Pergamon

Tetrahedron: *Asymmetry* 12 (2001) 2867–2873

TETRAHEDRON: *ASYMMETRY*

One-pot synthesis of a novel C_1-symmetric diphosphine from 1,3-cyclic sulfate. Asymmetric hydroformylation of styrene

Csaba Hegedüs,[b] József Madarász,[a] Henrik Gulyás,[b] Áron Szöllősy[c] and József Bakos[a,*]

[a]*Department of Organic Chemistry, University of Veszprém, H-8201 Veszprém, PO Box 158, Hungary*
[b]*Research Group for Petrochemistry, Hungarian Academy of Science, H-8201 Veszprém, PO Box 158, Hungary*
[c]*Department of General and Analytical Chemistry, Technical University of Budapest, H-1521 Budapest, Hungary*

Received 19 October 2001; accepted 2 November 2001

Abstract—Preparation of a novel homochiral diphosphine with C_1-symmetry from the cyclic sulfate of (2*R*,4*R*)-2,4-pentanediol is reported. Reaction of a lithium phosphide salt with the cyclic sulfate affords a γ-phospholylsulfate which can be converted to a diphosphine ligand on treatment with a second equivalent of lithium phosphide. Using this ligand in the platinum-catalyzed asymmetric hydroformylation of styrene, outstanding levels of regio- and enantiocontrol were obtained (89/11 *iso*/*n* isomeric ratio and 89% e.e.). The results are compared with those obtained with the analogous ligands (bdpp and bdbpp) having C_2-symmetry. The novel unsymmetric ligand possessed the advantageous catalytic features of the C_2-symmetric parent ligands.

1. Introduction

Asymmetric hydroformylation is an attractive catalytic approach to the synthesis of a large number of homochiral compounds.[1] The recently developed Rh-based asymmetric hydroformylation catalysts, which utilize chiral bidentate phosphine–phosphite[2] or diphosphite ligands[3] are generally superior to Pt–Sn–chiral phosphine systems in terms of regioselectivity.[4] Chiral ligands based on the 2,4-pentane-2,4-diyl skeleton found widespread application in asymmetric synthesis. The most well-known derivatives of this type are (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane[5] ((*S*,*S*)-bdpp, **2**), (2*S*,4*S*)-pentane-2,4-diyl-bis(5*H*-dibenzo[*b*]-phosphindole[6] ((*S*,*S*)-bdbpp, **5**), tetra-*para*-amino-functionalized [(*S*,*S*)-bdpp-(*p*-NMe_2)$_4$],[7] 3-benzyl-bdpp[8] or different diphosphite diastereomers, which contain stereogenic centers in the backbone as well as in the terminal groups.[9] As part of our research aimed at the synthesis and use of new chiral diphosphines, we have described the catalytic performance of Pt–diphosphine/$SnCl_2$ complexes for asymmetric hydroformylation of styrene in recent communications.[6,10]

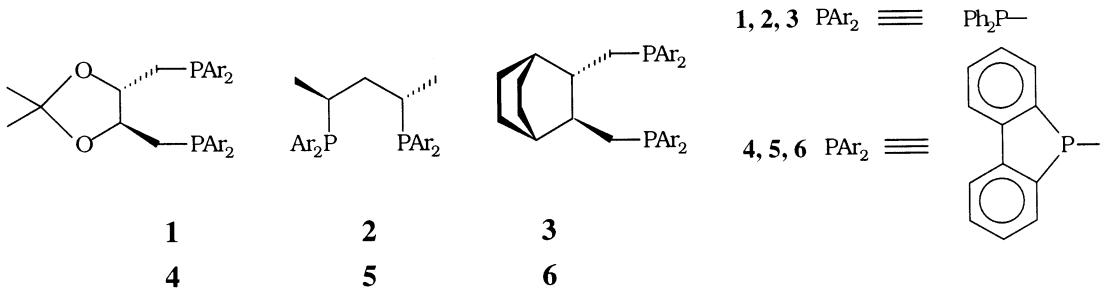
The regioselectivity is generally in favor of the linear aldehyde, and the reaction conditions have to be carefully controlled as hydroformylation can be accompanied by hydrogenation. The platinum systems are therefore not always the catalysts of choice for asymmetric hydroformylation. However, it has been found that if the diphenylphosphino groups of diop **1** or bdpp **2** are exchanged for dibenzophosphole (DBP) groups (**4** and **5**), the regioselectivity is reversed and branched, chiral product is predominantly formed (Scheme 1).[4,6]

For example, (*S*,*S*)-bdpp **2** readily provides good enantioselectivity, although with the expected moderate branched aldehyde selectivity (28% with 17% e.e. (*R*) at 100°C and 42% with 64.5% e.e. (*S*) at 70°C).[10] By the use of (*S*,*S*)-bdbpp **5**, the regioselectivity for the branched aldehyde is increased markedly; however, the enantioselectivity is dramatically decreased (79.3% with 11.6% e.e. (*S*) at 100°C and 86% with 18.8% e.e. (*S*) around 40°C).[6] Ligand **6** also gives better selectivities than its diphenylphosphino-analogue **3**.[4] As a result of these findings, phosphole derivatives of several other chiral ligands have been prepared.[1] Many of the catalysts derived from these ligands also show improved selectivity with respect to the branched aldehyde, when compared to the diphenylphosphino- counterparts, but none simultaneously gives high enantioselectivity without side reactions.

In the light of these findings we reasoned that by the exchange of a diphenylphosphino group for a dibenzo-

* Corresponding author. E-mail: bakos@almos.vein.hu

0957-4166/01/$ - see front matter
PII: S0957-4166(01)00498-0



1 **2** **3**
4 **5** **6**

Scheme 1.

phosphole unit in bdpp, the regioselectivity and enantioselectivity of the catalytic system could be improved. In order to prove the hypothesis we have developed a new methodology for the synthesis of chiral 1,3-ditertiary phosphines with two stereogenic centers and investigated the catalytic performance of the new phosphine–phosphole **9** in the asymmetric hydroformylation of styrene catalyzed by Pt and Rh complexes.

