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Asymmetric hydroformylation of styrene using rhodium and platinum complexes of diphosphites containing atropisomeric backbones and chiral 1,3,2-dioxaphosphorinane moieties

Stefánia Cserépi-Szűcs [a], Gottfried Huttner [b], László Zsolnai [b], József Bakos [c,*]

[a] *Research Group for Petrochemistry, Hungarian Academy of Science, PO Box 158, H-8201 Veszprém, Hungary*
[b] *Anorganisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany*
[c] *Department of Organic Chemistry, University of Veszprém, PO Box 158, H-8201 Veszprém, Hungary*

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Dedicated to: Professor László Markó on the occasion of his 70th birthday.

Abstract

Diastereomers of 2,2′-bis[4,6-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy]-1,1′-binaphthyl, *R*-bis(4*R*,6*R*)-**1**, and *S*-bis(4*R*,6*R*)-**2**, have been synthesized. The solid state structure of *S*-bis(4*S*,6*S*)-**1** and the platinum complex [$PtCl_2$(**1**)] (**3**) of its enantiomer pair have been determined. The structure of **3** shows a slightly distorted square-planar geometry. The dihedral angle defined by the naphthyl rings in **3** is smaller (77.6°(2)) than in the free ligand (103.0°(2)). In the platinum- and rhodium-catalyzed asymmetric hydroformylation of styrene, the axial chirality in the bridge has been found to be determinate for the product configuration with a cooperative effect from the terminal groups. The maximum enantioselectivity (39% ee) and a remarkable high regioselectivity (84%) towards branched aldehyde was obtained with platinum system of a matched constellation of the ligand (*S*-bis(4*R*,6*R*)-**2**).

Keywords: Hydroformylation; Catalysis; Diphosphite; Platinum; Rhodium

1. Introduction

Asymmetric hydroformylation is the most promising approach to the synthesis of optically active compounds of high synthetic value [1]. Diphosphite ligands are gaining increasing importance since their beneficial effect on the catalytic activity and/or regioselectivity of rhodium-catalyzed hydroformylation has been disclosed [2]. The recently developed Rh-based asymmetric hydroformylation catalysts, which utilize chiral bidentate phosphine–phosphite [3] or diphosphite ligands [4] are generally superior to Pt–Sn systems containing chiral diphosphines in terms of regioselectivity [5].

As part of our research aimed at the synthesis and use of new diphosphites we have described the first examples of the Pt–diphosphite/$SnCl_2$ catalytic system for asymmetric hydroformylation of styrene in a recent communication [6]. By the use of different 2,4-bis[naphtho[d,f][1,3,2]dioxaphosphepin-6-yloxy]-pentane diphosphite diastereomers as ligands, which contain stereogenic centers in the backbone and stereogenic axes in the terminal groups, remarkable enantioselective cooperative effects were observed (91% maximum enantioselectivity) in such reactions. Similar studies have been carried out with diphosphites derived from the reaction of 2,4-pentanediol or 1,3-diphenyl-1,3-propanediol enantiomers with (4*R*,6*R*)- or (4*S*,6*S*)-4,6-dimethyl-2-chloro-1,3,2-dioxaphosphorinane. Thus the chirality was varied both in the chelate backbone and in the terminal groups of the ligands [7]. These model ligands made possible to explore the notion of chiral cooperativity. This paper describes the catalytic proper-

* Corresponding author. Tel.: +36-88-422022; fax: +36-88-427492.
E-mail address: bakos@almos.vein.hu (J. Bakos)

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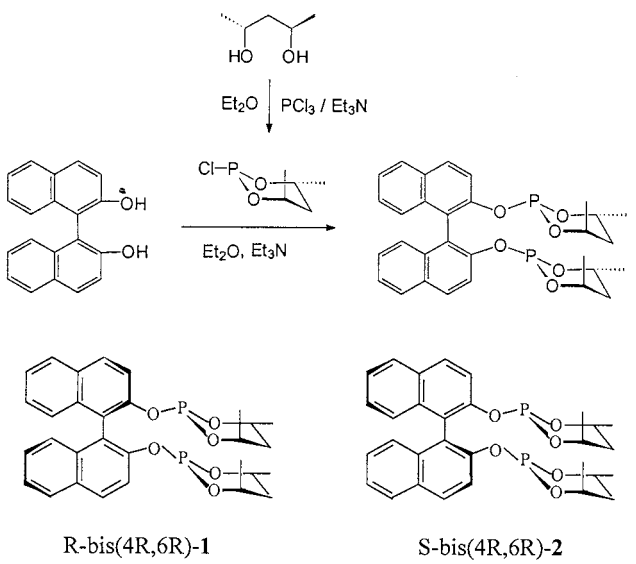
ties and stereochemistry of compounds **1** and **2** in Rh- and Pt-catalyzed hydroformylation. A comparison of their efficiency is presented. We also report here on the coordination chemistry and X-ray structure determination of these ligands and their platinum complex.

2. Results and discussion

2.1. Synthesis of 2,2′-bis[(4R,6R)-4,6-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy]-1,1′-binaphthyl (1 and 2)

The diastereomeric mixture of **1** and **2** was readily prepared by the reaction of the racemic 2,2′-dihydroxy-1,1′-binaphthyl with (4*R*,6*R*)-and (4*S*,6*S*)-4,6-dimethyl-2-chloro-1,3,2-dioxaphosphorinane, respectively (Scheme 1). The compounds (4*R*,6*R*)- and (2*S*,4*S*)-4,6-dimethyl-2-chloro-1,3,2-dioxaphosphorinane can be obtained from optically pure enantiomers of 2,4-pentanediol and PCl_3 in the presence of triethylamine [8]. The chirality of the dioxaphosphorinane groups makes a pair of diastereomers, differing only in the axial configuration of the binaphthalene core. The diastereomers can be separated by fractional crystallization from acetonitrile, thereby making a nice example of a self-resolving chiral diphosphite where the chirality in the terminal groups can be used to resolve a chiral axis. The configuration of this diastereomer was determined by the comparison of the optical rotation value with that of the product obtained by fractional crystallization.



