DOI: 10.1002/ejoc.200700533

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

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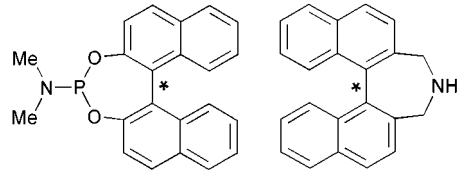
Keywords: Asymmetric catalysis / Hydrogenation / Rhodium / Phosphoramidites / Binaphthyl / Azepines / Binol

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)$_2$]BF_4, 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.

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 Reetz[15,16] independently found that easily accessible monodentate phosphoramidite as well as phosphite ligands, all containing a dinaphtho-fused 1,3-dioxa-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.



A **B**

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-

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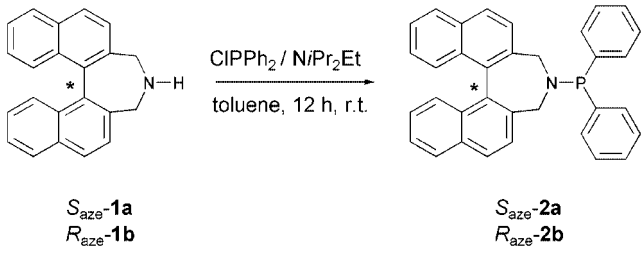
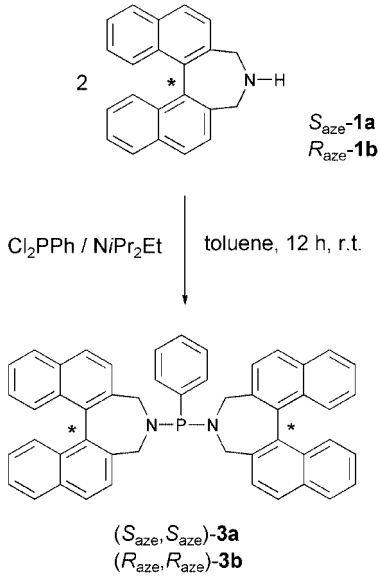
phanewith(*S*)-or(*R*)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]-azepine, respectively, in the presence of 1 equiv. of Hünig's base (diisopropylethylamine). Interestingly, replacing the latter with the less sterically hindered triethylamine produced large amounts of by-products. These enantiomers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



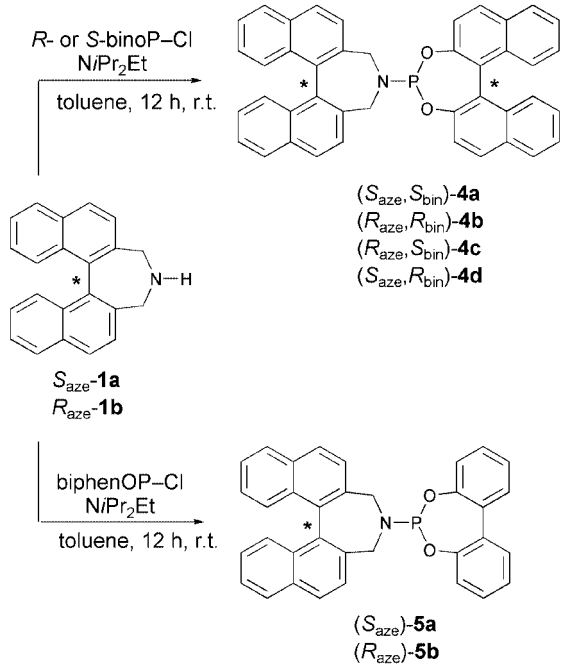
Scheme 1. Synthesis of aminophosphanes **2a** and **2b**.

