

Efficient, Rhodium-Catalyzed Hydrogenation of α -Dehydroamino Acid Esters with Chiral Monodentate Aminophosphanes Bearing Two Binaphthyl Groups

Luc Eberhardt,^[a] Dominique Armspach,^{*[a]} Dominique Matt,^{*[b]} Loic Toupet,^[b] and Benoît Oswald^[c]

Keywords: Asymmetric catalysis / Hydrogenation / Rhodium / Phosphoramidites / Binaphthyl / Azepines / Binol

All four stereoisomers of 4-[4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]azepin-4-yl]dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine have been prepared from (*R* or *S*)-1,1'-binaphthyl-2,2'-diyl chlorophosphite and the appropriate dinaphtho-azepine. When reacted with [Rh(1,5-cyclooctadiene)₂]BF₄, highly active catalysts for the hydrogenation of

α -dehydroamino acid esters were obtained. The highest enantioselectivities (up to 99% *ee*) were achieved with the phosphoramidites having two chiral binaphthyl groups with opposite configurations.

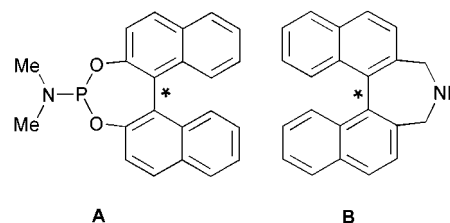
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

For over 30 years, chiral phosphanes have been used in combination with rhodium for the asymmetric hydrogenation of olefins.^[1] Researchers involved in this chemistry discovered very early on that chiral monodentate phosphanes are poorer ligands than their bidentate analogues in terms of enantioselectivity.^[2–5] As a result, considerable time and effort was dedicated in the 1970s and 1980s towards the design of bidentate chiral phosphorus ligands.^[6–10]

Recently, Feringa^[11–14] and Retz^[15,16] independently found that easily accessible monodentate phosphoramidite as well as phosphite ligands, all containing a dinaphthofused 1,3-dioxo-2-phosphacycloheptane unit, may be employed for the efficient enantioselective hydrogenation of dehydroamino acid esters. The prototype of such ligands is phosphoramidite **A**. Their good performance mainly arises from the presence of the binaphthyl ring system linked to the phosphorus atom. Following these results, a range of related binaphthyl phosphoramidites (also named as Feringa phosphoramidites) were synthesised in order to explore the scope of these catalysts.^[17–21] Most of them turned out to give high *ee*'s in asymmetric catalysis. Interestingly, de Vries et al. recently discovered that significant selectivity improvements may be achieved when integrating the nitrogen atom into a cyclic structure, such as in PipPhos and MorfPhos.^[19,22] Surprisingly, Feringa phosphoramidites in

which the nitrogen atom, like the phosphorus atom, forms a ring system with a chiral binaphthyl unit have not been reported.



In the present study, we describe the synthesis of several aminophosphanes, including Feringa-type phosphoramidites, containing the dinaphtho-azepine moiety (obtained from amine **B**). The new ligands were assessed in the rhodium-catalyzed hydrogenation of α -dehydroamino acid esters. It is noteworthy that ammonium salts derived from binaphthyl-based azepine derivatives^[23,24] have already been successfully employed as chiral phase-transfer catalysts.^[25,26] To date, only one phosphoramidite containing an azepinyl moiety has been reported.^[27] The latter led to *ee* values not higher than 74% for copper-catalysed alkylations of cinnamyl halides with dialkylzinc compounds. It should also be mentioned here that binol-based monophosphonites were also shown recently to result in good *ee*'s in asymmetric olefin hydrogenation.^[28]

Results and Discussion

In the following the subscripts “aze” and “bin” refer to molecules containing 4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]azepine and binaphtholate units, respectively. The aminophosphanes *S*_{aze}-**2a** and *R*_{aze}-**2b** (Scheme 1) were obtained in ca. 70% yield by treating chlorodiphenylphos-

[a] Laboratoire de Chimie Inorganique Moléculaire, Institut de Chimie, UMR 7177 CNRS,

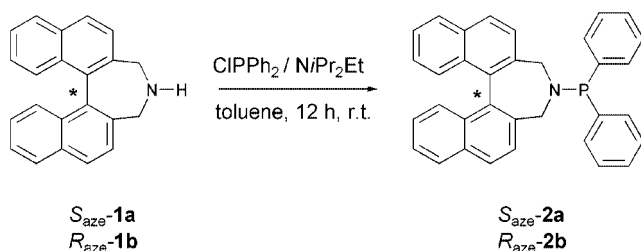
1 Rue Blaise Pascal, 67008 Strasbourg Cedex, France

[b] Groupe Matière Condensée et Matériaux, UMR 6626, Université de Rennes 1,

Campus de Beaulieu, 35042 Rennes cedex, France

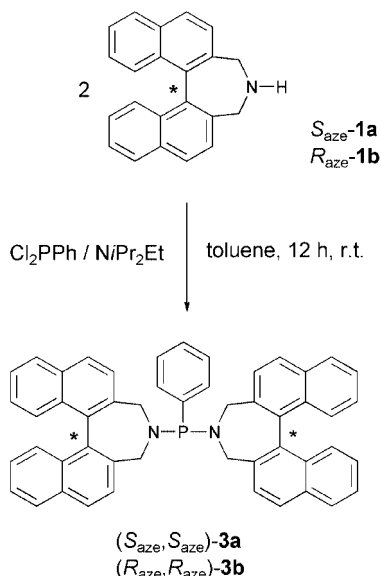
[c] Eichenweg 1, 4410 Liestal, Switzerland

phanewith(*S*)- or (*R*)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]azepine, respectively, in the presence of 1 equiv. of Hünig's base (diisopropylethylamine). Interestingly, replacing the latter with the less sterically hindered triethylamine produced large amounts of by-products. These enantiomers were air-stable and could be stored for months without particular care. The corresponding $^{31}\text{P}\{^1\text{H}\}$ NMR spectra display a single peak at $\delta = 63.7$ ppm, a value that lies in the range found for similar ligands.^[29,30]



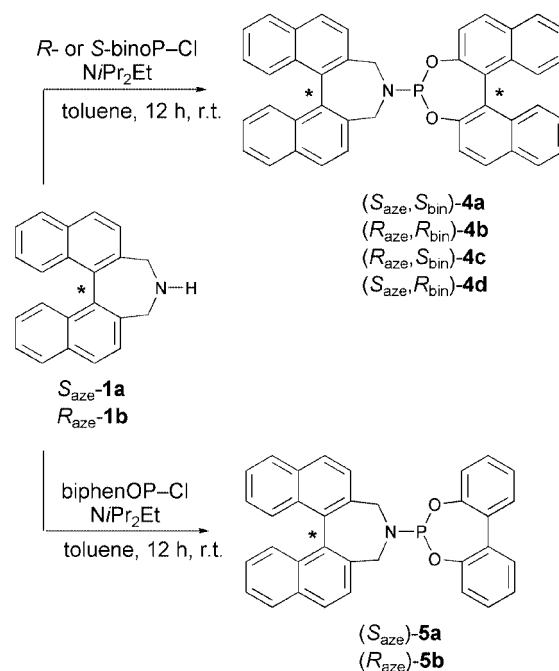
Scheme 1. Synthesis of aminophosphanes **2a** and **2b**.

The enantiomeric aminophosphanes ($S_{\text{aze}}, S_{\text{aze}}$)-**3a** and ($R_{\text{aze}}, R_{\text{aze}}$)-**3b**, containing two (aminoalkyl)binaphthyl moieties, were prepared in a similar manner, but using PhPCl_2 as the phosphorus precursor (Scheme 2). Both ligands were air stable. They were characterized by a signal at $\delta = 96.5$ ppm in the corresponding $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, a value in keeping with that reported for other diamino phosphanes.^[29–32]



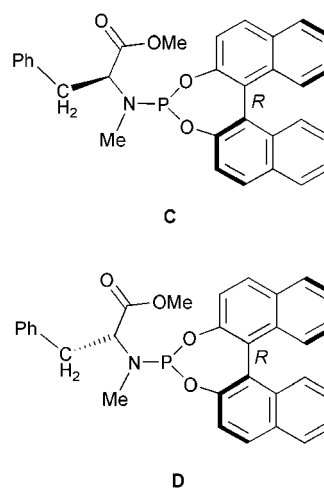
Scheme 2. Synthesis of diamino phosphanes **3a** and **3b**.

We further prepared the four diastereoisomers ($S_{\text{aze}}, S_{\text{bin}}$)-**4a**, ($R_{\text{aze}}, R_{\text{bin}}$)-**4b**, ($R_{\text{aze}}, S_{\text{bin}}$)-**4c** and ($S_{\text{aze}}, R_{\text{bin}}$)-**4d**, which were obtained from (*R* or *S*)-(1,1'-binaphthyl-2,2'-diyl)chlorophosphite (binoPCl) and the corresponding azepine in the presence of Hünig's base (Scheme 3).



