Application of P-Stereogenic Aminophosphine Phosphinite Ligands in Asymmetric Hydroformylation

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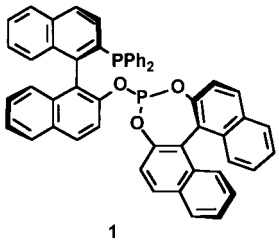
Abstract: New chiral aminophosphine phosphinite ligands with a stereogenic center at the aminophosphine phosphorus atom were prepared based on (*R*,*S*)-ephedrine as the chiral auxiliary and backbone. Substituents at the chiral aminophosphine as well as at the phosphinite phosphorus atom were varied. These new ligands were applied to the rhodium-catalyzed asymmetric hydroformylation of vinyl arenes. The enantiomeric excess reached up to 77%. ^{1}H and ^{31}P NMR studies of the Rh complexes under syngas pressure reveal that [HRh(CO)$_2$(P^P)] complexes with the NP* moiety in an axial position are responsible for enantioselectivity.

Keywords: aminophosphine · asymmetric hydroformylation · catalysts · P ligands · phosphinite · rhodium

Introduction

Aldehydes are among the most versatile building blocks in synthetic organic chemistry. A huge variety of functionalized compounds are available on this basis. Access to enantiomerically pure aldehydes from cheap olefinic substrates through asymmetric catalysis has therefore attracted enormous interest, spurred by the recent achievements made in this field.[1, 2] For many years, the platinum catalyst systems activated with tin chloride and modified by diphosphine ligands, as described by Stille,[3] were the only systems to give high enantiomeric excess (*ee*). These systems, however, suffer from low regioselectivity and large amounts of undesired byproducts as well as from racemization of the product due to the Lewis acidity of the promoter. In the rhodium-catalyzed reaction, the standard C_2-symmetrical diphosphine ligands lead to moderate to low enantioselectivity, but high regio- and chemoselectivity. The breakthrough in this field came with the work reported by Takaya and Nozaki,[4] and the results of Babin and van Leeuwen.[2, 5] In the first case the ligands are C_S-symmetrical phosphine phosphites based on a chiral binaphthalene backbone. The ligands used by Babin and van Leeuwen are C_2-symmetrical diphosphites based on a chiral 2,4-pentanediol backbone.

At a first glance, these two types of ligands seem to be quite different, since the phosphine phosphite (*R*,*S*)-BINAPHOS **1** adopts an equatorial–axial coordination in the catalytically



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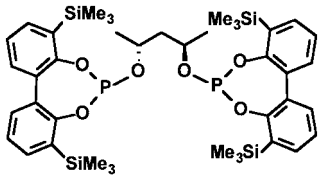

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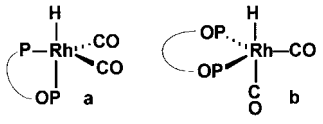
active hydrido-rhodiumcarbonyl complex (structure a),[4] whereas the diphosphite **2** coordinates in a bis-equatorial fashion (structure b).[2]



In situ NMR studies reveal that in both cases there is just one active hydridocarbonyl species present in solution under syngas pressure. This seems to be the key feature in controlling efficient chirality transfer, resulting from the conformationally more flexible rhodium systems compared with

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platinum catalysts. Only the combination of controlling the coordination mode of the ligand and differentiation between the two remaining possible coordination sites will give rise to high enantioselectivity. The coordination mode is efficiently controlled by the preferred chelation bite angle of the ligand. For BINAPHOS this is about 90°, while larger bite angles >100° result for the diphosphites.

Once the coordination mode of the ligand as well as the complex geometry and conformation are defined, efficient differentiation of the possible coordination sites is crucial. In order to accomplish this, it should be helpful to bring the center of chirality as close to the metal as possible. After our success with P-chiral ligands in the asymmetric hydrovinylation reaction,[6] we decided to design new P-chiral chelating ligands for use in asymmetric hydroformylation.

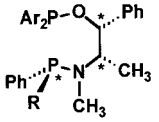
We report here on the synthesis of new diastereomerically pure aminophosphine phosphinites **6** that possess a stereogenic center at the nitrogen bound phosphorus atom and their application in the asymmetric hydroformylation of vinylarenes. Changing the electronic nature of the substituents in the phosphinite and aminophosphine moieties results in different coordination behavior of the ligands. This was studied by in situ high-pressure NMR techniques. The results obtained illustrate the power of a stereogenic phosphorus atom to control enantioselectivity in the hydroformylation reaction.

Results and Discussion

Ligand synthesis: Following a route described by Jugé et al.,[7] the borane-protected hydroxy aminophosphines **4** were prepared in high diastereomeric purity.[8] Starting from bis(diethylamino)phenyl phosphine with (−)-(*R,S*)-ephedrine as auxiliary, the borane-protected 1,3,2-oxazaphospholidines **3** can be obtained in high yields and diastereoselectivities (Scheme 1). Ring opening of the oxazaphospholidines with an organolithium reagent results in exclusive cleavage of the P–O bond to give the hydroxy compounds **4**. These intermediates represent ideal starting materials to produce a whole series of chelating ligands by conversion with a chlorophosphine in the presence of a base. The final products are obtained in good yields and with a high degree of diastereomeric purity. Deprotection is accomplished by refluxing the borane adduct in diethylamine. The products can be purified by simple flash chromatography over basic alumina (Scheme 1).

The absolute configuration of the aminophosphine phosphorus atom could not be assigned, but the diastereomeric excess was shown to be ≥92% *de* by $^{31}P\{^1H\}$ NMR spectroscopy. The route presented here allows the very variable synthesis of a large number of P-chiral ligands of this type. As was already shown by Petit and Mortreux, the aminophosphine phosphinite ligand family provides an enormous potential for variation and ligand fine-tuning for a number of transition metal catalyzed reactions.[9, 10] With the introduction of a stereogenic center at the phosphorus atom, the possibilities for variation are even larger. On the basis of (−)-ephedrine the ligands **6a–6i** listed in Table 1 were prepared.[11]

Table 1. Prepared aminophosphine phosphinite and phosphite ligands.



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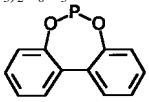
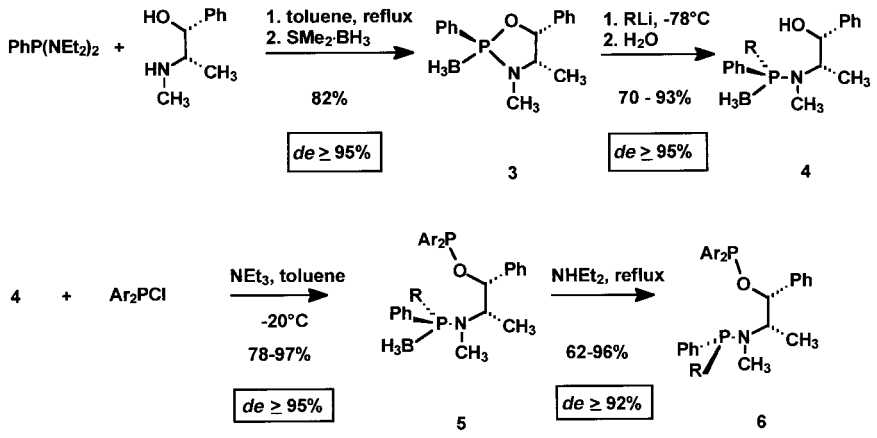
Ligand	R	Ar
6a	CH_3	Ph
6b	CH_3	4-CH_3-C_6H_5
6c	CH_3	3,5-$(CF_3)_2C_6H_3$
6d	CH_3	Ar_2P = 
6e	*n*-Bu	Ph
6f	*n*-Bu	4-CH_3-C_6H_5
6g	*n*-Bu	3,5-$(CF_3)_2C_6H_3$
6h	Ph	Ph
6i	1-naphth	Ph

Hydroformylation experiments: The diastereomerically pure P-chiral aminophosphine phosphinite ligands have been used in the rhodium-catalyzed asymmetric hydroformylation of styrene, other vinyl arenes, and vinyl acetate. The catalysts were prepared in situ by adding the chelating ligands L to [(acac)Rh(CO)$_2$] as the catalyst precursor. By converting the precursor complex with the chelating ligands, the CO was immediately replaced and bright yellow solutions formed. Under hydroformylation conditions the active catalyst [HRh(L)(CO)$_2$] was formed readily. In all experiments an excess of the ligand was used to avoid the formation of [HRh(CO)$_4$], which is a highly active but achiral hydroformylation catalyst.



Scheme 1. Diastereoselective route to aminophosphine phosphinite and phosphite ligands containing a stereogenic P atom.

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The results obtained in the asymmetric hydroformylation of styrene are summarized in Table 2. The substituents on the phosphorus atoms of the phosphinite and aminophosphine moieties were varied in order to study their influence on the catalyst activity and selectivity. The highest enantioselectivities are obtained with ligands bearing no substituent or an electron-donating group on the phenyl groups in the $-OPAr_2$ moiety (Entries 1, 2, 5, and 6). Lowering the electron density on the $-OPAr_2$ phosphorus atom by introducing electron-withdrawing groups or changing the phosphinite into a phosphite group significantly decreases the enantioselectivity (Entries 3, 4, and 7).

Table 2. Hydroformylation of styrene with $[HRh(L)(CO)_2]$, L = **6a**–**6i**.[a]

Entry	Ligand	TON	iso:*n* [%][b]	*ee* [%][c]
1	**6a**	39	98:2	75
2	**6b**	41	98:2	71
3	**6c**	104	95:5	32
4	**6d**	12	97:3	58
5	**6e**	71	98:2	75
6	**6f**	44	98:2	73
7	**6g**	244	95:5	46
8	**6h**	302	92:8	10
9	**6i**	151	80:20	10

[a] 17.4 mmol styrene; 20 mL toluene; styrene /Rh = 500; $p_{(CO/H_2)} = 20$ bar; $CO/H_2 = 1:1$; $T = 50\,^{\circ}C$; $t = 20$ h; L:Rh = 3:1; [Rh] = 1.74 mmol L^{-1}. [b] Selectivity to branched and linear aldehyde. [c] Determined by chiral GC after reduction of the aldehyde and conversion to the trifluoroacetate.