The simplest and most attractive way to prepare chiral ditertiary phosphines with C_1-symmetry would be via direct selective mono-substitution of readily available ditosylates or similar electrophiles. However, the direct nucleophilic substitution of ditosylates with conventional nucleophiles is usually non-selective, leading to mixtures of unreacted ditosylate and mono- and ditertiary phosphines.[11]

2. Results and discussion

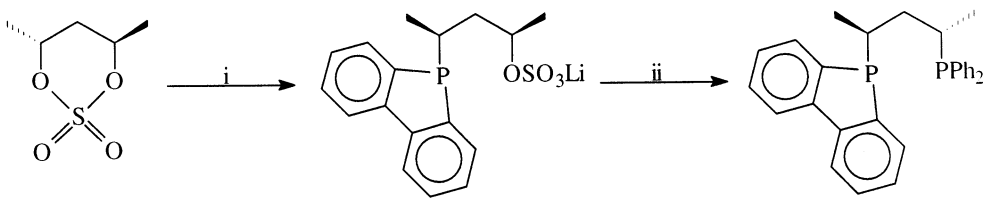
2.1. Synthesis of the ligand

The availability of homochiral diol from 2,4-pentanedione,[12] coupled with the highly electrophilic behavior of the derived cyclic sulfates,[13] has enabled us to develop an efficient route to a new ditertiary phosphine **9** having C_1-symmetry. The cyclic sulfate **7** of (2*R*,4*R*)-2,4-pentanediol was obtained by a simple one-pot reaction following the procedure developed for 1,2-cyclic sulfates by Gao and Sharpless.[14] The synthesis involves the treatment of diols with thionyl chloride followed by ruthenium-catalyzed oxidation. In this way, sulfate **7** could be obtained in high yield (82%).[13] The sulfate ester reacts smoothly with 1 equiv. of Li–DBP to give the 'sulfated' phosphole followed by the addition of a second equiv. of $LiPPh_2$ (Scheme 2).

Although it is known that an ionic sulfate group can act as a leaving group,[15] it was clear that its anionic nature renders it kinetically much less reactive than a $ROSO_2OR'$ group. The negative charge decreases the polarity of C–O bond, and the electrostatic repulsion between the leaving group and an attacking anionic group also increases the activation energy of the substitution. Accordingly, (i) the second substitution, the replacement of the $-OSO_3Li$ occurred at 60°C and (ii) in an independent experiment the sulfated phosphole could be isolated and fully characterized. Both nucleophilic attacks occur with complete inversion at the stereogenic centers to give a new homochiral phosphine–phosphole. This was proved by the synthesis of bdpp following the same methodology. A comparison of the configuration and specific rotation value of the product obtained from cyclic sulfate **7** with that of the known configuration and specific rotation of diastereomerically pure bdpp proves the complete enantioselectivity and diastereoselectivity of the double substitution. This is also supported by the presence of only two singlets in the $^{31}P\{^1H\}$ NMR spectrum of the product **9**. Recently, Werner et al. reported the synthesis of related enantiopure 1,2-bis(phosphanyl)ethane.[16]

2.2. Solution structure of the platinum complexes

The $[PtCl_2(\mathbf{9})]$ complex was prepared from the appropriate amount of $[PtCl_2(PhCN)_2]$ and 1 equiv. of the enantiopure ligand **9** in refluxing $CHCl_3$. The reaction resulted in a platinum complex possessing $^1J(^{195}Pt,^{31}P)$



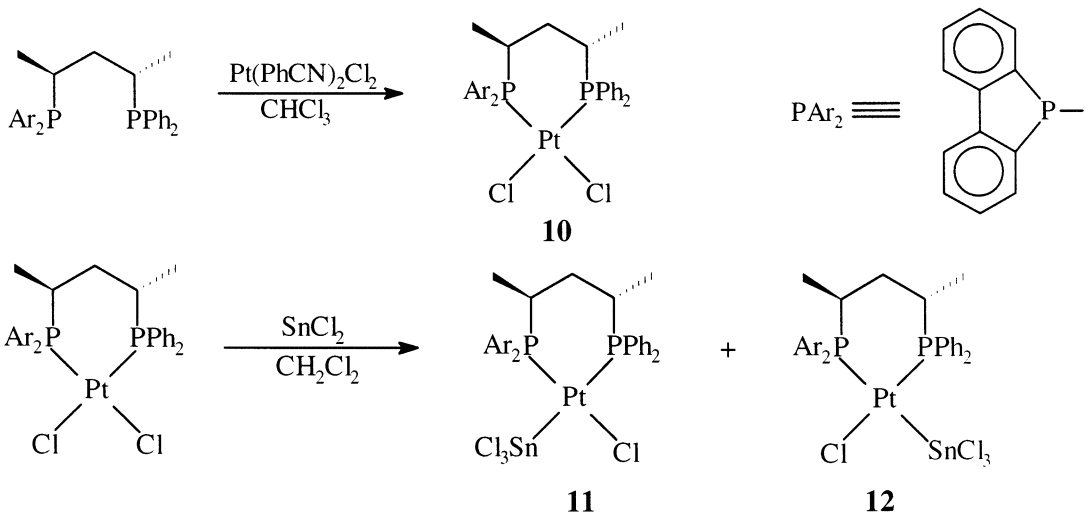
7 **8** **9**

Scheme 2. *Reagent and conditions*: (i) Li–DBP, THF, 0°C and then at room temperature 2 h; (ii) $LiPPh_2$, 60°C, 5 h (47% over two steps).