The enantiomeric aminophosphanes (S_{aze},S_{aze})-**3a** and (R_{aze},R_{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 δ = 96.5 ppm in the corresponding $^{31}P\{^1H\}$ NMR spectra, a value in keeping with that reported for other diaminophosphanes.[29–32]



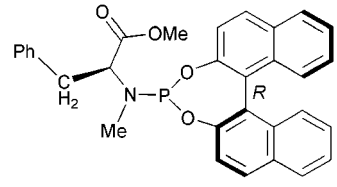
Scheme 2. Synthesis of diaminophosphanes **3a** and **3b**.

We further prepared the four diastereoisomers (S_{aze},S_{bin})-**4a**, (R_{aze},R_{bin})-**4b**, (R_{aze},S_{bin})-**4c** and (S_{aze},R_{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).

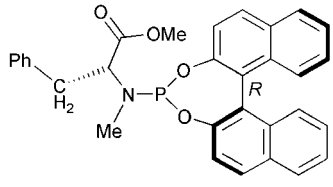


Scheme 3. Synthesis of phosphoramidites **4a**–**d**, **5a** and **5b**.

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_{aze},S_{bin})-**4a**/(R_{aze},R_{bin})-**4b** and (R_{aze},S_{bin})-**4c**/(S_{aze},R_{bin})-**4d** resonated at strikingly different chemical shifts (δ = 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.



C

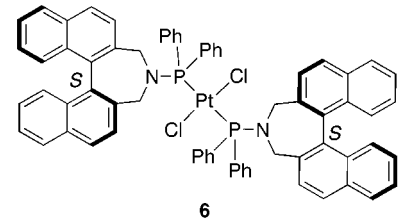


D

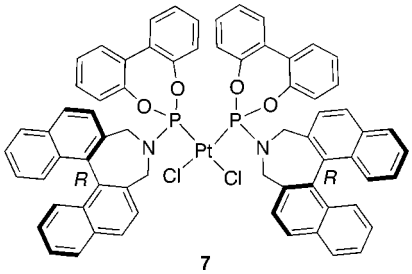
Finally, two enantiomeric phosphoramidites (S_{aze}-**5a**/R_{aze}-**5b**), which lack a stereogenic residue on phosphorus, but retain the general bicyclic structure of their aforementioned analogs, were synthesised by reacting either (*S*)- or (*R*)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepine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

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

The square-planar platinum(II) complex **6** was prepared from S_{aze}-**2a** and $[PtCl_2(PhCN)_2]$ in CH_2Cl_2. The *trans* stereochemistry of the complex was inferred from the corresponding $^{31}P\{^1H\}$ NMR spectrum, which consisted of a singlet flanked by two Pt satellites with a $J_{P,Pt}$ 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) ($^1J_{P,Pt}$ = 2678 Hz).[33]



6



7

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 $[PtCl_2(PhCN)_2]$ 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 $J_{P,Pt}$ 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).

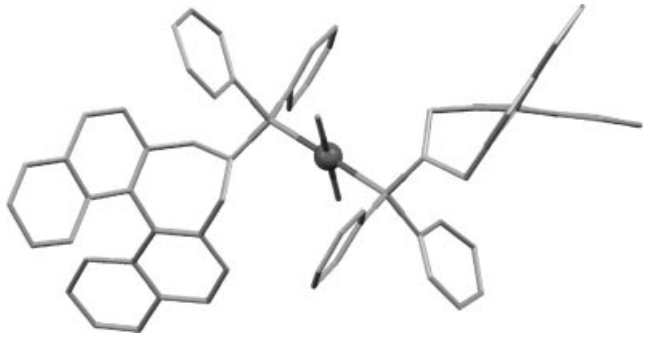


Figure 1. X-ray structure of compound **6** showing the *trans* configuration of the complex. Important bond lengths [Å] and angles [°]: P(1)–Pt 2.304(6); P(2)–Pt 2.328(4); Pt–Cl(1) 2.292(4); Pt–Cl(2) 2.305(5); P(1)–N(1) 1.690(16); P(2)–N(2) 1.727(18); P(1)–Pt–P(2) 178.9(3)°.