Scheme 1. Synthesis of chiral diphosphite with C_2 symmetry.

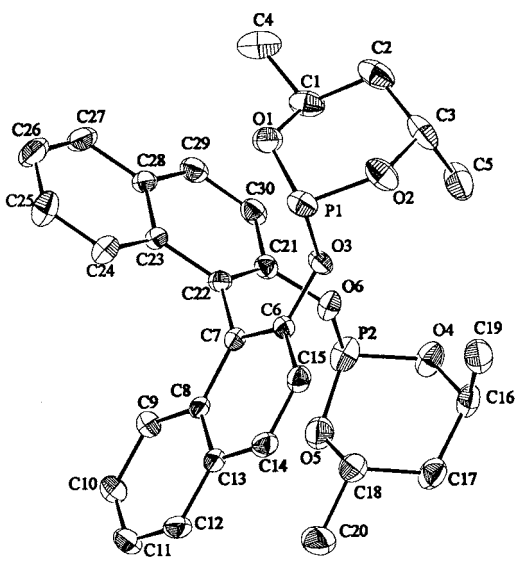


Fig. 1. Thermal ellipsoid (ORTEP) plot of the refined structure of compound *S*-bis(4*S*,6*S*)-**1**.

Optical resolution of 2,2′-dihydroxy-1,1′-binaphthyl was carried out by using (*R*,*R*)-(+)-2,3-dimethoxy-*N*,*N*,*N*′,*N*′-tetramethylsuccinamide [9] as host compound or (8*S*,9*R*)-(−)-*N*-benzylcinchonidium chloride [10] as a resolving agent. The reaction of homochiral (*S*)- and (*R*)-1,1′-bi-2-naphthol with (4*R*,6*R*)-4,6-dimethyl-2-chloro-1,3,2-dioxaphosphorinane gave the optically pure diastereomers (**1** and **2**), respectively.

The new ligands have been characterized by ^{1}H-, ^{13}C- and ^{31}P-NMR. Proton-decoupled ^{31}P-NMR spectra of the ligands gave singlets in the expected range (*R*-bis(4*R*,6*R*): δ 125.2 ppm, (*S*-bis(4*R*,6*R*): δ 124.5 ppm, (s)). Liquid-state spectroscopic studies proved that the dioxaphosphorinane rings are in the chair conformation (see Section 4).

The diastereomers differ only in the axial configuration in the 1,1′-binaphthalene backbone, the configurations of the carbon atoms in the terminal groups being the same. The appearance of one singlet in the ^{31}P-NMR spectra of the ligands indicates that only one diastereomer has been obtained.

Crystallization of *S*-bis(4*S*,6*S*)-**1** from acetonitrile at −20°C yielded crystals suitable for analysis by X-ray diffraction. The molecular structure of the diastereomer is shown in Fig. 1. The coordination sphere around the phosphorus atom is distorted tetrahedrally. The dihedral angle between the two naphthyl mean planes is 103.0° which is very similar to that value found in 1,1′-binaphthalene-2,2′-diol. The six-membered heterocyclic rings adopt the chair conformation. The selected bond lengths and angles for *S*-bis(4*S*,6*S*)-**1** are listed in Table 1.

2.2. Structure of [PtCl$_2$(R-bis(4R,6R)-1)]

Treatment of the atropisomers with $PtCl_2(PhCN)_2$ in $CDCl_3$ resulted in displacement of PhCN by the ligand. Phosphorus resonances consist of a singlet supplemented with $^{195}J_{PtP}$ satellites at δ 62.8 ppm (J_{PtP} = 5900

Table 1
Selected bond lengths (Å) and angles (°) for *S*-bis(4*S*,6*S*)-**1**

P(1)–O(1)	1.608(3)	O(1)–C(1)	1.462(4)
P(1)–O(2)	1.610(3)	O(2)–C(3)	1.470(4)
P(1)–O(3)	1.661(2)	O(3)–C(6)	1.395(4)
P(2)–O(5)	1.605(3)	O(4)–C(16)	1.460(4)
P(2)–O(4)	1.606(3)	O(5)–C(18)	1.459(5)
P(2)–O(6)	1.663(3)	O(6)–C(21)	1.396(4)
O(1)–P(1)–O(2)	102.40(13)	C(18)–O(5)–P(2)	120.8(2)
O(1)–P(1)–O(3)	100.57(13)	C(21)–O(6)–P(2)	118.7(2)
O(2)–P(1)–O(3)	98.49(13)	O(1)–C(1)–C(4)	106.8(3)
O(5)–P(2)–O(4)	102.66(14)	O(1)–C(1)–C(2)	108.3(3)
O(5)–P(2)–O(6)	101.01(14)	C(4)–C(1)–C(2)	112.9(3)
O(4)–P(2)–O(6)	98.19(13)	C(3)–C(2)–C(1)	113.6(3)
C(1)–O(1)–P(1)	121.4(2)	O(2)–C(3)–C(2)	110.1(3)
C(3)–O(2)–P(1)	123.9(2)	O(2)–C(3)–C(5)	110.6(3)
C(6)–O(3)–P(1)	119.1(2)	C(2)–C(3)–C(5)	114.8(4)
C(16)–O(4)–P(2)	125.0(2)		

Hz) and at δ 60.5 ppm ($J_{PtP} = 6021$ Hz) for $PtCl_2$(*R*-bis(4*R*,6*R*)) and for $PtCl_2$(*S*-bis(4*R*,6*R*)), respectively. The phosphorus resonances are 62.4 ppm (125.2 ppm) and 64.0 ppm (124.5 ppm) upfield from that of the free ligand.

