DOI: 10.1002/ejoc.200900918

1,1′-Binaphthyl-2,2′-diamine-Based Chiral Phosphorous Triamides: Synthesis and Application in Asymmetric Catalysis

Katalin Barta,[a] Matthias Eggenstein,[a] Markus Hölscher,[a] Giancarlo Franciò,*[a] and Walter Leitner*[a,b]

Keywords: P-ligands / Asymmetric catalysis / Hydrovinylation / Michael addition / Phosphoramidites

A set of chiral monodentate phosphorous triamides (PTA) comprising 1,1′-binaphthyl-2,2′-diamine as the common moiety have been synthesised. Electronic and steric tuning of the ligands was achieved by variation of the substituents at the diamine nitrogen atoms by incorporating methyl, *p*-tolyl and tosyl groups. Both chiral and achiral building blocks were used as monoamine components. Notably, (11b*R*)-3,5-dimethyl-*N*,*N*-bis[(*S*)-1-phenylethyl]-3,5-dihydro-4*H*-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]diazaphosphepin-4-amine, which is the PTA most closely related to the Feringa phosphoramidite ligand, was synthesised and characterised by NMR spectroscopy and X-ray diffraction. This PTA displays increased conformational rigidity in comparison with the corresponding phosphoramidite and adopts a C_1-symmetric structure both in the solid state and in solution, even at room temperature. The new PTA ligands were used in the copper-catalysed conjugate addition of diethylzinc to cyclohex-2-enone and the nickel-catalysed hydrovinylation of styrene giving good activities and chemoselectivities at moderate enantioselectivities in both reactions.

Introduction

Chiral ligands formally derived from phosphoric acid are gaining more and more importance as a valid alternative to phosphanes for asymmetric transition-metal catalysis.[1] These ligands are easily synthesised through modular approaches and their availability has grown rapidly in the last two decades.[2] Depending on the substitution pattern, these ligands may be stable towards hydrolysis as well as oxidation. Among phosphoric acid derivatives, binaphthol-based phosphoramidites (Figure 1, structure **A**) have proved to be very effective in asymmetric transformations.[3] One of the most efficient chiral phosphoramidites was introduced by Feringa et al. in 1997.[4] Ligand **1** (Figure 2) led to excellent enantioselectivities in a variety of metal-catalysed reactions and was therefore proposed by Woodward and co-workers as a new privileged ligand.[5] In some catalytic applications, the presence of substituents at the 3,3′-positions of the binaphthol moiety proved beneficial in terms of enantioselectivity and activity.[6] It was argued that the increase in the steric bulk near the phosphorus helps to transfer the chiral information from the axially chiral backbone closer to the phosphorus and hence to the metal centre (Figure 1, structure **B**). This effect should be even more pronounced for the corresponding binaphthyldiamine-based phosphorous triamide (PTA). Owing to the presence substituents on the nitrogen atoms, the phosphorus atom experiences greater steric crowding and this could affect the enantiomeric control more strongly (Figure 1, structure **C**). At present, however, very few studies have investigated the catalytic potential of PTA ligands.

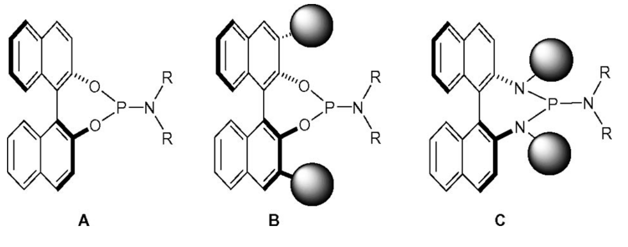


Figure 1. Possible modifications of the phosphoramidite ligand structure.

In 2003, Reetz et al. described the synthesis of the 1,1′-binaphthyl-2,2′-diamine-based phosphorous triamide (**2**) bearing an achiral monoamine substituent (Figure 2). This ligand was used in Rh-catalysed hydrogenation, but gave no conversion, and in the hydroformylation of styrene, in which it led to good conversion but poor enantioselectivity.[7] Ligand **2** is particularly prone to hydrolysis and was isolated as the borane adduct. The stability of the PTA structure could be significantly increased by introducing electron-withdrawing substituents at the nitrogen atoms in the heterocycle, as demonstrated by Gennari and co-

---

[a] Institut für Technische und Makromolekulare Chemie, RWTH Aachen University,
Worringerweg 1, 52074 Aachen, Germany
Fax: +49-241-80-22177
E-mail: francio@itmc.rwth-aachen.de
leitner@itmc.rwth-aachen.de
[b] Max-Planck-Institut für Kohlenforschung,
Kaiser-Wilhelm-Platz 1, 45470 Mülheim a.d. Ruhr, Germany

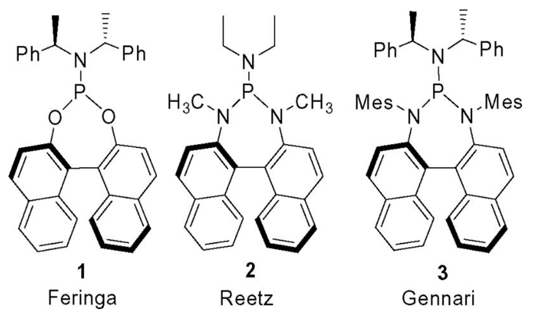


Figure 2. Phosphorous ligands bearing a binaphthyl backbone.

workers. A variety of ligands containing the electron-poor 1,3-bissulfonyl-1,3,2-diazaphosphepine moiety (e.g., Figure 2, ligand **3**) were prepared and tested in the copper-catalysed Michael addition of diethylzinc to cyclohex-2-en-one, obtaining enantioselectivities of up to 75% *ee*.[8]

P-Chiral phosphorous triamides based on the (*S*)-*N*-phenyl-2-(aminomethyl)pyrrolidine backbone have been synthesised by Tsarev et al. and used in Pd-catalysed asymmetric allylic alkylation reactions achieving low enantioselectivity.[9] More recently, we described a family of PTAs based on the same backbone and their application in Cu-catalysed Michael addition reactions of diethylzinc to cyclohex-2-enone and in the Ni-catalysed hydrovinylation of styrene with enantioselectivities of up to 60% *ee*.[10]

We describe herein the synthesis of a series of new chiral PTA ligands based on the 1,1′-binaphthyl-2,2′-diamine backbone in which both the steric and the electronic properties were systematically varied. Methyl, *p*-tolyl and tosyl substituents were incorporated at the nitrogen atoms of the diamine and both chiral and achiral building blocks were used as monoamine components. A structural comparison between the phosphoramidite (R_a,*S*,*S*)-**1** and the most closely related PTA analogue (R_a,*S*,*S*)-**8Aa** revealed that the latter possesses more conformational rigidity adopting a C_1-symmetric arrangement in solution at room temperature and in the solid state. All the new ligands were tested in two C–C bond-forming reactions with moderate enantioselectivity.