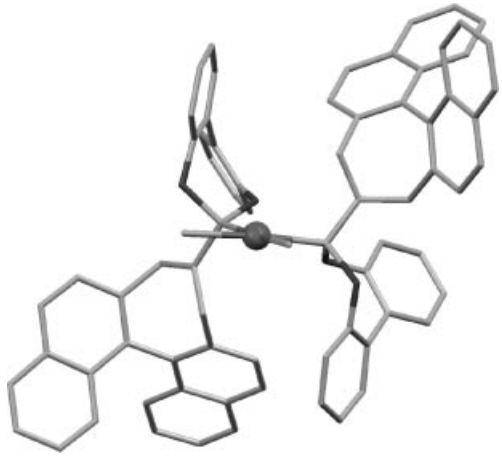
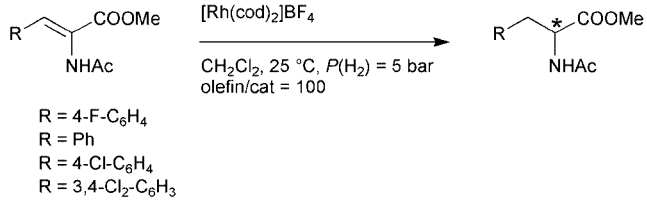


Figure 2. The molecular structure of complex **7** displaying its *cis* geometry. Important bond lengths [Å] and angles [°]: P(1)–Pt 2.2084(8); P(2)–Pt 2.2084(8); Pt–Cl(1) 2.3406(8); Pt–Cl(2) 2.3406(8); P(1)–N(1) 1.622(3); P(2)–N(2) 1.622(3); P(1)–Pt–P(2) 97.10(4)°. Dihedral angles between the linked 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-(acetylamino)-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, CH_2Cl_2), 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-(acetylamino)-3-phenylpropenoate.[a]

Entry	R	Solvent	Time / h	% Conv.[b]	% *ee*[c]	Config.
1	Ph	CH_2Cl_2	1	100	99	*R*
2[d]	Ph	CH_2Cl_2	4	100	99	*R*
3[e]	Ph	CH_2Cl_2	4	89	96	*R*
4	Ph	THF	1	100	74	*R*
5	Ph	MeOH	1	100	57	*R*
6	Ph	AcOEt	1	100	72	*R*

[a] General conditions: $P(H_2)$ = 5 bar; *T* = room temp.; [substrate/Rh/ligand = 100:1:2.2]. [b] Conversions were determined by means of ^{1}H 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.