Both ligands afforded only the *cis*-mononuclear nine-membered complexes without any oligomeric species. Oligomeric platinum complexes of diphospholes, dibenzophospholes and bisnaphthophospholes have been reported with *trans*-P–Pt–P arrangement [11]. The stereochemistry of the Pt complex is confirmed in the solid state by X-ray crystal structure determination.

When anhydrous $SnCl_2$ was added to this solution, a new complex was formed. The ^{31}P-NMR spectrum of this complex showed the presence of two different P-atoms, each being coupled to a platinum and phosphorus atom (δ 81.0 ppm (*trans* to $SnCl_3$), $J_{PtP} =$ 5118 Hz and 79.8 ppm (*cis* to $SnCl_3$), $J_{PtP} = 5785$, $J_{PP} = 23$ Hz). Phosphorus resonance *trans* to $SnCl_3$ is downfield from that of *cis* to $SnCl_3$. Accordingly, the complex was assigned to the structure of $Pt(SnCl_3)Cl$(*R*-bis(4*R*,6*R*)-**1**). When two equivalents of $SnCl_2$ (per Pt) were added, the phosphorus atoms became equivalent again leading to a new complex, $Pt(SnCl_3)_2$(*R*-bis(4*R*,6*R*)-**1**), which showed a ^{31}P resonance at δ 95.2 ppm, with $J_{PtP} = 5002$ Hz.

Upon growing suitable crystals from acetonitrile, the X-ray crystal structure of its acetonitrile solvate was determined. The crystal contains discrete mononuclear units of compound **3** in which *R*-bis(4*R*,6*R*)-**1** acts as a bidentate ligand providing a nine-membered ring with an irregular, partly chair–boat-like conformation [12]. The coordination around the platinum is essentially square planar with slight tetrahedral distortion (Fig. 2). Distances from mean plane: P(1) 0.077, Cl(2) 0.080, P(2) −0.089, Cl(1) −0.086 (Å). The dihedral angle defined by the planes of the naphthyl rings is 77.6°, which is considerably smaller than the 103.0°, found in the free ligand.

The large bite angle P(1)–Pt–P(2), 95.1(2)° may be attributed to the dihedral angle between the naphthyl units, so that the Cl(1)–Pt–Cl(2) 87.6(2)° angle is slightly less than 90°. The similar Cl(1)–Pt–P(1) (90.1°) and Cl(2)–Pt–P(2) (87.5°) angles are indicating that the two dioxaphosphorinane rings induce al-

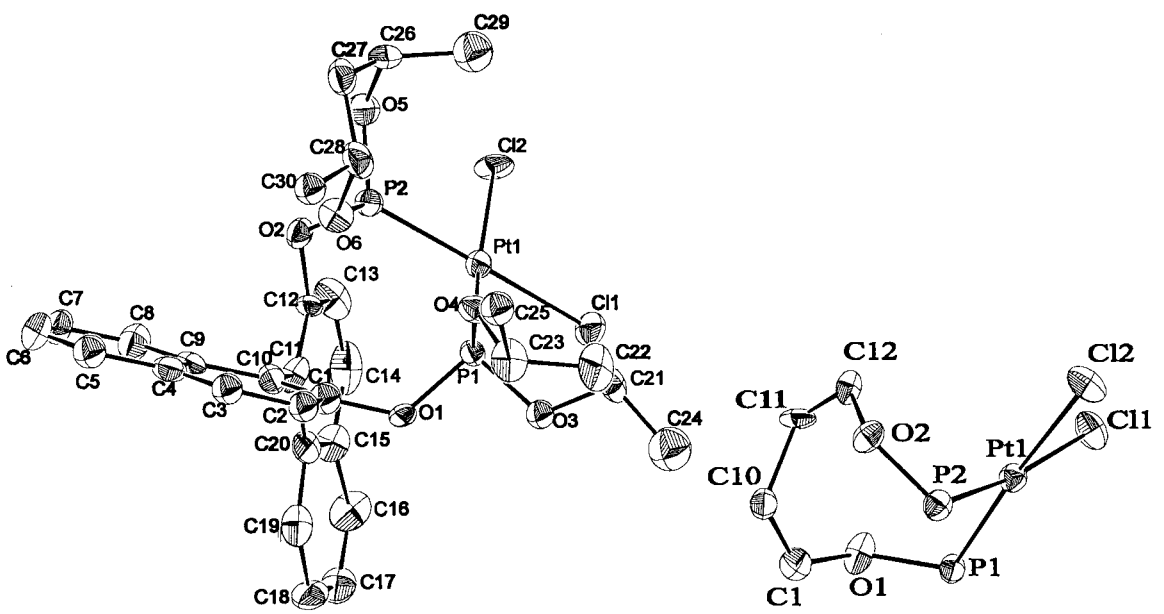


Fig. 2. (a) Thermal ellipsoid (ORTEP) plot of the refined structure of complex [$PtCl_2$(*R*-bis(4*R*,6*R*)-**1**)] and (b) perspective view of the nine-membered chelate ring.