coupling constants of 3224 Hz at 3.11 ppm and 3384 Hz at 10.10 ppm in the $^{31}P\{^1H\}$ NMR spectrum. These coupling constants are indicative for P–Pt–Cl *trans* arrangement and have been obtained for a number of *cis*-[$PtCl_2$(diphosphine)]-type complexes **10**.[17] In the case of bdpp and bdbpp the corresponding coupling constants are 3413 Hz (δ 7.21 ppm) and 3258 Hz (δ 8.30 ppm), respectively. From the platinum–phosphorus coupling constants it can be concluded that the coupling constant at 3.11 ppm belongs to the dibenzophosphole and that with a value of 3384 Hz at 10.10 ppm to the diphenylphosphine unit. It is interesting to note that ligand **5** initially gives a dimeric complex containing *trans*-bridging diphosphines, which rearranges to *cis*-[$PtCl_2$(**5**)] on stirring for a further 3 days.[6]

The platinum catalytic precursor [$Pt(SnCl_3)Cl$(**9**)] was prepared in CH_2Cl_2 at room temperature from the [$PtCl_2$(**9**)] complex with an equimolar amount of anhydrous tin(II) chloride (Scheme 3). The [$Pt(SnCl_3)Cl$(**9**)] complex was investigated using $^{31}P\{^1H\}$ NMR spectroscopy to elucidate the coordination mode of the ligand. For comparison the platinum/tin complexes of **2** and **5** having C_2-symmetry were included (Table 1). The platinum–phosphorus coupling constants (^1J(Pt,P)) of the square-planar [$Pt(SnCl_3)Cl$(diphosphine)] complexes are diagnostic values to differentiate between *cis*- and *trans*-coordination of the ligands.

At ambient temperature four signals were observed in the $^{31}P\{^1H\}$ NMR spectrum for the [$Pt(SnCl_3)Cl$(**9**)] complex containing the bdpp analogue with C_1-symmetry (Scheme 4). Based on the mutual phosphorus–phosphorus coupling ^2J(P,P), both the doublets at 11.95 and 12.85 ppm (complex **12**), furthermore the doublets at 17.95 and −6.65 ppm (complex **11**) are assigned to *cis* isomers.[18] The relatively large platinum–phosphorus coupling constant and the relatively small tin–phosphorus coupling constants ($^2J_{avg}$(Sn,P), the averaged value of $^2J_{cis}(^{117}Sn,^{31}P)$ and $^2J_{cis}(^{119}Sn,^{31}P)$) of 229 and 165 Hz of the signals at −6.65 and 11.95 ppm, respectively, are indicative of phosphine positioned *trans* to chlorine and *cis* to the tin and hence, are again indicative of *cis* complexes. From the chemical shifts and the platinum–phosphorus coupling constants it can be concluded that the doublets at 12.85 and 17.09 ppm belong to the phosphine positioned *trans* to tin, and those at 11.95 and −6.65 ppm to the phosphine positioned *trans* to chlorine. According to the relative intensities of the corresponding signals in the NMR spectrum, the diastereomeric ratio of the *cis* complexes [$Pt(SnCl_3)Cl$(**9**)] (**11** and **12**) is 1:1. This 1:1 ratio of the diastereomers (**11** and **12**) might reflect the

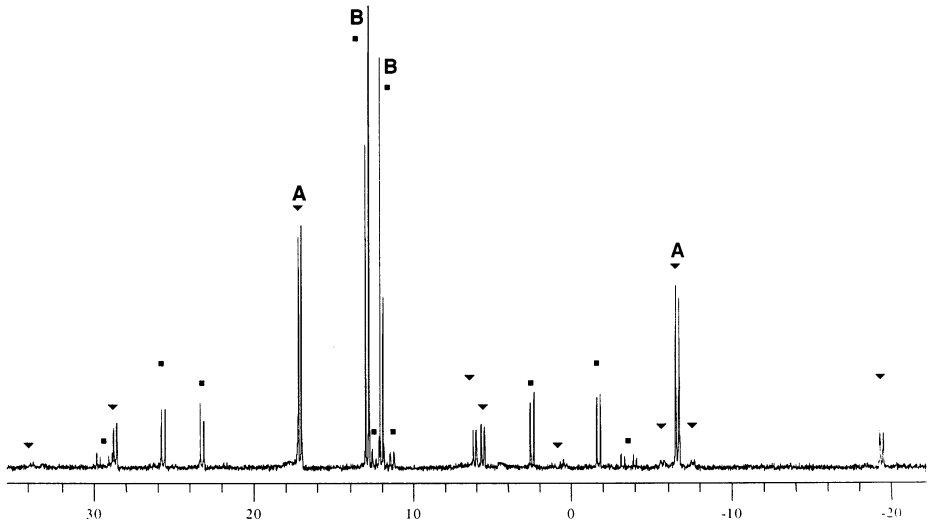


Scheme 3.