Scheme 3. Synthesis of phosphoramidites **4a–d**, **5a** and **5b**.

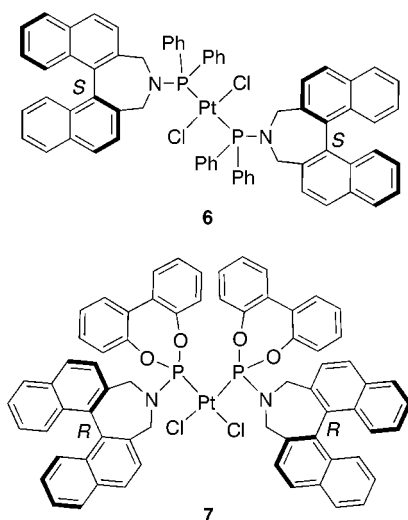
As expected for phosphoramidite ligands, all four compounds could be handled in air without noticeable oxidation, but underwent P–N cleavage in the presence of water. Interestingly, the P atoms in the two pairs of enantiomers ($S_{\text{aze}}, S_{\text{bin}}$)-**4a**/ $(R_{\text{aze}}, R_{\text{bin}})$ -**4b** and ($R_{\text{aze}}, S_{\text{bin}}$)-**4c**/ $(S_{\text{aze}}, R_{\text{bin}})$ -**4d** resonated at strikingly different chemical shifts ($\delta = 146.0$ and 143.0 ppm, respectively). In comparison, the chemical shift difference between the corresponding ^{31}P signals is only 0.4 ppm for the recently reported diastereoisomers **C** and **D**.^[21] Evidently, the P atoms experience very different environments in each diastereoisomeric pair.



Finally, two enantiomeric phosphoramidites (S_{aze})-**5a**/ R_{aze} -**5b**, which lack a stereogenic residue on phosphorus, but retain the general bicyclic structure of their aforementioned analogs, were synthesised by reacting either (*S*)- or (*R*)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]azepine with biphenyl-2,2'-diyl chlorophosphite (biphenOP-Cl)

(Scheme 3). In this instance, the ^{31}P chemical shift value ($\delta = 145.0$ ppm) for this enantiomeric pair lies between those observed for the previous diastereoisomers ($S_{\text{aze}}, S_{\text{bin}}$)-**4a**/ $(R_{\text{aze}}, R_{\text{bin}})$ -**4b** and $(R_{\text{aze}}, S_{\text{bin}})$ -**4c**/ $(S_{\text{aze}}, R_{\text{bin}})$ -**4d**.

The square-planar platinum(II) complex **6** was prepared from S_{aze} -**2a** and $[\text{PtCl}_2(\text{PhCN})_2]$ in CH_2Cl_2 . The *trans* stereochemistry of the complex was inferred from the corresponding $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, which consisted of a singlet flanked by two Pt satellites with a $J_{\text{P,Pt}}$ coupling constant of 2743 Hz. The latter value is close to that reported by Slawin et al. for a related *trans* complex, namely *trans*-dichloro-bis(*N*-diisopropylphosphino-*N*-methylpiperazine)-platinum(II) ($^1J_{\text{P,Pt}} = 2678$ Hz).^[33]



The *trans* stereochemistry of the complex was further confirmed by a single-crystal X-ray diffraction study (Figure 1). The structural analysis revealed an almost C_2 -symmetric structure, with the azepine moieties located on opposite sides of the coordination plane [N-atom-to-plane distances: 1.33(1) and 1.22(1) Å] (Figure 1). The dihedral angles between the linked naphthyl groups were respectively 49.5° and 54.0°. The formation of a complex with *trans*-disposed P atoms probably relies on a *trans* effect, rather than on a steric effect. Indeed, reaction of $[\text{PtCl}_2(\text{PhCN})_2]$

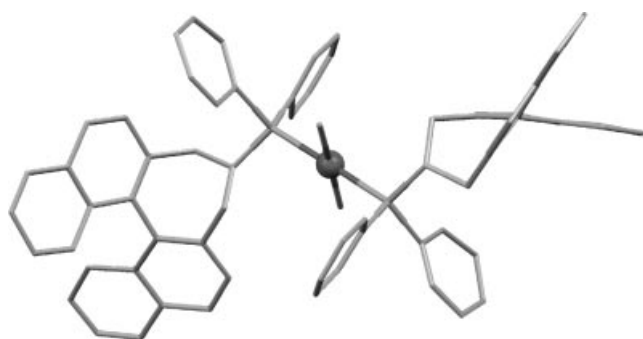


Figure 1. X-ray structure of compound **6** showing the *trans* configuration of the complex. Important bond lengths [Å] and angles [°]: P(1)–Pt 2.304(6); P(2)–Pt 2.328(4); Pt–Cl(1) 2.292(4); Pt–Cl(2) 2.305(5); P(1)–N(1) 1.690(16); P(2)–N(2) 1.727(18); P(1)–Pt–P(2) 178.9(3)°.

with ligand R_{aze} -**5b**, which is similar to S_{aze} -**2a** in size but has different electronic properties, afforded complex **7**, which adopts a *cis* stereochemistry. This geometry was deduced from the corresponding $J_{\text{P,Pt}}$ coupling constant, 5580 Hz (CDCl_3), which is in keeping with other *cis*-phosphoramidite-platinum complexes.^[21,34–36] This finding was further confirmed by an X-ray structure determination (Figure 2).

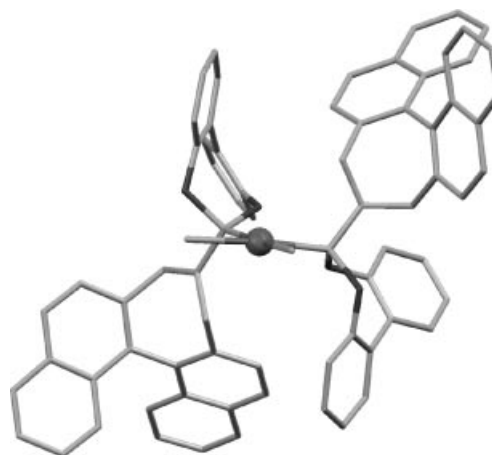
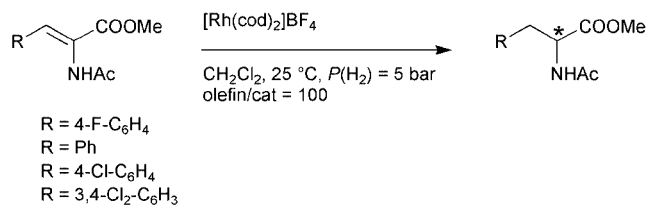


Figure 2. The molecular structure of complex **7** displaying its *cis* geometry. Important bond lengths [Å] and angles [°]: P(1)–Pt 2.2084(8); P(2)–Pt 2.2084(8); Pt–Cl(1) 2.3406(8); Pt–Cl(2) 2.3406(8); P(1)–N(1) 1.622(3); P(2)–N(2) 1.622(3); P(1)–Pt–P(2) 97.10(4)°. Dihedral angles between the linked naphthyl units: 54.3° and 54.4°. Dihedral angles between the linked phenyl units: –45.2° and –45.2°.

The asymmetric unit of **7** consists of a single molecule, which, as in **6**, is nearly C_2 -symmetric. The metal center lies in an almost planar coordination environment, but the P–Pt–P angle is considerably larger than 90° [97.10(4)°], thus reflecting the steric bulk of the azepine moieties. Again, the latter are located on opposite sides of the coordination plane (N-to-plane distance: 1.34 Å for both units), thereby minimizing steric repulsions within the molecule. Obviously, the chiral azepine units influence the orientation of the rings of the biphenyl residues, which both adopt a *pseudo*-(*S*) configuration in the solid state. Molecular models clearly reveal stronger steric interactions within a hypothetical analogue of R_{aze} -**5b** having the biphenyl moiety blocked in a *pseudo*-*R* configuration. The dihedral angles between the linked phenyl units in **7** (45.2°) are relatively small compared with those of the binaphthyl moieties (54.3°).

Performing the rhodium-catalyzed hydrogenation of various methyl 2-(acetylamino)-3-arylpropenoates with ligands **2–5** allowed us to study the influence of the binaphthyl-containing azepine residue on both catalyst activity and enantioselectivity (Scheme 4).

All catalytic runs (see Tables 1 and 2) were carried out with catalysts generated in situ under 5 bar pressure, using an olefin-to-rhodium ratio of 100:1. Operating with phosphoramidites at 0 °C led to selectivities similar to those at room temperature (Table 1, entries 1 and 2), but the catalyst was a little less active. On the other hand, a significant drop



Scheme 4. Hydrogenation of methyl 2-(acetyl-amino)-3-arylpropenoates.

of the TOF value was observed with a higher olefin-to-metal ratio (Table 1, entries 1 and 3). Further, among all the solvents tested (THF, MeOH, AcOEt, CH₂Cl₂), dichloromethane gave the best results (Table 1, entries 1 and 4–6). All the subsequent runs were therefore performed at room temperature in dichloromethane with a substrate to metal ratio of 100:1.