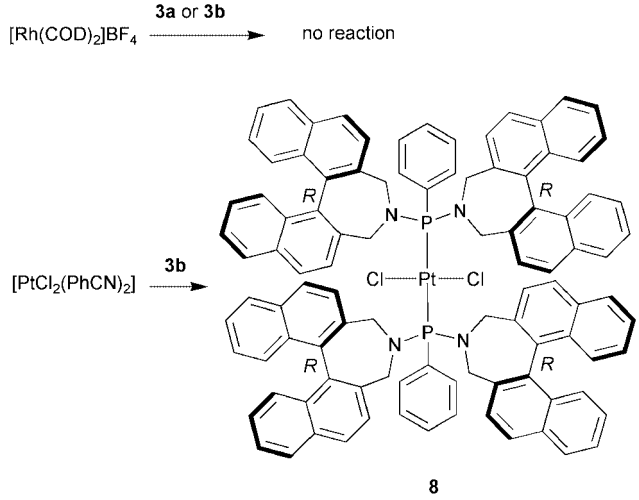
Generally, the use of chiral monodentate aminodiphenylphosphanes S_{aze}-**2a** and R_{aze}-**2b** as ligands in metal-catalyzed asymmetric hydrogenations gave lower activities (Table 2, entries 1 and 2) than that of their phosphoramidite analogues (conversion of ca. 70% after 16 h vs. full conversion 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 $[Rh(COD)_2]BF_4$ was treated with two equivalents of **3a** or **3b**. We also found that when hydrogenation of the substrate was repeated with $[Rh(COD)_2]BF_4$ 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 $[PtCl_2(PhCN)_2]$, leading quantitatively to *trans*-$[PtCl_2(\mathbf{3b})_2]$ (**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	S_{aze}-**2a**	16	63	0	
2	Ph	R_{aze}-**2b**	16	76	3	*R*
3	Ph	(S_{aze},S_{aze})-**3a**	24	6	n.d.	
4	Ph	(R_{aze},R_{aze})-**3b**	24	8	n.d.	
5	4-F-C_6H_4	(R_{aze},S_{bin})-**4c**	1	100	99	*R*
6	4-Cl-C_6H_4	(R_{aze},S_{bin})-**4c**	1	100	99	*R*
7	3,4-Cl_2-C_6H_3	(R_{aze},S_{bin})-**4c**	1	100	99	*R*
8	Ph	(S_{aze},R_{bin})-**4d**	1	100	96	*S*
9	4-F-C_6H_4	(S_{aze},R_{bin})-**4d**	1	100	97	*S*
10	4-Cl-C_6H_4	(S_{aze},R_{bin})-**4d**	1	100	98	*S*
11	3,4-Cl_2-C_6H_3	(S_{aze},R_{bin})-**4d**	1	100	99	*S*
12	Ph	(R_{aze},R_{bin})-**4b**	1	100	83	*S*
13	4-F-C_6H_4	(R_{aze},R_{bin})-**4b**	1	100	86	*S*
14	4-Cl-C_6H_4	(R_{aze},R_{bin})-**4b**	1	100	81	*S*
15	3,4-Cl_2-C_6H_3	(R_{aze},R_{bin})-**4b**	1	100	79	*S*
16	Ph	(S_{aze},S_{bin})-**4a**	1	100	82	*R*
17	4-F-C_6H_4	(S_{aze},S_{bin})-**4a**	1	100	85	*R*
18	4-Cl-C_6H_4	(S_{aze},S_{bin})-**4a**	1	100	81	*R*
19	3,4-Cl_2-C_6H_3	(S_{aze},S_{bin})-**4a**	1	100	79	*R*
20	Ph	none	63	12	0	
21	Ph	*S*-MonoPhos	15	100	92	*R*
22	4-F-C_6H_4	*S*-MonoPhos	15	100	97	*R*
23	4-Cl-C_6H_4	*S*-MonoPhos	15	100	95	*R*
24	3,4-Cl_2-C_6H_3	*S*-MonoPhos	15	100	93	*R*
25	Ph	S_{aze}-**5a**	1	98	50	*S*
26	4-F-C_6H_4	S_{aze}-**5a**	1	100	49	*S*
27	4-Cl-C_6H_4	S_{aze}-**5a**	1	96	50	*S*
28	3,4-Cl_2-C_6H_3	S_{aze}-**5a**	1	100	45	*S*
29	Ph	R_{aze}-**5b**	1	97	51	*R*
30	4-F-C_6H_4	R_{aze}-**5b**	1	98	49	*R*
31	4-Cl-C_6H_4	R_{aze}-**5b**	1	94	49	*R*
32	3,4-Cl_2-C_6H_3	R_{aze}-**5b**	1	100	44	*R*

[a] General conditions as for Table 1.



Scheme 5. Coordination properties of **3** towards $[Rh(COD)_2]BF_4$ and $[PtCl_2(PhCN)_2]$.