Table 2
Selected bond lengths (Å) and angles (°) for [$PtCl_2$ *R*-bis(4*R*,6*R*)-**1**]

Pt(1)–P(1)	2.211(4)	O(6)–C(28)	1.51(2)
Pt(1)–P(2)	2.212(4)	C(1)–C(10)	1.34(2)
Pt(1)–Cl(2)	2.366(4)	C(1)–C(2)	1.45(2)
Pt(1)–Cl(1)	2.373(4)	C(10)–C(11)	1.50(2)
P(1)–O(3)	1.554(11)	C(11)–C(12)	1.34(2)
P(1)–O(1)	1.594(12)	C(12)–C(13)	1.39(3)
P(1)–O(4)	1.598(13)	C(21)–C(24)	1.49(3)
P(2)–O(6)	1.550(12)	C(21)–C(22)	1.51(3)
P(2)–O(5)	1.585(13)	C(22)–C(23)	1.54(3)
P(2)–O(2)	1.606(11)	C(23)–C(25)	1.51(2)
O(1)–C(1)	1.38(2)	C(26)–C(27)	1.46(4)
O(2)–C(12)	1.42(2)	C(26)–C(29)	1.51(3)
O(3)–C(21)	1.48(2)	C(27)–C(28)	1.50(3)
O(4)–C(23)	1.55(2)	C(28)–C(30)	1.51(3)
O(5)–C(26)	1.49(2)		
P(1)–Pt(1)–P(2)	95.1(2)	C(1)–O(1)–P(1)	125.4(11)
P(1)–Pt(1)–Cl(2)	176.1(2)	C(12)–O(2)–P(2)	118.9(9)
P(2)–Pt(1)–Cl(2)	87.5(2)	C(21)–O(3)–P(1)	115.1(10)
P(1)–Pt(1)–Cl(1)	90.1(2)	C(23)–O(4)–P(1)	114.8(10)
P(2)–Pt(1)–Cl(1)	172.7(2)	C(26)–O(5)–P(2)	117.9(12)
Cl(2)–Pt(1)–Cl(1)	87.6(2)	C(28)–O(6)–P(2)	121.4(12)
O(3)–P(1)–O(1)	97.4(6)	C(10)–C(1)–O(1)	124(2)
P(1)–Pt(1)–P(2)	95.1(2)	C(10)–C(1)–C(2)	121(2)
P(1)–Pt(1)–Cl(2)	176.1(2)	O(1)–C(1)–C(2)	115(2)
P(2)–Pt(1)–Cl(2)	87.5(2)	C(11)–C(12)–O(2)	118.6(13)
P(1)–Pt(1)–Cl(1)	90.1(2)	C(13)–C(12)–O(2)	116(2)
P(2)–Pt(1)–Cl(1)	172.7(2)	O(3)–C(21)–C(24)	104(2)
Cl(2)–Pt(1)–Cl(1)	87.6(2)	O(3)–C(21)–C(22)	109(2)
O(3)–P(1)–O(1)	97.4(6)	C(24)–C(21)–C(22)	115(2)
O(3)–P(1)–O(4)	103.7(7)	C(21)–C(22)–C(23)	116.2(14)
O(1)–P(1)–O(4)	109.7(7)	C(22)–C(23)–C(25)	112(2)
O(3)–P(1)–Pt(1)	116.8(5)	C(22)–C(23)–O(4)	103(2)
O(1)–P(1)–Pt(1)	117.6(5)	C(25)–C(23)–O(4)	104(2)
O(4)–P(1)–Pt(1)	110.2(4)	C(27)–C(26)–O(5)	112(2)
O(6)–P(2)–O(5)	103.9(7)	C(27)–C(26)–C(29)	118(2)
O(6)–P(2)–O(2)	103.9(7)	O(5)–C(26)–C(29)	110(2)
O(5)–P(2)–O(2)	100.3(7)	C(26)–C(27)–C(28)	112(2)
O(6)–P(2)–Pt(1)	118.4(5)	C(27)–C(28)–C(30)	115(2)
O(5)–P(2)–Pt(1)	118.6(5)	C(27)–C(28)–O(6)	108(2)
O(2)–P(2)–Pt(1)	109.3(4)	C(30)–C(28)–O(6)	105(2)

most the same hindrance. Quite interestingly, the two dioxaphosphorinane rings in **3** have different ring conformations in the solid-state structure. One six-membered dioxaphosphorinane ring is in a chair conformation, the other six-membered ring in a twist conformation.

The sum of the bond angles (Table 2) about both P-atoms (310 and 308°) indicates a geometry intermediates between pyramidal and tetrahedral and is larger than that of the free ligand (301°). Similar geometry has been found in the Pt(II) complex of the sterically congested 2,2′-[biaryldiyl)bis(oxy)]bis[1,3,2-oxazaphospholidine] [17]. The observed geometry about both P-atoms suggests a significant amount of s character in the orbital containing the lone electron pair used in bonding to Pt(II) that is consistent with the observed large J_{PPt} [18].

The Pt–P bond lengths (2.211) Å fall in the normal range found for the interactions *trans* to a ligand with a poor *trans* influence [13]. The most interesting bond distances are those observed between platinum and chlorine, 2.373(4) and 2.366(4) Å. These distances are a useful measure of the X-ray *trans* influence of the ligand opposite to Cl and thus provide the opportunity to evaluate the bidentate ligand relative to others. Typically, ligands with a large *trans* influence show Pt–Cl distances in the range 2.36–2.42 Å, whereas the weaker *trans* influence cases have Pt–Cl distances of ca. 2.29–2.32 Å [14]. Our values 2.373 and 2.366 Å place the phosphite ligand at a lower end of the scale of ligands with large *trans* influence.

2.3. Catalysis

The pure diastereomers of compounds **1** and **2** have been tested both in the Pt- and Rh-catalyzed asymmetric hydroformylation of styrene (Table 3). Catalysts were prepared in situ by simply mixing $PtCl_2(PhCN)_2$ in toluene or $Rh(CO)_2(acac)$ in benzene with the ligand (**1**–**2**). In the case of platinum anhydrous $SnCl_2$ ($SnCl_2$:Pt molar ratio 1) was used as cocatalyst, which is essential for catalytic activity. In the case of rhodium systems an excess amount of diphosphite ligand was always added to the catalyst (P:Rh molar ratio 4.30) precursor to exclude the formation of $HRh(CO)_4$, which is an active achiral hydroformylation catalyst [15]. Catalytic reactions were carried out under classical conditions (Table 3) to give a mixture of the branched (2-phenylpropanal) and the normal (3-phenylpropanal) regioisomers.