Results and Discussion

The electronic tuning of the binaphthyldiamine backbone was accomplished by using substituents with different electron-donating properties at the diamine nitrogen atoms. From methyl, through *p*-tolyl, to tosyl, the electron density decreases whereas the steric bulk increases. Chiral secondary amines (*R*,*R*)- and (*S*,*S*)-bis(1-phenylethyl)amine (**5a**) and the achiral pyrrolidine (**5b**) and dimethylamine (**5c**) were selected as monoamine counterparts. The diamine and monoamine components used in the synthetic approach are depicted in Figure 3.

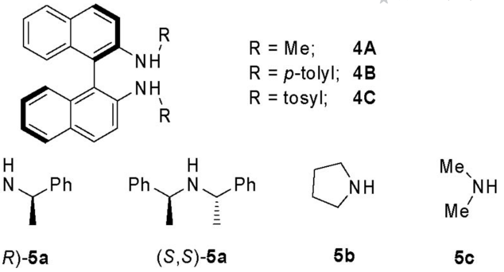
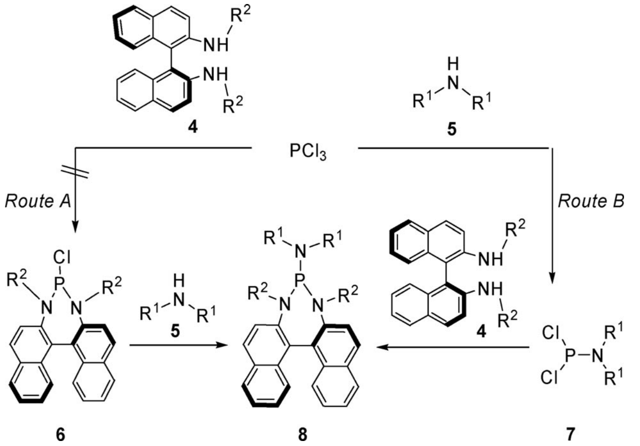


Figure 3. Selected diamines and monamines used in the PTA synthesis.

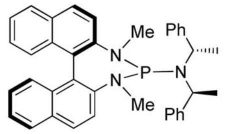
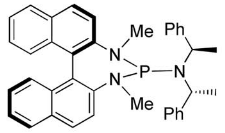
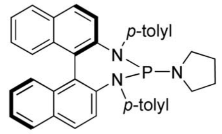
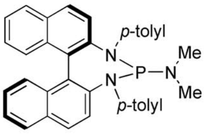
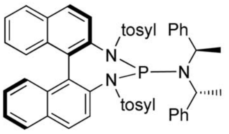
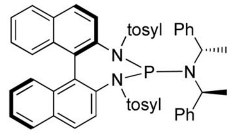
Phosphorous triamides, like other phosphorus acid derivatives, are accessible by two convergent synthetic routes starting from PCl_3 as described by Gennari,[8] although these routes are not in all cases equivalent.[10] Route A involves first the formation of the chlorodiaminophosphane **6**, which is subsequently converted into the final PTA **8** by reaction with a desired monoamine. Route B comprises first the formation of the dichloroaminophosphane **7**, which then reacts with a diamine **4**. These transformations can usually be accomplished in the presence of a base as hydrochloride acceptor (typically triethylamine or DMAP) or by previous deprotonation of the amine, for example, with *n*BuLi. In the present case, the ligand synthesis through Route A failed because the precursors of chlorodiaminophosphane **6**, (R_a)-2,2′-diaminobinaphthyl, (R_a)-*N*,*N*′-dimethyl-2,2′-diaminobinaphthyl and (R_a)-*N*,*N*′-ditosyl-2,2′-diaminobinaphthyl, turned out to be extremely sensitive towards moisture and quickly decomposed during isolation. Attempts to avoid the isolation of the chlorodiaminophosphane intermediate by carrying out the subsequent addition of **5a** in situ resulted in the formation of a mixture of phosphorus-containing species. Route A was, therefore, abandoned (Scheme 1).



Scheme 1. Possible synthetic routes for the preparation of PTAs.

Next, Route B was explored using different bases and various reaction conditions. The dichloroaminophosphane intermediates **7** were prepared by treating (*R*,*R*)- and (*S*,*S*)-**5a** and **5b** with PCl_3 in the presence of DMAP. Under optimised reaction conditions the desired dichloroaminophosphane (*S*,*S*)- and (*R*,*R*)-**7a** and **7b** were obtained in very good yields (95%) and with high purity.[10] Diamines **4A**,[11] **4B**[12] and **4C**[13] were synthesised following literature procedures. The coupling of **4** with **7** using DMAP or triethylamine as hydrochloride scavenger led to complex mixtures. In contrast, the use of *n*BuLi or TMEDA/*n*BuLi to deprotonate diamines **4A**, **4B** and **4C** followed by the addition of **7** resulted in the formation of the corresponding PTA ligands in moderate to high yields (31–95%). The structures, the ^{31}P NMR chemical shifts and selected ^{1}H NMR resonances of the newly synthesised PTA ligands are summarised in Table 1.

Table 1. Selected NMR-data and yields for the newly synthesised PTAs.

Ligand	% Yield	^{31}P-NMR δ (ppm)	^{1}H-NMR δ (ppm)
 (*R*$_a$,*S*,*S*)-**8Aa**	31	140.6 (CD$_2$Cl$_2$)	CHCH_3 1.59 and 1.93 NCH_3 1.96 and 3.21 CHCH$_3$ 4.18 and 4.56
 (*R*$_a$,*R*,*R*)-**8Aa**	67	137.5 (C$_6$D$_6$)	CHCH_3 1.14 and 1.68 NCH_3 2.59 and 3.02 CHCH$_3$ 4.07 and 4.67
 (*R*$_a$)-**8Bb**	94	130.7 (CDCl$_3$)	
 (*R*$_a$)-**8Bc**	65	136.0 (C$_6$D$_6$)	
 (*R*$_a$,*R*,*R*)-**8Ca**	32	129.4 (CDCl$_3$)	CHCH_3 2.05 and 2.09 CHCH$_3$ 4.77 and 5.10
 (*R*$_a$,*S*,*S*)-**8Ca**	38	123.3 (CDCl$_3$)	CHCH_3 1.93 and 2.26 CHCH$_3$ 4.78 and 5.03

Note that the stability of the PTA depends on the nature of the substituents on the diamine part of the structure. Thus, different purification procedures were applied. For instance, ligand **8Aa** turned out to be very sensitive towards air and moisture. Purification attempts by extraction with pentane or by column chromatography on silica were not successful. Even by careful handling under argon using Schlenk techniques, decomposition occurred, as indicated by the appearance in the ^{31}P NMR spectra of several peaks in the region between 130 and 20 ppm. However, pure **8Aa** was obtained by crystallisation from dry benzene by slow evaporation of the solvent under an inert atmosphere in a glove-box. Ligand **8Ca** bearing tosyl groups on the diamine moiety as well as ligands **8Bb** and **8Bc** bearing *p*-tolyl substituents are much more stable towards air and moisture and could be obtained in pure form after filtration through alumina.

