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Asymmetric hydrovinylation of styrene applying cationic allyl palladium complexes of a P-chiral ligand Prof. Dr. Dr. hc Friedrich Asinger on the occasion of his 90th birthday

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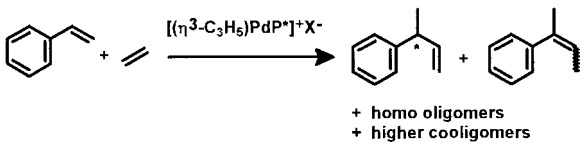
Abstract

Cationic allyl palladium complexes of the diasteriomerically pure P-chiral ligand *tert*-butyl(menthyl-*O*)phenylphosphinite **1** were prepared from $[(\eta^3\text{-}C_3H_5)PdI]_2$ and $[(\eta^3\text{-}C_3H_5)Pd(cod)]X$. Ligand **1** and the complex $[(\eta^3\text{-}C_3H_5)PdI(\mathbf{1})]$ **9** were characterized by X-ray crystallography. The absolute configuration at the phosphorus center of **1** was determined to be (*S*) for the (−)-menthol derivative. Crystals are orthorombic, space group $P2_12_12_1$, $a = 8.505(3)$ Å, $b = 10.82(1)$ Å, $c = 23.297(3)$ Å, $V = 2144(2)$ Å^3. Complex **9** shows distorted square planar geometry. Crystals are trigonal, space group $P3_2$, $a = 13.980(5)$ Å, $c = 11.292(3)$ Å, $V = 1911(2)$ Å^3. Asymmetric codimerization of styrene and ethylene was successfully applied. High enantioselectivities of up to 86% ee have been obtained at room temperature. The codimer 3-phenylbut-1-ene (3PB1) was formed in high selectivity (up to 96%) with only small amounts of the isomerization products *E*- and *Z*-2-phenylbut-2-ene. By addition of various coordinating solvents, the catalyst system was efficiently stabilized. Variation of the complex counter anion had significant effect on enantioselectivity. © 1998 Elsevier Science S.A.

Keywords: Palladium; Codimerization; Hydrovinylation; P-chiral; Styrene; Ethylene

1. Introduction

Asymmetric C–C coupling reactions are of high current interest. Especially catalytic versions attract increasing attention. Control of selectivity (chemo- and regio-) in C–C linkage reactions allows the specific synthesis of different frameworks starting from a particular feed stock [1]. Enantioselective codimerization can provide a route to chiral olefins as building blocks for fine chemicals. Hydrovinylation of vinyl arenes has been shown to open access to aryl propionic acids [2]. Several metals were used as catalysts in hydrovinylation reactions [3,4], among which nickel and palladium were the most



successful ones. Most catalysts are based on $(\eta^3$-allyl)nickel halide [5–8] or $(\eta^3$-allyl)palladium halide [9–11]. In the case of nickel, activation by a Lewis acid such as Et_2AlCl results in very active catalysts [5]. For palladium, the halide has to be abstracted by a silver salt of a noncoordinating anion [11]. But so far, in the asymmetric reaction, only nickel has been used.

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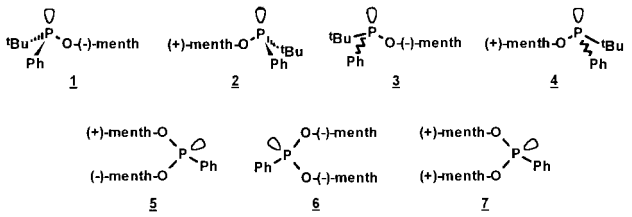
The first example for asymmetric hydrovinylation of styrene was given by Bogdanovic in 1979 using a nickel catalyst [12]. Wilke reported the most efficient system so far based on a nickel catalyst with a chiral azaphospholene ligand derived from myrthenal. The reaction has to be run at very low temperature (-70°C) to give high enantioselectivities of $>95\%$ ee [13]. Recently, the achiral nickel system *trans*-[Ni(2,4,6-$Me_3C_6H_2$)-(CH_3CN)(PBn_3)]BF_4 was reported to give nearly exclusive formation of the codimers at room temperature [14].

Recent reports from our laboratories have demonstrated that cationic Pd(II) complexes of hemilabile ligands are efficient and selective catalysts for C–C linkage reactions of olefins [15–17]. In the hydrovinylation high activity and selectivity towards 3PB1 was observed using phosphino carboxylic acid derivatives. Furthermore, these catalyst systems are stable under reaction conditions whereas similar complexes of monodentate ligands are known to be subtle to reduction and palladium black formation. Attempts to use chiral phosphino carboxylic acid esters derived from lactic and mandelic acid gave only moderate enantioselectivities of up to 33% ee [18]. In all these cases, the chirality was located in the ligand backbone. This prompted us to bring the chiral information closer to the metal center by using P-chiral ligands.

2. Results and discussion

The P-chiral phosphinite ligand **1** can be derived easily with high diastereomeric excess [19]. To overcome the problem of reduction of the monodentate Pd(II) complex yielding palladium black, we successfully applied coordinating cosolvents like acetic acid esters to mimic hemilabile ligand systems.

A series of phosphinite **1**–**4** and phosphonite **5**–**7** ligands were prepared from (−)- and (+)-menthol as chiral auxiliary. The ligands **1** and **2** resembling enantiomers were obtained in high diastereomeric purity ($\geq 98\%$ de, ^1H, ^{31}P NMR) from the two enantiomeric di(menthyl-*O*)-phenylphosphonites **6** and **7** by reaction with *t*-BuLi as described earlier by Richter and Neuffer [19]. These phosphinites were derived from dichlorophenylphosphine and (−)- and (+)-menthol, respectively. The meso compound **5** was prepared by subsequent reaction of dichlorophenylphosphine and the two menthol enantiomers. Ligands **3** and **4** were prepared from the corresponding chloro-(−)-menthyl-*O*- and chloro-(+)-menthyl-*O*-phenylphosphinite as a 1:1 diastereomeric mixture with (*R*) and (*S*) configuration at the stereogenic phosphorus atom.