Table 1. Solvent, temperature and Rh/L [L = (*R*_{aze},*S*_{bin})-**4c**] ratio variations in the catalytic hydrogenation of methyl 2-(acetyl-amino)-3-phenylpropenoate.^[a]

Entry	R	Solvent	Time / h	% Conv. ^[b]	% ee ^[c]	Config.
1	Ph	CH ₂ Cl ₂	1	100	99	<i>R</i>
2 ^[d]	Ph	CH ₂ Cl ₂	4	100	99	<i>R</i>
3 ^[e]	Ph	CH ₂ Cl ₂	4	89	96	<i>R</i>
4	Ph	THF	1	100	74	<i>R</i>
5	Ph	MeOH	1	100	57	<i>R</i>
6	Ph	AcOEt	1	100	72	<i>R</i>

[a] General conditions: *P*(H₂) = 5 bar; *T* = room temp.; [substrate/Rh/ligand = 100:1:2.2]. [b] Conversions were determined by means of ¹H NMR spectroscopy. [c] Enantioselectivities were determined by chiral GC analysis using a CHROMPAK chiral fused silica 25 m × 0.25 mm i.d. and/or specific rotation. Coating Chirasil-L-Val column. [d] Run carried out at 0 °C. [e] Substrate/Rh/ligand = 1000:1:2.2.

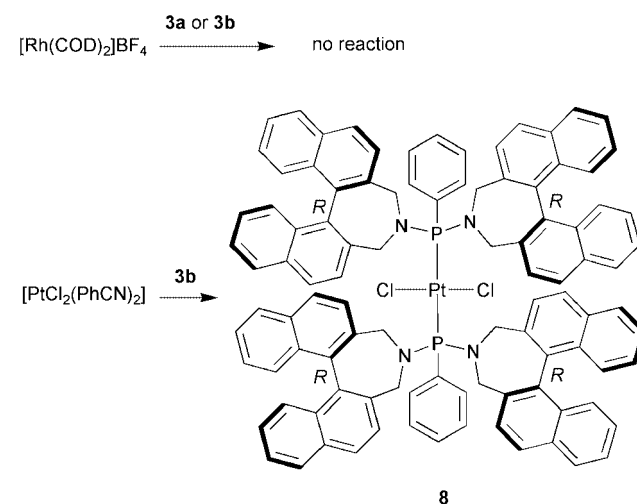
Generally, the use of chiral monodentate aminodiphenylphosphanes *S*_{aze}-**2a** and *R*_{aze}-**2b** as ligands in metal-catalyzed asymmetric hydrogenations gave lower activities (Table 2, entries 1 and 2) than that of their phosphoramidite analogues (conversion of ca. 70% after 16 h vs. full conversion after 1 h). Moreover, in terms of enantiodiscrimination, they proved to be extremely poor, as the measured *ee* values did not exceed 3%.

More surprising was the very low hydrogenation rate (Table 2, entries 3 and 4) observed when (diazepinyl)phenylphosphanes (*S*_{aze},*S*_{aze})-**3a** and (*R*_{aze},*R*_{aze})-**3b** were used as ligands. In fact, as revealed by a separate experiment, no reaction occurred when [Rh(COD)₂]BF₄ was treated with two equivalents of **3a** or **3b**. We also found that when hydrogenation of the substrate was repeated with [Rh(COD)₂]-BF₄ alone (Table 2, entry 20), the observed hydrogenation rate lay in the same range as when carried out in the presence of ligand. It must be emphasized here that despite its bulkiness, (*R*_{aze},*R*_{aze})-**3b** was able to bind transition metal centres, as revealed, e.g., by its reaction with [PtCl₂(PhCN)₂], leading quantitatively to *trans*-[PtCl₂(**3b**)₂] (**8**) (Scheme 5; see also Experimental Section). Bisaminophosphane–platinum complexes with *trans* stereochemistry have already been reported.^[37]

Table 2. Enantioselective hydrogenation of α-dehydroamino acid esters by Rh-monodentate phosphane catalysts in dichloromethane.^[a]

Entry	R	Ligand	Time / h	% Conv.	% ee	Config.
1	Ph	<i>S</i> _{aze} - 2a	16	63	0	
2	Ph	<i>R</i> _{aze} - 2b	16	76	3	<i>R</i>
3	Ph	(<i>S</i> _{aze} , <i>S</i> _{aze})- 3a	24	6	n.d.	
4	Ph	(<i>R</i> _{aze} , <i>R</i> _{aze})- 3b	24	8	n.d.	
5	4-F-C ₆ H ₄	(<i>R</i> _{aze} , <i>S</i> _{bin})- 4c	1	100	99	<i>R</i>
6	4-Cl-C ₆ H ₄	(<i>R</i> _{aze} , <i>S</i> _{bin})- 4c	1	100	99	<i>R</i>
7	3,4-Cl ₂ -C ₆ H ₃	(<i>R</i> _{aze} , <i>S</i> _{bin})- 4c	1	100	99	<i>R</i>
8	Ph	(<i>S</i> _{aze} , <i>R</i> _{bin})- 4d	1	100	96	<i>S</i>
9	4-F-C ₆ H ₄	(<i>S</i> _{aze} , <i>R</i> _{bin})- 4d	1	100	97	<i>S</i>
10	4-Cl-C ₆ H ₄	(<i>S</i> _{aze} , <i>R</i> _{bin})- 4d	1	100	98	<i>S</i>
11	3,4-Cl ₂ -C ₆ H ₃	(<i>S</i> _{aze} , <i>R</i> _{bin})- 4d	1	100	99	<i>S</i>
12	Ph	(<i>R</i> _{aze} , <i>R</i> _{bin})- 4b	1	100	83	<i>S</i>
13	4-F-C ₆ H ₄	(<i>R</i> _{aze} , <i>R</i> _{bin})- 4b	1	100	86	<i>S</i>
14	4-Cl-C ₆ H ₄	(<i>R</i> _{aze} , <i>R</i> _{bin})- 4b	1	100	81	<i>S</i>
15	3,4-Cl ₂ -C ₆ H ₃	(<i>R</i> _{aze} , <i>R</i> _{bin})- 4b	1	100	79	<i>S</i>
16	Ph	(<i>S</i> _{aze} , <i>S</i> _{bin})- 4a	1	100	82	<i>R</i>
17	4-F-C ₆ H ₄	(<i>S</i> _{aze} , <i>S</i> _{bin})- 4a	1	100	85	<i>R</i>
18	4-Cl-C ₆ H ₄	(<i>S</i> _{aze} , <i>S</i> _{bin})- 4a	1	100	81	<i>R</i>
19	3,4-Cl ₂ -C ₆ H ₃	(<i>S</i> _{aze} , <i>S</i> _{bin})- 4a	1	100	79	<i>R</i>
20	Ph	none	63	12	0	
21	Ph	<i>S</i> -MonoPhos	15	100	92	<i>R</i>
22	4-F-C ₆ H ₄	<i>S</i> -MonoPhos	15	100	97	<i>R</i>
23	4-Cl-C ₆ H ₄	<i>S</i> -MonoPhos	15	100	95	<i>R</i>
24	3,4-Cl ₂ -C ₆ H ₃	<i>S</i> -MonoPhos	15	100	93	<i>R</i>
25	Ph	<i>S</i> _{aze} - 5a	1	98	50	<i>S</i>
26	4-F-C ₆ H ₄	<i>S</i> _{aze} - 5a	1	100	49	<i>S</i>
27	4-Cl-C ₆ H ₄	<i>S</i> _{aze} - 5a	1	96	50	<i>S</i>
28	3,4-Cl ₂ -C ₆ H ₃	<i>S</i> _{aze} - 5a	1	100	45	<i>S</i>
29	Ph	<i>R</i> _{aze} - 5b	1	97	51	<i>R</i>
30	4-F-C ₆ H ₄	<i>R</i> _{aze} - 5b	1	98	49	<i>R</i>
31	4-Cl-C ₆ H ₄	<i>R</i> _{aze} - 5b	1	94	49	<i>R</i>
32	3,4-Cl ₂ -C ₆ H ₃	<i>R</i> _{aze} - 5b	1	100	44	<i>R</i>

[a] General conditions as for Table 1.



Scheme 5. Coordination properties of **3** towards [Rh(COD)₂]BF₄ and [PtCl₂(PhCN)₂].

In contrast, the four diastereoisomeric phosphoramidites **4a–d** proved to be much more effective ligands. Hydrogenation rates are well known to be higher for phosphoramidites than for aminophosphanes,^[21] and it came as no surprise that **4a–d** were ca. 16 times more active than **2a** and **2b**.