For the electron-withdrawing CF_3 substituents, the activity increased by a factor of 2–5 (Entries 3 and 7). Changing the R substituent on the chiral phosphorus atom from methyl to *n*-butyl did not change the stereoselectivity or activity of the catalyst. The introduction of a 1-naphthyl group resulted in a considerable decrease in enantioselectivity to only 10%, which was also observed for ligand **6h** without a stereogenic center at the phosphorus atom (Entries 8 and 9). Apart from ligand **6i** (Entry 9) the regioselectivity to the branched aldehyde 2-phenylpropanal always exceeds 90% as is expected for styrene and similar kind of substrates.[12] In all cases the configuration of the major stereoisomer of the 2-phenylpropanal was determined to be *S*. This was accomplished by comparing the retention times from gas chromatography (GC) with a sample obtained with the ligand (*R*,*S*)-BINAPHOS, for which the absolute configuration of the product is described to be always *R*. Under our reaction conditions (see footnotes in Table 2) the enantiomeric excess (*ee*) obtained with (*R*,*S*)-BINAPHOS is 92%.

For ligand **6a** the influence of different reaction parameters on the performance of the catalyst system was examined. Lowering the reaction temperature from 60 °C to 40 °C increases the *ee* from 50% to 77%. On the other hand, the activity decreases by a factor of 10. Temperatures higher than 60 °C caused deterioration of the catalyst system and the *ee* was reduced to almost zero at 80 °C. The brown color of the reaction mixture after reaction indicated that rhodium carbonyl clusters had been formed, probably due to decomposition of the ligand. However, at 60 °C the ligand is stable. Conversion can be completed by applying longer reaction times without loss of enantioselectivity.

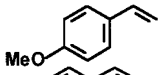
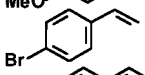
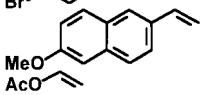
Increasing the syngas pressure from 20 to 60 bar CO/H_2 (1:1) had a negative effect both on activity and enantioselectivity. It was expected that increasing the pressure would have a negative effect on the activity, since dissociation of CO and coordination of the olefin is commonly regarded as the rate-determining step.[13] It was shown by Buisman et al. for the asymmetric hydroformylation of styrene using diphosphite ligands, that an increased hydrogen partial pressure has a negative influence on the enantioselectivity.[2c] However, this effect is not very pronounced in the systems studied here.

In order to obtain high enantiomeric excess, it is essential to apply a larger excess of ligand (4 equiv with respect to Rh). Also at lower L/Rh ratios, $[HRh(CO)_4]$ can be formed.

In contrast to the results obtained with diphosphites, the preformation time of the catalyst with the new AMPP ligands had only little or no influence on the catalyst performance. This is in accordance with our NMR studies, which indicate that the active species, $[HRh(L)(CO)_2]$, is formed rapidly in the presence of syngas.

After the promising results we obtained in the hydroformylation of styrene, which gave an *ee* of up to 77% in 2-phenylpropanal and high selectivity to the branched aldehyde (98:2), we applied the new P-chiral AMPP ligands in the hydroformylation of other vinyl derivatives (see Table 3).

Table 3. Hydroformylation of vinylic substrates with $[HRh(L)(CO)_2]$, L = **6a**.[a]

Entry	Substrate	TON	iso:*n* [%][b]	*ee* [%]
10		20	92:8	58
11[c]		76	98:2	71
12		20	98:2	64
13		23	82:18	62

[a] 17.4 mmol styrene; 20 mL toluene; styrene/Rh = 500; $p(CO/H_2) = 20$ bar; $CO/H_2 = 1:1$; $T = 50\,^{\circ}C$; $t = 20$ h; L:Rh = 3:1; [Rh] = 1.74 mmol L^{-1}. [b] Selectivity to branched and linear aldehyde. [c] $T = 40\,^{\circ}C$.

The 4-bromo-styrene derivative shows a considerably higher reactivity, even when the temperature is 10 °C lower (Entry 11). The *ee* obtained is also slightly higher than for the other substrates and is comparable with that found for styrene.

Structures of hydroformylation catalysts in solution: The catalysts were prepared in situ by treating the precursor complex $[Rh(acac)(CO)_2]$ with the appropriate amount of ligand (Scheme 2).

On mixing solutions of $[Rh(acac)(CO)_2]$ and ligands **6a**–**6i**, displacement of CO was observed immediately. Bright yellow solutions were formed, and IR and ^{31}P NMR spectroscopy showed that both carbonyl ligands had been removed and the phosphorus ligands formed a chelate with the rhodium center. In the $^{31}P\{^1H\}$ NMR spectra of the complexes, a doublet of doublets occurred in addition to the signals of the free ligand. Spectra of the solutions prepared with a 1:1 ratio

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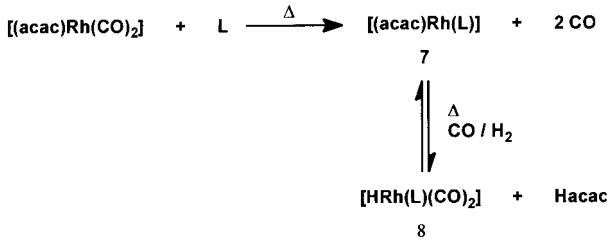
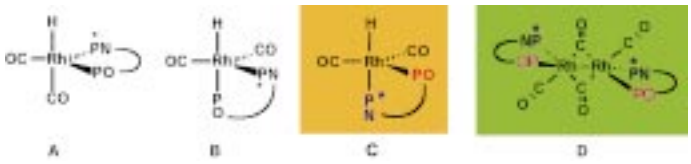


Scheme 2. In situ preparation of catalysts.

of $[Rh(acac)(CO)_2]$ and ligand only contain the signals of the $[(L)Rh(acac)]$ complex indicating that the complex formation is quantitative.

Characterization of $[HRh(L)(CO)_2]$ complexes: The $[HRh(L)(CO)_2]$ complexes were generated in situ by treating $[Rh(acac)(CO)_2]$ with two equivalents of ligand at 40 °C under a syngas pressure of 50 bar ($CO/H_2 = 1:1$) over three hours. The resulting complexes were characterized by ^1H and ^{31}P NMR, and IR spectroscopy. The NMR spectra were recorded at 303 K under a syngas pressure of 20 bar CO/H_2 (1:1).

In principle, three different isomeric mononuclear hydrido rhodium complexes **A**–**C** with a trigonal bipyramidal structure can be formed.



It turned out that in the case of ligands giving rise to high enantiomeric excesses (**6a**, **6b**, **6e**, and **6f**), only two species are formed under these conditions. In addition to a catalytically inactive dinuclear carbonyl-bridged complex **D**, only species **C** with the PN moiety in the axial position and the PO moiety bound in the equatorial position is observed. Figure 1 shows the $^{31}P\{^1H\}$ NMR and the $^{31}P,^1H$ NMR spectra for ligand **6a**. The two singlets at $\delta = 50.7$ (PN) and 113.9 (PO)

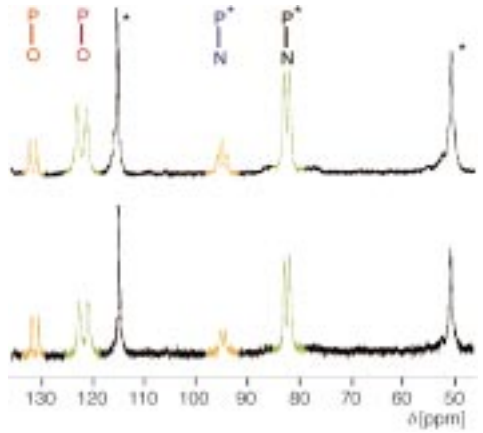


Figure 1. $^{31}P\{^1H\}$ NMR (lower trace) and $^{31}P,^1H$ NMR spectra (upper trace) of $[HRh(L)(CO)_2]$, L = **6a**, at 20 bar ($CO:H_2 = 1:2$) and 303 K; L:Rh = 2:1.

are the signals of the free ligand, which is present in excess. Two broad double doublets at $\delta = 82.1$ (PN, $^1J_{(NP\text{-}Rh)} = 123$ Hz, $^2J_{(NP\text{-}PO)} = 15$ Hz), and 121.1 (PO, $^1J_{(OP\text{-}Rh)} = 216$ Hz) are assigned to the dinuclear complex **D**.[14]

Complex **C** gives rise to a doublet of doublets at $\delta = 94.5$ (PN, $^1J_{(NP\text{-}Rh)} = 112$ Hz, $^2J_{(NP\text{-}PO)} = 17$ Hz), and 130.4 (PO, $^1J_{(OP\text{-}Rh)} = 157$ Hz). These assignments are confirmed by correlation of the peak integration areas of the signals. In the $^{31}P,^1H$ NMR spectrum, only the signal of the PN moiety of the hydrido complex shows further splitting, due to a large coupling $^2J_{(NP\text{-}H)} = 118$ Hz with the axial hydride in a *trans* position. Large $J_{(P\text{-}H)}$ constants have been reported before for hydrogen and phosphorus with a *trans* relation at a rhodium center.[4a, 15] In the coupled spectrum, there is no indication of a species with a PO moiety *trans* to the hydride. The signal of the PO is slightly broadened due to the small *cis* coupling ($^2J_{(OP\text{-}H)} = 12$ Hz). In the ^1H NMR spectrum, the hydride signal is a doublet of pseudo triplets resulting from the large 118 Hz $^2J_{(H\text{-}PN)}$ coupling and two couplings $^1J_{(H\text{-}Rh)}$ and $^2J_{(H\text{-}PO)}$ both with a value of 12 Hz (Figure 2).