Table 1. $^{31}P\{^1H\}$ NMR data for the platinum complexes of [$Pt(SnCl_3)Cl$(diphosphine)][a] obtained in the [$PtCl_2$(diphosphine)] + $SnCl_2$ reaction

	P (*trans* to $SnCl_3$)				P (*cis* to $SnCl_3$)		
Ligand	δ (ppm)	^1J(Pt,P) (Hz)	^2J(Sn,P)[b] (Hz)	^2J(P,P) (Hz)	δ (ppm)	^1J(Pt,P) (Hz)	^2J(Sn,P)[c] (Hz)
9[d]	17.09	2798	4031, 3873	23.1	−6.65	3091	229
9[e]	12.85	2519	4085, 3904	26.2	11.95	3320	165

[a] [$Pt(SnCl_3)Cl$(**2**)]:[10] δ 13.79 ppm (*trans* to $SnCl_3$), ^1J(Pt,P) 2759 Hz, ^2J(Sn,P) 4090 Hz, ^2J(P,P) 23.7 Hz, δ 7.43 ppm (*cis* to $SnCl_3$), ^1J(Pt,P) 3348 Hz, ^2J(Sn,P) 187 Hz; [$Pt(SnCl_3)Cl$(**5**)]:[6] δ 15.6 (*trans* to $SnCl_3$), ^1J(Pt,P) 2556 Hz, ^2J(P,P) 20.8 Hz, δ −0.70 ppm (*cis* to $SnCl_3$), ^1J(Pt,P) 3120 Hz.
[b] $^2J_{trans}(^{117}Sn,^{31}P)$; $^2J_{trans}(^{119}Sn,^{31}P)$.
[c] $^2J_{cis}(^{117}Sn,^{31}P)$ and $^2J_{cis}(^{119}Sn,^{31}P)$ coincide.
[d] Complex **11**.
[e] Complex **12**.



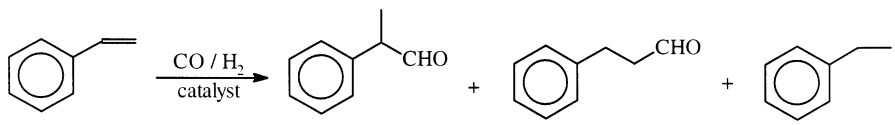
Scheme 4. $^{31}P\{^{1}H\}$ NMR of the solution of [**9**-Pt($SnCl_3$)Cl]. Complex **11** (▼): A. Complex **12** (■): B.

relative *trans* influences of the non-equivalent phosphorus atoms (Scheme 3).

2.3. Hydroformylation of styrene

The hydroformylation reactions were performed under classical conditions shown in Table 2. The in situ preparation of the catalyst by simply mixing [$PtCl_2(PhCN)_2$] or [$Rh(CO)_2(acac)$] in toluene with the ligand was revealed to be advantageous. The exchange of a diphenylphosphino group for a dibenzophospholyl group in bdpp **2** was found to have a favorable effect on the catalytic performance of the resulting C_1 symmetric ligand. A remarkable increase in regio- and enantioselectivities from 47/53 with 20% e.e. up to 79/21 with 86% e.e. (entries 1–4) was seen on lowering the reaction temperature from 100 to 24°C. It is interesting to note that with [Pt(Cl)($SnCl_3$)(*S*,*S*)(**2**)] at low temperatures (20–40°C) (*S*)-2-phenylpropanal predominates up to 85% e.e., while at temperature above 100°C

Table 2. Asymmetric hydroformylation of styrene with chiral Pt and Rh diphosphine catalysts[a]



13 **14** **15**

Entry	*T* (°C)	Time (h)	Conv. (%)[b]	TOF[c]	RCHO (%)[b,d]	(*b*/*n*)[b]	E.e. of **13** (%)[e]
1	100	8	100	207	83	47/53	20 (*S*)
2	70	8	64	139	87	56/44	43 (*S*)
3	40	66	65	19	94	67/33	69 (*S*)
4	24	165	48	6	97	79/21	86 (*S*)
5[f]	24	45	70	29	94	85/15	89 (*S*)
6[g]	24	27	43	27	84	89/11	88 (*S*)
7[h]	70	9	74	–	93	36/74	26 (*S*)
8[i]	70	27	90	49	73	86/14	19 (*S*)
9[j]	40	46	57	24	100	92/8	47 (*R*)

[a] *Reactions conditions*: H_2 and CO (1:1) at 70 atm initial total pressure. Catalyst: 0.05 mmol [$Pt(PhCN)_2Cl_2$], 0.05 mmol $SnCl_2$ and 0.055 mmol chiral ligand in 35 mL toluene, substrate/catalyst molar ratio is 2000.

[b] For determination see Section 4.

[c] Amount of RCHO **13**+**14** in mol (mol Rh)$^{-1}$ h^{-1} determined at the end of the reaction time.

[d] Aldehydes/(aldehydes+ethylbenzene).

[e] Determined by GC analysis of the distilled product (β-DEX 225, 30 m, id 0.25 mm, 0.25 μm film).

[f] H_2 and CO (2:1) at 195 atm initial total pressure.

[g] (9:1) at 155 atm initial total pressure.

[h] Data from Ref. 10. (*S*,*S*)-bdpp **2** was used as a ligand.

[i] Data from Ref. 6. (*S*,*S*)-bdbpp **5** was used as a ligand.

[j] *Reactions conditions*: H_2 and CO (1:1) at 30 atm initial total pressure. Catalyst: 0.0125 mmol [$Rh(CO)_2(acac)$] and 0.075 mmol chiral ligand in 7 mL toluene, substrate/catalyst molar ratio is 2000.

the (*R*)-enantiomer predominates with a maximum of 28% e.e.[10] In the case of **5** the temperature dependence is less significant.[6] Furthermore, ligand **9** give chemoselectivities similar to those obtained with ligand **5** (entries 2 and 7) and both ligands give higher chemoselectivities than ligand **2** (entry 8).