The absolute configuration at the phosphorus atom was determined for compound **1** to be (S_P) by X-ray crystal structure analysis of the borane complex (Fig. 1). Suitable crystals were obtained from hexane solution at −28°C. Selected distances and angles are given in Table 1.

The crystal structure of the iodo allylpalladium complex of ligand **1** shows a distorted square planar geometry (Fig. 2). Remarkably, there is no disorder of the allyl fragment observed in the solid state, while in dichloromethane solution, a 3:2 mixture of diastereomers is observed by NMR. Crystals were grown from a solution of the complex in CH_2Cl_2/Pentane at −28°C. Selected bond distances and angles are given in Table 2.

The catalysts applied were generated in situ by either ligand exchange in [(η^3-C_3H_5)Pd(cod)]X or conversion with [(η^3-C_3H_5)PdI]$_2$ and subsequent halide abstraction with AgX (X = OTf, BF_4^-, PF_6^-, SbF_6^-) (Scheme 1). High selectivity to the codimers and high enantioselectivity was observed. Total turn over numbers were in the range of 200–800 mol/mol.

At 0–22°C, enantioselectivities up to 86% ee were obtained. Only small amount of isomerization to the *E*/*Z*-2-phenylbut-2-ene was obtained. However, with

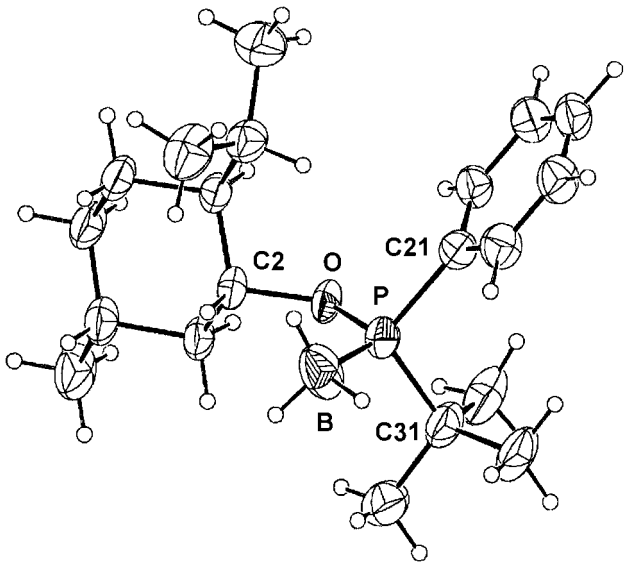


Fig. 1. Thermal ellipsoid plot (PLATON [20]) of the borane aduct of **1**. Ellipsoids are scaled to 30% probability.

Table 1
Selected bond distances and angles of $\mathbf{1}\cdot BH_3$

Distances (Å)			
P–O	1.607(3)	P–B	1.857(8)
P–C21	1.810(6)	O–C2	1.487(5)
P–C31	1.823(6)		
Angles (deg)			
O–P–C21	102.9(2)	C21–P–B	113.8(4)
O–P–C31	101.8(2)	C31–P–B	114.4(4)
O–P–B	116.4(3)	P–O–C2	124.9(3)
C21–P–C31	106.1(3)		

Table 2
Selected bond distances and angles of **9**

Distances (Å)			
I–Pd	2.639(1)	P–O	1.603(4)
Pd–P	2.304(2)	P–C11	1.869(6)
Pd–C30	2.142(7)	P–C20	1.821(6)
Pd–C31	2.157(7)	C30–C31	1.38(1)
Pd–C32	2.193(7)	C31–C32	1.36(1)
Angles (deg)			
I–Pd–P	108.03(4)	O–P–C11	102.1(2)
I–Pd–C30	155.1(2)	O–P–C20	101.9(3)
I–Pd–C31	124.2(3)	C11–P–C20	102.5(3)
I–Pd–C32	90.2(2)	P–O–C1	121.9(4)
P–Pd–C30	95.2(2)	Pd–C31–C32	73.2(4)
P–Pd–C31	126.2(3)	C30–C31–C32	120.7(8)
P–Pd–C32	161.8(2)	Pd–C32–C31	70.3(4)
Pd–P–O	116.2(2)	Pd–C30–C31	71.9(4)
Pd–P–C11	121.0(2)	Pd–C31–C30	70.6(4)
Pd–P–C20	110.6(2)		

only one equivalent of the monodentate ligand, reduction to Pd(0) occurred in the course of the reaction, while applying two equivalents of ligand significantly decreased the catalytic activity. This is also known from chelating diphosphines, which show only little to no activity.

Therefore, we applied donating cosolvents to stabilize the catalyst and, hence, mimic the effect known from the hemilabile ligands. Acetic acid esters appeared to stabilize the Pd(II) species efficiently. No Pd(0) formation occurred during the reaction. Furthermore, the selectivity of the codimerization was increased without affecting the enantioselectivity. More strongly coordinating solvents like acetonitrile inhibited the reaction.