The data in Table 3 show that in the platinum-catalyzed asymmetric hydroformylation the absolute configuration of the axial chirality in the bridge is of primary importance in asymmetric induction. In the case of *S*-bis(4*R*,6*R*)-**2** and its enantiomers (matched constellations), there is a cooperative effect of the axial chirality of the bridge and the central chirality of the dioxaphosphorinane ring. Diastereomers afforded the opposite prevailing enantiomers in the product when the configuration of the stereogenic axis on the backbone linking the two P atoms are changed (39% (*S*) versus 23% (*R*)). Diastereomers differing in the configuration of the terminal groups would afford the same prevailing enantiomer in the product.

Significant differences in regioselectivities were noted between diastereomers. The most interesting feature of these catalysts is that they favor the formation of the branched aldehyde with regioselectivity that is among the highest (84%) for platinum catalysts [1,16]. Both diastereomers of **1** and **2** afforded higher enantioselectivity and catalytic activity in com-

bination with platinum than with rhodium, but the rhodium system gave complete chemoselectivity towards aldehydes and slightly higher regioselectivity.

3. Conclusions

In the extension of our study on asymmetric hydroformylation, we reported herein the detailed synthesis and spectroscopic characterization of new bisphosphite **1**–**2**, which afforded the highly active platinum catalysts for asymmetric hydroformylation. The highest enantioselectivity (39%) has been obtained with the platinum(II)–$SnCl_2$ catalytic system associated with *S*-bis(4*R*,6*R*)-**2**. In this regard, these model ligands make possible exploration of chiral cooperativity.

4. Experimental

4.1. General procedures

All reaction were carried out in oven-dried glasswork using Schlenk techniques under an atmosphere of argon. Benzene and toluene were distilled from sodium/benzophenone. Triethylamine and dichloromethane were distilled from CaH_2 and stored under an atmosphere of argon. ^{31}P- (121.421 MHz), ^{13}C- (75 MHz), and ^{1}H- (300 MHz) NMR spectra were obtained on a Varian Unity. Optical rotations were measured on Schmidt Haensch 21245 polarimeter. Gas chromatographic analyses were run on a Hewlett–Packard 5830A gas chromatograph (SPB-1 30 m column, film thickness 0.1 μm, carrier gas 2 ml min^{-1}). GC and MS analyses were carried out on a Hewlett–Packard 5980 II gas chromatograph (ULTRA-2 25 m column, film thickness 0.3 μm, carrier gas helium) and 5971A mass spectrometer (70 eV).

4.2. Catalysis

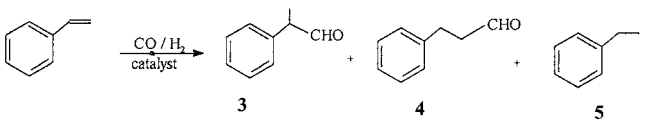
4.2.1. Platinum-catalyzed asymmetric hydroformylation of styrene

In a typical experiment, 0.05 mmol of $Pt(PhCN)_2Cl_2$ and 0.056 mmol of ligand, 0.05 mmol of $SnCl_2$, 25 ml of toluene, 50 mmol of styrene and 5 mmol of decane as an internal standard were placed under argon into a Schlenk tube. 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 gas mixture. At the end of the reaction the autoclave was cooled and depressurized. The reaction mixture was directly distilled in vacuum to remove the catalyst. The reaction mixture and the distilled products were analyzed by GC. The enantiomeric excess was determined by optical rotation of the aldehyde and GC analysis of the corresponding acid obtained by $KMnO_4$ oxidation of a sample of a distilled product (β-DEX, 30 m, id 0.25 mm).

4.2.2. Rhodium-catalyzed asymmetric hydroformylation of styrene

In a typical experiment, 0.0310 mmol of $Rh(acac)(CO)_2$ and 0.0668 mmol of ligand, 2 ml of benzene and 31 mmol of styrene were placed under

Table 3
Hydroformylation of styrene with chiral Pt and Rh diphosphite catalysts [a]



3 4 5

Entry	Ligand	Catalyst precursor	*t* (h)	*T* (°C)	Conversion (%) [b]	**5** (%) [b]	(*b*/*n*) [b]	ee of **3** (%) [c]	Configuration [d]
1	*R*-bis(4*R*,6*R*)-**1** [e]	$Pt(PhCN)_2Cl_2$	12	60	100	42	70/30	23	(*R*)
2	*R*-bis(4*R*,6*R*)-**1** [e]	$Pt(PhCN)_2Cl_2$	5	60	37	40	72/28	23	(*R*)
3	*S*-bis(4*R*,6*R*)-**2** [e]	$Pt(PhCN)_2Cl_2$	5	60	65	29	84/16	39	(*S*)
4	*R*-bis(4*R*,6*R*)-**1** [f]	$Rh(CO)_2(acac)$	19	60	92	0	88/12	16	(*R*)
5	*S*-bis(4*R*,6*R*)-**2** [f]	$Rh(CO)_2(acac)$	4	60	71	0	81/19	20	(*S*)

[a] Reactions were carried out in stainless steel autoclaves under an atmosphere of H_2 and CO (1:1) at 100 atm initial total pressure.
[b] Conversions and composition of the reaction mixture (b:l:h, branched:linear:hydrogenated) were determined by GC (SPB-1) using decane as an internal standard.
[c] Determined by GC analysis (β-DEX, 30 m, id 0.25 mm) of the corresponding acid.
[d] Determined by the sign of optical rotation of the corresponding aldehyde.
[e] Catalyst, $Pt(PhCN)_2Cl_2$-$SnCl_2$-L; solvent, toluene; substrate/catalyst molar ratio, 1000.
[f] Catalyst, $Rh(CO)_2(acac)$; solvent, benzene; substrate/catalyst/ligand molar ratio, 1000/1/2.15.

argon into a Schlenk tube. The stainless steel autoclave (20 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 the gas mixture. The experiment was carried out in the same way as in platinum-catalyzed hydroformylation.