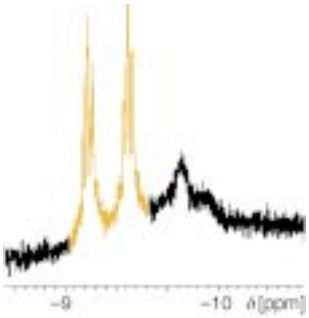
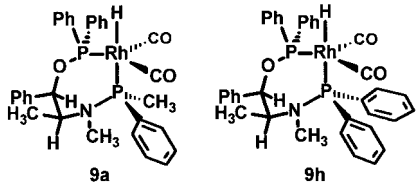


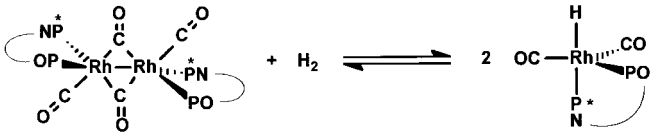
Figure 2. Hydride region of the ^1H NMR spectrum of $[HRh(L)(CO)_2]$, L = **6a**.

Similar results have been described by Pottier with the EPHOS ligand **6h**. They also showed that there is only one hydride species present in solution containing NP in axial and OP in equatorial positions, as well as a dinuclear complex.[16] The important point is that both ligands **6a** and **6h** show the same coordination mode, while in **9a** the aminophosphine phosphorus atom represents an additional homochiral stereogenic center. Complex **9h** gives an *ee* of only 10% under our reaction conditions, whereas **9a** gives 77%.



This clearly demonstrates the importance of the additional chirality at the phosphorus atom. From this point of view, the chiral phosphorus atom bearing one relatively small and one larger group gives rise to efficient stereodifferentiation of the two possible coordination sites. This also explains why the P-chiral ligand **6i** with two substituents similar in shape gives poor enantioselectivity.

The catalytically inactive dinuclear complex **D** is in equilibrium with the hydrido complex **C** under the NMR experimental conditions. This was shown by varying the hydrogen partial pressure as well as by lowering the rhodium complex concentration during the measurements.



Increasing the hydrogen partial pressure from 10 bar ($P_{(CO/H_2)} = 20$ bar, $CO:H_2 = 1:1$) to 20 and 40 bar caused the ratio of complexes **D**:**C** to vary from 17:1 to 2.5:1 and 2:1, respectively. A similar effect was observed by lowering the complex concentration from 51 mmol L^{-1} to 33 mmol L^{-1} at a syngas pressure of 20 bar ($CO:H_2 = 1:1$).[14] This increased the amount of the active hydride from the initial 17:1 ratio to 3.5:1 **D**:**C**. After releasing the syngas pressure from the NMR tube, only the dinuclear complex **D** remained as could be seen from the ^{31}P NMR spectrum and no hydride was observed in the ^{1}H NMR spectrum. The IR spectrum of this solution shows a band at 1788 cm^{-1} that results from the bridging CO groups and a band at 1988 cm^{-1}, which is typical for a terminal CO group. This is also in agreement with the C_2-symmetrical structure we assigned for **D** from the ^{31}P NMR data.

Since the rhodium concentrations for the NMR experiments were about 30 times higher than those of the catalytic reactions (51 mmol L^{-1} versus 1.74 mmol L^{-1}), we also performed high pressure in situ IR spectroscopy. At a rhodium concentration of 1.74 mmol L^{-1} under a syngas pressure of 20 bar ($CO:H_2 = 1:1$) at 323 K there was no indication for bridging CO groups. The spectrum shows three bands in the carbonyl and hydride region at 2021, 1994, and 1943 cm^{-1} (Figure 3).

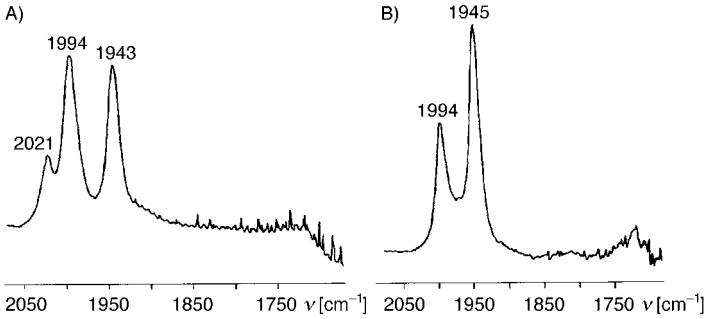


Figure 3. In situ IR spectrum of $[HRh(L)(CO)_2]$, L = **6a** (L:Rh = 2:1), 323 K. A) 20 bar ($CO:H_2 = 1:1$). B) 20 bar ($CO:D_2 = 1:1$).

The band at 2021 cm^{-1} could be assigned to the Rh–H vibration by replacing CO/H_2 with CO/D_2. The two bands at 1994 and 1943 cm^{-1} remained unchanged, while the band at 2021 cm^{-1} disappeared. This underlines the results of the NMR experiments, that there is no bis-equatorial complex present because these would lead to frequency shifts of the carbonyl bands upon the exchange.[17]

In contrast to the behavior described for the ligands **6a**, **6b**, **6e**, and **6f** that gives rise to high enantiomeric excess, the ligands bearing electron-withdrawing groups in the phosphinite part show a mixture of several different species in solution. The signals obtained in the ^{31}P NMR under syngas pressure are very broad, indicative of a fluctional behavior of the complexes.[5c] By using ligand **6g**, however, four sets of signals were obtained that were interpreted as a mixture of all four possible complexes **A**–**D** present in solution under these conditions. Signals remained broad and unresolved for ligands **6c**, **6d**, and **6g** on cooling down to 223 K. By introducing electron-withdrawing groups in the phosphinite part, the donor character is decreased and the acceptor ability is increased. When the two different phosphorus atoms in the ligand have similar electronic properties, there is no longer a preference for either an axial or an equatorial mode of coordination.

Conclusions

Aminophosphine phosphinite ligands derived from (−)-ephedrine with a stereogenic center at the aminophosphine phosphorus atom are successful ligands in the asymmetric hydroformylation of styrene and other vinylic substrates. High enantioselectivity (up to 77%) and high selectivity to the branched aldehydes (up to 98%) is obtained under mild reaction conditions (40–50 °C, 20 bar CO/H_2). The results highlight that the presence of the additional stereogenic center at the aminophosphine phosphorus atom increases the enantioselectivity significantly. Investigation of the hydrido rhodium complexes under syngas pressure by NMR and IR spectroscopy showed that the actual structure of these complexes has a great influence on the enantioselectivity. Ligands that give high *ee*'s coordinate in a stable axial/equatorial manner, with the aminophosphine moiety in the axial position of the trigonal bipyramidal complex. We assign this species to be responsible for good enantioselection. The ligands, which form seven-membered ring chelates with a flexible ligand backbone, prefer bite angles of about 90° and hence equatorial/axial coordination. By changing the electronic properties of the phosphinite part to become more electron-accepting, the complexes become fluctional and the *ee*'s drop considerably. It is therefore evident that in order to control the complex configuration and conformation, the two phosphorus atoms must have different donor/acceptor properties. This is the case for the ligands **6a**, **6b**, **6e**, and **6f**. Once the complex configuration is defined, differentiation between the two remaining coordination sites should be brought about. For the new AMPP ligands, this task is achieved by the chiral phosphorus atom bearing two different substituents. It is evident that these should be different in size and shape. In the case of the (*R*,*S*)-BINAPHOS ligand, the differentiation is achieved by the fixed conformation of the (*S*)-binaphthalene part of the phosphite, which efficiently shields one coordination site.

So far, the activity of the catalyst systems with our P-chiral AMPP ligands is too low for practical purposes. Based on the encouraging results obtained by using this new type of ligands, work is in progress to make use of this concept for more active and stable catalysts.

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Experimental Section

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 over molecular sieves (Linde 4 Å). Solvents were freshly distilled under argon atmosphere and dried by standard procedures. Air and moisture sensitive solutions and reagents were handled by 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 (^{1}H, ^{13}C, respectively), or external 85 % H_3PO_4 (^{31}P). ^{31}P and ^{13}C NMR spectra were measured ^{1}H decoupled unless otherwise stated. IR spectra were recorded on a Nicolet 5130-FT-IR spectrometer and processed with the OMNIC software. Chemicals were purchased from Fluka and Aldrich. Styrene was distilled under argon atmosphere after drying over CaH_2. All other substrates were distilled prior to use and stored under argon at −30 °C. 2-Methoxy-6-vinylnaphthalene was dissolved in toluene and filtered over neutral alumina. The syngas used was mixed in house in a 1:1 ratio from 3.0 quality CO and H_2. The phosphorus compounds $PhP(NEt_2)_2$,[18] $Cl_2P(NEt_2)$,[18] $ClP(3,5\text{-}(CH_3)_2\text{-}C_6H_3)_2$,[19] and $ClP(4\text{-}CH_3\text{-}C_6H_3)_2$[19] were prepared by literature procedures. Elemental analyses were performed on a Carlo Erba CHN-Analyzer 1106. Gas chromatographic analyses for styrene, 4-methoxy styrene, 2-methoxy-6-vinylnaphthalene, and 4-bromo styrene were run on a Siemens Sichromat 2 apparatus (split/splitless injector, 25 m Ultra 2 column, carrier gas 101.3 kPa N_2, FID detector). The analyses for vinyl acetate were run on the same apparatus, but with a different capillary column (50 m Pona (HP), carrier gas 152 kPa He). The integration system HP 3359 was used for all GC analyses. Enantiomeric excess for styrene, 4-methoxy styrene, and 4-bromo styrene was determined after reduction of the aldehydes and conversion to the corresponding trifluoroacetates. For styrene and 4-bromo styrene the trifluoro acetates are analyzed on a 25 m Lipodex E cyclodextrin column (carrier gas 50.6 kPa H_2). For 4-methoxy styrene a 25 m FS-Cyclodex β I/P column (carrier gas 81 kPa H_2) was used, and for 2-acetoxypropanal from vinyl acetate, which was analyzed without derivatization, a 50 m β I/P (7 %) column (carrier gas 141.8 kPa H_2) was used. For the enantiomer analyses in all cases a Carlo Erba 2300 apparatus was used (split/splitless injector, FID detector). For 2-methoxy-6-vinylnaphthalene the enantiomeric excess was determined from the alcohol after reduction with $LiAlH_4$ using HPLC on a (*S*,*S*)-Whelk-O 1 (4 × 250 mm) column with cyclohexane/*iso*-propanol (95:5) as eluent (303 K, UV detector).