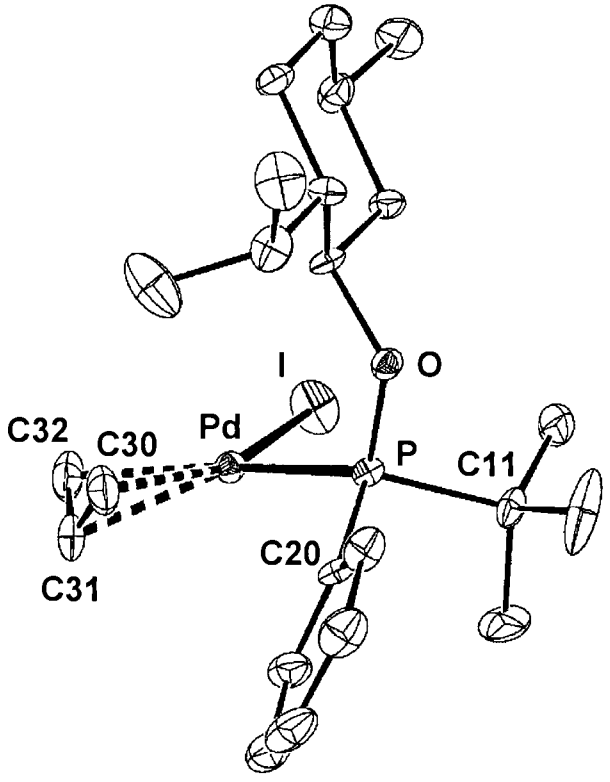
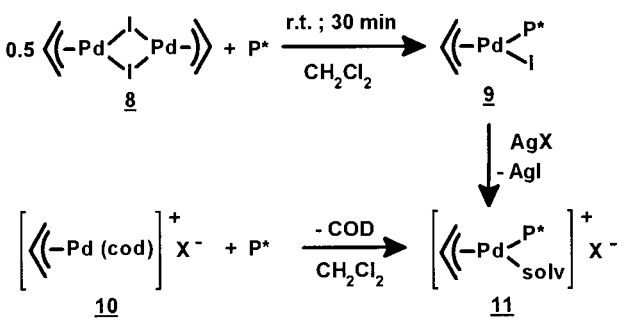


Fig. 2. Thermal ellipsoid plot (PLATON [20]) of complex **9**. Ellipsoids are scaled to 30% probability.

Results comparing different acetic acid esters are shown in Table 3.

In order to study the contribution of the chiral centers in the menthol auxiliary and at the phosphorus atom to the asymmetric induction, ligands **1**–**7** were applied in catalysis (Table 4). The enantiomeric phosphinite ligands **1** and **2** give the opposite product enantiomers with almost the same ee. Ligand **1** derived from (−)-menthol gave (*S*)-3PB1 in 86% ee, while the phosphinite **2** from (+)-menthol gave the (*R*)-enantiomer.

Ligands **3** and **4** which were prepared as 1:1 diastereomeric mixtures with (*R*) and (*S*) configuration at the stereogenic phosphorus center showed the same direction of stereochemical induction as their diastereomerically pure counterparts **1** and **2**, but with significantly lower ee. The two enantiomeric phosphonites, **6** and **7**, gave the opposite induction, (*R*)- for (−)-menthol and (*S*)- for (+)-menthol. As expected, the meso compound **5** showed no induction at all. These results underline the great potential of the use of ligands with a homochiral stereogenic phosphorus atom in order to achieve high asymmetric induction in the codimerization reaction.



Scheme 1. Catalyst complex preparation.

Table 3
Effect of cosolvents

Run	Cosolv.	Conv.[a] /%	Yield[b] /%	$S^{c}_{codimers}$ /%	S^{d}_{3PB1} /%	% ee
1	–	76	48	64	98	85
2	EtOAc	91	70	80	96	82
3	*t*-BuOAc	77	52	70	96	85
4	menthOAc	76	53	72	97	86

$T = 0$°C; reaction time = 2 h; 10 bar initial pressure; P/Pd = 1; styrene/Pd = 500–1000; 20 ml CH_2Cl_2; 2 ml styrene (17.4 mmol); 3 ml cosolvent added; complex **8** as precursor.
[a]Conversion of styrene.
[b]Yield of 3PB1.
[c]Σ(codimers)/conv.
[d](3PB1)/Σ(codimers).

Table 4
Cooperativity of chiral auxiliary and chiral phosphorus

Ligand	Conv.[b] /%	Yield[c] /%	$S^{d}_{codimers}$ /%	S^{e}_{3PB1} /%	% ee	Config.
1	95	79	89	94	86	*S*
2	100	74	91	82	83	*R*
3	89	70	86	92	37	*S*
4	84	65	83	93	29	*R*
5[a]	74	39	77	68	–	–
6[a]	75	44	94	62	42	*R*
7[a]	49	34	85	81	38	*S*

$T = 10$°C; reaction time = 1 h; 10 bar initial pressure, P/Pd = 1; styrene/Pd = 500–1000; 20 ml CH_2Cl_2; 2 ml styrene (17.4 mmol); complex **10** as precursor.
[a]Complex **8** as precursor; reaction time = 4 h.
[b]Conversion of styrene.
[c]Yield of 3PB1.
[d]Σ(codimers)/conv.
[e](3PB1)/Σ(codimers).

For the nickel catalyzed reaction, a strong influence of the complex counter anion on the enantioselectivity was reported. Wilke et al. [21] and Angermund et al. [22] found that the more coordinating anions gave the highest ee's. In contrast to these findings, we observed the opposite effect for the cationic palladium systems (Table 5). With triflate no asymmetric induction was observed while PF_6^- and SbF_6^- gave the highest ee's.

Table 5
Asymmetric hydrovinylation of styrene catalyzed by [(allyl)Pd(**1**)]X, influence of the anion X

Run	Anion	Conv.[a] /%	Yield[b] /%	$S^{c}_{codimers}$ /%	S^{d}_{3PB1} /%	% ee	Config.
1	OTf^-	23	6	25	97	0	–
2	BF_4^-	93	49	55	95	77	*S*
3	PF_6^-	100	12	47	25	87	*S*
4	SbF_6^-	83	46	58	95	87	*S*

$T = 0$°C; reaction time = 2 h; 10 bar initial pressure; P/Pd = 1; styrene/Pd = 500–1000; 20 ml CH_2Cl_2; 2 ml styrene (17.4 mmol); 3 ml cosolvent added.
[a]Conversion of styrene.
[b]Yield of 3PB1.
[c]Σ(codimers)/conv.
[d](3PB1)/Σ(codimers).