4.3. Materials and methods

Enantiomerically pure 2,4-pentanediols were synthesized by asymmetric hydrogenation of 2,4-pentanedions over Raney nickel catalyst modified with the corresponding enantiomer of tartaric acid and NaBr (TA–NaBr–MRNi) [19]. Resolution of 2,2′-dihydroxy-1,1′-binaphthyl was carried out by using (*R*,*R*)-(+)-2,3-dimethoxy-*N*,*N*,*N*′,*N*′-tetramethylsuccinamide [9] as host compound or (8*S*,9*R*)-(−)-*N*-benzylcinchonidium chloride [10] as a resolving agent.

4.4. Preparations

4.4.1. Synthesis of 2,2′-bis[(4R,6R)-4,6-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy]-R-1,1′-binaphthyl R-bis-(4R,6R)-**1**

The compound (4*R*,6*R*)-4,6-dimethyl-2-chloro-1,3,2-dioxaphosphorinane [7,8] 8.4 g (50 mmol) was dissolved in 200 ml of dry ether. Optically pure (*R*)-1,1′-binaphthalene-2,2′-diol (7.15 g, 25 mmol), and triethylamine (7.65 ml, 50 mmol) were dissolved in 50 ml ether and added dropwise to the (4*R*,6*R*)-4,6-dimethyl-2-chloro-1,3,2-dioxaphosphorinane solution at 0°C. After 1 h of stirring at 0°C, the reaction mixture was allowed to warm to room temperature. The precipitated amine salts were removed by filtration. The ether was removed under reduced pressure. Yield 12.4 g white solid (90%). M.p. = 118–121°C. $[\alpha]_D^{20} = 211.0°$ (*c* 1, $CHCl_3$). Anal. Calc. for $C_{30}H_{32}O_6P_2$: C, 65.45; H, 6.22. Found: C, 65.50; H, 6.77%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 0.54 (6H, d, $^3J_{HH} = 6.2$ Hz, CH_3 eq.), 0.97 (6H, d, $^3J_{HH} = 6.8$ Hz, CH_3 ax.), 1.2 (4H, m, CH_2 eq.), 1.6 (4H, m, CH_2 ax.), 3.4 (2H, m, CH ax.), 4.13 (2H, m, CH eq.), 7.1–7.8 (12H, m); ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 22.0 (s, CH_3 ax.), 22.0 (s, CH_3 eq.), 38.8 (d, $^3J_{POCC} = 8.3$ Hz, CH_2), 60.5 (s, CH ax.), 69.6 (d, $^2J_{POC} = 7.1$ Hz, CH eq.), 119.9 (d, $^3J_{POCC} = 16$ Hz, C-30, C-15), 123.5 (d, $^3J_{POCC} = 16.7$ Hz, C-22, C-7), 124.8 (s, C-24, C-9), 126.6 (s, C-26, C-11), 127.0 (s, C-25, C-10), 129.9 (s, C-27, C-12), 130.4 (s, C-14, C-29), 130.8 (s, C-28, C-13), 135.05 (s, C-8, C-23), 150.3 (d, $^2J_{POC} = 8.8$ Hz, C-6, C-21); ^{31}P-NMR (121 MHz, $CDCl_3$): δ (ppm) 125.2 (s).

4.4.2. Synthesis of 2,2′-bis[(4S,6S)-4,6-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy]-S-1,1′-binaphthyl S-bis-(4S,6S)-**1**

This compound was prepared in the same way as *R*-bis(4*R*,6*R*)-**1**. $[\alpha]_D^{20} = -205.0°$ (*c* 1.3, $CHCl_3$). Suitable crystals for X-ray diffraction were obtained from acetonitrile.

4.4.3. Synthesis of 2,2′-bis[(4R,6R)-4,6-dimethyl-1,3,2-dioxaphosphorinan-2-yloxy]-1,1′-binaphthyl S-bis(4R,-6R))-**2**

This compound was prepared as previously described. $[\alpha]_D^{20} = 53.3°$ (*c* 1, $CHCl_3$), ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 0.66 (6H, d, $^3J_{HH} = 6.8$ Hz, CH_3 eq.), 0.94 (6H, d, $^3J_{HH} = 6.2$ Hz, CH_3 ax.), 1.4 (4H, m, CH_2 eq.), 1.7 (4H, m, CH_2 ax.), 3.7 (2H, m, CH ax.), 4.15 (2H, m, CH eq.), 7.1–7.8 (12H, m); ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 22.5 (s, CH_3 ax.), 22.6 (s, CH_3 eq.), 38.8 (d, $^3J_{POCC} = 8.1$ Hz, CH_2), 61.1 (s, CH ax.), 69.6 (d, $^2J_{POC} = 6.8$ Hz, CH eq.), 120.2 (d, $^3J_{POCC} = 16.3$ Hz, C-30, C-15), 124.0 (s, C-24, C-9), 124.7 (d, $^3J_{POCC} = 18.1$ Hz, C-22, C-7), 126.7 (s, C-26, C-11), 127.0 (s, C-25, C-10), 128.6 (s, C-27, C-12), 130.4 (s, C-14, C-29), 130.8 (s, C-28, C-13), 134.6 (s, C-8, C-23), 149.0 (d, $^2J_{POC} = 9.0$ Hz, C-6, C-21); ^{31}P-NMR ($CDCl_3$): δ (ppm) 124.5 (s).