Hydroformylation experiments: In a typical experiment, the autoclave was heated to 60 °C, dried under reduced pressure for about 1 h, and filled with argon. The catalyst precursor $[Rh(acac)(CO)_2]$ (0.035 mmol) and the ligand (0.104 mmol, P/Rh ratio of 3) were each dissolved in toluene (5 mL). After mixing and stirring for 15 min the solution was transferred into the autoclave by syringe. The autoclave was purged three times with syngas ($CO/H_2 = 1:1$), pressurized to the appropriate initial pressure, and put into a preheated bath. In runs with separate catalyst preformation the mixture was stirred for the appropriate time (1 h or 15 h). Styrene (2.0 mL, 17.4 mmol in 5 mL of toluene, total solvent volume 20 mL) was introduced into the autoclave and the reaction mixture was stirred for the desired time. The autoclave was then cooled, depressurized, and vented with argon. A weighed amount of standard (1.50 g) was added and the reaction mixture was directly distilled under high vacuum into a dry ice trap to remove the catalyst. A sample was analyzed by GC. For measuring the enantiomeric excess a sample of the distilled reaction mixture was dropped to a suspension of $LiAlH_4$ in diethyl ether under ice cooling. This reaction mixture was stirred at room temperature for additional 3 h and quenched with water. The mixture was extracted three times with diethyl ether. The combined organic layers were dried over sodium sulfate, and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and trifluoroacetic acid anhydride was added at room temperature. After removing the solvent, the resulting trifluoroacetate was distilled in vacuum and analyzed on a chiral GC column.

Preparation of $[HRhL(CO)_2]$ complexes and NMR measurements: In a typical experiment a dried 13 mL autoclave was filled with $[Rh(acac)(CO)_2]$ (0.0922 mmol), ligand (0.191 mmol, ligand to Rh ratio of 2), and $[D_8]$toluene (1.8 mL). The autoclave was purged three times with syngas ($CO/H_2 = 1:1$) and pressurized to 50 bar. After 3 h at 40 °C the autoclave was cooled and depressurized and the solution was transferred into the NMR tube, which was immediately pressurized again to the appropriate pressure and analyzed.

Ligand Preparation

(Ξ_P,4*S*,5*R*)-2,5-Diphenyl-3,4-dimethyl-1,3,2-oxazaphospholidine-2-borane (3): This compound was prepared according to a procedure reported by Jugé.[7] (*R*,*S*)-Ephedrin (37 mmol, 6.08 g) was azeotropically dried by three cycles of dissolving in toluene and evaporating. It was then dissolved in toluene (180 mL) together with fresh distilled $PhP(NEt_2)_2$. The mixture was refluxed for 18 h, during which the diethylamine was removed from the top of the reflux condenser. To assure complete conversion, the reaction mixture was degassed three times in between by means of vacuum. The mixture was allowed to cool to room temperature and a solution of $BH_3 \cdot CS_2$ (0.074 mmol, 36.8 mL of a 2 M solution in toluene) was added. After stirring at room temperature for 12 h, the solvent was removed in vacuum to yield a viscous oil. The crude product was recrystallized from methanol (30 mL) at −20 °C. Yield: 82 % (30.3 mmol, 8.58 g). Mp: 98 °C; *de* ≥ 95 % (^{31}P{^{1}H} NMR); ^{31}P NMR ($CDCl_3$): $\delta = 133.4$ (q, $^1J_{(P\text{-}B)} = 65.8$ Hz); ^{13}C NMR ($CDCl_3$): $\delta = 136.8 - 127.2$ (C arom), 84.8 (O*C*HPh), 59.2 (N*C*H(CH_3)), 29.8 (N*C*H$_3$), 14.1 (CH*C*H$_3$); ^{1}H NMR ($CDCl_3$): $\delta = 7.78 - 7.19$ (m, 10 H; arom), 5.52 (dd, $^3J = 3.0$ Hz, $^3J_{(H\text{-}P)} = 6.0$ Hz, 1 H; O*CH*Ph), 3.64 – 3.57 (m, 1 H; N*CH*(CH_3), 2.60 (d, $^3J_{(H\text{-}P)} = 11.0$ Hz, 3 H; N*CH*$_3$), 0.75 (d, $^3J = 6.5$ Hz, CH(*CH*$_3$)), 1.6 – 0.4 (br m, 3 H; BH_3).

(Ξ_P,1*R*,2*S*)-2-*N*-Methyl-*N*-(methylphenylphosphinoborane)-2-amino-1-phenylpropane-1-ol (4a): The oxazaphospholidine **3** (18 mmol, 5.02 g) was dissolved in THF (60 mL) in a Schlenk flask equipped with a rubber septum. At −78 °C MeLi (20 mmol, 25.1 mL of a 0.8 M solution in diethyl ether) was introduced dropwise through a syringe. After complete addition the mixture was stirred for an additional 2 h at −78 °C and was allowed to warm to room temperature overnight. The reaction was monitored by TLC (5 % EtOAc/toluene (v/v), $R_f = 0.20$, starting material $R_f = 0.55$). The reaction mixture was hydrolyzed with water (20 mL) and the THF was removed in vacuum. The mixture was taken up in CH_2Cl_2 (20 mL) and separated, and the aqueous phase was extracted with CH_2Cl_2. The combined and dried ($MgSO_4$) organic phases were evaporated to dryness. Yield: 97 % (17.5 mmol, 5.30 g) of a white powder; *de* ≥ 95 % (^{31}P{^{1}H} NMR); ^{31}P NMR ($CDCl_3$): $\delta = 66.7 - 66.0$ (m); ^{13}C NMR ($CDCl_3$): $\delta =$ 141.6 – 125.8 (C arom), 76.5 (O*C*HPh), 57.0 (N*C*H(CH_3)), 27.9 (N*C*H$_3$), 13.1 (CH(*C*H$_3$)), 10.2 (d, $^1J_{(C\text{-}P)} = 41.0$ Hz, P*C*H$_3$); ^{1}H NMR ($CDCl_3$): $\delta = 7.42 -$ 7.00 (m, 10 H; arom), 4.67 (d, $^3J = 7.2$ Hz, 1 H; O*CH*(Ph)), 3.98 (dq, $^3J =$ 7.2 Hz, $^3J = 6.7$ Hz, 1 H; N*CH*(CH_3)), 2.40 (d, $^3J_{(H\text{-}P)} = 7.8$ Hz, 3 H; N*CH*$_3$), 2.32 (br s, 1 H; O*H*), 1.45 (d, $^2J_{(H\text{-}P)} = 8.9$ Hz, 3 H; P*CH*$_3$), 1.17 (d, $^3J = 6.7$ Hz, 3 H; CH(*CH*$_3$)), 2.0 – 0.1 (br m, 3 H; B*H*$_3$).

(Ξ_P,1*R*,2*S*)-2-*N*-Methyl-*N*-(*n*-butylphenylphosphinoborane)-2-amino-1-phenylpropane-1-ol (4b): This compound was prepared by the procedure described for **4a**. The oxazaphospholidine **3** (5.30 mmol, 1.51 g) in THF (40 mL) was converted with *n*-BuLi (5.83 mmol, 2.8 mL of a 2.1 M solution in hexane). The reaction was monitored by TLC (5 % EtOAc/toluene (v/v), $R_f = 0.29$). Yield: 97 % (5.14 mmol, 1.77 g) of a colorless oil; *de* ≥ 95 % (^{31}P{^{1}H} NMR); ^{31}P NMR ($CDCl_3$): $\delta = 71.4 - 70.7$ (m); ^{13}C NMR ($CDCl_3$): $\delta = 141.5 - 124.2$ (C arom), 77.4 (O*C*H(CH_3)), 57.0 (N*C*H(CH_3)), 28.1 (C(*C*H$_3$)), 24.2 – 23.0 ((*C*H$_2$)$_3$), 12.6 (N*C*H$_3$), 11.9 (H$_3$*C*(CH$_2$)$_3$); ^{1}H NMR ($CDCl_3$): $\delta = 7.40 - 7.23$ (m, 10 H; arom), 4.80 (d, $^3J = 6.0$ Hz, 1 H; O*CH*(Ph)), 4.02 – 3.90 (dq, $^3J = 6.0$ Hz, $^3J = 6.9$ Hz, 1 H; N*CH*(CH_3)), 2.53 (d, $^3J_{(H\text{-}P)} = 7.8$ Hz, 3 H; N*CH*$_3$), 1.80 – 1.34 (m, 7 H; P(*CH*$_2$)$_3$, O*H*), 1.15 (d, $^3J = 6.9$ Hz, 3 H; CH(*CH*$_3$)), 0.91 (t, $^3J = 6.9$ Hz, 3 H; CH$_2$*CH*$_3$), 1.80 – 0.32 (br m, 3 H; B*H*$_3$).