3. Conclusions

The presented P-chiral phosphinite ligands give excellent selectivities to 3PB1 in the codimerization of styrene and ethylene. High enantiomeric excess is obtained even at room temperature. The importance of the phosphorus atom being a stereogenic center was demonstrated. The cationic palladium catalyst systems could be efficiently stabilized by addition of acetic acid esters as coordinating cosolvents. Combining both, the chiral phosphorus atom and the weaker coordinating ester group in a hemilabile, P-chiral ligand is presently in progress in our group.

4. Experimental

4.1. General

All manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. The argon was deoxygenated by BASF catalyst R-3-11 and dried using molsieve Linde 4 Å. Solvents were freshly distilled under argon atmosphere and dried by standard procedures. Air and moisture sensitive solutions and reagents were handled using syringe techniques. Catalytic experiments under pressure were carried out in 75 ml stainless steel autoclaves equipped with a magnetic stirring bar. NMR spectra were acquired on Bruker AC-300 and Bruker DPX-300 spectrometer. Chemical shifts are referenced to internal or external TMS (^1H, ^{13}C) respectively external 85% H_3PO_4 (^{31}P). IR spectra were recorded on a Nicolet 505-FT-IR spectrometer. Styrene was purchased from Fluka and distilled from CaH_2 under argon. The ethylene used had a purity of > 99.5%. [(η^3-C_3H_5)Pd(cod)]BF_4 [23] and [(η^3-C_3H_5)PdI]$_2$ [24,25] were prepared by literature procedures.

4.2. General procedure for preparation of the cationic (allyl)PdP* complexes

A solution of 1.00 equivalent of the phosphorus ligand (0.1 mmol) in dichloro methane (5 ml) was added to a solution of 0.05 mmol [(η^3-C_3H_5)PdI]$_2$ in 5 ml CH_2Cl_2. After stirring for 30 min the solution was transferred to a flask containing 1.03 eq $AgSbF_6$ in 2 ml CH_2Cl_2. After stirring vigorously for 5 min, the mixture was filtered through a pad of celite into a flask kept at −20°C. The Celite was washed with CH_2Cl_2 (2 × 4 ml) and the resulting solution used for catalysis.

4.3. Hydrovinylation reaction

The cold catalyst solution was transferred into a 75 ml stainless steel autoclave via syringe with a PTFE cannula. The autoclave was cooled in an ice bath. The cosolvent and 2.01 g (19.3 mmol) of chilled styrene were added and the autoclave was pressurized with ethylene. After the reaction the autoclave was slowly vented and the reaction mixture separated from the catalyst and higher oligomers by flash distillation. Products were analyzed by GC and the enantiomeric excess also determined by GC using chiral capillary column [26].

4.4. Ligand Preparation

4.4.1. Di((±)-menthyl-O)-phenylphosphonite **5** (general procedure 1)

Dichloro phenylphosphine (64.1 mmol) was dissolved in 80 ml of toluene and the solution cooled to 0°C. (−)-Menthol 10.02 g (64.1 mmol, 1.0 eq) was azeotropically dried by three subsequent cycles of dissolving in 20 ml of toluene and evaporating again. The menthol was then dissolved in 100 ml of toluene together with triethylamine 7.78 g (77 mmol, 1.2 eq). This mixture was added dropwise to the cooled solution of the chlorophosphine so that the temperature was kept at 0°C. After the addition was complete, the whole mixture was heated to 80°C for 1 h and stirred at room temperature over night. After filtering off the ammonium salt, the solution was evaporated to a volume of about 100 ml and cooled to 0°C. A solution of azeotropically dried (+)-menthol 10.02 g (64.1 mmol) and triethylamine 7.78 g (77 mmol, 1.2 eq) in 100 ml of toluene was added slowly at 0°C. The mixture was then heated to 100°C for 12 h. After cooling down and filtering off the ammonium salt, the solution was evaporated to dryness. The product, which can be recrystallized from pentane, was obtained as white crystalline solid (22 g, 82%). Mp: 32°C. Calculated for $C_{26}H_{43}O_2P$: C 74.600% H 10.353%; found: C 73.57% H 9.91%.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.69$ (d, 3H, J(HH) = 6.9 Hz, $HCCH_3$), 0.70, 1.62 (2H, m $CHCH_2CH_2$), 0.81 (3H, d, J(HH) = 7.2 Hz, $HCCH_3$), 0.91 (3H, d, J(HH) = 6.3 Hz, $HCCH_3$), 0.95, 1.62 (2H, m, CH_2CH_2CH), 1.19 (1H, m, $CHCHCH$), 1.42 (1H, m, $CHCH_3$), 2.02 (2H, m, $CHCH_2CHO$), 2.09 (1H, m, $CH(CH)(CH_3)_2$), 3.81 (1H, m, $HCOP$), 7.43, 7.23 (5H, m, H_{aromat}). ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 15.86$ (d, J(CP) = 3.3 Hz, $CHCH_3$), 21.29 ($CHCH_3$), 22.39 (CCH_3), 23.04 (CH_2CH_2CH), 25.29 ($CH(CH_3)_2$), 32.06 ($CHCH_3$), 34.46 (CH_2CH_2CH), 44.38 (d, $CHCH_2CHO$), 49.33 (d, J(CP) = 5.5 Hz, CH_2CHCHO), 79.52, 79.56 (d, J(CP) = 17.3, 17.0 Hz, $HCOP$), 128.16 (d, J(CP) = 6.6 Hz, C_{meta}), 128.42, 129.23 (C_{para}), 129.74 (d, J(CP) = 18.5 Hz, C_{ortho}), 143.26 (d, J(CP) = 10.8 Hz, C_{ipso}). ^{31}P NMR (121.28 MHz, $CDCl_3$): $\delta = 165.75$ ppm. IR (CH_2Cl_2): $\nu = 1024$ cm^{-1} (P–O), 1389, 1365 cm^{-1} (CH_3), 2959, 2923, 2874 cm^{-1} (CH_3, $CH_2)_{as,s}$, 1462 cm^{-1} $(CH_2)_s$, 1439 cm^{-1} (P–Phenyl), 760, 699 cm^{-1} (Phenyl).