NMR spectroscopic analysis clearly showed that all four PTA ligands bearing the bis(1-phenylethyl)amine moiety do not present C_2 symmetry as each nucleus gives rise to an individual resonance in the ^{13}C and ^{1}H NMR spectra even at room temperature. For instance, in the ^{1}H NMR spectrum of (*R*$_a$,*S*,*S*)-**8Aa** the two methyl groups of the secondary amine moiety appear as doublets at δ = 1.59 and 1.93 ppm. An even larger shift of $\Delta\delta$ = 1.25 ppm is observed between the two methyl signals (δ = 3.21 and 1.96 ppm) attached to the binaphthyldiamine backbone. The latter unusually low chemical shift of an *N*-methyl group could be a result of its proximity to the shielding zone caused by the diamagnetic ring current of the phenyl groups belonging to the secondary amine moiety, as confirmed by the X-ray structure analysis of (*R*$_a$,*S*,*S*)-**8Aa** (see below). The methine protons give rise to two distinct multiplets, a quartet at δ = 4.18 ppm and a doublet of quartets at δ = 4.56 ppm. The multiplicity of the latter signal is due to additional ^{1}H–^{31}P coupling (Figure 4). These data indicate that the rotation around the exocyclic P–N bond is blocked even at room temperature and that the most stable conformer is C_1-symmetric.

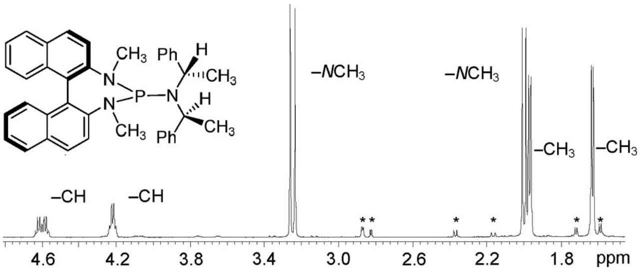


Figure 4. Aliphatic region of the ^{1}H NMR spectrum of (*R*$_a$,*S*,*S*)-**8Aa** in C$_6$D$_6$ at room temperature. Signals of trace amounts of hydrolysis products are labeled with an asterisk *.

In contrast, the ^{1}H NMR spectrum in CD$_2$Cl$_2$ of the phosphoramidite ligand (*R*$_a$,*S*,*S*)-**1** presents one signal (doublet, δ = 1.62 ppm) for both methyl groups and one signal (quartet, δ = 4.40 ppm) for both methine protons at room temperature, which split at –80 °C (methyl groups: δ = 1.45 and 1.85 ppm; methine protons: δ = 4.22 and 4.58 ppm).[14] Thus, in the phosphoramidite (*R*$_a$,*S*,*S*)-**1**, free rotation around the exocyclic P–N bond occurs at room temperature, which can be frozen at –80 °C to give a conformer with C_1 symmetry.

It is surprising in this context that both diastereomers of the related PTA **3** reported by Gennari and co-workers[8] display only one signal for the methyl groups, one for the mesylate groups and one for the methine protons although the mesylate substituents in **3** are significantly bulkier than the corresponding methyl groups in **8Aa**.

The PTA (R_a,S,S)-**8Aa** also exhibits a C_1-symmetric arrangement in the solid state, as evidenced in the X-ray structural analysis (Figure 5). The secondary amine part is twisted towards one side of the binaphthyl backbone. All three P–N bond lengths are different: 1.716 (P–N^1) and 1.742 Å (P–N^2) for the P–N bonds in the phosphorus heterocycle and 1.680 Å for the exocyclic P–N^3 bond. The exocyclic nitrogen displays a nearly trigonal planar geometry with the sum of all the angles around the nitrogen being 359.5°. Also, the two nitrogen atoms embedded in the heterocycle show a pronounced sp^2 character with the sum of all angles equal to 353.9° around N^2 and 339.9° around N^1.

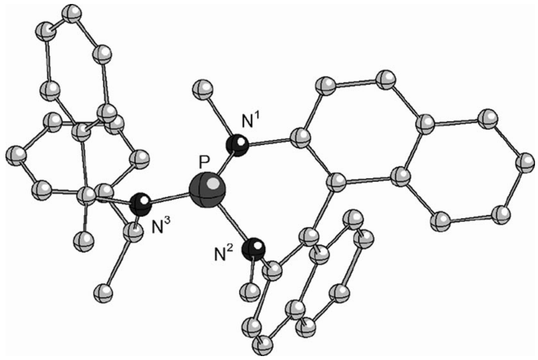


Figure 5. Structure of (R_a,S,S)-**8Aa** in the solid state as determined by single-crystal X-ray diffraction. Selected atom distances [Å] and angles [°]: P–N^3 1.6801(12); P–N^1 1.7163(13); P–N^2 1.7416(12); N^1–P–N^3 109.62(6); N^2–P–N^3 99.13(6); N^1–P–N^2 97.22(6).

Interestingly, the methyl group on the N^1 nitrogen is very close to one of the phenyl rings of the secondary amine (Figure 5). Assuming a similar arrangement in solution, this conformation would explain the large difference in the ^{1}H NMR chemical shifts of the two methyl groups, δ = 1.96 and 3.21 ppm. Although the two methyl groups at the nitrogen atoms are "forced" to reside almost in the plane defined by N^1–P–N^2 in the free ligand due to the nearly planar nature of N^1 and N^2, this arrangement could change significantly in metal complexes, as shown for phosphoramidite ligands. There, the geometry of the nitrogen changes from planar to pyramidal upon coordination of the phosphorus to a metal centre.[15] The two methyl groups of the chiral secondary amine point in the same direction and the phenyl rings reside nearly perpendicular to each other.