(Ξ_P,1*R*,2*S*)-2-*N*-Methyl-*N*-(1-naphthylphenylphosphinoborane)-2-amino-1-phenylpropane-1-ol (4c): In a 100 mL Schlenk flask equipped with a rubber septum, sec-BuLi (19 mmol, 16.56 mL of a 1.165 M solution in diethyl ether) in diethyl ether (10 mL) was cooled to −78 °C. A solution of 1-bromonaphthalene (23 mmol, 4.79 g) in diethyl ether (10 mL) was added dropwise by using syringe. During addition, the naphthyllithium precipitated as a white solid. The reaction was monitored by TLC (5 % EtOAc/toluene (v/v), R_f (bromonaphthalene) = 0.65) and upon complete conversion of the bromonaphthalene, THF (20 mL) was added to the mixture. The oxazaphospholidine **3** (17 mmol, 5.00 g) was dissolved in THF (30 mL) in a second flask and cooled to −78 °C. The suspension of naphthyllithium was transferred by using syringe and added slowly in order to keep the

temperature at −78 °C. After the addition was complete, the mixture was allowed to warm to room temperature overnight. The mixture was hydrolyzed with water (30 mL), and the THF was removed in vacuum. The remaining suspension was mixed with CH_2Cl_2 (20 mL) and separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave the product **4c** as a pale yellow, highly viscous oil, which was further purified by column chromatography (5% EtOAc/toluene (v/v), $R_f = 0.31$). Yield: 61% (10.37 mmol, 4.42 g) of a colorless viscous oil; $de \geq 95\%$ ($^{31}P\{^1H\}$ NMR); ^{31}P NMR ($CDCl_3$): $\delta = 71.5$ (m); ^{13}C NMR ($CDCl_3$): $\delta = 143.7-124.5$ (C arom), 78.5 (O*C*HPh), 57.0 (N*C*H(CH_3)), 28.1 (N*C*H$_3$), 13.9 (CH(*C*H$_3$)); ^1H NMR ($CDCl_3$): $\delta = 7.40-7.23$ (m, 10H; arom), 5.01 (d, $^3J = 3.7$ Hz, 1H; OC*H*(Ph)), 4.53 (dq, $^3J = 3.7$ Hz, $^3J = 6.6$ Hz, 1H; NC*H*(CH_3)), 2.65 (d, $^3J_{(H\text{-}P)} = 7.5$ Hz, 3H; NC*H*$_3$), 1.97 (br s, 1H; O*H*), 1.33 (d, $^3J = 6.6$ Hz, 3H; CH(C*H*$_3$)), 2.36–0.91 (br m, 3H; B*H*$_3$).

(Ξ_P1*R*,2*S*)-2-*N*-Methyl-*N*-(methylphenylphosphino)-2-amino-1-phenyl-1-(diphenylphosphinoxy)propane (6a): In a 50 mL Schlenk flask equipped with a rubber septum, compound **4a** (3.5 mmol, 1.06 g) and triethylamine (7.34 mmol, 0.78 g) were dissolved in toluene (15 mL) and cooled to −20 °C. A solution of freshly distilled $ClPPh_2$ in toluene (5 mL) was slowly added by using syringe. The resulting suspension was allowed to warm to room temperature overnight and the ammonium salt was filtered off over a 3 cm pad of Celite. The solvent was evaporated, and the residue dried in high vacuum. Yield: 92% (3.22 mmol, 1.57 g) of **5a** as a highly viscous colorless oil; $de \geq 95\%$ ($^{31}P\{^1H\}$ NMR); ^{31}P NMR (C_6D_6): $\delta = 113.8$ (s, PO), 68.3 (m, PN); ^{13}C NMR (C_6D_6): $\delta = 142.7-125.7$ (C arom), 86.4 (O*C*HPh), 58.3 (N*C*H(CH_3)), 28.3 (CH(*C*H$_3$)), 15.6 (N*C*H$_3$), 11.1 (P*C*H$_3$); ^1H NMR (C_6D_6): $\delta = 7.67-6.80$ (m, 20H; arom), 4.88 (dd, $^3J = 8.7$ Hz, $^3J_{(H\text{-}PO)} = 8.7$ Hz, 1H; OC*H*(Ph)), 4.72 (dq, $^3J = 8.7$ Hz, $^3J = 8.7$ Hz, 1H; NC*H*(CH_3)), 1.96 (d, $^3J_{(H\text{-}PN)} = 8.4$ Hz, 3H; NC*H*$_3$), 1.30 (d, $^3J_{(H\text{-}PN)} = 6.6$ Hz, 3H; PC*H*$_3$), 1.14 (d, $^3J = 8.7$ Hz, 3H; CH(C*H*$_3$)), 2.27–0.76 (br m, 3H; B*H*$_3$).

For deprotection the borane adduct **5a** (0.68 mmol, 0.33 g) was dissolved in diethylamine (20 mL) and heated to 55 °C for 15 h. The reaction was monitored by ^{31}P NMR. After quantitative removal of the BH_3 the mixture was evaporated to dryness and the residue was taken up in a hexane/toluene mixture (2 mL, 1:1). The amine–borane adduct was removed by filtration over basic alumina. Evaporation and drying in high vacuum afforded the product **6a**. Yield: 84% (0.57 mmol, 0.27 g) of a colorless highly viscous oil; $de \geq 95\%$ ($^{31}P\{^1H\}$ NMR); ^{31}P NMR (C_6D_6): $\delta = 113.9$ (s, PO), 50.7 (s, PN); ^{13}C NMR (C_6D_6): $\delta = 143.2-126.3$ (C arom), 85.4 (O*C*HPh), 63.9 (N*C*H(CH_3)), 28.9 (N*C*H$_3$), 16.0 (CH(*C*H$_3$)), 11.3 (P*C*H$_3$); ^1H NMR (C_6D_6): $\delta = 7.75-6.77$ (m, 20H; arom), 4.94 (dd, $^3J = 8.7$ Hz, $^3J_{(H\text{-}PO)} = 8.7$ Hz, 1H; OC*H*(Ph)), 3.97 (dq, $^3J = 8.7$ Hz, $^3J = 6.0$ Hz, 1H; NC*H*(CH_3)), 2.05 (d, $^3J_{(H\text{-}PN)} = 3.6$ Hz, 3H; NC*H*$_3$), 1.45 (d, $^3J_{(H\text{-}PN)} = 6.6$ Hz, 3H; PC*H*$_3$), 1.16 (d, $^3J = 6.0$ Hz, 3H; CH(C*H*$_3$)).

(Ξ_P1*R*,2*S*)-2-*N*-Methyl-*N*-(methylphenylphosphino)-2-amino-1-phenyl-1-[di-(4-methyl-phenyl)phosphinoxy]propane (6b): This compound was prepared by the procedure described for **6a**. Compound **4a** (3.8 mmol, 1.15 g) and $ClP(4\text{-}CH_3C_6H_4)_2$ (4.2 mmol, 1.04 g) were converted in the presence of triethylamine (8.4 mmol, 0.85 g). Yield: 82% (3.12 mmol, 1.60 g) of **5b** as a highly viscous colorless oil; $de \geq 95\%$ ($^{31}P\{^1H\}$ NMR); ^{31}P NMR (C_6D_6): $\delta = 114.4$ (s, PO), 68.4 (m, PN); ^{13}C NMR (C_6D_6): $\delta = 141.1-125.6$ (C arom), 86.3 (O*C*HPh), 58.4 (N*C*H(CH_3)), 28.4 (N*C*H$_3$), 21.2 (PhC*H*$_3$), 15.6 (CH(*C*H$_3$)), 11.1 (P*C*H$_3$); ^1H NMR (C_6D_6): $\delta = 7.68-6.86$ (m, 18H; arom), 4.93 (dd, $^3J = 8.4$ Hz, $^3J_{(H\text{-}PO)} = 8.4$ Hz, 1H; OC*H*(Ph)), 4.60 (dq, $^3J = 8.4$ Hz, $^3J = 6.6$ Hz, 1H; NC*H*(CH_3)), 2.08 (s, 3H; PhC*H*$_3$), 2.01 (d, $^3J_{(H\text{-}PN)} = 8.4$ Hz, 3H; NC*H*$_3$), 2.00 (s, 3H; PhC*H*$_3$), 1.33 (d, $^3J = 6.6$ Hz, 3H; CH(C*H*$_3$)), 1.15 (d, $^3J_{(H\text{-}PN)} = 8.7$ Hz, 3H; PC*H*$_3$), 2.00–0.80 (br m, 3H; B*H*$_3$).

Deprotection of the borane adduct **5b** (0.7 mmol, 0.38 g) in triethylamine (15 mL) afforded **6b** as a viscous colorless oil. Yield: 62% (0.43 mmol, 0.23 g); $de \geq 95\%$ ($^{31}P\{^1H\}$ NMR); ^{31}P NMR (C_6D_6): $\delta = 114.3$ (s, PO), 52.1 (s, PN); ^{13}C NMR (C_6D_6): $\delta = 140.6-126.3$ (C arom), 85.3 (O*C*HPh), 64.1 (N*C*H(CH_3)), 28.9 (N*C*H$_3$), 19.9 (PhC*H*$_3$) 16.0 (CH(*C*H$_3$)), 11.3 (P*C*H$_3$); ^1H NMR (C_6D_6): $\delta = 7.08-6.65$ (m, 18H; arom), 5.29 (dd, $^3J = 7.5$ Hz, $^3J_{(H\text{-}PO)} = 9.6$ Hz, 1H; OC*H*(Ph)), 3.57 (dq, $^3J = 6.6$ Hz, $^3J = 9.6$ Hz, 1H; NC*H*(CH_3)), 2.02 (s, PhC*H*$_3$), 2.01 (d, $^3J_{(H\text{-}PN)} = 3.9$ Hz, 3H; NC*H*$_3$), 1.30 (d, $^3J_{(H\text{-}PN)} = 6.6$ Hz, 3H; CH(C*H*$_3$)), 1.08 (d, $^3J = 6.3$ Hz, 3H; PC*H*$_3$).