Comparing entries 4–6 shows that regio- and enantioselectivities are slightly increased by increasing the partial pressure of H_2 (*iso*/*n* isomeric ratio = 89/11 with 88% e.e.) and the activities were best at high P_{H_2}/P_{CO} ratios. This is in line with detailed mechanistic studies into platinum-catalyzed hydroformylation with ditertiary phosphines, which showed that the rate-determining step is the hydrogenolysis of the acyl–platinum complex.[19]

With the platinum precursor, anhydrous $SnCl_2$ was used as co-catalyst, which is essential for catalytic activity. $SnCl_2$ may act as a Lewis acid or as a ligand ($SnCl_3$), directly bonded to platinum,[19] or as a counter anion ($SnCl_3$).[18] Theoretical studies on the olefin insertion suggest that the major role of the $SnCl_3$ ligand is to stabilize the pentacoordinated intermediates as well as to weaken the Pt–H bond *trans* to it.[20] Recent theoretical[21] and spectroscopic studies[22] suggest that the presence a single catalytically active species in solution is the key to controlling efficient chirality transfer. Based on the coordination chemistry and catalytic results of the new ligand it can be concluded that the selective insertion of tin(II) chloride into the Pt–Cl bond is not a prerequisite for achieving high regioselectivity and enantioselectivity in the platinum/tin-catalyzed asymmetric hydroformylation.

It has recently been reported that for the rhodium catalyst containing the chiral ligand **2**, the enantioselectivity heavily depends on the ligand to metal ratio.[23] Thus, the highest enantioselectivity (54%) for **13** at a **2**:Rh ratio of 6:1 was obtained. At a similar ratio, ligand **9** induced slightly lower enantioselectivity (entry 9, e.e. = 47%) and regioselectivity (92%).

3. Conclusions

We have developed a highly practical one-pot synthesis of an unsymmetrical 1,3-bis(phosphanyl)propane from 1,3-cyclic sulfate. This methodology is remarkable because of its easy synthetic approach, short reaction time and high efficiency. Moreover, the strategy can be extended to related phosphines. In the presence of the novel chiral phosphine–phosphole, the platinum-catalyzed asymmetric hydroformylation of styrene results in outstanding levels of regio- and enantiocontrol (89/11 *iso*/*n* isomeric ratio and 89% e.e.). These results are similar to those obtained with the most efficient diphosphine-based catalytic systems previously reported[1] and are in agreement with the concept that C_1-symmetric diphosphines may provide better results than C_2-symmetric diphosphines.[24]

4. Experimental

4.1. General techniques

All reactions were carried out in oven-dried glasswork using Schlenk techniques under an atmosphere of argon. Infrared (IR) spectra were recorded on a Specord IR-75A spectrometer. $^{31}P\{^1H\}$ NMR spectra were recorded on either a VARIAN UNITY 300 spectrometer operating at 121.42 MHz or a Bruker DRX-500 spectrometer operating at 202.45 MHz. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.15 and at 75.43 MHz, respectively, on a VARIAN UNITY 300 spectrometer or at 500.13 and 125.76 MHz, respectively, on a Bruker DRX-500 spectrometer. Chemical shifts are relative to tetramethylsilane as external reference or calibrated against solvent resonances. Optical rotations were measured on Schmidt Haensch 21245 polarimeter using 10 cm cells. Gas chromatographic analyses were performed on a Hewlett–Packard 5830A gas chromatograph equipped with a flame-ionization detector and a SPB-1 column (30 m, film thickness 0.1 μm, carrier gas 2 mL/min). Mass spectrometric measurement was performed using a PE SCIEX API 2000 triple quadrupole instrument. Electrospray ionization was used and negative ion was detected.

4.2. Materials and methods

Tetrahydrofuran (THF), diethyl ether (Et_2O), toluene and hexane were distilled from sodium benzophenone ketyl under argon. Methylene chloride (CH_2Cl_2) was distilled from CaH_2 and methanol (MeOH) from $Mg(OMe)_2$ under argon. Water (H_2O) was distilled twice under argon. Deuterated water (D_2O) was deoxygenated by bubbling with argon for 10 min. Deuterated chloroform and methylene chloride ($CDCl_3$ and CD_2Cl_2) were deoxygenated by distillation under argon. Enantiomerically pure pentane-2,4-diol is conveniently prepared by asymmetric hydrogenation of 2,4-pentanedione over Raney nickel catalyst modified with the corresponding enantiomer of tartaric acid and NaBr (TA–NaBr–MRNi).[12] Li–DBP was prepared according to the literature procedure.[6] All the other chemicals were commercial products and were used as received without further purification.

4.3. (2*R*,4*S*)-4-(Dibenzophospholyl)-pent-2-yl-sulfate lithium salt 8

A solution of (4*R*,6*R*)-4,6-dimethyl-2,2-dioxide-1,3,2-dioxathiane **7** (610 mg, 3.7 mmol) in dry THF (4 mL) was added at 0°C to a solution of $LiPAr_2$·dioxane adduct (1.2 g, 4.3 mmol) in dry THF (15 mL), meanwhile the bright red color of the phosphide solution turned light brown. The mixture was stirred at ambient temperature for 1 h. The THF was removed under reduced pressure, then deoxygenated water (30 mL) and Et_2O (20 mL) were added. The aqueous phase was separated and washed with Et_2O (20 mL) again. The remained ether was removed from the aqueous solution

