel autoclave. The reaction vessel was pressurized to 80 bar total pressure ($CO/H_2 = 1/1$) and placed in an oil bath of appropriate temperature and the mixture was stirred with a magnetic stirrer. Samples were taken from the mixture and the pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed and immediately analyzed by GC and chiral GC (on a capillary Cyclodex-column, (*S*)-2-phenylpropanal was eluted before the (*R*) enantiomer).

3.3. Theoretical calculations

The structures for the conformational analysis of the *cis* structures were built up by PCMODEL [37]. The calculations were performed in gas phase by Gaussian '03 [38]. A mixed basis set was used with B3LYP hybrid density functional: 6-31G** for H, C, P, Cl atoms and LANL2DZ effective core potential for Pt atom. Only positive normal mode frequencies were obtained for the accepted geometries.

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