(Ξ_P1*R*,2*S*)-2-*N*-Methyl-*N*-(methylphenylphosphino)-2-amino-1-phenyl-1-(di-{[3,5-bis-(trifluoromethyl)phenyl]}phosphinoxy)propane (6c): This compound was prepared by the procedure described for **6a**. Compound **4a** (1.7 mmol, 0.50 g) and $ClP(3,5\text{-}(CF_3)_2C_6H_3)_2$ (1.9 mmol, 0.91 g) were converted in the presence of triethylamine (5.0 mmol, 0.51 g). Yield: 96% (1.63 mmol, 1.21 g) of **5c** as a highly viscous pale yellow oil; $de \geq 95\%$ ($^{31}P\{^1H\}$ NMR); ^{31}P NMR (C_6D_6): $\delta = 106.6$ (s, PO), 69.1 (m, PN); ^{19}F NMR (C_6D_6): $\delta = -63.2$ (d, $J = 13.5$ Hz); ^{13}C NMR (C_6D_6): $\delta = 144.4-121.5$ (C arom), 87.8 (O*C*HPh), 57.2 (N*C*H(CH_3)), 28.1 (N*C*H$_3$), 15.9 (CH(*C*H$_3$)), 11.1 (P*C*H$_3$); ^1H NMR ($CDCl_3$): $\delta = 7.85-6.59$ (m, 16H; arom), 4.76 (dd, $^3J = 8.0$ Hz, $^3J_{(H\text{-}PO)} = 9.3$ Hz, 1H; OC*H*(Ph)), 4.38 (m, 1H; NC*H*(CH_3)), 2.25 (d, $^3J_{(H\text{-}PN)} = 8.1$ Hz, 3H; NC*H*$_3$), 1.46 (d, $^3J = 8.8$ Hz, 3H; CH(C*H*$_3$)), 1.31 (d, $^3J_{(H\text{-}PN)} = 6.5$ Hz, 3H; PC*H*$_3$), 2.00–0.50 (br m, 3H; B*H*$_3$).

Deprotection of the borane adduct **5c** (1.6 mmol, 1.20 g) in triethylamine (20 mL) afforded **6c** as a viscous colorless oil. Yield: 96% (1.54 mmol, 1.13 g); $de = 92\%$ ($^{31}P\{^1H\}$ NMR); ^{31}P NMR (C_6D_6): $\delta = 104.9$ (s, PO), 51.3 (s, PN); ^{19}F NMR (C_6D_6): $\delta = -63.2$ (d, $J = 13.5$ Hz); ^{13}C NMR (C_6D_6): $\delta = 144.1-122.1$ 5 (C arom), 87.7 (O*C*HPh), 57.2 (N*C*H(CH_3)), 28.2 (N*C*H$_3$), 15.9 (CH(*C*H$_3$)), 10.8 (P*C*H$_3$); ^1H NMR (C_6D_6): $\delta = 7.95-6.65$ (m, 16H; arom), 4.87 (dd, $^3J = 7.9$ Hz, $^3J_{(H\text{-}PO)} = 8.6$ Hz, 1H; OC*H*(Ph)), 3.93 (dq, $^3J = 7.9$ Hz, $^3J = 7.2$ Hz, 1H; NC*H*(CH_3)), 2.19 (d, $^3J_{(H\text{-}PN)} = 3.3$ Hz, 3H; NC*H*$_3$), 1.38 (d, $^3J = 7.2$ Hz, 3H; CH(C*H*$_3$)), 1.31 (d, $^3J_{(H\text{-}PN)} = 6.3$ Hz, 3H; PC*H*$_3$).

(Ξ_P1*R*,2*S*)-2-*N*-Methyl-*N*-(methylphenylphosphino)-2-amino-1-phenyl-1-(1,3,2-dioxa-[d,f]-dibenzo-phosphepinoxy)propane (6d): This compound was prepared by the procedure described for **6a**. Compound **4a** (1.3 mmol, 0.40 g) and 2,2′-biphenylphosphorchloridite (1.5 mmol, 0.37 g) were converted in the presence of triethylamine (3.0 mmol, 0.41 g). Yield: 81% (1.05 mmol, 0.55 g) of **5d** as a white solid; $de \geq 95\%$ ($^{31}P\{^1H\}$ NMR); ^{31}P NMR (C_6D_6): $\delta = 145.4$ (s, PO), 68.1–67.5 (m, PN); ^{13}C NMR (C_6D_6): $\delta = 149.4-121.2$ (C arom), 79.5 (O*C*HPh), 63.7 (N*C*H(CH_3)), 30.3 (N*C*H$_3$), 15.3 (CH(*C*H$_3$)), 12.0 (P*C*H$_3$); ^1H NMR (C_6D_6): $\delta = 7.48-6.76$ (m, 18H; arom), 5.48 (dd, $^3J = 6.6$ Hz, $^3J_{(H\text{-}PO)} = 9.6$ Hz, 1H; OC*H*(Ph)), 4.33 (dq, $^3J = 6.6$ Hz, $^3J = 8.1$ Hz, 1H; NC*H*(CH_3)), 2.19 (d, $^3J_{(H\text{-}PN)} = 8.7$ Hz, 3H; NC*H*$_3$), 1.15 (d, $^3J = 8.1$ Hz, 3H; CH(C*H*$_3$)), 1.13 (d, $^3J_{(H\text{-}PN)} = 6.1$ Hz, 3H; PC*H*$_3$), 2.00–0.80 (br m, 3H; B*H*$_3$).

Deprotection of the borane adduct **5d** (1.1 mmol, 0.55 g) in triethylamine (20 mL) afforded **6d** as a white solid. Yield: 82% (0.90 mmol, 0.44 g); $de \geq 95\%$ ($^{31}P\{^1H\}$ NMR); ^{31}P NMR (C_6D_6): $\delta = 149.2$ (s, PO), 49.9 (s, PN); ^{13}C NMR (C_6D_6): $\delta = 149.3-121.1$ (C arom), 79.2 (O*C*HPh), 63.8 (N*C*H(CH_3)), 29.9 (N*C*H$_3$), 14.9 (CH(*C*H$_3$)), 11.2 (P*C*H$_3$); ^1H NMR (C_6D_6): $\delta = 7.19-6.66$ (m, 18H; arom), 5.27 (dd, $^3J = 8.5$ Hz, $^3J_{(H\text{-}PO)} = 8.5$ Hz, 1H; OC*H*(Ph)), 3.56 (dq, $^3J = 8.5$ Hz, $^3J = 6.6$ Hz, 1H; NC*H*(CH_3)), 2.01 (d, $^3J_{(H\text{-}PN)} = 3.9$ Hz, 3H; NC*H*$_3$), 1.29 (d, $^3J = 6.6$ Hz, 3H; CH(C*H*$_3$)), 1.08 (d, $^3J_{(H\text{-}PN)} = 6.3$ Hz, 3H; PC*H*$_3$).

(Ξ_P1*R*,2*S*)-2-*N*-Methyl-*N*-(*n*-butylphenylphosphino)-2-amino-1-phenyl-1-(diphenylphosphinoxy)propane (6e): This compound was prepared by the procedure described for **6a**. Compound **4b** (1.5 mmol, 0.50 g) and $ClPPh_2$ (1.7 mmol, 0.37 g) were converted in the presence of triethylamine (3.4 mmol, 0.34 g). Yield: 78% (1.33 mmol, 0.60 g) of **5e** as a colorless, highly viscous oil; $de \geq 95\%$ ($^{31}P\{^1H\}$ NMR); ^{31}P NMR (C_6D_6): $\delta = 112.1$ (s, PO), 71.1 (m, PN); ^{13}C NMR (C_6D_6): $\delta = 141.9-126.4$ (C arom), 85.8 (O*C*HPh), 64.0 (N*C*H(CH_3)), 28.3 (N*C*H$_3$), 27.05 ($CH_2CH_2CH_3$), 26.7 (PCH_2CH_2), 23.3 (CH(*C*H$_3$)), 15.5 (CH_2CH_3), 12.7 (P*C*H$_2$); ^1H NMR (C_6D_6): $\delta = 7.50-6.92$ (m, 20H; arom), 4.83 (dd, $^3J = 8.0$ Hz, $^3J_{(H\text{-}PO)} = 8.0$ Hz, 1H; OC*H*(Ph)), 4.17 (dq, $^3J = 8.0$ Hz, $^3J = 6.6$ Hz, 1H; NC*H*(CH_3)), 2.39 (d, $^3J_{(H\text{-}PN)} = 7.8$ Hz, 3H; NC*H*$_3$), 1.89–1.31 (m, 6H; $(CH_2)_3$), 1.26 (d, $^3J = 6.6$ Hz, 3H; CH(C*H*$_3$)), 0.90 (t, $^3J = 7.1$ Hz, 3H; CH_2CH_3), 1.89–0.30 (br m, 3H; B*H*$_3$).

Deprotection of the borane adduct **5e** (1.14 mmol, 0.60 g) in triethylamine (20 mL) afforded **6e** as a colorless highly viscous oil. Yield: 84% (0.96 mmol, 0.49 g); $de \geq 95\%$ ($^{31}P\{^1H\}$ NMR); ^{31}P NMR (C_6D_6): $\delta = 112.6$ (s, PO), 62.2 (s, PN); ^{13}C NMR (C_6D_6): $\delta = 141.8-126.3$ (C arom), 85.8 (O*C*HPh), 64.1 (N*C*H(CH_3)), 28.3 (N*C*H$_3$), 27.1 ($CH_2CH_2CH_3$), 26.6 (PCH_2CH_2), 23.3 (CH(*C*H$_3$)), 15.5 (CH_2CH_3), 12.7 (P*C*H$_2$); ^1H NMR (C_6D_6): $\delta = 7.75-6.77$ (m, 20H; arom), 4.98 (dd, $^3J = 8.7$ Hz, $^3J_{(H\text{-}PO)} = 8.7$ Hz, 1H; OC*H*(Ph)), 4.05 (dq, $^3J = 8.7$ Hz, $^3J = 5.7$ Hz, 1H; NC*H*(CH_3)), 2.16 (d, $^3J_{(H\text{-}PN)} = 3.6$ Hz, 3H; NC*H*$_3$), 1.52 (d, $^3J = 5.7$ Hz, 3H; CH(C*H*$_3$)), 1.85–1.20 (m, 6H; $(CH_2)_3$), 0.92 (t, $^3J = 6.9$ Hz, 3H; CH_2CH_3).