4.4.2. Di((−)-menthyl-O)-phenylphosphonite **6**

Following the general procedure 1, dichloro phenylphosphine (50 mmol) was converted with (−)-menthol and triethylamine. Yield: 15.9 g (76%), mp: 61°C. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.70$, 0.77 (3H, d, J(HH) = 6.9 Hz, $CH_3(HC)CH_3$), 0.86, 0.90 (3H, d, J(HH) = 7.2, 6.6 Hz, $CH_3(HC)CH_3$), 0.88, 1.66 (2H, m, CH_2CH_2CH), 0.92 (3H, d, J(HH) = 6.9 Hz, $HCCH_3$), 0.95, 1.67 (2H, m, $CHCH_2CH_2$), 1.35 (1H, m, $CHCH(CH_3)_2$), 1.46 (1H, m, $CHCH_3$), 2.09, 2.31 (1H, m, $CH(CH)(CH_3)_2$), 2.15 (2H, m, $CHCH_2CHO$), 3.73, 3.83 (1H, m, J(PH) = 7.8, 8.9 Hz, $HCOP$), 7.40, 7.65 (5H, m, H_{aromat}). ^{13}C NMR (75.34 MHz, $CDCl_3$): $\delta = 15.83$ (J(CP) = 3.6 Hz), 16.26 ($CHCH_3$); 21.31, 21.52 ($CHCH_3$), 22.37 (CCH_3); 23.03, 23.08 (CH_2CH_2CH), 25.11, 25.35 ($CH(CH_3)_2$), 31.85, 32.12 ($CHCH_3$), 34.44, 34.48 (CH_2CH_2CH), 44.62, 44.91 (d, J(CP) = 2.9, 5.0 Hz, $CHCH_2CHO$), 49.31, 49.42 (d, J(CP) = 4.8, 6.3 Hz, CH_2CHCHO), 77.99, 79.82 (d, J(CP) = 11.2, 17.7 Hz, $HCOP$), 128.20 (d, J(CP) = 6.3 Hz, C_{meta}), 129.86 (C_{para}), 130.02 (d, J(CP) = 23.4 Hz, C_{ortho}), 143.28 (d, J(CP) = 13.4 Hz, C_{ipso}). ^{31}P NMR (121.28 MHz, $CDCl_3$): $\delta = 161.07$ ppm. IR (CH_2Cl_2): $\nu = 1019$ cm^{-1} (P–O), 1375 cm^{-1} (CH_3), 2973, 2934, 2868 cm^{-1} (CH_3, $CH_2)_{as,s}$, 1392 cm^{-1} $(CH_2)_s$, 1452 cm^{-1} (P–Phenyl), 723, 693 cm^{-1} (Phenyl).

4.4.3. Di((+)-menthyl-O)-phenylphosphonite **7**

Following the general procedure 1, dichloro phenylphosphine (50 mmol) was converted with (+)-menthol and triethylamine. Yield: 17.2 g (82%), mp: 69°C. Calculated for $C_{26}H_{43}O_2P$: C 74.600% H 10.353%; found: C 74.26% H 9.79%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.70$, 0.76 (3H, d, J(HH) = 6.9 Hz, $CH_3(HC)CH_3$), 0.86, 0.90 (3H, d, J(HH) = 7.2, 6.6 Hz, $CH_3(HC)CH_3$), 0.88, 1.66 (2H, m, CH_2CH_2CH), 0.92 (3H, d, J(HH) = 6.9 Hz, $HCCH_3$), 0.95, 1.66 (2H, m, $CHCH_2CH_2$), 1.36 (1H, m, $CHCH(CH_3)_2$), 1.45 (1H, m, $CHCH_3$), 2.10, 2.31 (1H, m, $CH(CH)(CH_3)_2$), 2.14 (2H, m, $CHCH_2CHO$), 3.73, 3.83 (1H, m, J(PH) = 7.8, 8.9 Hz, $HCOP$), 7.40, 7.65 (5H, m, H_{aromat}). ^{13}C NMR (75.34 MHz, $CDCl_3$): $\delta = 15.85$ (J(CP) = 3.3 Hz), 16.28 ($CHCH_3$); 21.33, 21.53 ($CHCH_3$), 22.38 (CCH_3); 23.04, 23.10 (CH_2CH_2CH), 25.12, 25.36 ($CH(CH_3)_2$), 31.87, 32.14 ($CHCH_3$), 34.46, 34.50 (CH_2CH_2CH), 44.64, 44.92 (d, J(CP) = 2.8, 5.0 Hz, $CHCH_2CHO$), 49.34, 49.43 (d, J(CP) = 5.3, 7.6 Hz, CH_2CHCHO), 78.01, 79.84 (d, J(CP) = 11.4, 17.8 Hz, $HCOP$), 128.22 (d, J(CP) = 6.3 Hz, C_{meta}), 129.88 (C_{para}), 130.03 (d,

J(CP) = 23.4 Hz, C_{ortho}), 143.30 (d, J(CP) = 13.4 Hz, C_{ipso}). ^{31}P NMR (121.28 MHz, $CDCl_3$): δ = 161.05 ppm. IR (CH_2Cl_2): ν = 1022 cm^{-1} (P–O), 1386, 1370 cm^{-1} (CH_3), 2964, 2934, 2879 cm^{-1} (CH_3, CH_2)$_{as,s}$, 1457 cm^{-1} (CH_2)$_s$, 1436 cm^{-1} (P–Phenyl).