in vacuum. The pH of the solution was adjusted to ~6.8 using diluted H_2SO_4 solution. The water was removed under reduced pressure, then CH_2Cl_2 (20 mL) was added. Li_2SO_4 was removed by filtration. Evaporation of the solvent under vacuum yielded the product as a white powder (900 mg, 68%). $[\alpha]_{22}^{D}=+39.5$ ($c=4.1$, H_2O). $^{31}P\{^1H\}$ NMR (202.45 MHz, D_2O): δ 2.13 ppm. ^1H NMR (500 MHz, D_2O): δ 0.47 (dd, $^3J(P,H)=13.0$ Hz, $^3J(H,H)=7.0$ Hz, 3H, CH_3CHPAr_2), 0.84 (d, $^3J(H,H)=6.0$ Hz, 3H, CH_3CHOSO_3Li), 0.84 (overlapped by the signal of CH_3, 1H, diastereotopic CH_2), 1.33 (m, 1H, diastereotopic CH_2), 2.02 (m, 1H, $CHPAr_2$), 4.33 (m, 1H, $CHOSO_3Li$), 6.81–7.36 (m, 8H, aromatic protons). $^{13}C\{^1H\}$ NMR (125.76 MHz, D_2O): δ 15.45 (d, $^2J(P,C)=6.3$ Hz, CH_3CHPAr_2), 20.95 (s, CH_3CHOSO_3Li), 28.88 (d, $^1J(P,C)=17.0$ Hz, $CHPAr_2$), 40.07 (d, $^2J(P,C)=7.7$ Hz, CH_2), 75.67 (d, $^3J(P,C)=10.6$ Hz, $CHOSO_3Li$), 121.52 (s), 127.57 (pseudo t, $\Delta\delta\approx{}^3J(P,C)\approx8.8$ Hz), 128.77 (s), 128.91 (s), 130.58 (d, $^2J(P,C)=20.1$ Hz), 130.81 (d, $^2J(P,C)=21.4$ Hz), 140.05 (d, $^1J(P,C)=6.4$ Hz), 140.63 (d, $^1J(P,C)=5.0$ Hz), 144.25 (s), 144.35 (s). MS (ESI, m/z) 349 [M−Li$^+$].

4.4. (2*S*,4*S*)-2-(Dibenzophospholyl)-4-(diphenylphosphino)pentane 9

A solution of (4*R*,6*R*)-4,6-dimethyl-2,2-dioxide-1,3,2-dioxathiane **7** (1.5 g, 8.8 mmol) in dry THF (15 mL) was added to a solution of Li–DBP·dioxane adduct (2.4 g, 8.8 mmol) in THF (20 mL) at 0°C, wherein the bright red color turned light brown. The mixture was stirred at ambient temperature for 2 h. $LiPPh_2$·dioxane adduct (2.5 g, 8.8 mmol) in THF (15 mL) was added and the reaction mixture was heated for 5 h at 60°C. The THF was removed under reduced pressure, then Et_2O (30 mL) and deoxygenated water (15 mL) were added. The organic phase was separated and the aqueous phase was washed with Et_2O (2×10 mL). The organic phase was filtered through a pad of $MgSO_4$–Al_2O_3–$MgSO_4$. The solvent was removed under reduced pressure. The remaining dense liquid was crystallized from hot MeOH. Yield: 1.8 g (47%) mp 107–109°C; $[\alpha]_{20}^{D}=-67.3$ ($c=4.1$, $CHCl_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$): $\delta=0.64$ (s), 1.05 (s). ^1H NMR (500.13 MHz, $CDCl_3$): $\delta=0.68$ (dd, $^3J(P,H)=12.5$ Hz, $^3J(H,H)=7.0$ Hz, 3H; CH_3), 0.84 (dd, $^3J(P,H)=15.2$ Hz, $^3J(H,H)=7.0$ Hz, 3H; CH_3), 1.37 (m, 1H; CH_2), 1.44 (m, 1H; CH_2), 1.95 (m, 1H; CH), 2.34 (m, 1H; CH), 7.1–7.8 (m, 18H; aromatic protons). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): $\delta=14.97$ (d, $^2J(P,C)=7.4$ Hz, CH_3), 15.69 (d, $^2J(P,C)=15.7$ Hz, CH_3), 27.49 (t, $^1J(P,C)\sim{}^3J(P,C)\sim9.6$ Hz, CH), 30.95 (dd, $^1J(P,C)=17.1$ Hz, $^3J(P,C)=11.9$ Hz, CH), 36.85 (t, $^2J(P,C)\sim{}^2J(P,C)\sim15.7$ Hz, CH_2), 121.33 (s), 121.36 (s), 127.10 (d, $^3J(P,C)=7.7$ Hz), 127.24 (d, $^3J(P,C)=7.4$ Hz), 128.56 (d, $^3J(P,C)=10.5$ Hz), 128.55 (s), 128.58 (s), 129.07 (d, $^4J(P,C)=3.2$ Hz), 130.35 (d, $^2J(P,C)=21.1$ Hz), 130.63 (d, $^2J(P,C)=20.8$ Hz), 135.83 (d, $^2J(P,C)=19.0$ Hz), 136.29 (d, $^1J(P,C)=9.3$ Hz), 136.63 (d, $^1J(P,C)=9.3$ Hz), 140.85 (d, $^1J(P,C)=7.5$ Hz), 141.27 (d, $^1J(P,C)=7.5$ Hz), 144.39 (s), 144.71 (s). Anal. calcd for $C_{29}H_{28}P_2$: C 79.45, H 6.39%. Found: C 79.38, H 6.43%.

4.5. (2*S*,4*S*)-2,4-Bis(diphenylphosphino)pentane 2

A solution of (4*R*,6*R*)-4,6-dimethyl-2,2-dioxide-1,3,2-dioxathiane (**7**) (1.5 g, 8.8 mmol) in dry THF (15 mL) was added dropwise at 0°C to a solution of $LiPPh_2$·dioxane (2.4 g, 8.8 mmol) in dry THF (20 mL), meanwhile the bright red color turned light brown. The mixture was stirred at ambient temperature for 2 h. $LiPPh_2$·dioxane adduct (2.5 g, 8.8 mmol) in THF (15 mL) was added and the reaction mixture was heated for 5 h at 60°C. The THF was removed under reduced pressure, then Et_2O (30 mL) and deoxygenated water (15 mL) were added. The organic phase was separated and the aqueous phase was washed with Et_2O (2×10 mL). The organic phase was filtered through a pad of $MgSO_4$–Al_2O_3–$MgSO_4$. The solvent was removed under reduced pressure. The remained dense liquid was crystallized from hot MeOH. Yield: 1.8 g (58%). mp 79–80°C; $[\alpha]_{20}^{D}=-123.5$ ($c=4.1$, $CHCl_3$).