(Ξ_P1*R*,2*S*)-2-*N*-Methyl-*N*-(*n*-butylphenylphosphino)-2-amino-1-phenyl-1-[di-(4-methyl-phenyl)phosphinoxy]propane (6f): This compound was

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prepared by the procedure described for **6a**. Compound **4b** (3.8 mmol, 1.30 g) and $ClP(4\text{-}CH_3C_6H_4)_2$ (4.2 mmol, 1.04 g) were converted in the presence of triethylamine (8.4 mmol, 0.85 g). Yield: 76% (2.89 mmol, 1.60 g) of **5f** as a pale yellow, highly viscous oil; $de \geq 95\%$ ($^{31}P\{^1H\}$ NMR); ^{31}P NMR (C_6D_6): $\delta = 114.1$ (s, PO), 68.3 (m, PN); ^{13}C NMR (C_6D_6): $\delta =$ 141.2–125.6 (C arom), 86.3 (O*C*HPh), 58.4 (N*C*H(CH_3)), 28.4 (N*C*H$_3$), 27.05 ($CH_2CH_2CH_3$), 26.7 (PCH_2CH_2), 23.3 (CH(*C*H$_3$)), 15.5 (CH_2CH_3), 12.7 (PCH_2); ^1H NMR (C_6D_6): $\delta = 7.50-6.92$ (m, 18H; arom), 4.83 (dd, $^3J = 8.0$ Hz, $^3J_{(H\text{-}PO)} = 8.0$ Hz, 1H; OC*H*(Ph)), 4.17 (dq, $^3J = 8.0$ Hz, $^3J =$ 6.6 Hz, 1H; NC*H*(CH_3)), 2.33 (d, $^3J_{(H\text{-}PN)} = 6.0$ Hz, 3H; NC*H*$_3$), 2.26 (s, 3H; PhC*H*$_3$), 2.20 (s, 3H; PhC*H*$_3$), 1.89–1.31 (m, 6H; (CH_2)$_3$), 1.26 (d, $^3J =$ 6.6 Hz, 3H; CH(C*H*$_3$)), 1.16 (d, $^3J = 9.0$ Hz, 3H; CH(C*H*$_3$)), 0.83 (t, $^3J =$ 6.0 Hz, 3H; CH_2CH_3), 2.00–0.20 (br m, 3H; BH_3).

Deprotection of the borane adduct **5f** (0.7 mmol, 0.39 g) in triethylamine (15 mL) afforded **6f** as a pale yellow, highly viscous oil. Yield: 70% (0.49 mmol, 0.26 g); $de \geq 95\%$ ($^{31}P\{^1H\}$ NMR); ^{31}P NMR (C_6D_6): $\delta = 113.4$ (s, PO), 62.2 (s, PN); ^{13}C NMR (C_6D_6): $\delta = 142.8-121.7$ (C arom), 87.1 (m, O*C*HPh), 65.6 (m, N*C*H(CH_3)), 29.6 (N*C*H$_3$), 28.4 ($CH_2CH_2CH_3$), 28.1 (PCH_2CH_2), 24.7 (CH(*C*H$_3$)), 21.2 (Ph*C*H$_3$), 16.8 (CH_2CH_3), 14.1 (PCH_2); ^1H NMR (C_6D_6): $\delta = 7.74-6.84$ (m, 18H; arom), 5.03 (dd, $^3J = 8.7$ Hz, $^3J_{(H\text{-}PO)} = 8.7$ Hz, 1H; OC*H*(Ph)), 4.07 (dq, $^3J = 8.7$ Hz, $^3J = 6.7$ Hz, 1H; NC*H*(CH_3)), 2.18 (d, $^3J_{(H\text{-}PN)} = 3.4$ Hz, 3H; NC*H*$_3$), 2.09 (s, 3H; PhC*H*$_3$), 2.00 (s, 3H; PhC*H*$_3$), 1.49 (d, $^3J = 6.7$ Hz, 3H; CH(C*H*$_3$)), 1.95–1.20 (m, 6H; (CH_2)$_3$), 0.91 (t, $^3J = 6.9$ Hz, 3H; CH_2CH_3).

(Ξ_P,1*R*,2*S*)-2-*N*-Methyl-*N*-(*n*-butylphenylphosphino)-2-amino-1-phenyl-1-(di-{[3,5-bis-(trifluoromethyl)phenyl]}phosphinoxy)propane (6g): This compound was prepared by the procedure described for **6a**. Compound **4b** (1.3 mmol, 0.45 g) and $ClP(3,5\text{-}(CF_3)_2C_6H_3)_2$ (1.5 mmol, 0.71 g) were converted in the presence of triethylamine (2.9 mmol, 0.29 g). Yield: 96% (1.25 mmol, 1.01 g) of **5g** as a pale yellow, highly viscous oil; $de \geq 95\%$ ($^{31}P\{^1H\}$ NMR); ^{31}P NMR (C_6D_6): $\delta = 107.1$ (s, PO), 72.5 (m, PN); ^{13}C NMR (C_6D_6): $\delta = 144.7-121.2$ (C arom), 87.0 (O*C*HPh), 59.3 (N*C*H(CH_3)), 28.3 (N*C*H$_3$), 27.05 ($CH_2CH_2CH_3$), 26.7 (PCH_2CH_2), 23.3 (CH(*C*H$_3$)), 15.9 (CH_2CH_3), 14.6 (PCH_2); ^1H NMR (C_6D_6): $\delta = 7.95-6.65$ (m, 16H; arom), 4.84 (dd, $^3J = 8.4$ Hz, $^3J_{(H\text{-}PO)} = 8.4$ Hz, 1H; OC*H*(Ph)), 4.37 (dq, $^3J = 8.4$ Hz, $^3J = 6.6$ Hz, 1H; NC*H*(CH_3)), 2.40 (d, $^3J_{(H\text{-}PN)} = 7.3$ Hz, 3H; NC*H*$_3$), 1.93–1.26 (m, 6H; (CH_2)$_3$), 1.37 (d, $^3J = 6.6$ Hz, 3H; CH(C*H*$_3$)), 0.91 (t, $^3J =$ 7.0 Hz, 3H; CH_2CH_3), 2.00–0.20 (br m, 3H; BH_3).

Deprotection of the borane adduct **5g** (1.30 mmol, 1.01 g) in triethylamine (20 mL) afforded **6g** as a pale yellow, highly viscous oil. Yield: 81% (1.05 mmol, 0.80 g); $de = 94\%$ ($^{31}P\{^1H\}$ NMR); ^{31}P NMR (C_6D_6): $\delta = 104.9$ (s, PO), 60.8 (s, PN); ^{19}F NMR (C_6D_6): $\delta = -63.2$ (s); ^{13}C NMR (C_6D_6): $\delta =$ 143.6–120.2 (C arom), 87.1 (O*C*HPh), 62.9 (N*C*H(CH_3)), 28.8 (N*C*H$_3$), 27.1 ($CH_2CH_2CH_3$), 26.6 (PCH_2CH_2), 23.3 (CH(*C*H$_3$)), 15.9 (CH_2CH_3), 12.7 (PCH_2); ^1H NMR (C_6D_6): $\delta = 7.85-6.66$ (m, 16H; arom), 4.73 (dd, $^3J =$ 8.4 Hz, $^3J_{(H\text{-}PO)} = 8.4$ Hz, 1H; OC*H*(Ph)), 3.78 (dq, $^3J = 8.4$ Hz, $^3J = 6.6$ Hz, 1H; NC*H*(CH_3)), 1.95 (d, $^3J_{(H\text{-}PN)} = 3.0$ Hz, 3H; NC*H*$_3$), 1.26 (d, $^3J = 6.6$ Hz, 3H; CH(C*H*$_3$)), 1.63–1.00 (m, 6H; (CH_2)$_3$), 0.78 (t, $^3J = 7.2$ Hz, 3H; CH_2CH_3).

(Ξ_P,1*R*,2*S*)-2-*N*-Methyl-*N*-(diphenylphosphino)-2-amino-1-phenyl-1-(diphenylphosphinoxy)propane (6h, EPHOS): The azeotropically dried ($3 \times$ 10 mL toluene) ephedrine (13.7 mmol, 2.27 g) and triethylamine (40.9 mmol, 4.14 g) were dissolved in toluene (100 mL). At $-78\,^\circ C$ a solution of $ClPPh_2$ (30.1 mmol, 6.65 g) in toluene (10 mL) was slowly added by a syringe. The mixture was allowed to warm to room temperature overnight, and the ammonium salt was filtered off. Evaporation of the solvent yielded raw **6h** 94% (12.9 mmol, 6.8 g) as a yellow, highly viscous oil. The product was purified by dissolving in hexane/toluene (2:1) and filtration over carefully dried basic alumina. Evaporation of the solvents gave **6h** as colorless, highly viscous oil. Yield: 84% (11.5 mmol, 5.7 g); ^{31}P NMR (C_6D_6): $\delta = 111.1$ (s, PO), 65.3 (s, PN); ^{13}C NMR (C_6D_6): $\delta = 141.8-$ 126.3 (C arom), 85.8 (O*C*HPh), 64.3 (N*C*H(CH_3)), 30.5 (N*C*H$_3$), 15.8 (CH(*C*H$_3$)); ^1H NMR (C_6D_6): $\delta = 7.75-6.77$ (m, 20H; arom), 4.94 (dd, $^3J =$ 8.7 Hz, $^3J_{(H\text{-}PO)} = 8.7$ Hz, 1H; OC*H*(Ph)), 3.97 (dq, $^3J = 8.7$ Hz, $^3J = 6.0$ Hz, 1H; NC*H*(CH_3)), 2.05 (d, $^3J_{(H\text{-}PN)} = 3.6$ Hz, 3H; NC*H*$_3$), 1.45 (d, $^3J_{(H\text{-}PN)} =$ 6.6 Hz, 3H; PC*H*$_3$), 1.16 (d, $^3J = 6.0$ Hz, 3H; CH(C*H*$_3$)).