4.4.4. Synthesis of cis-[$PtCl_2$(R-bis(4R,6R)-**1**] (**3**)

CH_2Cl_2 (2.0 ml) was added to a mixture of 0.0184 mmol of bisphosphite (10.1 mg) and $PtCl_2(PhCN)_2$ (15.0 mg) with stirring. The solvent was removed under reduced pressure. Suitable crystals for X-ray diffraction were obtained from acetonitrile. Anal. Calc. for $C_{30}H_{34}O_6P_2Cl_2Pt$: C, 42.91; H, 4.20. Found: C, 42.76; H, 3.74%. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ (ppm) 0.95 (6H, d, $^3J_{HH} = 6$ Hz, CH_3 eq.), 1.40 (6H, d, $^3J_{HH} = 6$ Hz, CH_3 ax.), 1.75 (4H, m, CH_2 eq.), 2.05 (4H, m, CH_2 ax.), 4.60 (2H, m, CH ax.), 4.80 (2H, m, CH eq.), 7.4 –7.8 (12H, m); ^{31}P-NMR (CD_2Cl_2): δ (ppm) 62.8 (s, $J_{PtP} = 5900$ Hz, satellites).

4.4.5. Synthesis of [$PtCl_2$(S-bis(4R,6R)-**2**] (**3**)

The compound was prepared by in situ mixing of 0.0184 mmol each of bisphosphite (10.1 mg) and $PtCl_2(PhCN)_2$ (15.0 mg) in 0.6 ml CD_2Cl_2. ^{31}P-NMR (121.4 MHz, CD_2Cl_2): δ (ppm) 60.4 (s, $J_{PtP} = 6021.4$ Hz, satellites).

4.4.6. Synthesis of cis-PtCl($SnCl_3$)(R-bis(4R,6R)-**1**

A 0.6 ml amount of CD_2Cl_2 was added to a mixture of 0.0184 mmol of $PtCl_2(PhCN)_2$ (15.0 mg), bisphosphite (10.1 mg) and damp-proof $SnCl_2$ (3.5 mg) with stirring at r.t. The mixture turned orange–red immediately. ^{31}P-NMR (121.4 MHz, CD_2Cl_2): δ

Table 4
Crystal data and details of structure refinement for compounds *S*-bis(4*S*,6*S*)-**1** and [$PtCl_2$(*R*)-bis(4*R*,6*R*)-**1**] (**3**)

	S-bis(4*S*,6*S*)-**1**	[$PtCl_2$(*R*)-bis(4*R*,6*R*)-**1**] (**3**)
Empirical formula	$C_{30}H_{32}O_6P_2$	$C_{30}H_{32}Cl_2O_6P_2Pt$ (0.75 CH_3CN)
Molecular mass (g mol^{-1})	550.50	847.28
Temperature (K)	200	200
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorombic	Monoclinic
Space group	$P2_12_1$	$P2_1$
Unit cell dimensions		
a (Å)	9.235(2)	9.2760(10)
b (Å)	12.450(2)	16.294(2)
c (Å)	24.691(4)	11.2960(10)
α (°)	90	90
β (°)	90	82.340(10)
γ (°)	90	90
V (Å^3)	2838.9(9)	1692.1(3)
Z	4	2
D_{calc} (g m^{-3})	1.288	1.663
Absorption coefficient (mm^{-1})	0.194	4.441
F(000)	1160	837
Crystal size (mm)	0.30×0.30×0.30	0.30×0.25×0.15
θ Range for data collection (°)	2.32–27.00	2.21–27.01
Index ranges	$0\le h\le 11$, $0\le k\le 15$, $0\le l\le 31$	$-10\le h\le 11$, $-17\le k\le 20$, $-14\le l\le 14$
Reflections collected	3494	4053
Independent reflections	3494 [R_{int} = 0.0000]	3823 [R_{int} = 0.0240]
Data/restraints/parameters	3494/0/381	3823/0/346
Goodness-of-fit on F^2	0.993	1.527
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0419, wR_2 = 0.1009	R_1 = 0.0464, wR_2 = 0.1357
R indices (all data)	R_1 = 0.0607, wR_2 = 0.1124	R_1 = 0.0548, wR_2 = 0.1797
Absolute structure parameter	−0.35(13)	0.02(2)
Largest difference peak and hole (e Å^{-3})	0.212 and −0.262	2.065 and −2.324
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2

(ppm) 81.0 (d, J_{PtP} = 5118 Hz, satellites, (*trans* to $SnCl_3$), J_{PP} = 23 Hz), 79.8 (d, J_{PtP} = 5785 Hz, satellites, (*cis* to $SnCl_3$), J_{PP} = 23 Hz).

4.4.7. Synthesis of $Pt(SnCl_3)_2$(R-bis(4R,6R)-**1**)

A 0.0184 mmol amount (3.5 mg) of anhydrous $SnCl_2$ was added to the mixture of *cis*-$PtCl(SnCl_3)$(*R*-bis(4*R*,6*R*)-**1** in 0.6 ml CD_2Cl_2. ^{31}P-NMR (121.4 MHz, CD_2Cl_2): δ (ppm) 95.2 (s, J_{PtP} = 5002 Hz, satellites).

4.5. X-ray crystallography

Crystals of the compounds **1** and **3** were obtained as described above. Data were collected on a Siemens (Nicolet Syntex) R3m/V diffractometer, and the structures were solved by direct methods [20,21]. The crystallographic data and the data collection and refinement details for **1** and **3** are presented in Table 4. Final atomic coordinates and equivalent isotropic thermal parameters of *S*-bis(4*S*,6*S*)-**1** and **3** are given in Tables 5 and 6, respectively. Sources of scattering factors are as in Ref. [22]. Graphical management of the data was performed using XPMA [23].