Regardless of the unsaturated substrate used, *ee* values higher than 99% were obtained with enantiomeric phosphoramidites ($R_{\text{aze}}, S_{\text{bin}}$)-**4c** and ($S_{\text{aze}}, R_{\text{bin}}$)-**4d**, which is well above the values reported for Feringa's MonoPhos ligand, (binoP)NMe₂ (Table 1, entry 1 and Table 2, entries 5–7, 21–24). These findings contrast with the results of de Vries et al., who showed that replacing the amino group of MonoPhos by some seven-membered, cyclic amino groups decreases the enantioselectivity.^[22] Interestingly, the counterparts of the two above ligands, namely ($S_{\text{aze}}, S_{\text{bin}}$)-**4a** and ($R_{\text{aze}}, R_{\text{bin}}$)-**4b** gave poorer results (up to 20% decrease) whatever the substrates used (Table 2, entries 12–19). Switching the chiral configuration of the azepine moiety from *R*, as in ($R_{\text{aze}}, S_{\text{bin}}$)-**4c**, to *S*, as in ($S_{\text{aze}}, S_{\text{bin}}$)-**4a**, clearly led to a significant drop of enantioselectivity (Table 1, entry 1 and Table 2, entries 5–7 and 16–19; compare also with the results obtained for MonoPhos, Table 2, entries 21–24). Such a match and mismatch effect between diastereoisomeric pairs has already been reported for other phosphoramidites containing two stereogenic centres but not to such an extent.^[21,38] This means that the chiral information provided by the azepine residue undoubtedly plays a significant role in the enantiodiscrimination process, with the chirality of the binoP group being dominant. Overall, having opposite configurations of the two binaphthyl units enhances the enantioselectivity, while identical configurations result in a drop in selectivity. The ability of the dinaphthoazepine moiety having a given configuration (*R* or *S*) to favor hydrogenation products with the same configuration (*R* or *S*, respectively) was further verified by performing tests with the biphenyl phosphoramidites S_{aze} -**5a** or R_{aze} -**5b** (Table 2, entries 25–32). Remarkably, in spite of having azepine groups as their only stereogenic moieties, these ligands, which are somewhat remote from the phosphorus atom, are able to give rise to significant *ee*'s (up to 51%, Table 2, entries 25–32). The question is whether the chiral information is passed directly from the azepine residue onto the substrate to be hydrogenated or, as the X-ray crystal structure of **7** indicates, it is transferred onto the latter via the 1,1'-biphenolate group.

Conclusions

In this study, we have described the synthesis and catalytic properties of the first Feringa-type phosphoramidites incorporating chiral dinaphthoazepine units. These ligands, which contain two bridged binaphthyl units, display high catalytic activity in the hydrogenation of α -dehydroamino acid esters. Provided these phosphoramidites contain binaphthyl units having the opposite configuration, enantioselectivities higher than those observed for existing monophosphanes, such as MonoPhos and MorfPhos, were obtained. For instance, ligand **4c**, gives rise to *ee*'s as high as 99% for all the substrates tested. Overall, **4c** is the best-performing reported phosphoramidite bearing a chiral amino moiety. To address the question of whether its high performance originates directly from the steric crowding

and the rigidity of the azepinyl group, therefore allowing control of the substrate orientation, or a domino effect involving the P-bound binaphthyl unit requires further investigations, in particular the chemical modification of the dinaphthoazepine fused-ring system.

Experimental Section

General Procedures: All manipulations involving aminophosphanes were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. CDCl₃ was passed through a column (diameter 5 cm) filled with alumina and stored under nitrogen over molecular sieves (4 Å). Routine ¹H, ¹³C{¹H} and ³¹P{¹H} spectra were recorded with Bruker FT Instruments (AC-200 and AC-300). ¹H NMR spectra were referenced to residual protonated solvents ($\delta = 7.26$ ppm for CDCl₃ and 7.16 ppm for C₆D₆), ¹³C chemical shifts are reported relative to deuterated solvents ($\delta = 77.16$ ppm for CDCl₃ and 128.06 ppm for C₆D₆), and the ³¹P NMR spectroscopic data are given relative to external H₃PO₄. Chemical shifts and coupling constants are reported in ppm and in Hertz, respectively. Mass spectra were recorded with a Bruker MicroTOF spectrometer (ESI) using CH₂Cl₂ as solvent. Optical rotations were measured on a Perkin-Elmer 341 digital polarimeter with a 1-dm cell. The two enantiomeric azepines used in this study, S_{aze} -**1a** and R_{aze} -**1b**, were obtained according to a published procedure.^[25] The corresponding elemental analyses and $[\alpha]_{\text{D}}^{20}$ values (specific rotations in deg cm² g⁻¹) are given below.

(S)-4,5-Dihydro-3H-dinaphtho[2,1-c:1',2'-e]azepine (S_{aze} -1a**):** C₂₂H₁₇N (295.38): calcd. C 89.5, H 5.8, N 4.7; found C 89.6, H 5.9, N 4.8. M.p. 147–149 °C (ref.^[25] 145–147 °C); $[\alpha]_{\text{D}}^{20} = +685.3$ (*c* = 0.22, CHCl₃).

(R)-4,5-Dihydro-3H-dinaphtho[2,1-c:1',2'-e]azepine (R_{aze} -1b**):** C₂₂H₁₇N (295.38): calcd. C 89.5, H 5.8, N 4.7; found C 89.5, H 5.6, N 4.6. M.p. 145–147 °C (ref.^[25] 145–147 °C); $[\alpha]_{\text{D}}^{20} = -686.8$ (*c* = 0.22, CHCl₃).

General Procedure for the Synthesis of Aminophosphanes **2a and **2b**:** To a solution of azepine in toluene (50 mL) were added 1 equiv. of diisopropylethylamine and 1 equiv. of chlorodiphenylphosphane. The mixture was stirred for 3 h at room temperature before being filtered through dried Al₂O₃. The solvent was removed in vacuo to afford the product as a white solid.

(S)-Phosphane (S_{aze} -2a**):** This compound was prepared according to the above procedure from S_{aze} -**1a** (0.800 g, 2.71 mmol), chlorodiphenylphosphane (0.598 g, 2.71 mmol, ca. 0.49 mL) and diisopropylethylamine (0.350 g, 2.71 mmol, ca. 0.47 mL); yield 0.800 g, 62%. C₃₄H₂₆NP (479.55): calcd. C 85.2, H 5.5, N 2.9; found C 85.3, H 5.4, N 3.0. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.95$ (d, *J*_{H,H} = 7.9 Hz, 2 H, arom. H), 7.94 (d, *J*_{H,H} = 8.2 Hz, 2 H, arom. H), 7.59–7.35 (m, 13 H, arom. H), 7.29–7.24 (m, 5 H, arom. H), 4.19 and 3.73 (ABX spectrum, *J*_{AX} = 6.3, *J*_{BX} = 6.4, *J*_{AB} = 12.4 Hz, 4 H, ArCH₂) ppm. ¹³C NMR (75 MHz, CDCl₃) (*J*_{C,P} values were obtained from decoupling experiments): $\delta = 140.01$ (d, *J*_{C,P} = 11.8 Hz, *ipso*-C of Ph), 139.31 (d, *J*_{C,P} = 15.5 Hz, *ipso*-C of Ph), 134.70 (s, quat. C of naphthyl), 134.58 (d, *J*_{C,P} = 3.7 Hz, quat. C of naphthyl), 133.08 (s, quat. C), 132.28 (d, *J*_{C,P} = 20.4 Hz, *o*-C of Ph), 131.62 (d, *J*_{C,P} = 18.9 Hz, *o*-C of Ph), 131.44 (s, quat. C), 129.11 (s, arom. CH), 128.60 (s, arom. CH), 128.49 (d, *J*_{C,P} = 3 Hz, arom. CH), 128.46 (d, *J*_{C,P} = 2 Hz, arom. CH), 128.36 (s, arom. CH), 128.22 (d, *J*_{C,P} = 6.2 Hz, arom. CH), 127.60 (s, arom. CH), 127.28 (s, arom. CH), 125.86 (s, arom. CH), 125.53 (s, arom. CH),

53.64 (d, $^2J_{C,P} = 16.7$ Hz, NCH₂) ppm. ^{31}P NMR (121 MHz, CDCl₃): $\delta = 63.7$ (s) ppm. M.p. 196–198 °C; $[\alpha]_D^{20} = 183.0$ ($c = 0.44$, CHCl₃). MS (EI): $m/z = 479.3$ (71%, [M]⁺; C₃₄H₂₆NP requires 479.2).

(R)-Phosphane *R*_{aze}-2b: This compound was prepared as above from *R*_{aze}-1b (0.917 g, 3.10 mmol), chlorodiphenylphosphane (0.750 g, 3.40 mmol, ca. 0.61 mL) and diisopropylethylamine (0.401 g, 3.10 mmol, ca. 0.54 mL); yield 1.150 g, 77%. C₃₄H₂₆NP (479.55): calcd. C 85.2, H 5.5, N 2.9; found C 85.4, H 5.5, N 2.8. NMR as for *S*_{aze}-2a. M.p. 195–197 °C; $[\alpha]_D^{20} = -198.6$ ($c = 0.22$, CHCl₃). MS (ESI-TOF): $m/z = 480.2$ (100%, [M + H]⁺; C₃₄H₂₇NP requires 480.2).