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_{aze},S_{bin})-**4c** and (S_{aze},R_{bin})-**4d**, which is well above the values reported for Feringa's MonoPhos ligand, (binoP)NMe_2 (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_{aze},S_{bin})-**4a** and (R_{aze},R_{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_{aze},S_{bin})-**4c**, to *S*, as in (S_{aze},S_{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 dinaphtho-azepine 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 dinaphtho-azepine 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 dinaphtho-azepine 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. $CDCl_3$ was passed through a column (diameter 5 cm) filled with alumina and stored under nitrogen over molecular sieves (4 Å). Routine ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra were recorded with Bruker FT Instruments (AC-200 and AC-300). ^1H NMR spectra were referenced to residual protonated solvents (δ = 7.26 ppm for $CDCl_3$ and 7.16 ppm for C_6D_6), ^{13}C chemical shifts are reported relative to deuterated solvents (δ = 77.16 ppm for $CDCl_3$ and 128.06 ppm for C_6D_6), and the ^{31}P NMR spectroscopic data are given relative to external H_3PO_4. Chemical shifts and coupling constants are reported in ppm and in Hertz, respectively. Mass spectra were recorded with a Bruker MicroTOF spectrometer (ESI) using CH_2Cl_2 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, $\boldsymbol{S}_{aze}$-**1a** and $\boldsymbol{R}_{aze}$-**1b**, were obtained according to a published procedure.[25] The corresponding elemental analyses and $[\alpha]_D^{20}$ values (specific rotations in deg $cm^2\,g^{-1}$) are given below.

(*S*)-4,5-Dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepine (S_{aze}-1a): $C_{22}H_{17}N$ (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); $[\alpha]_D^{20}$ = +685.3 (*c* = 0.22, $CHCl_3$).

(*R*)-4,5-Dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepine (R_{aze}-1b): $C_{22}H_{17}N$ (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); $[\alpha]_D^{20}$ = –686.8 (*c* = 0.22, $CHCl_3$).

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 Al_2O_3. 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%. $C_{34}H_{26}NP$ (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, $CDCl_3$): δ = 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, ArCH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) ($J_{C,P}$ values were obtained from decoupling experiments): δ = 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, NCH$_2$) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 63.7 (s) ppm. M.p. 196–198 °C; $[\alpha]_D^{20}$ = 183.0 (c = 0.44, $CHCl_3$). MS (EI): m/z = 479.3 (71%, $[M]^+$; $C_{34}H_{26}NP$ 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%. $C_{34}H_{26}NP$ (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, $CHCl_3$). MS (ESI-TOF): m/z = 480.2 (100%, $[M + H]^+$; $C_{34}H_{27}NP$ 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 Al_2O_3. The solvent was removed in vacuo to afford the product as a white solid.

Bis[(*S*)-(4,5-dihydro-3*H*-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), 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%. $C_{50}H_{37}N_2P$ (696.82): calcd. C 86.2, H 5.4, N 4.0; found C 86.3, H 5.4, N 4.2. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 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, ArCH_2), 4.38 and 3.91 (AB spectrum, J_{AB} = 12.1 Hz, 2 H, ArCH_2), 4.12 and 3.72 (AB spectrum, J_{AB} = 12.4 Hz, 2 H, ArCH_2), 4.10 and 3.72 (AB spectrum, J_{AB} = 12.4 Hz, 2 H, ArCH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) ($J_{C,P}$ values were obtained via decoupling experiments): δ = 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, NCH$_2$), 52.57 (d, $^2J_{C,P}$ = 15.1 Hz, NCH$_2$) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 96.49 (s) ppm. M.p. 224–226 °C; $[\alpha]_D^{20}$ = 284.0 (c = 0.2, $CHCl_3$). MS (ESI-TOF): m/z = 697.2 (100%, $[M + H]^+$; $C_{50}H_{38}N_2P$ 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%. $C_{50}H_{37}N_2P$ (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, $CHCl_3$); m/z (EI) 696.5 (100%, $[M]^+$; $C_{50}H_{37}N_2P$ 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 Al_2O_3. The solvent was removed in vacuo to afford the product as a white solid.