Table 5
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for *S*-bis(4*S*,6*S*)-**1**

	x	*y*	*z*	U_{eq} [a]
P(1)	5319(1)	5720(1)	8621(1)	29(1)
P(2)	−804(1)	3466(1)	8159(1)	34(1)
O(1)	4349(3)	6678(2)	8864(1)	33(1)
O(2)	5701(3)	6153(2)	8023(1)	37(1)
O(3)	4038(3)	4844(2)	8454(1)	24(1)
O(4)	−567(3)	3386(2)	7516(1)	35(1)
O(5)	−303(3)	2302(2)	8366(1)	37(1)
O(6)	649(3)	4198(2)	8308(1)	26(1)
C(1)	3248(4)	7216(3)	8536(2)	33(1)
C(2)	3973(5)	7644(3)	8024(2)	39(1)
C(3)	4694(5)	6779(3)	7687(2)	38(1)
C(4)	2605(5)	8095(3)	8884(2)	48(1)
C(5)	3659(5)	6043(4)	7390(2)	44(1)
C(6)	3949(3)	3875(2)	8735(1)	20(1)
C(7)	2799(3)	3704(2)	9081(1)	19(1)
C(8)	2716(3)	2688(2)	9353(1)	19(1)
C(9)	1571(4)	2443(3)	9714(1)	26(1)
C(10)	1529(4)	1481(3)	9983(1)	32(1)
C(11)	2624(4)	709(3)	9903(1)	32(1)
C(12)	3729(4)	911(3)	9547(1)	30(1)
C(13)	3812(4)	1902(2)	9266(1)	22(1)
C(14)	4969(4)	2134(3)	8908(1)	27(1)
C(15)	5035(4)	3100(3)	8646(1)	25(1)
C(16)	575(4)	2768(3)	7251(1)	31(1)
C(17)	787(5)	1690(3)	7531(1)	34(1)
C(18)	979(5)	1783(3)	8141(2)	34(1)
C(19)	1946(4)	3427(3)	7203(2)	38(1)
C(20)	1135(6)	704(3)	8410(2)	52(1)
C(21)	661(4)	4781(2)	8791(1)	22(1)
C(22)	1706(4)	4567(2)	9168(1)	20(1)
C(23)	1746(4)	5216(2)	9653(1)	22(1)
C(24)	2777(4)	5045(3)	10 068(1)	30(1)
C(25)	2782(4)	5669(3)	10 525(2)	37(1)
C(26)	1773(5)	6509(3)	10 586(2)	38(1)
C(27)	776(4)	6696(3)	10 195(1)	33(1)
C(28)	724(4)	6060(2)	9718(1)	24(1)
C(29)	−331(4)	6233(3)	9315(1)	28(1)
C(30)	−359(4)	5605(3)	8860(1)	26(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for [$PtCl_2$(*R*)-bis(4*R*,6*R*)]

	x	*y*	*z*	U_{eq} [a]
Pt(1)	8471(1)	4993	836(1)	23(1)
Cl(1)	10 715(4)	4517(3)	−188(4)	33(1)
Cl(2)	7730(4)	3604(2)	1033(5)	33(1)
P(1)	9198(4)	6275(2)	520(4)	21(1)
P(2)	6413(4)	5316(3)	1963(4)	25(1)
O(1)	9553(12)	6794(8)	1642(10)	30(3)
O(2)	6611(11)	5204(7)	3344(10)	27(3)
O(3)	10 678(12)	6406(7)	−280(11)	25(2)
O(4)	8067(13)	6766(7)	−164(11)	30(3)
O(5)	5028(14)	4757(8)	1897(12)	36(3)
O(6)	5825(13)	6203(7)	1895(11)	28(3)
C(1)	8535(18)	7097(11)	2538(16)	30(3)
C(2)	7987(18)	7909(11)	2322(16)	28(3)
C(3)	6962(18)	8221(11)	3189(16)	29(3)
C(4)	6476(17)	7858(12)	4256(17)	32(4)
C(5)	5415(19)	8196(11)	5148(17)	33(4)
C(6)	5000(22)	7767(16)	6189(21)	46(5)
C(7)	5590(19)	6991(16)	6399(17)	40(4)
C(8)	6595(20)	6643(14)	5562(17)	36(4)
C(9)	7057(17)	7046(11)	4478(15)	28(3)
C(10)	8105(17)	6708(10)	3568(15)	25(3)
C(11)	8736(19)	5886(11)	3798(19)	26(4)
C(12)	8043(15)	5176(9)	3666(13)	23(4)
C(13)	8598(30)	4399(15)	3840(21)	41(6)
C(14)	10 032(36)	4312(19)	4126(27)	52(8)
C(15)	10 810(15)	5069(18)	4241(13)	31(4)
C(16)	12 297(20)	4915(23)	4503(17)	44(6)
C(17)	13 097(20)	5639(17)	4615(19)	46(5)
C(18)	12 526(21)	6464(19)	4498(18)	53(6)
C(19)	11 117(22)	6522(13)	4226(16)	36(4)
C(20)	10 195(24)	5829(15)	4105(20)	33(5)
C(21)	10 625(22)	6347(11)	−1581(15)	33(4)
C(22)	9718(24)	7049(16)	−1955(17)	47(5)
C(23)	8728(21)	7488(14)	−941(16)	37(5)
C(24)	12 180(26)	6365(17)	−113(24)	56(6)
C(25)	7419(20)	7884(12)	−1375(18)	34(4)
C(26)	4021(16)	4991(18)	1033(16)	37(4)
C(27)	3533(19)	5841(13)	1201(18)	36(4)
C(28)	4783(24)	6431(13)	1027(17)	41(4)
C(29)	4661(26)	4733(14)	−210(22)	49(5)
C(30)	4397(19)	7319(11)	1297(16)	30(3)
N(1)	6389(33)	4587(20)	6810(29)	62(7)
C(31)	8574(34)	3883(21)	7407(30)	51(7)
C(32)	7274(38)	4302(22)	7072(33)	54(8)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

5. Supplementary material

Full crystallographic details including thermal parameters and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre (CCDC). Any request to CCDC for this material should quote the full literature citation.

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