4.6. Preparation of *cis*-[$PtCl_2$(9)]

$CHCl_3$ (10 mL) was added to a mixture of [$PtCl_2(PhCN)_2$] (387 mg, 0.82 mmol) and (2*S*,4*S*)-2-(dibenzophospholyl)-4-(diphenylphosphino)pentane **9** (359 mg, 0.82 mmol) with stirring. The formed yellow solution was refluxed for 1 h, upon which the solution went lighter in color. After cooling hexane (20 mL) was added and the formed precipitate was filtered. The solid was washed with hexane (10 mL) and dried under vacuo, yielding product as a white powder (575 mg). $^{31}P\{^1H\}$ NMR (202.45 MHz, $CDCl_3$): $\delta=3.11$ (d, $^2J(P,P)=24.8$ Hz, $^1J(P,Pt)=3224.0$ Hz), 10.10 (d, $^2J(P,P)=24.8$ Hz, $^1J(P,Pt)=3384.0$ Hz). ^1H NMR (500.13 MHz, $CDCl_3$): $\delta=0.31$ (dd, $^3J(P,H)=14.9$ Hz, $^3J(H,H)=6.7$ Hz, 3H; CH_3), 1.35 (dd, $^3J(P,H)=16.3$ Hz, $^3J(H,H)=7.0$ Hz, 3H; CH_3), 2.23 (m, 2H; CH_2), 2.46 (m, 1H; CH), 3.00 (m, 1H; CH), 6.5–8.3 (m, 18H; aromatic protons). ^{195}Pt NMR ($CDCl_3$, Na_2PtCl_6): $\delta=-4647.70$ (dd, $^1J(P,Pt)=3224.0$ Hz, $^1J(P,Pt)=3384.0$ Hz).

4.7. Preparation of *cis*-[PtCl($SnCl_3$)(9)]

CH_2Cl_2 (25 mL) was added to a mixture of *cis*-[$PtCl_2$(**9**)] (150 mg, 0.21 mmol) and anhydrous $SnCl_2$ (40 mg 0.21 mmol) with stirring. After 4 h, the yellow solution was filtered and the filtrate was concentrated under reduced pressure giving *cis*-[**9**-PtCl($SnCl_3$)] as an orange solid. Yield: 178 mg (95%) $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2): $\delta=11.95$, d, 12.85, d, ($^1J(P,Pt)=3320.6$ Hz, $^2J_{cis}(P,^{117,119}Sn)=165.2$ Hz (Cl *trans* to diphenylphosphino group), satellites, $^1J(P,Pt)=2519.4$ Hz, $^2J_{trans}(P,^{117}Sn)=3904.1$ Hz, $^2J_{trans}(P,^{119}Sn)=4084.7$ Hz ($SnCl_3$ *trans* to dibenzophospholyl group), satellites, $^2J(P,P)=26.2$ Hz), $\delta=-6.65$, d, 17.09, d, ($^1J(P,Pt)=3091.0$ Hz, $^2J_{cis}(P,^{117,119}Sn)=229.0$ Hz (Cl *trans* to dibenzophospholyl group), satellites, $^1J(P,Pt)=2798.8$ Hz,

$^2J_{trans}$(P,^{117}Sn) = 3873.0 Hz, $^2J_{trans}$(P,^{119}Sn) = 4031.0 Hz ($SnCl_3$ *trans* to diphenylphosphino group), satellites, ^2J(P,P) = 23.1 Hz). ^{195}Pt NMR (CD_2Cl_2, Na_2PtCl_6): δ = −4891.37 (dd, ^1J(P,Pt) = 3091.0 Hz, ^1J(P,Pt) = 2798.8 Hz), −4909.6 (dd, ^1J(P,Pt) = 3320.6 Hz, ^1J(P,Pt) = 2519.4 Hz).

4.8. Catalytic experiments

In a typical experiment, [Pt(PhCN)$_2$Cl$_2$] (0.05 mmol), the ligand (0.055 mmol), $SnCl_2$ (0.05 mmol), toluene (35 mL), styrene (100 mmol) and decane (5 mmol used as an internal standard) were placed in a Schlenk-tube under argon. The stainless-steel autoclave (100 mL) was filled with this solution and then purged with syn gas [CO–H_2 (1:1)] and pressurized to the appropriate initial pressure with this gas mixture. At the end of the reaction the autoclave was cooled, and depressurized. The reaction mixture was directly vacuum distilled to remove the catalyst. The reaction mixture and the distilled products were analyzed by gas chromatography. The enantiomeric excess of the aldehyde was determined by GC analysis of the distilled product on a Hewlett–Packard HP 4890 gas chromatograph equipped with a split/splitless injector and a β-DEX 225 column (30 m, internal diameter 0.25 mm, film thickness 0.25 μm, carrier gas: 100 kPa nitrogen, F.I.D. detector; the retention times of the enantiomers are 30.4 min (*R*), 31.4 min (*S*)). The configuration of the prevailing enantiomer in the product was determined by the sign of optical rotation of the corresponding aldehyde. Conversions and composition of the reaction mixture (**13**:**14**:**15** branched:linear:hydrogenated) were determined by GC (SPB-1) using decane as an internal standard.

Acknowledgements

Financial support from the Hungarian National Science Foundation (OTKA-T016269) is gratefully acknowledged. We are grateful to Mr. Béla Édes for skilful technical assistance.