The solid-state structure of (R_a,S,S)-**8Aa** compares well with that of (R_a,S,S)-**1**, as demonstrated in Figure 6 in which the two structures are superimposed. The bond lengths in the phosphorus heterocycle are shorter in (R_a,S,S)-**1** with 1.664 Å (P–O^1) versus 1.716 Å (P–N^1), 1.661 Å (P–O^2) versus 1.742 Å (P–N^2) as well as the exocyclic P–N^3 distance with 1.658 Å versus 1.680 Å. The two dihedral angles of the binaphthyl moiety are also slightly different with values of 59° for (R_a,S,S)-**8Aa** and 52.2° for (R_a,S,S)-**1**. Despite these relatively small differences in their geometrical arrangements, the PTA ligand (R_a,S,S)-**8Aa** shows a very distinct catalytic behaviour compared with the phosphoramidite ligand (R_a,S,S)-**1** (see below).

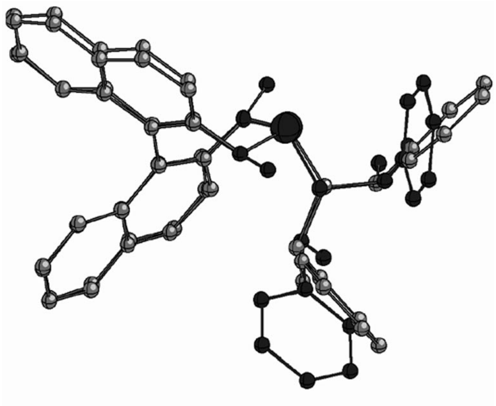


Figure 6. Superimposition of the crystal structures of the phosphoramidite (R_a,S,S)-**1** and the PTA ligand (R_a,S,S)-**8Aa**.

Asymmetric Catalysis

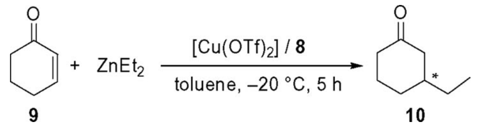
The newly synthesised PTAs were used in metal catalytic asymmetric reactions in which chiral monodentate phosphorus ligands and especially phosphoramidites have already shown a high potential. First, we focused our attention on the Cu-catalysed conjugate addition of diethylzinc to cyclohex-2-enone.

The phosphoramidite ligand (R_a,S,S)-**1** gave excellent enantioselectivities of up to 98 % in this asymmetric transformation,[16] whereas the related PTA **3** led to an *ee* of just 19 %.[8] Up to now, the highest enantioselectivities obtained with PTAs have been achieved with a ligand analogous to **3** but bearing the achiral dimethylamino moiety (75 %)[8] and with a PTA based on (S)-N-phenyl-2-(aminomethyl)-pyrrolidine (60 %).[10]

All the new PTA ligands were tested under standard conditions in the Cu-catalysed Michael addition of diethylzinc to cyclohex-2-enone, leading in all cases to the complete conversion of **9**. The results are summarised in Table 2. Interestingly, ligand (R_a,R,R)-**8Aa** afforded **10** with an almost identical enantioselectivity to the diastereomeric ligand (R_a,S,S)-**8Aa** although with an opposite absolute configuration (Table 2, entry 1 vs. entry 2). This result indicates that, in contrast to the corresponding phosphoramidite **1**,[4] the enantioinduction is dominated by the monoamine moiety of the ligand and synergistic effects between the central and the axial chirality elements are negligible for this ligand. A lower enantioselectivity of (R)-**10** was observed with both tosyl-substituted PTAs (R_a,R,R)-**8Ca** (29 % *ee*, matched diastereomer) and (R_a,S,S)-**8Ca** [3 % *ee* (R), mismatched diastereomer]. Interestingly, ligands (R_a)-**8Bb** and

(R_a)-**8Bc**, both missing the central chirality elements, led preferentially to the formation of the (S)-configured products, albeit with low enantioselectivities of 20 and 30%, respectively (entries 5 and 6). In general, the results obtained here are in line with those reported by Gennari and co-workers for the dimesylated binaphthyldiamine-based phosphorous triamides.[8]

Table 2. Cu-catalysed addition of $ZnEt_2$ to cyclohex-2-enone.[a]

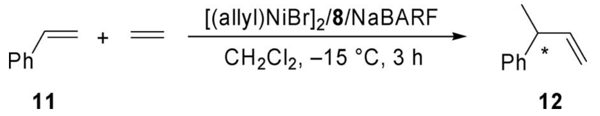


Entry	Ligand	Conv. [%]	*ee* [%]
1	(R_a,S,S)-**8Aa**	>99	55 (S)
2	(R_a,R,R)-**8Aa**	>99	53 (R)
3	(R_a,S,S)-**8Ca**	>99	3 (R)
4	(R_a,R,R)-**8Ca**	>99	29 (R)
5	(R_a)-**8Bb**	>99	20 (S)
6	(R_a)-**8Bc**	>99	30 (S)

[a] Reaction conditions: [Cu] = 0.01 mmol, **8** = 0.02 mmol, **9** = 0.1 mmol, toluene = 2 mL.

Next, we used the new PTAs in another C–C bond-forming reaction, the asymmetric hydrovinylation of styrene. The state-of-the-art conditions for this transformation are defined by the Wilke azaphospholene ligand[17] and by phosphoramidites bearing at least one 1-arylethyl moiety at the nitrogen atom.[18] All reactions were conducted under the same conditions. $[Ni(allyl)Br]_2$ was used as the precursor and NaBARF {tetrakis[3,5-bis(trifluoromethyl)phenyl] boron sodium} as the activator at –50 °C. The same catalyst loading of 0.17 mol-% was used in all experiments to compare the relative activities. The results are summarised in Table 3.

Table 3. Hydrovinylation of styrene with various PTAs.[a]



Entry	Ligand	Conv. [%]	Select. for **12** [%]	*ee* [%]
1	(R_a,S,S)-**8Aa**	82	95	32 (S)
2	(R_a,R,R)-**8Aa**	50	98	33 (R)
3	(R_a,S,S)-**8Ca**	34	>99	37 (R)
4	(R_a,R,R)-**8Ca**	35	>99	34 (S)
5	(R_a)-**8Bb**	84	97	40 (R)
6	(R_a)-**8Bc**	78	91	11 (R)

[a] Reaction conditions: $[Ni(allyl)Br]_2$ = 0.006 mmol, **8** = 0.012 mmol, NaBARF = 0.014 mmol, **11** = 0.36 mmol, ethylene 1 bar, CH_2Cl_2 = 3 mL.