4.4.4. [(S_P,1R,2S,5R)-(−)-menthyl-O]tert-butyl-phenylphosphinite **1** (general procedure 2)

To a solution of Di((−)-menthyl-*O*) phenylphosphonite 14.18 g (33.87 mmol) in a mixture of ether (85 ml) and benzene (26 ml) 1 eq. of *tert*-butyllithium (22.7 ml, 1.56 M in pentane) was added at −78°C. The reaction mixture was allowed to warm to room temperature over night and the solvent was removed in vacuum. The residue was distilled in high vacuum. The resulting colorless oil solidifies upon storage at −20°C. This raw material had a diastereomeric purity of about 90% (^{1}H NMR and ^{31}P NMR). Diastereomerically pure product was obtained from the borane adduct of the ligand. Therefore, **1** was reacted with an excess (1.6 eq.) of a BH_3 solution in THF (54.2 ml, 1 M) at −40°C. The reaction mixture was stirred for 1 h at −40°C and an additional hour at 23°C. The solvent was evaporated yielding an airstable white solid (7.7 g, 68%). After four recrystallizations from hexane the product was diastereomerically pure. Mp: 76–78°C. Calculated for $C_{20}H_{36}$BOP: C 71.86% H 10.85%; found: C 71.05% H 10.22%.

The borane was removed by heating the adduct with 2 eq. of DABCO in toluene at 100°C for 16 h. The solvent was removed and the residue taken up in ether. Filtration over a short column with dry silica (5–8 cm) gave the pure compound **1**, which can be recrystallized from hexane. Calculated for $C_{20}H_{33}$OP: C 74.96% H 10.38%; found: C 74.40% H 10.48%.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.60 (3H, d, J(HH) = 6.9 Hz, CH_3HCCH_3), 0.89 (3H, d, J(HH) = 7 Hz, CH_3HCCH_3), 0.91, 1.66 (2H, m, $CHCH_2CH_2$), 0.94 (3H, d, J(HH) = 6.6 Hz, $HCCH_3$), 0.95 (9H, d J(PH) = 12 Hz, $C(CH_3)_3$), 1.35 (2H, m, $CHCH_3$, CHCHCH), 0.87, 1.62 (2H, m, CH_2CH_2CH), 2.32 (2H, m, $CHCH_2CHO$), 2.34 (1H, m, $CH(CH)(CH_3)_2$), 3.46 (1H, m, J(PH) = 14.6 Hz, HCOP), 7.32, 7.52 (5H, m, H_{aromat}). ^{13}C NMR (75.34 MHz, $CDCl_3$): δ = 15.67 ($CHCH_3$), 21.46 ($CHCH_3$), 22.47 (CCH_3), 22.91 (CH_2CH_2CH), 25.38 ($CH(CH_3)_2$), 25.39 (d, J(CP) = 15.6 Hz, $C(CH_3)_3$), 32.00 ($CHCH_3$), 32.58 (d, J(CP) = 10.8 Hz, $C(CH_3)_3$), 34.64 (CH_2CH_2CH), 43.37 (d, J(CP) = 7.7 Hz, $CHCH_2CHO$), 49.95 (d, J(CP) = 4.5 Hz, CH_2CHCHO), 79.84 (d, J(CP) = 14.9 Hz, HCOP), 127.42 (d, J(CP) = 7.4 Hz, C_{meta}), 128.95 (C_{para}), 131.25 (d, J(CP) = 22.2 Hz, C_{ortho}), 140.62 (d, J(CP) = 28.1 Hz, C_{ipso}). ^{31}P NMR (121.28 MHz, $CDCl_3$): δ = 121.46 ppm. IR (CH_2Cl_2): ν = 1012 cm^{-1} (P–O), 1363 cm^{-1} (CH_3), 2993, 2930, 2874 cm^{-1} (CH_3, CH_2)$_{as,s}$, 1460 cm^{-1} (CH_2)$_s$, 1435 cm^{-1} (P–Phenyl), 749, 708 cm^{-1} (Phenyl).

4.4.5. [(R_P,1R,2S,5R)-(+)-menthyl-O]tert-butyl-phenylphosphinite **2**

Following the general procedure 2, Di((+)-menthyl-*O*)-phenylphosphonite **7** 14,24 g (34.0 mmol) was converted with *tert*-butyllithium, resulting in the borane adduct of **2** as colorless crystals. Yield: 8.3 g (73%), mp: 79–83°C. Calculated for $C_{20}H_{36}$BOP: C 71.86% H 10.85%; found: C 71.80% H 10.15%. The borane was removed as described for **1**.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.59 (3H, d, J(HH) = 6.9 Hz, CH_3HCCH_3), 0.87 (3H, d, J(HH) = 7.2 Hz, CH_3HCCH_3), 0.91, 1.65 (2H, m, $CHCH_2CH_2$), 0.93 (3H, d, J = 6.6 Hz, $HCCH_3$), 0.94 (9H, d J(PH) = 12.6 Hz, $C(CH_3)_3$), 1.35 (2H, m, $CHCH_3$, CHCHCH), 0.85, 1.61 (2H, m, CH_2CH_2CH), 2.33 (2H, m, $CHCH_2CHO$), 2.34 (1H, m, $CH(CH)(CH_3)_2$), 3.45 (1H, m, J(PH) = 14.7 Hz, HCOP), 7.32, 7.51 (5H, m, H_{aromat}). ^{13}C NMR (75.34 MHz, $CDCl_3$): δ = 15.67 ($CHCH_3$); 21.45 ($CHCH_3$), 22.45 (CCH_3); 22.92 (CH_2CH_2CH), 25.32 (d, J(CP) = 14.2 Hz, $C(CH_3)_3$), 25.42 ($CH(CH_3)_2$), 32.00 ($CHCH_3$), 32.56 (d, J(CP) = 8.3 Hz, $C(CH_3)_3$), 34.61 (CH_2CH_2CH), 43.28 (d, J(CP) = 8.3 Hz, $CHCH_2CHO$), 49.92 (d, J(CP) = 4.1 Hz, CH_2CHCHO), 80.20 (d, J(CP) = 16.8 Hz, HCOP), 127.56 (d, J(CP) = 4.5 Hz, C_{meta}), 129.22 (C_{para}), 131.39 (d, J(CP) = 21.2 Hz, C_{ortho}), 141.62 (d, J(CP) = 26.0 Hz, C_{ipso}). ^{31}P NMR (121.28 MHz, $CDCl_3$): δ = 122.46 ppm. IR (CH_2Cl_2): ν = 1012 cm^{-1} (P–O), 1371 cm^{-1} (CH_3), 2993, 2874 cm^{-1} (CH_3, CH_2)$_{as,s}$, 1452 cm^{-1} (CH_2)$_s$, 1420 cm^{-1} (P–Phenyl), 743, 699 cm^{-1} (Phenyl).