4-{(*S*)-4,5-Dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4-yl}-(*S*)-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine (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%. $C_{42}H_{28}NO_2P$ (609.65): calcd. C 82.7, H 4.6, N 2.3; found C 82.7, H 4.7, N 2.3. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 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, ArCH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 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, ArCH$_2$) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 146.0 (s) ppm. M.p. 157–159 °C; $[\alpha]_D^{20}$ = 153.6 (c = 0.46, $CHCl_3$). MS (EI): m/z = 609.3 (12%, $[M]^+$; $C_{42}H_{28}NO_2P$ 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%. $C_{42}H_{28}NO_2P$ (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, $CHCl_3$). MS (ESI-TOF): m/z = 610.2 (100%, $[M + H]^+$; $C_{42}H_{29}NO_2P$ 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%. $C_{42}H_{28}NO_2P$ (609.65): calcd. C 82.7, H 4.6, N 2.3; found C 82.8, H 4.7, N 2.4. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 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, ArCH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 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, ArCH$_2$) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 143.0 (s) ppm. M.p. 155–157 °C; $[\alpha]_D^{20}$ = 61.8 (c = 0.28, $CHCl_3$). MS (EI): m/z = 609.4 (9%, $[M]^+$; $C_{42}H_{28}NO_2P$ 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%. $C_{42}H_{28}NO_2P$ (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**. $[\alpha]_D^{20}$ = 62.4 (*c* = 0.28, $CHCl_3$). MS (ESI-TOF): *m*/*z* = 610.2 (100%, $[M + H]^+$; $C_{42}H_{29}NO_2P$ 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%. $C_{34}H_{24}NO_2P$ (509.53): calcd. C 80.1, H 4.8, N 2.8; found C 80.3, H 4.8, N 2.8. ^{1}H NMR (300 MHz, $CDCl_3$): 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, ArCH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 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, $^2J_{C,P}$ = 21.1 Hz, Ar*C*H_2) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 144.9 (s) ppm. $[\alpha]_D^{20}$ = 120.0 (*c* = 1.60, CH_2Cl_2). MS (EI): *m*/*z* = 509.1 (37%, $[M]^+$; $C_{34}H_{24}NO_2P$ 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%. $C_{34}H_{24}NO_2P$ (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; $[\alpha]_D^{20}$ = –118.8 (*c* = 1.60, CH_2Cl_2). MS (EI): *m*/*z* = 509.1 (38%, $[M]^+$; $C_{34}H_{24}NO_2P$ requires 509.2).

***trans*-Dichloroplatinum(II) Complex 6:** A solution of S_{aze}-**2a** (0.133 g, 0.277 mmol) in CH_2Cl_2 (8 mL) was added to a solution of $[PtCl_2(PhCN)_2]$ (0.066 g, 0.139 mmol) in CH_2Cl_2 (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 **5** to precipitate as a white solid, which was filtered; yield 0.161 g, 95%. $C_{68}H_{52}Cl_2N_2P_2Pt$ (1225.09): calcd. C 66.7, H 4.3, N 2.3; found C 66.7, H 4.4, N 2.2. ^{1}H NMR (300 MHz, $CDCl_3$): 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, $^3J_{H,P}$ + $^5J_{H,P'}$ = 7.8 Hz, 2 H, ArCH_2), 4.73 (virtual t, $^3J_{H,P}$ + $^5J_{H,P'}$ = 7.8 Hz, 2 H, ArCH_2), 3.75 (virtual t, $^3J_{H,P}$ + $^5J_{H,P'}$ = 5.5 Hz, 2 H, ArCH_2), 3.70 (virtual t, $^3J_{H,P}$ + $^5J_{H,P'}$ = 5.2 Hz, 2 H, ArCH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.15 (s, quat. C), 133.63 (virtual t, $^1J_{C,P}$ + $^3J_{C,P'}$ = 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, $^2J_{C,P}$ + $^4J_{C,P'}$ = 6.8 Hz, Ar*C*H_2) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 81.4 ($^1J_{Pt,P}$ = 2743 Hz) ppm. M.p. > 250 °C. MS (ESI-TOF): *m*/*z* = 1230.32 (82%, $[M + Li]^+$; $C_{68}H_{52}Cl_2N_2P_2PtLi$ requires 1230.28).