General Procedure for the Synthesis of Diaminophosphanes 3a and 3b: To a solution of the appropriate azepine derivative in toluene (50 mL) were added 1 equiv. of diisopropylethylamine and 0.5 equiv. of dichlorophenylphosphane. The mixture was stirred for 3 h at room temperature before being filtered through dried Al₂O₃. The solvent was removed in vacuo to afford the product as a white solid.

Bis[(S)-(4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]azepin-4-yl)]-phenylphosphane (*S*_{aze},*S*_{aze})-3a: This compound was prepared according to the above procedure from *S*_{aze}-1a (0.633 g, 2.14 mmol) and dichlorophenylphosphane (0.185 g, 1.03 mmol, ca. 0.14 mL) and diisopropylethylamine (0.277 g, 2.14 mmol, ca. 0.37 mL); yield 0.539 g, 75%. C₅₀H₃₇N₂P (696.82): calcd. C 86.2, H 5.4, N 4.0; found C 86.3, H 5.4, N 4.2. 1H NMR (300 MHz, CDCl₃): $\delta = 7.79$ (t, $J_{H,H} = 7.5$ Hz, 4 H, arom. H), 7.61–7.13 (m, 23 H, arom. H), 7.07 (d, $J_{H,H} = 8.2$ Hz, 2 H, arom. H), 4.36 and 3.96 (AB spectrum, $J_{AB} = 12.3$ Hz, 2 H, ArCH₂), 4.38 and 3.91 (AB spectrum, $J_{AB} = 12.1$ Hz, 2 H, ArCH₂), 4.12 and 3.72 (AB spectrum, $J_{AB} = 12.4$ Hz, 2 H, ArCH₂) ppm. ^{13}C NMR (75 MHz, CDCl₃) ($J_{C,P}$ values were obtained via decoupling experiments): $\delta = 139.65$ (d, $J_{C,P} = 5.0$ Hz, quat. C), 134.74 (s, quat. C), 134.59 (s, quat. C), 134.08 (d, $J_{C,P} = 7.5$ Hz, quat. C), 133.20 (s, quat. C), 132.83 (s, quat. C), 131.51 (d, $J_{C,P} = 15.5$ Hz, *o*-C of Ph, tentative assignment), 131.45 (s, quat. C), 131.27 (s, quat. C), 129.01 (s, arom. CH), 128.70 (s, arom. CH), 128.67 (s, arom. CH), 128.53 (s, arom. CH), 128.45 (s, arom. CH), 128.39 (s, arom. CH), 128.36 (s, quat. C), 127.98 (s, arom. CH), 127.50 (s, arom. CH), 127.44 (s, arom. CH), 126.76 (s, arom. CH), 126.66 (s, arom. CH), 125.94 (s, arom. CH), 125.73 (s, arom. CH), 125.40 (s, arom. CH), 125.23 (s, arom. CH), 53.37 (d, $^2J_{C,P} = 18.1$ Hz, NCH₂), 52.57 (d, $^2J_{C,P} = 15.1$ Hz, NCH₂) ppm. ^{31}P NMR (121 MHz, CDCl₃): $\delta = 96.49$ (s) ppm. M.p. 224–226 °C; $[\alpha]_D^{20} = 284.0$ ($c = 0.2$, CHCl₃). MS (ESI-TOF): $m/z = 697.2$ (100%, [M + H]⁺; C₅₀H₃₈N₂P requires 697.3).

Phosphane (*R*_{aze},*R*_{aze})-3b: This compound was prepared as above from *R*_{aze}-1b (0.914 g, 3.09 mmol), dichlorophenylphosphane (0.264 g, 1.47 mmol, ca. 0.20 mL) and diisopropylethylamine (0.400 g, 3.09 mmol, ca. 0.54 mL); yield 0.760 g, 74%. C₅₀H₃₇N₂P (696.82): calcd. C 86.2, H 5.4, N 4.0; found C 86.1, H 5.6, N 3.9. NMR as for (*S*_{aze},*S*_{aze})-3a. $[\alpha]_D^{20} = -276.3$ ($c = 0.2$, CHCl₃); m/z (EI) 696.5 (100%, [M]⁺; C₅₀H₃₇N₂P requires 696.3).

General Procedure for the Synthesis of Phosphoramidites 4a–d and 5: To a solution of azepine in toluene (50 mL) was added 1 equiv. of diisopropylethylamine and 1 equiv. of chlorophosphite. The mixture was stirred overnight at room temperature before being filtered through dried Al₂O₃. The solvent was removed in vacuo to afford the product as a white solid.

4-{(S)-4,5-Dihydro-3H-dinaphtho[2,1-c:1',2'-e]azepin-4-yl}-(S)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphine (*S*_{aze},*S*_{bin})-4a: This compound was prepared according to the above procedure from *S*_{aze}-1a (0.560 g, 1.90 mmol), (*S*)-1,1'-binaphthyl-2,2'-diyl chlorophosphite (0.680 g, 1.90 mmol) and diisopropylethylamine (0.245 g, 1.90 mmol, ca. 0.33 mL); yield 0.763 g, 66%. C₄₂H₂₈NO₂P (609.65): calcd. C 82.7, H 4.6, N 2.3; found C 82.7, H 4.7, N 2.3. 1H NMR (300 MHz, CDCl₃): $\delta = 8.16$ (d, $J_{H,H} = 8.7$ Hz, 1 H, arom. H), 8.08 (d, $J_{H,H} = 8.2$ Hz, 1 H, arom. H), 7.98 (d, $J_{H,H} = 8.2$ Hz, 2 H, arom. H), 7.96 (d, $J_{H,H} = 8.8$ Hz, 1 H, arom. H), 7.95 (d, $J_{H,H} = 8.7$ Hz, 2 H, arom. H), 7.92 (d, $J_{H,H} = 8.8$ Hz, 1 H, arom. H), 7.51–7.17 (m, 16 H, arom. H), 4.14 and 3.61 (ABX spectrum, $J_{AX} = 7.7$ Hz, $J_{BX} = 5.9$ Hz, $J_{AB} = 13.0$ Hz, 4 H, ArCH₂) ppm. ^{13}C NMR (75 MHz, CDCl₃): $\delta = 149.81$ (s, quat. C), 149.62 (d, $J_{C,P} = 5.6$ Hz, quat. C), 135.04 (s, quat. C), 133.18 (d, $J_{C,P} = 4.3$ Hz, quat. C), 133.13 (s, quat. C), 132.88 (d, $J_{C,P} = 4.3$ Hz, quat. C), 131.40 (s, quat. C), 131.33 (s, quat. C), 130.91 (s, quat. C), 130.41 (s, arom. CH), 130.03 (s, arom. CH), 129.07 (s, arom. CH), 129.03 (s, arom. CH), 128.39 (s, arom. CH), 128.27 (s, arom. CH), 127.38 (s, arom. CH), 127.27 (s, arom. CH), 127.12 (s, arom. CH), 127.04 (s, arom. CH), 126.30 (s, arom. CH), 126.18 (s, arom. CH), 125.93 (s, arom. CH), 125.66 (s, arom. CH), 124.86 (s, arom. CH), 123.91 (d, $J_{C,P} = 5.0$ Hz, quat. C), 122.93 (s, arom. CH), 122.88 (s, quat. C), 122.01 (s, arom. CH), 48.36 (d, $^2J_{C,P} = 21.7$ Hz, ArCH₂) ppm. ^{31}P NMR (121 MHz, CDCl₃): $\delta = 146.0$ (s) ppm. M.p. 157–159 °C; $[\alpha]_D^{20} = 153.6$ ($c = 0.46$, CHCl₃). MS (EI): $m/z = 609.3$ (12%, [M]⁺; C₄₂H₂₈NO₂P requires 609.2).

(*R*_{aze},*R*_{bin})-4b: This compound was obtained as described above from *R*_{aze}-1b (0.896 g, 3.03 mmol), (*R*)-1,1'-binaphthyl-2,2'-diyl chlorophosphite (1.130 g, 3.03 mmol) and diisopropylethylamine (0.392 g, 3.03 mmol, ca. 0.53 mL); yield 1.570 g, 85%. C₄₂H₂₈NO₂P (609.65): calcd. C 82.7, H 4.6, N 2.3; found C 82.7, H 4.6, N 2.3. NMR as for (*S*_{aze},*S*_{bin})-4a. $[\alpha]_D^{20} = -154.8$ ($c = 0.46$, CHCl₃). MS (ESI-TOF): $m/z = 610.2$ (100%, [M + H]⁺; C₄₂H₂₉NO₂P requires 610.2).