4.4.6. [(R / S_P,1R,2S,5R)-(−)-menthyl-O]tert-butyl-phenylphosphinite **3** (general procedure 3)

At 0°C, a solution of triethylamine 2.65 g (26.2 mmol) and (−)-menthol 3.72 g (23.79 mmol) in 12 ml of toluene was added dropwise to the solution of dichloro phenylphosphine 4.26 g (23.79 mmol) in 14.4 ml of toluene. The appearing clouding was redissolved by heating the mixture for 1 h at 80°C after complete addition. The mixture was allowed to cool to room temperature over night, filtered through a glass sinter fritte (G4) and the solvent was removed resulting in a colorless oil. The ^{31}P NMR spectrum ($CDCl_3$) showed two signals for the diastereoisomers at 178.9 ppm and 176.0 ppm. The chloro menthyl-*O* phenylphosphinite was dissolved in a mixture of 100 ml ether and 30 ml benzene and cooled to −78°C. Addition of *tert*-butyllithium (23.79 mmol; 14.87 ml, 1.6 M in pentane) resulted in the formation of a suspension which turned to a clear orange solution after adding half of the butyllithium. After half an hour LiCl, began to deposit. The mixture was allowed to warm to room temperature over 12 h. The solvent was removed and the product

distilled in high vacuum. Yield: 4.93 g (62%), bp: 135–142°C ($2.5 \cdot 10^{-1}$ mbar).

^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.59$, 0.81 (3H, d, J(HH) = 6.9 Hz, CH_3HCCH_3), 0.77, 0.92 (3H, d, J(HH) = 6.9 Hz, CH_3HCCH_3), 0.83, 1.64 (2H, m, $CHCH_2CH_2$), 0.87, (3H, d, J(HH) = 6.6 Hz, $HCCH_3$), 0.93, 0.94 (9H, d, J(PH) = 12.6 Hz, $C(CH_3)_3$), 1.37 (2H, m, $CHCH_3$, $CHCH(CH_3)_2$), 0.97, 1.64 (2H, m, CH_2CH_2CH), 0.82, 1.94, 0.93, 2.38 (2H, m, $CHCH_2CHO$), 2.33, 2.47 (1H, m, $CH(CH)(CH_3)_2$), 3.45, 3.59 (1H, m, J(PH) = 17.7, 15.3 Hz, HCOP), 7.34, 7.50 (5H, m, H_{aromat}). ^{13}C NMR (75.34 MHz, $CDCl_3$): $\delta = 15.66$, 15.86 ($CHCH_3$); 21.46, 21.49 ($CHCH_3$), 22.94, 22.48 (CCH_3); 22.93 (CH_2CH_2CH), 25.38 ($CH(CH_3)_2$), 25.32, 25.40 (d, J(CP) = 15.5, 15.7 Hz, $C(CH_3)_3$), 31.89, 31.99 ($CHCH_3$), 32.58, 32.88 (d, J(CP) = 10.7, 10.4 Hz, $C(CH_3)_3$), 34.61, 34.64 (CH_2CH_2CH), 43.37, 43.56 (d, J(CP) = 7.9, 7.5 Hz, $CHCH_2CHO$), 49.95, 50.01 (d, J(CP) = 3.7, 5.5 Hz, CH_2CHCHO), 79.83, 81.13 (d, J(CP) = 15, 16.4 Hz, HCOP), 127.35, 127.43 (d, J(CP) = 6.5, 5.8 Hz, C_{meta}), 128.75, 128.96 (C_{para}), 130.87, 131.25 (d, J(CP) = 21.2, 22.2 Hz, C_{ortho}), 140.63, 141.67 (d, J(CP) = 26.6, 26.9 Hz, C_{ipso}). ^{31}P NMR (121.28 MHz, $CDCl_3$): $\delta = 121.63$ ppm/122.27 ppm. IR (CH_2Cl_2): $\nu = 1017$ cm^{-1} (P–O), 1360 cm^{-1} (CH_3), 2959, 2924, 2874 cm^{-1} (CH_3, $CH_2)_{as,s}$, 1460 cm^{-1} $(CH_2)_s$, 1450 cm^{-1} (P–Phenyl), 754, 702 cm^{-1} (Phenyl).

*4.4.7. [(R / S_P,1R,2S,5R)-(+)-menthyl-O]tert-butylphenylphosphinite **4***

Following the general procedure 3, (+)-menthol (22.84 mmol) was converted to give **4** as a colorless liquid. Yield: 5.65 g (74%), bp: 110°C ($3 \cdot 10^{-2}$ mbar).