***cis*-Dichloroplatinum(II) Complex 7:** A solution of (R_{aze})-**5a** (0.156 g, 0.306 mmol) in CH_2Cl_2 (8 mL) was added to a solution of $[PtCl_2(PhCN)_2]$ (0.072 g, 0.153 mmol) in CH_2Cl_2 (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%. $C_{68}H_{48}Cl_2N_2O_4P_2Pt$ (1285.05): calcd. C 63.6, H 3.8, N 2.2; found C 63.4, H 3.7, N 2.0. ^{1}H NMR (300 MHz, $CDCl_3$): 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, ArCH_2), 3.19 (d, $^2J_{H,H}$ = 11.7 Hz, 4 H, ArCH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 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, Ar*C*H_2) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 85.3 ($^1J_{Pt,P}$ = 5580 Hz) ppm. M.p. > 250 °C. MS (ESI-TOF): *m*/*z* = 1323.74 (93%, $[M + K]^+$; $C_{68}H_{48}Cl_2KN_2O_4P_2Pt$ requires 1323.18).

***trans*-Dichloroplatinum(II) Complex 8:** A solution of (R_{aze},R_{bin})-**3b** (0.121 g, 0.174 mmol) in CH_2Cl_2 (8 mL) was added to a solution of $PtCl_2(PhCN)_2$ (0.041 g, 0.087 mmol) in CH_2Cl_2 (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%. $C_{100}H_{74}Cl_2N_4P_2Pt$ (1659.62): calcd. C 72.4, H 4.5, N 3.4; found C 72.4, H 4.4, N 3.4. ^{1}H NMR (300 MHz, $CDCl_3$): 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, $^3J_{H,P}$ + $^5J_{H,P'}$ = 6.3 Hz, 2 H, ArCH_2), 4.95 (virtual t, $^3J_{H,P}$ + $^5J_{H,P'}$ = 7.3 Hz, 2 H, ArCH_2), 4.72 (virtual t, $^3J_{H,P}$ + $^5J_{H,P'}$ = 7.4 Hz, 2 H, ArCH_2), 4.67 (virtual t, $^3J_{H,P}$ + $^5J_{H,P'}$ = 7.4 Hz, 2 H, ArCH_2), 3.89–3.83 (m, 8 H, ArCH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 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, $^2J_{C,P}$ + $^4J_{C,P'}$ = 6.8 Hz, Ar*C*H_2), 50.64 (virtual t, $^2J_{C,P}$ + $^4J_{C,P'}$ = 6.8 Hz, Ar*C*H_2) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 81.4 ($^1J_{Pt,P}$ = 2945 Hz) ppm. M.p. > 250 °C. MS (MALDI-TOF): *m*/*z* = 1622.54 (5%, $[M – Cl]^+$; $C_{100}H_{74}ClN_4P_2Pt$ 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. $PtCl_2P_2C_{75}H_{60}N_2$, M = 1317.18, triclinic, space group $P\bar{1}$, a = 10.5246(7), b = 13.1551(6), c = 14.2077(9) Å, V = 1799.25(2) Å^3, 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 ($2.76 < \theta < 32.09°$), 12472 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 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) Å^3, Z = 2, D_x = 1.614 Mg cm^{-3}, λ(Mo-K_α) = 0.71073 Å, μ = 25.44 cm^{-1}, F(000) = 1752, T = 110(1) K. The sample (0.22 × 0.18 × 0.16 mm) was studied on an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite-monochromatized Mo-K_α radiation. The data collection was carried out using CrysAlis RED.[39] 11731 Reflections were collected ($2.90 < \theta < 32.08°$), 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 ^{1}H NMR spectroscopy. Enantioselectivities were determined by chiral GC analysis using a CHROMPAK chiral fused silica Chirasil-L-Val column (25 m × 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/ejic.
[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. Welvart, *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. Francio, 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