(*R*_{aze},*S*_{bin})-4c: This compound was obtained as above from *R*_{aze}-1b (0.957 g, 3.24 mmol), (*S*)-1,1'-binaphthyl-2,2'-diyl chlorophosphite (1.250 g, 3.56 mmol) and diisopropylethylamine (0.419 g, 3.24 mmol, ca. 0.56 mL); yield 1.600 g, 81%. C₄₂H₂₈NO₂P (609.65): calcd. C 82.7, H 4.6, N 2.3; found C 82.8, H 4.7, N 2.4. 1H NMR (300 MHz, CDCl₃): $\delta = 7.92$ –8.01 (m, 6 H, arom. H), 7.67 (dd, $J_{H,H} = 8.7$, 1.0 Hz, 1 H, arom. H), 7.58 (d, $J_{H,H} = 8.3$ Hz, 2 H, arom. H), 7.57 (dd, $J_{H,H} = 8.7$, 0.9 Hz, 1 H, arom. H), 7.50 (td, $J_{H,H} = 8.0$, 1.2 Hz, 2 H, arom. H), 7.45–7.37 (m, 4 H, arom. H), 7.35–7.16 (m, 7 H, arom. H), 6.61 (d, $J_{H,H} = 8.9$ Hz, 1 H, arom. H), 4.34 and 3.37 (ABX spectrum, $J_{AX} = 7.5$ Hz, $J_{BX} = 8.9$ Hz, $J_{AB} = 12.8$ Hz, 4 H, ArCH₂) ppm. ^{13}C NMR (75 MHz, CDCl₃): $\delta = 150.38$ (d, $J_{C,P} = 5.0$ Hz, quat. C), 149.54 (s, quat. C), 135.29 (s, quat. C), 133.47 (d, $J_{C,P} = 3.1$ Hz, quat. C), 133.24 (s, quat. C), 132.88 (d, $J_{C,P} = 1.2$ Hz, quat. C), 132.40 (s, quat. C), 131.47 (s, quat. C), 131.38 (s, quat. C), 130.63 (s, quat. C), 130.38 (s, arom. CH), 130.09 (s, arom. CH), 129.22 (s, arom. CH), 129.11 (s, arom. CH), 128.40 (s, arom. CH), 128.29 (s, arom. CH), 128.24 (s, arom. CH), 127.47 (s, arom. CH), 127.31 (s, arom. CH), 127.09 (s, arom. CH), 126.87 (s, arom. CH), 126.13 (s, arom. CH), 126.05 (s, arom. CH), 125.99 (s, arom. CH), 125.71 (s, arom. CH), 125.37 (s, quat. C), 124.88 (s, arom. CH), 124.51 (s, arom. CH), 124.09 (d, $J_{C,P} = 5.0$ Hz, quat. C), 122.08 (d, $J_{C,P} = 1.2$ Hz, arom. CH), 121.61 (s, arom. CH), 47.46 (d, $^2J_{C,P} = 20.5$ Hz, ArCH₂) ppm. ^{31}P NMR (121 MHz, CDCl₃): $\delta = 143.0$ (s) ppm. M.p. 155–157 °C; $[\alpha]_D^{20} = 61.8$ ($c = 0.28$, CHCl₃). MS (EI): $m/z = 609.4$ (9%, [M]⁺; C₄₂H₂₈NO₂P requires 609.2).

(*S*_{aze},*R*_{bin})-4d: This compound was prepared as above from *S*_{aze}-1a (0.560 g, 1.90 mmol), (*R*)-1,1'-binaphthyl-2,2'-diyl chlorophosphite (0.680 g, 1.90 mmol) and diisopropylethylamine (0.245 g, 1.90 mmol, ca. 0.33 mL); yield 0.878 g, 76%. C₄₂H₂₈NO₂P (609.65): calcd. C 82.7, H 4.6, N 2.3; found C 82.8, H 4.6, N 2.3. NMR as for (*R*_{aze},*S*_{bin})-4c. [α]_D²⁰ = 62.4 (*c* = 0.28, CHCl₃). MS (ESI-TOF): *m/z* = 610.2 (100%, [M + H]⁺; C₄₂H₂₉NO₂P requires 610.2).

(*S*_{aze})-5a: This compound was prepared as above from *S*_{aze}-1a (0.119 g, 0.40 mmol), 1,1'-binaphthyl-2,2'-diyl chlorophosphite (0.101 g, 0.40 mmol) and diisopropylethylamine (0.052 g, 0.40 mmol, ca. 0.07 mL); yield 0.160 g, 78%. C₃₄H₂₄NO₂P (509.53): calcd. C 80.1, H 4.8, N 2.8; found C 80.3, H 4.8, N 2.8. ¹H NMR (300 MHz, CDCl₃): δ = 7.98 (t, *J*_{H,H} = 7.7 Hz, 4 H, arom. H), 7.53–7.05 (m, 15 H, arom. H), 6.81 (d, *J*_{H,H} = 7.9 Hz, 1 H, arom. H), 4.40 and 3.57 (ABX spectrum, *J*_{AX} = 7.5 Hz, *J*_{BX} = 6.9 Hz, *J*_{AB} = 12.8 Hz, 4 H, ArCH₂) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 152.04 (d, *J*_{C,P} = 5.6 Hz, 1 C, quat. C), 151.22 (d, *J*_{C,P} = 4.4 Hz, quat. C), 135.30 (s, quat. C), 133.52 (d, *J*_{C,P} = 3.7 Hz, quat. C), 133.30 (s, quat. C), 131.48 (s, quat. C), 131.45 (s, quat. C), 131.07 (d, *J*_{C,P} = 2.5 Hz, quat. C), 129.99 (s, arom. CH), 129.73 (s, arom. CH), 129.36 (s, arom. CH), 129.24 (s, arom. CH), 128.42 (s, arom. CH), 127.53 (s, arom. CH), 127.41 (s, arom. CH), 126.03 (s, arom. CH), 125.76 (s, arom. CH), 124.90 (s, arom. CH), 124.55 (s, arom. CH), 122.53 (s, arom. CH), 121.91 (s, arom. CH), 47.83 (d, ²*J*_{C,P} = 21.1 Hz, ArCH₂) ppm. ³¹P NMR (121 MHz, CDCl₃): δ = 144.9 (s) ppm. [α]_D²⁰ = 120.0 (*c* = 1.60, CH₂Cl₂). MS (EI): *m/z* = 509.1 (37%, [M]⁺; C₃₄H₂₄NO₂P requires 509.2).

(*R*_{aze})-5b: This compound was obtained as above using *R*_{aze}-1b (0.080 g, 0.27 mmol), 1,1'-binaphthyl-2,2'-diyl chlorophosphite (0.068 g, 0.27 mmol) and diisopropylethylamine (0.035 g, 0.27 mmol, ca. 0.05 mL); yield 0.090 g, 65%. C₃₄H₂₄NO₂P (509.53): calcd. C 80.1, H 4.8, N 2.8; found C 80.0, H 4.8, N 2.7. NMR as for (*S*_{aze})-5a. M.p. 144–146 °C; [α]_D²⁰ = –118.8 (*c* = 1.60, CH₂Cl₂). MS (EI): *m/z* = 509.1 (38%, [M]⁺; C₃₄H₂₄NO₂P requires 509.2).

trans-Dichloroplatinum(II) Complex 6: A solution of *S*_{aze}-2a (0.133 g, 0.277 mmol) in CH₂Cl₂ (8 mL) was added to a solution of [PtCl₂(PhCN)₂] (0.066 g, 0.139 mmol) in CH₂Cl₂ (10 mL). After stirring for 24 h, the solution was concentrated to 6 mL, whereupon *n*-pentane (30 mL) was added. Cooling the solution to –10 °C caused complex **6** to precipitate as a white solid, which was filtered; yield 0.161 g, 95%. C₆₈H₅₂Cl₂N₂P₂Pt (1225.09): calcd. C 66.7, H 4.3, N 2.3; found C 66.7, H 4.4, N 2.2. ¹H NMR (300 MHz, CDCl₃): δ = 7.91 (d, *J*_{H,H} = 8.1 Hz, 4 H, arom. H), 7.84 (d, *J*_{H,H} = 8.3 Hz, 4 H, arom. H), 7.73–7.66 (m, 4 H, arom. H), 7.59–7.51 (m, 4 H, arom. H), 7.47–7.38 (m, 14 H, arom. H), 7.32–7.16 (m, 14 H, arom. H), 4.77 (virtual t, ³*J*_{H,P} + ⁵*J*_{H,P'} = 7.8 Hz, 2 H, ArCH₂), 4.73 (virtual t, ³*J*_{H,P} + ⁵*J*_{H,P'} = 7.8 Hz, 2 H, ArCH₂), 3.75 (virtual t, ³*J*_{H,P} + ⁵*J*_{H,P'} = 5.5 Hz, 2 H, ArCH₂), 3.70 (virtual t, ³*J*_{H,P} + ⁵*J*_{H,P'} = 5.2 Hz, 2 H, ArCH₂). ¹³C NMR (75 MHz, CDCl₃): δ = 135.15 (s, quat. C), 133.63 (virtual t, ¹*J*_{C,P} + ³*J*_{C,P'} = 5.0 Hz, quat. C), 133.29 (s, quat. C), 133.15 (d, *J*_{C,P} = 13.0 Hz, arom. CH), 133.07 (d, *J*_{C,P} = 13.0 Hz, arom. CH), 131.35 (s, quat. C), 130.44 (s, arom. CH), 130.18 (s, arom. CH), 129.11 (s, arom. CH), 128.40 (s, arom. CH), 127.99 (s, arom. CH), 127.91 (s, arom. CH), 127.82 (s, arom. CH), 127.79 (s, arom. CH), 127.78 (s, quat. C), 127.64 (s, arom. CH), 125.87 (s, arom. CH), 125.73 (s, arom. CH), 52.30 (virtual t, ²*J*_{C,P} + ⁴*J*_{C,P'} = 6.8 Hz, ArCH₂) ppm. ³¹P NMR (121 MHz, CDCl₃): δ = 81.4 (¹*J*_{Pt,P} = 2743 Hz) ppm. M.p. > 250 °C. MS (ESI-TOF): *m/z* = 1230.32 (82%, [M + Li]⁺; C₆₈H₅₂Cl₂N₂P₂PtLi requires 1230.28).