^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.59$, 0.83 (3H, d, J(HH) = 6.6, 6.9 Hz, CH_3HCCH_3), 0.78, 0.92 (3H, d, J(HH) = 6.9 Hz, CH_3HCCH_3), 0.83, 1.63 (2H, m, $CHCH_2CH_2$), 0.88 (3H, d, J(HH) = 6.9 Hz, $HCCH_3$), 0.94, 0.95 (9H d J(PH) = 12.6 Hz, $C(CH_3)_3$), 1.36 (2H, m, $CHCH_3$, $CHCH(CH_3)_2$), 0.97, 1.63 (2H, m, CH_2CH_2CH), 0.89, 1.94, 0.94, 2.38 (2H, m, $CHCH_2CHO$), 2.32, 2.48 (1H, m, $CH(CH)(CH_3)_2$), 3.46, 3.59 (1H, m, J(PH) = 14.8, 15.1 Hz, HCOP), 7.35, 7.50 (5H, m, H_{aromat}). ^{13}C NMR (75.34 MHz, $CDCl_3$): $\delta = 15.67$, 15.86 ($CHCH_3$); 21.47, 21.50 ($CHCH_3$), 22.32, 22.48 (CCH_3); 22.92 (CH_2CH_2CH), 25.39 ($CH(CH_3)_2$), 25.32, 25.40 (d, J(CP) = 15.7, 15.6 Hz, $C(CH_3)_3$), 31.90, 32.00 ($CHCH_3$), 32.60, 32.90 (d, J(CP) = 10.6, 10.3 Hz, $C(CH_3)_3$), 34.61, 34.65 (CH_2CH_2CH), 43.39, 43.56 (d, J(CP) = 7.8, 7.4 Hz, $CHCH_2CHO$), 49.95, 50.01 (d, J(CP) = 3.8, 5.4 Hz, CH_2CHCHO), 79.84, 81.13 (d, J(CP) = 14.8, 16.2 Hz, HCOP), 127.35, 127.44 (d, J(CP) = 5.6, 7.2 Hz, C_{meta}), 128.76, 128.96 (C_{para}), 130.88, 131.26 (d, J(CP) = 21.1, 22.1 Hz, C_{ortho}), 140.63, 141.67 (d, J(CP) = 26.5, 26.7 Hz, C_{ipso}). ^{31}P NMR (121.28 MHz, $CDCl_3$): $\delta = 122.20$ ppm/121.59 ppm. $\nu = 1025$ cm^{-1} (P–O), 1383, 1361 cm^{-1} (CH_3), 2959, 2922 cm^{-1} (CH_3, $CH_2)_{as,s}$, 1484 cm^{-1} $(CH_2)_s$, 1460 cm^{-1} (P–Phenyl), 737, 703 cm^{-1} (Phenyl).

5. X-ray structure determinations

Geometry and intensity data were collected on an ENRAF–Nonius CAD4 diffractometer with graphite monochromated radiation. A summary of crystallographic data, data collection parameters, and convergence results is compiled in Table 6. In the case of both **1** · BH_3 and **9**, a numerical absorption correction [27] was applied to the data before averaging over symmetry related reflections. The structures were solved by direct methods [28]; refinement for the ligand **1** · BH_3 was performed on F^2 with the SHELXL-93 program [29], whereas the model of **9** was refined on structure factors with the local version of the MOLEN program suite [30].

Table 6
Crystallographic data, data collection parameters, and convergence results for **1** · BH_3 and **9**

	1 · BH_3	**9**
Formula	$C_{20}H_{36}BOP$	$C_{23}H_{38}IOPdP$
fw	340.78	594.84
System	orthorhombic	trigonal
Space group (no.)	$P2_12_12_1$ (19)	$P3_2$ (145)
a, Å	8.505(3)	13.980(5)
b, Å	10.82(1)	
c, Å	23.297(3)	11.292(3)
V, Å^3	2144(2)	1911(2)
Z	4	3
d_{calc}, g cm^{-3}	1.04	1.550
T, K	293	203
Radiation (λ,Å)	Cu K α (1.5418)	Mo K α (0.7107)
μ, cm^{-1}	11.25	19.89
Θ_{max}, deg	69	26
Crystal color and shape	colorless platelet	yellow rod
Crystal dimens, mm^3	0.76×0.70×0.30	0.35×0.10×0.10
Min transmission	0.456	0.780
Max transmission	0.724	0.875
No reflns.	12289	9411
Indep reflns. in refinement	3897	3865
No vars.	240	243
Unweighted agreement factor[a]	0.069	0.030
Weighted agreement factor	0.180[b]	0.037[c]
GOF[d]	0.848	0.794
Res el dens, eÅ^{-3}	0.26	0.78

[a] $R = \Sigma| |F_o| - |F_c| / \Sigma|F_o|$.
[b] $wR^2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0868 P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.
[c] $R_W = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(F_o)$.
[d] GOF = $[\Sigma w(|F_o| - |F_c|)^2 / n_{obs} - n_{var}]^{1/2}$; n_{obs}: no. of observations; n_{var}: no. of variables refined.

In the full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic displacement parameters. Hydrogen atoms (C–H = 0.98 Å). In the case of $\mathbf{1} \cdot BH_3$, a total of six groupwise defined isotropic displacement parameters was refined for the hydrogen atoms and a value of 0.07(5) was calculated for Flack's enantiopol parameter [31]. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, 76344 Eggenstein–Leopoldshafen, on quoting the depository numbers CSD-407756 (for $\mathbf{1} \cdot BH_3$) and CSD-407757 (for **9**).

Supporting information available: X-ray data for $\mathbf{1} \cdot BH_3$ and **9** including tables of positional parameters, displacement parameters and interatomic distances and angles (12 pages). Ordering information is given on any current masthead page.

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