In contrast to the very active catalytic system involving the phosphoramidite ligand (R_a,S,S)-**1**, no conversion was observed after 3 h at –50 °C in the presence of PTA **8Aa**. At –15 °C, however, 82% conversion was achieved within 3 h with (R_a,S,S)-**8Aa** and the desired 3-phenyl-1-butene (**12**) was obtained with very high chemoselectivity and an enantioselectivity of 32% (Table 2, entry 1). Ligand (R_a,R,R)-**8Ab** turned out to be less active and led to a conversion of 50% under the same conditions (entry 2). The chemo- and enantioselectivities were the same as for (R_a,S,S)-**8Aa**. Hence, as already observed in the Cu-catalysed Michael addition reaction, the two diastereomers (R_a,S,S)-**8Aa** and (R_a,R,R)-**8Aa** behave in the hydrovinylation almost as enantiomers as they favour the formation of products with nearly identical enantioselectivity but opposite configuration. Very similar results were achieved with the diastereomeric pair (R_a,S,S)-**8Ca** and (R_a,R,R)-**8Ca**. Again the same levels of enantioselectivity and the opposite product enantiomers were obtained. Note that the highest enantioselectivity (40%) in this series was achieved in the presence of ligand (R_a)-**8Bb** lacking the chiral monoamine moiety. Probably, a tolyl group in (R_a)-**8Bb** serves as a hemilabile donor, which accounts for the catalyst stability and the control of enantioselectivity in the process.[14,19] In contrast, ligand (R_a)-**8Bc** gave a very modest enantioselectivity. Thus, in the Ni-catalysed hydrovinylation reaction PTAs are also less effective in comparison with the corresponding phosphoramidites.[18a]

Conclusions

A set of chiral monodentate phosphorous triamide ligands bearing substituents with different steric and electronic properties have been synthesised. Among them, the phosphorous triamide analogue closest to the Feringa ligand was prepared and compared with the corresponding phosphoramidite structure both in solution and the solid state. In solution PTA (R_a,S,S)-**8Aa** shows greater rigidity and adopts a C_1 symmetry even at room temperature. The overall geometrical arrangements of the preferred conformations in the solid state are almost superimposable for both ligand types. The new PTAs were tested in two different C–C bond-forming reactions. Full conversions and moderate enantioselectivities were achieved in the copper-catalysed Michael addition of diethylzinc to cyclohex-2-enone. The new PTAs formed also active and highly chemoselective Ni catalysts for the hydrovinylation of styrene. However, in this reaction only a modest level of enantioselectivity was achieved. Although PTAs are not competitive yet with, for example, the corresponding phosphoramidite, the exploitation of their large structural diversity on the basis of a better understanding can lead in the future to efficient catalytic systems.

Experimental Section

General: All reactions were carried out under an inert atmosphere of dry and oxygen-free argon either with the use of standard Schlenk techniques or in a glove-box. All solvents were dried and distilled prior to use. NMR spectra were measured at room temperature with a Bruker AV-600 spectrometer. Chemical shifts are given relative to TMS using the solvent signal as the internal reference for ^1H and ^{13}C NMR spectra and H_3PO_4 (85%) as the external reference for ^{31}P NMR spectra. (R)-N,N'-Dimethyl-1,1′-binaphthyl-2,2′-diamine,[20] (R)-N,N'-di-p-tolyl-1,1′-binaphthyl-2,2′-

diamine,[12] (*R*)-*N*,*N*′-di-*p*-tolylsulfonyl-1,1′-binaphthyl-2,2′-diamine,[21] (*R*,*R*)- and (*S*,*S*)-bis(1-phenylethyl)aminophosphorusdichloridite (**7a**),[10] and [Ni(allyl)Br]$_2$,[22] were prepared according to literature procedures. Styrene and cyclohex-2-enone were distilled prior to use. *n*-Butyllithium was titrated with *N*-benzylbenzamide.[23] All other reagents were purchased from Acros or Sigma–Aldrich and used as received.

(11b*R*)-3,5-Dimethyl-*N*,*N*-bis[(*S*)-1-phenylethyl]-3,5-dihydro-4*H*-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]diazaphosphepin-4-amine [(R_a,*S*,*S*)-8Aa]: TMEDA (180 µL, 1.2 mmol) and *n*-butyllithium (1.6 M in hexane, 0.85 mL, 1.2 mmol) were added through a syringe to a solution of (*R*)-*N*,*N*′-dimethyl-1,1′-binaphthyl-2,2′-diamine (150 mg, 0.6 mmol) in THF (4 mL) at –78 °C. The solution was warmed to room temperature for 30 min and then cooled again to –78 °C. A solution of (*S*,*S*)-**7a** (0.196 mg, 0.6 mmol) in toluene (1 mL) was added dropwise through a rubber septum. The mixture was warmed to room temperature and stirred overnight during which time a white precipitate was formed. All solvents were removed under reduced pressure. The residue was suspended in toluene (5 mL) and filtered through alumina. Toluene was removed under reduced pressure and a white solid was obtained. This solid was redissolved in benzene and upon slow evaporation of the solvent in a glove-box, the title compound was obtained as colourless crystals suitable for X-ray diffraction. Yield 104 mg, 31%. ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 1.59 (d, *J* = 7.0 Hz, 3 H), 1.93 (d, *J* = 7.3 Hz, 3 H), 1.96 (d, J_{PH} = 11.3 Hz, 3 H), 3.21 (d, J_{PH} = 16.1 Hz, 3 H), 4.18 (q, *J* = 7.0 Hz, 1 H), 4.56 (dq, *J* = 7.3, J_{PH} = 21.3 Hz; 1 H), 6.83 (d, *J* = 8.7 Hz, 1 H), 6.92 (d, *J* = 6.7 Hz, 2 H), 7.06 (t, *J* = 8.7 Hz, 1 H), 7.07–7.13 (m, 5 H), 7.14–7.21 (m, 5 H), 7.28 (t, *J* = 7.4 Hz, 1 H), 7.35 (d, *J* = 8.4 Hz, 1 H), 7.42 (d, *J* = 8.9 Hz, 1 H), 7.82 (d, *J* = 8.8 Hz, 2 H), 7.87 (m, 2 H), 7.93 (d, ^{3}J = 8.9 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2): δ = 21.4, 25.4 (d, J_{PC} = 15 Hz), 36.5 (d, J_{PC} = 26 Hz), 38.9 (d, J_{PC} = 41 Hz), 52.0 (d, J_{PC} = 28 Hz), 54.5 (d, J_{PC} = 7 Hz), 121.1, 122.0, 124.0, 124.5, 125.7, 125.9, 126.8, 127.2, 127.3, 127.5, 127.6, 127.7, 127.9, 128.0, 128.1 (d, ^{4}J = 2 Hz), 128.2, 128.3, 128.5, 128.8 (d, J_{PC} = 5 Hz), 128.9, 129.2, 130.9 (d, J_{PC} = 4 Hz), 133.2 (d, J_{PC} = 19 Hz), 142.8, 144.5 (d, J_{PC} = 9 Hz), 145.2 (d, J_{PC} = 3.0 Hz), 147.2 (d, J_{PC} = 6.3 Hz) ppm. ^{31}P NMR (242 MHz, CD_2Cl_2): δ = 140.6 ppm. HRMS (EI): calcd. for $C_{38}H_{36}N_3P$ 565.2647; found 565.2659.