References

1. Recent reviews see: (a) Gladiali, S.; Bayón, J.; Claver, C. *Tetrahedron: Asymmetry* **1995**, *7*, 1453; (b) Agbossou, F.; Carpentier, J. F.; Mortreux, A. *Chem. Rev.* **1995**, *95*, 2485; (c) Consiglio, G. In *Catalytic Asymmetric Syntheses*; Ojima, I. Ed.; VCH Publishers: Weinheim, 1993, 273; (d) Beller, M.; Cornils, B.; Frohning, C. D.; Kohlpainter, V. W. *J. Mol. Catal.* **1995**, *104*, 17; (e) Brunner, H.; Zettlmeier, W. *Handbook of Enantioselective Catalysis*; VCH: Weinheim, 1993.
2. (a) Sakai, N.; Nozaki, K.; Mashima, K.; Takaya, H. *Tetrahedron: Asymmetry* **1992**, *3*, 583; (b) Sakai, N.; Mano, S.; Nozaki, K.; Takaya, H. *J. Am. Chem. Soc.* **1993**, *115*, 7033; (c) Horiuchi, T.; Ohta, T.; Nozaki, K.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1996**, *1*, 155.
3. (a) van Leeuwen, P. W. N. M.; Roobeek, C. F. *Eur. Pat. Appl.* (to Shell), EP 54986 (1982); (b) Buisman, G. J. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1993**, *4*, 1625; (c) Buisman, G. J. H.; Martin, M. E.; Vos, E. J.; Klootwijk, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1995**, *7*, 719.
4. (a) Parenillo, G.; Stille, J. K. *J. Org. Chem.* **1986**, *51*, 4189; (b) Stille, J. K.; Su, H.; Brechot, P.; Parenillo, G.; Hegedus, L. S. *Organometallics* **1991**, *10*, 1183; (c) Consiglio, G.; Nefkens, S. C. A.; Borer, A. *Organometallics* **1991**, *10*, 2046; (d) Scrivanti, A.; Zeggio, S.; Beghetto, V.; Matteoli, U. *J. Mol. Catal.* **1995**, *101*, 217.
5. (a) Mac Neil, P. A.; Roberts, N. K.; Bosnich, B. *J. Am. Chem. Soc.* **1981**, *103*, 2273; (b) Bakos, J.; Tóth, I.; Heil, B.; Markó, L. *J. Organomet. Chem.* **1985**, *279*, 23.
6. Tóth, I.; Elseiver, C. J.; de Vries, J. G.; Bakos, J.; Smeets, W. J. J.; Spek, A. *J. Organomet. Chem.* **1997**, *540*, 15.
7. Tóth, I.; Guo, I.; Hanson, B. E. *Organometallics* **1993**, *12*, 848.
8. Bianchini, C.; Barbaro, P.; Scapacci, G.; Zanobini, F. *Organometallics* **2000**, *19*, 2450.
9. (a) Billig, E.; Abatjoglou, A. G.; Bryant, D. R. US Pat. 4,769,498 (to Union Carbide) 1988; (b) Babin, J. E.; Whiteker G. T. W.O. US Pat. 911 518 (to Union Carbide) 1992.
10. (a) Kollár, L.; Bakos, J.; Tóth, I.; Heil, B. *J. Organomet. Chem.* **1988**, *350*, 277; (b) Kollár, L.; Kégl, T.; Bakos, J. *J. Organomet. Chem.* **1993**, *453*, 155.
11. Morimoto, T.; Chiba, M.; Achiwa, K. *Tetrahedron Lett.* **1988**, *29*, 4755.
12. (a) Ito, K.; Harada, T.; Tai, A.; Izumi, Y. *Chem. Lett.* **1979**, 1049; (b) Ito, K.; Harada, T.; Tai, A. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3367.
13. (a) Gulyás, H.; Árva, P.; Bakos, J. *Chem. Commun.* **1997**, *1*, 2385; (b) Gulyás, H.; Dobó, A.; Bakos, J. *Can. J. Chem.* **2001**, *73*, 1040.
14. Gao, Y.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 7538.
15. Burk, M. J.; Pizzano, A.; Martin, J. A.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **2000**, *19*, 250.
16. Fries, G.; Wolf, J.; Pfeiffer, M.; Stalke, D.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 564.
17. Pregosin, P. S. In *Phosphorus*-31 *NMR Spectroscopy*; Verkade, D. L.; Quin, Eds.; VCH Publishers: Deerfield Beach, Florida, 1987; pp. 465–530.
18. Tóth, I.; Kégl, T.; Elsevier, C. J.; Kollár, L. *Inorg. Chem.* **1994**, *33*, 5704 and references cited therein.
19. (a) Scrivanti, A.; Botteghi, C.; Toniolo, L.; Berton, A. *J. Organomet. Chem.* **1988**, *344*, 261; (b) Scrivanti, A.; Berton, A.; Toniolo, L.; Botteghi, C. *J. Organomet. Chem.* **1986**, *314*, 369.
20. Rocha, W.; De Almeida, W. B. *Organometallics* **1998**, *17*, 1961.
21. Gleich, D.; Herrmann, W. A. *Organometallics* **1999**, *18*, 4354 and references cited therein.
22. (a) Buisman, G. J. H.; van deer Veen, L. A.; Klootwijk, A.; de Lange, W. G. J.; Kramer, P. C. J.; van Leeuwen, P. W. N. M.; Vogt, D. *Organometallics* **1997**, *16*, 2929; (b) Nozaki, K.; Sakai, N.; Nanno, T.; Higashijima, T.; Mano, S.; Horiuchi, T.; Takaya, H. *J. Am. Chem. Soc.* **1997**, *119*, 4413.
23. (a) Masdeu-Bultó, A. M.; Orejón, A.; Castellanos, A.; Castillón, S.; Claver, C. *Tetrahedron: Asymmetry* **1996**, *7*, 1829; (b) Diéguez, M.; Pereira, M. M.; Masdeu-Bultó, A. M.; Claver, C.; Bayón, J. C. *J. Mol. Catal. A.: Chem.* **1999**, *143*, 111.
24. RajanBabu, T. V.; Casalnuovo, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 6325 and references cited therein.