(Ξ_P,1*R*,2*S*)-2-*N*-Methyl-*N*-(1-naphthylphenylphosphinoborane)-2-amino-1-phenyl-1-(diphenylphosphinoxy)propane (6i): This compound was prepared by the procedure described for **6a**. Compound **4c** (2.2 mmol, 0.92 g) and $ClPPh_2$ (2.4 mmol, 0.54 g) were converted in the presence of triethylamine (4.9 mmol, 0.50 g). Yield: 83% (1.83 mmol, 1.10 g) of **5i** as a highly viscous, colorless oil. It turned out that during synthesis a scrambling of the BH_3 group occurred between the PN and the newly introduced PO terminus. ^{31}P NMR (C_6D_6): $\delta = 111.2$ (s, *P*OÇNP(BH_3)), 107.0 ((BH_3)*P*OÇNP), 71.8 (m, POÇN*P*(BH_3)), 58.7 (s, (BH_3)POÇN*P*). The ^{13}C NMR and ^1H NMR spectra show a mixture of compounds.

Deprotection of the borane adduct **5i** (1.8 mmol, 1.07 g) in triethylamine (20 mL) afforded **6i** as a highly viscous, colorless oil. Yield: 95% (1.71 mmol, 0.99 g); $de = 93\%$ ($^{31}P\{^1H\}$ NMR); ^{31}P NMR (C_6D_6): $\delta =$ 111.8 (s, PO), 57.6 (s, PN); ^{13}C NMR (C_6D_6): $\delta = 141.8-124.1$ (C arom), 85.7 (O*C*HPh), 64.4 (N*C*H(CH_3)), 30.5 (N*C*H$_3$), 15.8 (CH(*C*H$_3$)); ^1H NMR (C_6D_6): $\delta = 8.22-6.60$ (m, 27H; arom), 4.85 (dd, $^3J = 7.5$ Hz, $^3J_{(H\text{-}PO)} =$ 7.5 Hz, 1H; OC*H*(Ph)), 4.12 (dq, $^3J = 7.5$ Hz, $^3J = 6.0$ Hz, 1H; NC*H*(CH_3)), 2.29 (d, $^3J_{(H\text{-}PN)} = 3.0$ Hz, 3H; NC*H*$_3$), 1.43 (d, $^3J_{(H\text{-}PN)} = 6.0$ Hz, 3H; CH(C*H*$_3$)).

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[1] a) N. Sakai, S. Mano, K. Nozaki, H. Takaya, *J. Am. Chem. Soc.* **1993**, *115*, 7033; for review see: S. Gladiali, J. C. Bayón, C. Claver, *Tetrahedron: Asymmetry* **1995**, *6*, 1453.

[2] a) J. E. Babin, G. T. Whiteker (Union Carbide Chem. Plastics Techn. Co.) US 5491266, **1996** [*Chem. Abs.* **1993**, *119*, P159872h]; b) J. E. Babin, G. T. Whiteker (Union Carbide Chem. Plastics Techn. Co.) WO 93/03839, **1993** [*Chem. Abs.* **1993**, *119*, P159872h]; c) G. J. H. Buisman, E. J. Vos, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Chem. Soc. Dalton Trans.* **1995**, 409; d) G. J. H. Buisman, L. A. van der Veen, A. Klootwijk, W. G. J. de Lange, P. C. J. Kamer, P. W. N. M. van Leeuwen, D. Vogt, *Organometallics* **1997**, *16*, 2929.

[3] a) G. Parinello, J. K. Stille, *J. Am. Chem. Soc*. **1987**, *109*, 7122; b) J. K. Stille, G. Parinello (Colorado State Univ. Res. Found.), WO 88/08835, **1988** [*Chem. Abs.* **1988**, *111*, P996656]; c) G. Parinello, J. K. Stille, *J. Mol. Catal*. **1983**, *21*, 203; d) J. K. Stille, H. Su, P. Brechot, G. Parrinello, L. S. Hegedus, *Organometallics* **1991**, *10*, 1183.

[4] a) N. Sakai, K. Nozaki, K. Mashima, H. Takaya, *Tetrahedron: Asymmetry* **1992**, *3*, 583; b) N. Sakai, S. Mano, K. Nozaki, H. Takaya, *J. Am. Chem. Soc.* **1993**, *115*, 7033; c) K. Nozaki, N. Sakai, T. Nanno, T. Higashijima, S. Mano, T. Horiuchi, H. Takaya, *J. Am. Chem. Soc.* **1997**, *119*, 4413; d) K. Nozaki, W.-g. Li, T. Horiuchi, H. Takaya, *Tetrahedron Lett.* **1997**, *38*, 4611; e) N. Sakai, K. Nozaki, H. Takaya, *J. Chem. Soc. Chem. Commun.* **1994**, 395; f) T. Nanno, N. Sakai, K. Nozaki, *Tetrahedron: Asymmetry* **1995**, *6*, 2583; g) T. Horiuchi, T. Ohta, K. Nozaki, H. Takaya, *Chem. Commun*. **1996**, 155; h) T. Horiuchi, T. Ohta, E. Shirakawa, K. Nozaki, H. Takaya, *Tetrahedron* **1997**, *53*, 7795; i) K. Nozaki, T. Nanno, H. Takaya, *J. Organomet. Chem*. **1997**, *527*, 103; j) K. Nozaki, W.-g. Li, T. Horiuchi, H. Takaya, *J. Org. Chem.* **1996**, *61*, 7658; k) T. Horiuchi, T. Ohta, E. Shirikawa, K. Nozaki, H. Takaya, *J. Org. Chem.* **1997**, *62*, 4285.

[5] a) G. J. H. Buisman, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Tetrahedron: Asymmetry.* **1993**, *4*, 1625; b) G. J. H. Buisman, M. E. Martin, E. J. Vos, A. Klootwijk, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Tetrahedron: Asymmetry* **1995**, *6*, 719; c) G. J. H. Buisman, L. A. van der Veen, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Organometallics* **1997**, *16*, 5681.

[6] R. Bayersdörfer, B. Ganter, U. Englert, W. Keim, D. Vogt, *J. Organomet. Chem.* **1998**, *552*, 183.

[7] a) S. Jugé, J. P. Genet, *Tetrahedron Lett.* **1989**, *30*, 2786; b) S. Jugé, M. Stephan, J. A. Laffitte, J. P. Genet, *Tetrahedron Lett.* **1990**, *31*, 6357; c) V. Peper, K. Stingl, H. ThümLer, W. Saak, D. Haase, S. Pohl, S. Jugé, J. Martens, *Liebigs Ann. Chem.* **1995**, 2123.

[8] a) J. Wilken, J. Martens, *Synth. Commun.* **1996**, *26*, 4477; b) V. Peper, J. Martens, *Tetrahedron Lett.* **1996**, *37*, 8351.
[9] a) C. Hatat, N. Kokel, A. Mortreux, F. Petit, *Tetrahedron Lett*. **1990**, *31*, 4139; b) F. Hapiot, F. Agbossou, A. Mortreux, *Tetrahedron: Asymmetry* **1994**, *5*, 515; c) F. Agbossou, J.-F. Carpentier, C. Hatat, N. Kokel, A. Mortreux, *Organometallics* **1995**, *14*, 2480; d) F. Hapiot, F. Agbossou, A. Mortreux, *Tetrahedron: Asymmetry* **1995**, *6*, 11; e) J.-F. Carpentier, F. Agbossou, A. Mortreux, *Tetrahedron: Asymmetry* **1995**, *6*, 39; f) J.-F. Carpentier, F. Agbossou, C. Hatat, N. Kokel, A. Mortreux, *Organometallics* **1995**, *14*, 2480; g) A. Roucoux, M. Devocelle, J.-F. Carpentier, F. Agbossou, A. Mortreux, *Synlett* **1995**, 358; h) P. Cros, G. Buono, G. Pfeiffer, D. Denis, A. Mortreux, F. Petit, *New J. Chem*. **1987**, *11*, 573; i) I. Suisse, H. Bricout, A. Mortreux, *Tetrahedron Lett*. **1994**, *35*, 413; j) M. A. ElAmrani, I. Suisse, N. Knouzi, A. Mortreux, *Tetrahedron Lett*. **1995**, *36*, 5011; k) A. Mortreux, F. Petit, *J. Organomet. Chem*. **1994**, *483*, C1; l) S. Mutez, E. Paumard, A. Mortreux, F. Petit, *Tetrahedron Lett*. **1989**, *30*, 5759.
[10] a) H. W. Krause, U. Schmidt, S. Taudien, B. Costisella, M. Michalik, *J. Mol. Catal*. **1995**, *104*, 147; b) D. Heller, R. Kadyrov, M. Michalik, T. Freier, U. Schmidt, H. W. Krause, *Tetrahedron: Asymmetry* **1996**, *7*, 3025.
[11] R. Ewalds, Ph.D. Thesis, RWTH Aachen (Germany), **1997**.
[12] T. J. Kwok, D. J. Wink, *Organometallics* **1993**, *12*, 1954.
[13] P. W. N. M. van Leeuwen, G. van Koten, *Stud. Surf. Sci. Catal.* **1993**, *79*, 199 – 222.
[14] A. Castellanos-Páez, S. Castillón, C. Claver, P. W. N. M. van Leeuwen, W. G. J. de Lange, *Organometallics*, **1998**, *17*, 2543.
[15] a) P. Meakin, E. L. Muetterties, J. P. Jesson, *J. Am. Chem. Soc.* **1972**, *94*, 5271; b) P. Meakin, J. P. Jesson, F. N. Tebbe, E. L. Muetterties, *J. Am. Chem. Soc.* **1971**, *93*, 1797; c) E. M. Hyde, J. R. Swain, J. G.Verkade, P. Meakin, *J. Chem. Soc. Dalton Trans.* **1976**, 1169.
[16] Y. Pottier, A. Mortreux, F. Petit, *J. Organomet. Chem*. **1989**, *370*, 333.
[17] L. A. van der Veen, M. D. K. Boele, F. R. Bregman, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, H. Schenk, C. Bo, *J. Am. Chem. Soc.* **1998**, *120*, 11616.
[18] H. Nöth, H. J. Vetter, *Chem. Ber.* **1963**, *96*, 1116.
[19] A. L. Casalnuovo, T. V. RajanBabu, T. A. Ayers, T. H. Warren, *J. Am. Chem. Soc.* **1994**, *116*, 9869.

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