(11b*R*)-3,5-Dimethyl-*N*,*N*-bis[(*R*)-1-phenylethyl]-3,5-dihydro-4*H*-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]diazaphosphepin-4-amine [(R_a,*R*,*R*)-8Aa]: The same procedure applied to the synthesis of (R_a,*S*,*S*)-**8Aa** was followed using (*R*,*R*)-**7a** instead of (*S*,*S*)-**7a**. Yield 230 mg, 67%. ^{1}H NMR (600 MHz, C_6D_6): δ = 1.14 (d, *J* = 6.8 Hz, 3 H), 1.68 (d, *J* = 6.9 Hz, 3 H), 2.59 (d, J_{PH} = 13.9 Hz, 3 H), 3.02 (d, J_{PH} = 10.0 Hz, 3 H), 4.07 (dq, *J* = 6.9, J_{PH} = 18.7 Hz, 1 H), 4.67 (q, *J* = 6.8 Hz, 1 H), 6.79 (d, *J* = 8.9 Hz, 1 H), 6.84–6.90 (m, 2 H), 7.01 (d, *J* = 7.5 Hz, 1 H), 7.03–7.14 (m, 10 H), 7.20 (d, *J* = 8.5 Hz, 1 H), 7.26 (d, *J* = 9.1 Hz, 1 H), 7.48 (m, 2 H), 7.57 (d, *J* = 8.2 Hz, 1 H), 7.71 (d, *J* = 8.2 Hz, 1 H), 7.75 (d, *J* = 9.1 Hz, 1 H), 7.85 (d, *J* = 9.1 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ = 20.2, 21.4, 37.6 (d, $^{3}J_{PC}$ = 27 Hz), 38.9 (d, $^{3}J_{PC}$ = 42 Hz), 53.7 (d, $^{2}J_{PC}$ = 8 Hz), 56.1 (d, $^{2}J_{PC}$ = 25 Hz), 112.1, 113.4, 121.5, 122.0, 123.4, 124.1, 124.5, 125.8, 125.9, 126.4, 126.7, 127.4, 127.6 (d, J_{PC} = 13 Hz), 127.8, 128.1, 128.3, 129.0, 129.4, 129.8, 131.1, 131.5, 133.2, 133.5, 144.1 (d, J_{PC} = 9 Hz), 145.4, 146.8, 147.2 (d, J_{PC} = 6 Hz) ppm. ^{31}P NMR (242 MHz, C_6D_6): δ = 137.5 ppm. HRMS (EI): calcd. for $C_{38}H_{36}N_3P$ 565.2647; found 565.2641.

(11b*R*)-*N*,*N*-Bis[(*S*)-1-phenylethyl]-3,5-ditosyl-3,5-dihydro-4*H*-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]diazaphosphepin-4-amine [(R_a,*S*,*S*)-8Ca]: TMEDA (290 µL, 2.0 mmol) and *n*-butyllithium (1.6 M in hexane, 1.25 mL, 2.0 mmol) were added through a syringe to a solution of (*R*)-*N*,*N*′-bis(*p*-tolylsulfonyl)-1,1′-binaphthyl-2,2′-diamine (593 mg, 1.0 mmol) in THF (10 mL) at –78 °C. The solution was warmed to room temperature for 30 min and then cooled again to –78 °C. A solution of (*S*,*S*)-**7a** (326.0 mg, 1.0 mmol) in toluene (3 mL) was added dropwise through a rubber septum. The mixture was warmed to room temperature and stirred overnight during which time a white precipitate formed. All solvents were removed under reduced pressure. The residue was suspended in toluene (5 mL) and filtered through alumina. Toluene was removed under reduced pressure and the product was obtained as a white solid. Yield 320 mg, 38%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.89 (s, 3 H), 1.99 (s, 3 H), 2.05 (d, *J* = 7.2 Hz, 3 H), 2.09 (d, *J* = 7.2 Hz, 3 H), 4.72–4.82 (m, 1 H), 5.05–5.15 (m, 1 H), 6.25 (d, *J* = 8.1 Hz, 2 H), 6.31 (d, *J* = 8.1 Hz, 2 H), 6.37 (d, *J* = 8.4 Hz, 1 H), 6.46 (d, *J* = 8.4 Hz, 1 H), 6.60 (d, *J* = 8.7 Hz, 2 H), 6.84–6.91 (m, 4 H), 7.27–7.48 (m, 10 H), 7.68 (d, *J* = 7.7 Hz, 2 H), 7.73 (d, *J* = 8.2 Hz, 1 H), 7.75 (d, *J* = 8.7 Hz, 1 H), 7.83 (d, *J* = 8.2 Hz, 1 H), 7.86 (d, *J* = 8.7 Hz, 1 H), 7.98 (d, *J* = 8.8 Hz, 1 H), 8.21 (d, *J* = 8.8 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 21.5 (d, J_{PC} = 14.3 Hz), 22.5, 23.4 (d, J_{PC} = 19.6 Hz), 25.4, 58.7 (d, J_{PC} = 36.8 Hz), 61.9 (d, J_{PC} = 9.9 Hz), 125.5, 125.9 126.6, 126.7, 127.0, 127.4, 127.7, 127.8, 128.24, 128.27, 128.3, 128.4, 128.5, 128.6, 128.72, 128.74, 129.00, 129.04, 129.06, 129.6, 129.7, 130.0, 131.7, 131.9, 132.1, 132.4, 132.9, 133.1, 133.2, 134.61, 134.64, 135.73, 135.78, 135.8, 137.25, 137.27 ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 242 MHz): δ = 123.3 ppm. MS (SIMS): *m*/*z* (%) = 846 (51) [M]$^+$, 845 (17), 742 (10), 740 (11), 691 (19), 690 (38), 634 (10), 615 (10), 344 (17), 343 (22), 312 (11), 282 (10), 281 (15), 280 (14), 279 (14), 267 (13), 266 (19), 226 (51), 109 (11), 105 (100), 95 (11), 83 (20), 81 (18), 71 (15).