cis-Dichloroplatinum(II) Complex 7: A solution of (*R*_{aze})-5a (0.156 g, 0.306 mmol) in CH₂Cl₂ (8 mL) was added to a solution

of [PtCl₂(PhCN)₂] (0.072 g, 0.153 mmol) in CH₂Cl₂ (10 mL). After stirring for 24 h, the solution was concentrated to 6 mL, whereupon *n*-pentane (30 mL) was added. Cooling the solution to –10 °C caused complex **7** to precipitate as a white solid, which was collected by filtration; yield 0.190 g, 97%. C₆₈H₄₈Cl₂N₂O₄P₂Pt (1285.05): calcd. C 63.6, H 3.8, N 2.2; found C 63.4, H 3.7, N 2.0. ¹H NMR (300 MHz, CDCl₃): δ = 7.93 (d, *J*_{H,H} = 8.2 Hz, 4 H, arom. H), 7.80 (d, *J*_{H,H} = 8.1 Hz, 4 H, arom. H), 7.58 (d, *J*_{H,H} = 7.9 Hz, 2 H, arom. H), 7.49 (t, *J*_{H,H} = 7.3 Hz, 4 H, arom. H), 7.59–7.12 (m, 18 H, arom. H), 7.15 (t, *J*_{H,H} = 7.1 Hz, 4 H, arom. H), 6.83 (t, *J*_{H,H} = 7.2 Hz, 2 H, arom. H), 6.56 (d, *J*_{H,H} = 5.5 Hz, 2 H, arom. H), 4.68 (br. s, 4 H, ArCH₂), 3.19 (d, ²*J*_{H,H} = 11.7 Hz, 4 H, ArCH₂) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 149.77 (br. s, quat. C), 148.92 (br. s, quat. C), 135.29 (s, quat. C), 133.38 (s, quat. C), 131.76 (s, quat. C), 131.21 (s, quat. C), 130.47 (s, arom. CH), 130.16 (s, arom. CH), 129.60 (s, arom. CH), 129.55 (s, quat. C), 129.15 (s, arom. CH), 129.06 (s, quat. C), 128.41 (s, arom. CH), 127.47 (s, arom. CH), 126.42 (s, arom. CH), 126.04 (s, arom. CH), 123.51 (s, arom. CH), 121.21 (s, arom. CH), 48.99 (s, ArCH₂) ppm. ³¹P NMR (121 MHz, CDCl₃): δ = 85.3 (¹*J*_{Pt,P} = 5580 Hz) ppm. M.p. > 250 °C. MS (ESI-TOF): *m/z* = 1323.74 (93%, [M + K]⁺; C₆₈H₄₈Cl₂KN₂O₄P₂Pt requires 1323.18).

trans-Dichloroplatinum(II) Complex 8: A solution of (*R*_{aze},*R*_{bin})-3b (0.121 g, 0.174 mmol) in CH₂Cl₂ (8 mL) was added to a solution of PtCl₂(PhCN)₂ (0.041 g, 0.087 mmol) in CH₂Cl₂ (10 mL). After stirring for 24 h, the solution was concentrated to 6 mL, upon which *n*-pentane (30 mL) was added. Cooling the solution to –10 °C caused complex **8** to precipitate as a white solid, which was filtered; yield 0.134 g, 93%. C₁₀₀H₇₄Cl₂N₄P₂Pt (1659.62): calcd. C 72.4, H 4.5, N 3.4; found C 72.4, H 4.4, N 3.4. ¹H NMR (300 MHz, CDCl₃): δ = 7.95–7.90 (m, 8 H, arom. H), 7.82–7.69 (m, 13 H, arom. H), 7.57–7.37 (m, 29 H, arom. H), 7.28–7.21 (m, 8 H, arom. H), 4.99 (virtual t, ³*J*_{H,P} + ⁵*J*_{H,P'} = 6.3 Hz, 2 H, ArCH₂), 4.95 (virtual t, ³*J*_{H,P} + ⁵*J*_{H,P'} = 7.3 Hz, 2 H, ArCH₂), 4.72 (virtual t, ³*J*_{H,P} + ⁵*J*_{H,P'} = 7.4 Hz, 2 H, ArCH₂), 4.67 (virtual t, ³*J*_{H,P} + ⁵*J*_{H,P'} = 7.4 Hz, 2 H, ArCH₂), 3.89–3.83 (m, 8 H, ArCH₂) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 135.26 (s, quat. C), 133.80 (s, arom. CH), 133.54 (d, *J*_{C,P} = 5.6 Hz, quat. C), 133.50 (d, *J*_{C,P} = 5.6 Hz, quat. C), 133.19 (s, quat. C), 133.18 (d, *J*_{C,P} = 5.0 Hz, arom. CH), 131.41 (s, quat. C), 131.27 (s, quat. C), 130.36 (s, arom. CH), 129.53 (s, arom. CH), 128.89 (s, arom. CH), 128.62 (s, arom. CH), 128.36 (s, arom. CH), 128.28 (s, arom. CH), 127.67 (s, arom. CH), 127.59 (s, arom. CH), 125.79 (s, arom. CH), 125.71 (s, arom. CH), 125.61 (s, arom. CH), 125.54 (s, arom. CH), 50.82 (virtual t, ²*J*_{C,P} + ⁴*J*_{C,P'} = 6.8 Hz, ArCH₂), 50.64 (virtual t, ²*J*_{C,P} + ⁴*J*_{C,P'} = 6.8 Hz, ArCH₂) ppm. ³¹P NMR (121 MHz, CDCl₃): δ = 81.4 (¹*J*_{Pt,P} = 2945 Hz) ppm. M.p. > 250 °C. MS (MALDI-TOF): *m/z* = 1622.54 (5%, [M – Cl]⁺; C₁₀₀H₇₄ClN₄P₂Pt requires 1622.48).

Crystal Data for 6: Crystals of **6** suitable for X-ray diffraction were obtained by slow diffusion of *n*-heptane into a toluene solution of the complex. PtCl₂P₂C₇₅H₆₀N₂, *M* = 1317.18, triclinic, space group *P*1, *a* = 10.5246(7), *b* = 13.1551(6), *c* = 14.2077(9) Å, *V* = 1799.25(2) Å³, *Z* = 1, *D*_x = 1.216 g cm^{–3}, λ (Mo-*K*_α) = 0.71073 Å, μ = 2.107 cm^{–1}, *F*(000) = 666, *T* = 293(2) K. The sample (0.32 × 0.32 × 0.22 mm) was studied with an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite-monochromatized Mo-*K*_α radiation. The data collection was carried out using Crysalis RED.^[39] 17184 Reflections were collected (2.76 < θ < 32.09°), 12472 observations with *I* > 2.0σ(*I*). The structure was solved with SIR-97^[40], which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms could be localized with a Fourier difference. The whole structure was refined with SHELXL-97^[41] Hydrogen atoms were included and refined using

a riding mode in SHELX-97. Final results: $R_1 = 0.0819$, $wR_2 = 0.2048$, goodness of fit 0.977, 804 parameters, residual electron density: min./max. = $-0.957/1.526$. Flack's parameter: 0.050 (10).