(11b*R*)-*N*,*N*-Bis[(*R*)-1-phenylethyl]-3,5-ditosyl-3,5-dihydro-4*H*-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]diazaphosphepin-4-amine [(R_a,*R*,*R*)-8Ca]: The same procedure applied to the synthesis of (R_a,*S*,*S*)-**8Ca** was followed using (*R*,*R*)-**7a** instead of (*S*,*S*)-**7a**. Yield 250 mg, 32%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.84 (s, 3 H), 1.93 (d, *J* = 6.9 Hz, 3 H), 1.97 (s, 3 H), 2.26 (m, 3 H), 4.78 (m, 1 H), 5.03 (m, 1 H), 6.17 (d, *J* = 8.0 Hz, 2 H), 6.27 (d, *J* = 8.6 Hz, 1 H), 6.31 (d, *J* = 8.0 Hz, 2 H), 6.39 (d, *J* = 8.7 Hz, 1 H), 6.65 (d, *J* = 8.9 Hz, 1 H), 6.69 (d, *J* = 8.3 Hz, 2 H), 6.77 (d, *J* = 8.3 Hz, 2 H), 6.82 (m, 2 H), 7.15–7.45 (m, 10 H), 7.56 (d, *J* = 8.9 Hz, 1 H), 7.59 (d, *J* = 7.4 Hz, 2 H), 7.66 (d, *J* = 8.3 Hz, 1 H), 7.72 (d, *J* = 8.2 Hz, 1 H), 7.85 (d, *J* = 8.8 Hz, 1 H), 8.22 (d, *J* = 8.8 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 19.9, 21.4 (d, J_{PC} = 9.9 Hz), 25.6, 25.9, 57.37 (d, J_{PC} = 29.1 Hz), 58.5 (d, J_{PC} = 7.9 Hz), 125.2, 125.6, 125.7, 126.2, 126.3, 126.4, 126.5, 127.1, 127.4, 127.6, 127.7, 127.9, 128.0, 128.2, 128.3, 128.5, 128.6, 128.9, 129.0, 129.3, 129.8, 130.3, 131.1, 131.3 131.7, 132.3, 132.4 (d, J_{PC} = 10.4 Hz), 132.9, 133.7, 134.2, 135.7, 137.2, 141.7, 142.5, 143.6, 144.2 ppm. ^{31}P NMR ($CDCl_3$, 242 MHz): δ = 129.4 ppm. MS (EI): *m*/*z* (%) = 845.02 (0.1) [M$^+$], 362.3 (5), 272.2 (43), 257.2 (37), 210.2 (90), 182.1 (81), 167.1 (85), 165.1 (65), 154.1 (22), 105.0 (100), 91.0 (31), 77.0 (45). HRMS (ESI): calcd. for $C_{50}H_{44}N_3O_4PS_2$: 845.251091; found 845.248468.

(11b*R*)-4-(Pyrrolidin-1-yl)-3,5-di-*p*-tolyl-3,5-dihydro-4*H*-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]diazaphosphepine [(R_a)-8Bb]: TMEDA (290 µL, 2.0 mmol) and *n*-butyllithium (1.6 M in hexane, 1.25 mL, 2.0 mmol) were added through a syringe to a solution of (*R*)-*N*,*N*′-bis(*p*-tolyl)-1,1′-binaphthyl-2,2′-diamine (464.3 mg, 1.0 mmol) in THF (10 mL) at –78 °C. The solution was warmed to room temperature for 30 min and then cooled again to –78 °C. A solution of 1-(dichlorophosphanyl)pyrrolidine (172.0 mg, 1.0 mmol) in toluene (3 mL) was added dropwise through a rubber septum. The mixture was warmed to room temperature and stirred overnight during which time a white precipitate formed. All solvents were removed under reduced pressure. The residue was suspended in toluene (5 mL) and filtered through alumina. Toluene was removed under reduced pressure and the product was obtained as a crystalline yellow solid. Yield 530 mg, 94%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.24 (m, 2 H), 1.38 (m 2 H), 2.21 (s, 3 H), 2.28 (s, 3 H), 2.82 (m, 4 H), 6.91 (m, 4 H), 6.98 (m, 4 H), 7.18–7.24 (m, 2 H), 7.28 (m, 1 H), 7.34–7.38 (m, 2 H), 7.41 (d, J = 8.6 Hz, 1 H), 7.49–7.52 (m, 2 H), 7.74 (d, J = 8.8 Hz, 1 H), 7.80 (d, J = 8.2 Hz, 1 H), 7.87 (d, J = 8.6 Hz, 1 H), 7.94 (d, ^3J = 8.2 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 20.7, 21.0, 25.7 (d, J_{PC} = 4.2 Hz), 46.9 (d, J_{PC} = 14.4 Hz), 121.3 (d, J_{PC} = 16.6 Hz), 124.6, 125.1 (d, J_{PC} = 5.9 Hz), 125.4, 126.0, 126.2,126.6, 127.2, 127.3, 127.4, 128.2, 128.3,129.0, 129.20, 129.21,129.4, 130.2, 130.9, 131.5, 132.0, 132.1, 133.2 (d, ^2J = 5.8 Hz), 133.7, 142.8 (d, ^2J = 5.6 Hz), 145.7 (d, J_{PC} = 12.9 Hz), 145.90, 145.94, 146.2 (d, J_{PC} = 27.6 Hz) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 242 MHz): δ = 130.7 ppm. MS (EI): m/z (%) = 564 (31) $[M]^+$, 563 (74) $[M]^+$, 494 (38), 493 (100), 389 (16), 388 (55), 367 (14), 358 (25), 357 (84), 232 (11), 136 (19). HRMS (ESI): calcd. for $C_{38}H_{34}N_3PNa$ $[M + Na]^+$: 586.238113; found 586.238258.

(11b*R*)-*N*,*N*-Dimethyl-3,5-di-*p*-tolyl-3,5-dihydro-4*H*-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]diazaphosphepin-4-amine [(R_a)-8Bc]: The same procedure applied to the synthesis of (R_a)-**8Bb** was followed using dimethylaminodichlorophosphane instead of 1-(dichlorophosphanyl)pyrrolidine. Yield 350 mg, 65%. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.17 (s, 3 H), 2.25 (s, 3 H), 2.13–2.30 (m, 6 H), 6.75–7.04 (m, 8 H), 7.16–7.55 (m, 8 H), 7.72–7.99 (m, 4 H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ = 20.4, 20.6, 35.8 (d, J_{PC} = 35.8 Hz), 117.6, 121.0, 121.4 (d, J_{PC} = 17.0 Hz), 123.3, 124.2, 124.8, 125.3, 126.1 (d, J_{PC} = 22.8 Hz), 126.5, 127.1 (d, J_{PC} = 20.2 Hz), 127.5, 128.3 (d, J_{PC} = 8.0 Hz), 128.4, 129.2 (d, J_{PC} = 6.0 Hz), 129.3 (d, J_{PC} = 2.7 Hz), 129.9, 130.6, 131.3, 131.8 (d, J_{PC} = 86.2 Hz), 132.2 (d, J_{PC} = 72.6 Hz), 133.1, 133.2 (d, J_{PC} = 30.6 Hz), 134.2, 140.0, 141.5, 142.4 (d, J_{PC} = 5.2 Hz), 145.5 (d, J_{PC} = 23.6 Hz), 146.0 (d, J_{PC} = 27.8 Hz) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 242 MHz): δ = 136.0 ppm. MS (EI): m/z (%) = 537 (56) $[M]^+$, 494 (37), 493 (100), 388 (19), 367 (10), 358 (18), 357 (57), 246 (10), 232 (10), 136 (12). HRMS (EI): calcd. for $C_{36}H_{334}N_3P$ $[M + H]^+$: 538.240299; found 538.240658.

General Procedure for a Typical Hydrovinylation Reaction: A solution of the ligand (0.012 mmol) in CH_2Cl_2 (1.5 mL) was added to a solution of $[Ni(allyl)Br]_2$ (0.006 mmol) in CH_2Cl_2 (1.5 mL) at room temperature. After stirring for 15 min, styrene (0.41 mL, 3.6 mmol) and NaBARF (12.4 mg, 0.014 mmol) were added sequentially. The solution was cooled to the desired reaction temperature and saturated with ethylene. After 3 h, the reaction was quenched by the addition of aqueous ammonia (1 mL). The organic phase was washed with water (3 × 2 mL), dried with Na_2SO_4 and analysed by GC and chiral GC.

General Procedure for a Typical Conjugate Addition Reaction of Et_2Zn to Cyclohex-2-enone: $Cu(OTf)_2$ (3.6 mg, 0.01 mmol) was added to a solution of the ligand (0.021 mmol) in toluene (1 mL). The reaction mixture was stirred at room temperature for 30 min and then cooled to –20 °C. Et_2Zn (290 µL, 1.5 M in toluene, 0.44 mmol) was added followed by cyclohex-2-enone (20 µL, 0.20 mmol). The mixture was stirred for 5 h and quenched by the addition of a saturated, aqueous NH_4Cl solution (1 mL). The organic phase was washed with water (3 × 2 mL) and analysed by chiral GC.

Acknowledgments

We thank the European Community (contract NMP-3CT-2003-505267, LIGBANK) and the Deutsche Forschungsgemeinschaft (DFG) (project CALAPAI, FR2487/1-1) for financial support of this work and Prof. Klaus Ditrich (BASF) for a generous gift of chiral amines.

---

[1] E. N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), *Comprehensive Asymmetric Catalysis*, Springer, Berlin, **2004**.
[2] J. Ansell, M. Wills, *Chem. Soc. Rev.* **2002**, *31*, 259–268.
[3] C. Bruneau, J.-L. Renaud, in: *Phosphorus Ligands in Asymmetric Catalysis* (Ed.: A. Börner), Wiley-VCH, Weinheim, **2008**, vol. 1, pp. 36–69.
[4] B. L. Feringa, M. Pineschi, L. A. Arnold, R. Imbos, A. H. M. de Vries, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2620–2624.
[5] a) V. E. Albrow, A. J. Blake, R. Fryatt, C. Wilson, S. Woodward, *Eur. J. Org. Chem.* **2006**, 2549–2557; b) T. P. Yoon, E. N. Jacobsen, *Science* **2003**, *299*, 1691–1693.
[6] For selected examples, see: a) A. Rimkus, N. Sewald, *Org. Lett.* **2003**, *5*, 79–80; b) Z. Hua, V. C. Vassar, I. Ojima, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5411–5416; c) F. Giacomina, A. Meetsma, L. Panella, L. Lefort, A. H. M. de Vries, J. G. de Vries, *Angew. Chem. Int. Ed.* **2007**, *46*, 1497–1500.
[7] M. T. Reetz, H. Oka, R. Goddard, *Synthesis* **2003**, 1809–1814.
[8] C. Monti, C. Gennari, R. M. Steele, U. Piarulli, *Eur. J. Org. Chem.* **2004**, 3557–3565.
[9] V. N. Tsarev, S. E. Lyubimov, A. A. Shiryaev, S. V. Zheglov, O. G. Bondarev, V. A. Davankov, A. A. Kabro, S. K. Moiseev, V. N. Kalinin, K. N. Gavrilov, *Eur. J. Org. Chem.* **2004**, 2214–2222.
[10] K. Barta, M. Hölscher, G. Franciò, W. Leitner, *Eur. J. Org. Chem.* **2009**, 4102–4116.
[11] S. C. Benson, P. Cai, M. Colon, M. A. Haiza, M. Tokles, J. K. Snyder, *J. Org. Chem.* **1988**, *53*, 5335–5341.
[12] Š. Vyskočil, S. Jaracz, M. Smrčina, M. Šticha, V. Hanuš, M. Polášek, P. Kočovský, *J. Org. Chem.* **1998**, *63*, 7727–7737.
[13] J. Y. Jamieson, R. R. Schrock, W. M. Davis, P. J. Bonitatebus, S. Sherry Zhu, A. H. Hoveyda, *Organometallics* **2000**, *19*, 925–930.
[14] M. Hölscher, G. Franciò, W. Leitner, *Organometallics* **2004**, *23*, 5606–5617.
[15] G. Franciò, C. G. Arena, F. Faraone, C. Graiff, M. Lanfranchi, A. Tiripicchio, *Eur. J. Inorg. Chem.* **1999**, 1219–1227.
[16] B. L. Feringa, *Acc. Chem. Res.* **2000**, *33*, 346–353.
[17] G. Wilke, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 185–206.
[18] a) G. Franciò, F. Faraone, W. Leitner, *J. Am. Chem. Soc.* **2002**, *124*, 736–737; b) W.-J. Shi, Q. Zhang, J.-H. Xie, S.-F. Zhu, G.-H. Hou, Q.-L. Zhou, *J. Am. Chem. Soc.* **2006**, *128*, 2780–2781; c) C. R. Smith, T. V. RajanBabu, *Org. Lett.* **2008**, *10*, 1657; d) N. Lassauque, G. Franciò, W. Leitner, *Adv. Synth. Catal.*, manuscript accepted for publication.
[19] J. Joseph, T. V. RajanBabu, E. D. Jemmis, *Organometallics* **2009**, *28*, 3552–3566.
[20] S. Miyano, M. Nawa, A. Mori, H. Hashimoto, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2171–2176.
[21] J. Y. Jamieson, R. R. Schrock, W. M. Davis, P. J. Bonitatebus, S. S. Zhu, A. H. Hoveyda, *Organometallics* **2000**, *19*, 925–930.
[22] G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, H. Zimmermann, *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 151–164.
[23] A. F. Burchat, J. M. Chong, N. Nielsen, *J. Organomet. Chem.* **1997**, *542*, 281–283.

Received: August 13, 2009