Crystal Data for 7: Crystals of **7** suitable for X-ray diffraction were obtained by slow diffusion of *n*-pentane into a chloroform solution of the complex. $C_{68}H_{48}Cl_2N_2O_4P_2Pt$, 4 $CHCl_3$, $M = 1762.48$, orthorhombic, space group $P2_12_12$, $a = 24.8457(7)$, $b = 12.8647(3)$, $c = 11.3484(3)$ Å, $V = 3627.3(2)$ Å³, $Z = 2$, $D_x = 1.614$ Mg cm⁻³, $\lambda(Mo-K\alpha) = 0.71073$ Å, $\mu = 25.44$ cm⁻¹, $F(000) = 1752$, $T = 110(1)$ K. The sample ($0.22 \times 0.18 \times 0.16$ mm) was studied on an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite-monochromatized Mo- $K\alpha$ radiation. The data collection was carried out using CrysAlis RED.^[39] 11731 Reflections were collected ($2.90 < \theta < 32.08^\circ$), 10174 observations with $I > 2.0\sigma(I)$. The structure was solved with SIR-97^[40], which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms could be localized with a Fourier difference. The whole structure was refined with SHELXL97.^[41] Hydrogen atoms were included and refined using a riding mode in SHELX-97. Final results: $R_1 = 0.035$, $wR_2 = 0.089$, goodness of fit 1.025, 430 parameters; residual electron density: min./max. = $-2.144/2.047$. Flack's parameter: -0.012 (4)

CCDC-631059 (for **6**) and -643952 (for **7**) contain supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for Asymmetric Hydrogenation and Determination of Enantiomeric Excesses: To a solution of $[Rh(COD)_2]BF_4$ (1 equiv.) in CH_2Cl_2 (10 mL) was added a solution of the ligand (2.2 equiv.) in CH_2Cl_2 (10 mL), and the resulting mixture was stirred for 30 min. before being used in the catalytic run. For those runs carried out in another solvent, the complex was prepared in CH_2Cl_2 as above, then after evaporation of CH_2Cl_2 , the residue was dissolved in the desired solvent (20 mL). Using a syringe, the solution was introduced into a 100 mL glass-lined, stainless steel autoclave containing a magnetic stirring bar and the substrate (2.5 mmol). The autoclave was then placed under the required hydrogen pressure (1 or 5 bar). The tests were carried out at room temperature. At the end of the catalytic run, the autoclave was depressurized, and the mixture was passed through a short silica column to remove the catalyst. Conversions were monitored by ¹H NMR spectroscopy. Enantioselectivities were determined by chiral GC analysis using a CHROMPAK chiral fused silica Chirasil-L-Val column (25 m \times 0.25 mm i.d.) and/or specific rotation.

Acknowledgments

The authors thank Prof. J. B. Harrowfield for interesting discussions. Financial support by Genzyme Pharmaceuticals is gratefully acknowledged.

- [1] T. P. Dang, H. B. Kagan, *J. Chem. Soc. Chem. Commun.* **1971**, 481.
 [2] L. Horner, H. Siegel, H. Büthe, *Angew. Chem.* **1968**, *80*, 1034–1035.
 [3] W. S. Knowles, M. J. Sabacky, *Chem. Commun. (London)* **1968**, 1445–1446.
 [4] W. S. Knowles, M. J. Sabacky, B. D. Vineyard, *J. Chem. Soc. Chem. Commun.* **1972**, 10–11.

- [5] B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman, D. J. Weinkauff, *J. Am. Chem. Soc.* **1977**, *99*, 5946–5952.
 [6] A. Miyashita, A. Yasuda, H. Takaya, K. Toriumi, T. Ito, T. Souchi, R. Noyori, *J. Am. Chem. Soc.* **1980**, *102*, 7932–7934.
 [7] H. Takaya, S. Akutagawa, R. Noyori, *Org. Synth.* **1988**, *67*, 20–28.
 [8] M. J. Burk, *J. Am. Chem. Soc.* **1991**, *113*, 8518–8519.
 [9] M. J. Burk, J. E. Feaster, W. A. Nugent, R. L. Harlow, *J. Am. Chem. Soc.* **1993**, *115*, 10125–10138.
 [10] A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, *J. Am. Chem. Soc.* **1994**, *116*, 4062–4066.
 [11] M. van den Berg, A. J. Minnaard, E. P. Schudde, J. van Esch, A. H. M. de Vries, J. G. de Vries, B. L. Feringa, *J. Am. Chem. Soc.* **2000**, *122*, 11539–11540.
 [12] R. Hulst, N. K. de Vries, B. L. Feringa, *Tetrahedron: Asymmetry* **1994**, *5*, 699–708.
 [13] D. Pena, A. J. Minnaard, J. G. de Vries, B. L. Feringa, *J. Am. Chem. Soc.* **2002**, *124*, 14552–14553.
 [14] M. van den Berg, A. J. Minnaard, R. M. Haak, M. Leeman, E. P. Schudde, A. Meetsma, B. L. Feringa, A. H. M. de Vries, C. E. P. Maljaars, C. E. Willans, D. Hyett, J. A. F. Boogers, H. J. W. Henderickx, J. G. de Vries, *Adv. Synth. Catal.* **2003**, *345*, 308–323.
 [15] M. T. Reetz, T. Sell, *Tetrahedron Lett.* **2000**, *41*, 6333–6336.
 [16] M. T. Reetz, G. Mehler, *Angew. Chem. Int. Ed.* **2000**, *39*, 3889–3890.
 [17] D. Ager, M. van den Berg, A. J. Minnaard, B. L. Feringa, A. H. M. de Vries, C. E. Willans, J. A. F. Boogers, J. G. de Vries, *ACS Symp. Ser. ACS Symp. Ser.* **2004**, 115–119.
 [18] M. T. Reetz, J.-A. Ma, R. Goddard, *Angew. Chem. Int. Ed.* **2005**, *44*, 412–415.
 [19] H. Bernsmann, M. van den Berg, R. Hoen, A. J. Minnaard, G. Mehler, M. T. Reetz, J. G. de Vries, B. L. Feringa, *J. Org. Chem.* **2005**, *70*, 943–951.
 [20] L. Panella, A. M. Aleixandre, G. J. Kruidhof, J. Robertus, B. L. Feringa, J. G. de Vries, A. J. Minnaard, *J. Org. Chem.* **2006**, *71*, 2026–2036.
 [21] L. Eberhardt, D. Armspach, D. Matt, L. Toupet, B. Oswald, *Eur. J. Inorg. Chem.*, DOI: 10.1002/iejc.
 [22] L. Lefort, J. A. F. Boogers, A. H. M. de Vries, J. G. de Vries, *Org. Lett.* **2004**, *6*, 1733–1735.
 [23] N. Maigrot, J. P. Mazaleyrat, Z. Welvert, *J. Org. Chem.* **1985**, *50*, 3916–3918.
 [24] J. M. Hawkins, G. C. Fu, *J. Org. Chem.* **1986**, *51*, 2820–2822.
 [25] T. Ooi, M. Kameda, K. Maruoka, *J. Am. Chem. Soc.* **2003**, *125*, 5139–5151.
 [26] S. Superchi, M. Nardiello, M. I. Donnoli, P. Scafato, R. Menicagli, C. Rosini, *C. R. Chim.* **2005**, *8*, 867–874.
 [27] W.-J. Shi, L.-X. Wang, Y. Fu, S.-F. Zhu, Q.-L. Zhou, *Tetrahedron: Asymmetry* **2003**, *14*, 3867–3872.
 [28] A. Gillon, K. Heslop, D. J. Hyett, A. Martorell, A. G. Orpen, P. G. Pringle, C. Claver, E. Fernandez, *Chem. Commun.* **2000**, 961–962.
 [29] A. W. Verstuyft, D. A. Redfield, L. W. Cary, J. H. Nelson, *Inorg. Chem.* **1977**, *16*, 2776–2786.
 [30] G. A. Gray, J. H. Nelson, *Org. Magn. Reson.* **1980**, *14*, 8–13.
 [31] G. A. Gray, T. A. Albright, *J. Am. Chem. Soc.* **1977**, *99*, 3243–3250.
 [32] W. B. Jennings, M. Rutherford, *Tetrahedron Lett.* **1984**, *25*, 3131–3132.
 [33] M. L. Clarke, A. M. Z. Slawin, J. D. Woollins, *Polyhedron* **2003**, *22*, 19–26.
 [34] G. Franco, C. G. Arena, F. Faraone, C. Graiff, M. Lanfranchi, A. Tiripicchio, *Eur. J. Inorg. Chem.* **1999**, 1219–1227.
 [35] J. Fawcett, E. G. Hope, A. M. Stuart, A. J. West, *Polyhedron* **2006**, *25*, 1182–1186.
 [36] I. S. Mikhel, G. Bernardinelli, A. Alexakis, *Inorg. Chim. Acta* **2006**, *359*, 1826–1836.
 [37] I. C. F. Vasconcelos, G. K. Anderson, N. P. Rath, C. D. Spilling, *Tetrahedron: Asymmetry* **1998**, *9*, 927–935.

- [38] Q. H. Zeng, X. P. Ping Hu, X. M. Liang, Z. Zheng, *Chin. Chem. Lett.* **2005**, *16*, 1321–1323.
- [39] O. D. L. *CrysAlis RED software*, version 1.171.29.9.
- [40] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1998**, *31*, 74–77.
- [41] S. G. M. Sheldrick, *Program for the Refinement of Crystal Structures*, Univ. of Göttingen, Germany, **1997**.

Received: June 11, 2007

Published Online: August 29, 2007