Binaphthyldiamine-Based Diazaphospholidines as a New Class of Chiral Monodentate P-Ligands

Manfred T. Reetz,* Hiromasa Oka, Richard Goddard

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim/Ruhr, Germany
Fax +49(208)3062985; E-mail: reetz@mpi-muelheim.mpg.de

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Dedicated to Professor Wolfgang Steglich on the occasion of his 70th birthday.

Abstract: A new family of chiral diazaphospholidines is readily accessible by phosphorylating commercially available (*S*)-1,1′-binaphthyl-2,2′-diamine. NMR spectroscopy, mass spectrometry and X-ray crystallographic analysis reveal their unique structures. In preliminary studies these novel monodentate P-ligands were tested in Rh-catalyzed hydrogenation and hydroformylation (31% ee) reactions. The modular nature of the ligands allows for further structural diversity.

Key words: asymmetric catalysis, rhodium, phosphorus, hydrogenation, hydroformylation

Recently, we and others have shown that BINOL-based monodentate phosphites,[1] phosphonites[2,3] and phosphoramidites[4] are excellent ligands in a number of transition metal catalyzed reactions. For example, in Rh-catalyzed olefin-hydrogenation unexpectedly high enantioselectivities were achieved in a number of cases (ee > 90%), which is of significant academic and industrial interest.[1–4] As a consequence of these findings the long-standing dogma that chelating bidentate ligands are necessary in order to obtain high enantioselectivity no longer pertains.[5] Moreover, these P-ligands are cheaper than the traditional chiral diphosphines by a factor of at least 50. In recent studies we extended the value of these compounds by demonstrating that mixtures of two different monodentate P-ligands can lead to dramatically enhanced enantioselectivities.[6]

In contrast to the extensive use of BINOL as a building block in a variety of chiral catalysts,[1–5] little is known concerning similar ligands based on 1,1′-binaphthyl-2,2′-diamine (**1**), bis-ketimines derived thereof being one prominent example.[7] This may be due to the distinctly higher price of **1** relative to that of BINOL. Nevertheless, we were interested in the synthesis of monodentate diazaphospholidines derived from **1**. In this paper we describe the synthesis and characterization of the first representatives of this novel class of chiral P-ligands **2** (Figure 1). Moreover, preliminary results concerning their application in several asymmetric transition metal catalyzed reactions are presented. These ligands are modular in nature because the substituents at nitrogen (R) and at phosphorus (X) can be varied.

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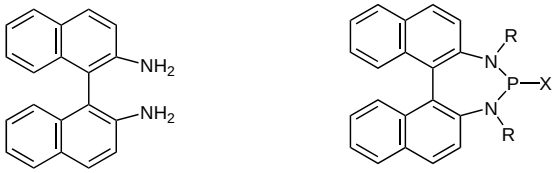
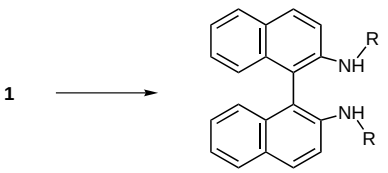


1 **2 a** R = CH_3; X = OCH_3
b R = CH_3; X = NEt_2
c R = C_6H_5; X = OCH_3
d R = C_6H_5; X = CH_3
e R = C_6H_5; X = $CH(CH_3)_2$
f R = C_6H_5; X = c-C_6H_{11}
g R = C_6H_5; X = $C(CH_3)_3$

Figure 1 Diazaphospholidines **2** derived from dinaphthyldiamine **1**

The first step in the synthesis of compounds **2** from the starting material **1** involves the introduction of the R-substituents at nitrogen with formation of the secondary diamines **3** (Scheme 1). Compounds **3a**,**b** were prepared by procedures described in the literature.[7b,8,9] The new mesityl-derivative was synthesized by Pd-catalyzed arylation using the Buchwald–Hartwig method[10] (94% yield).

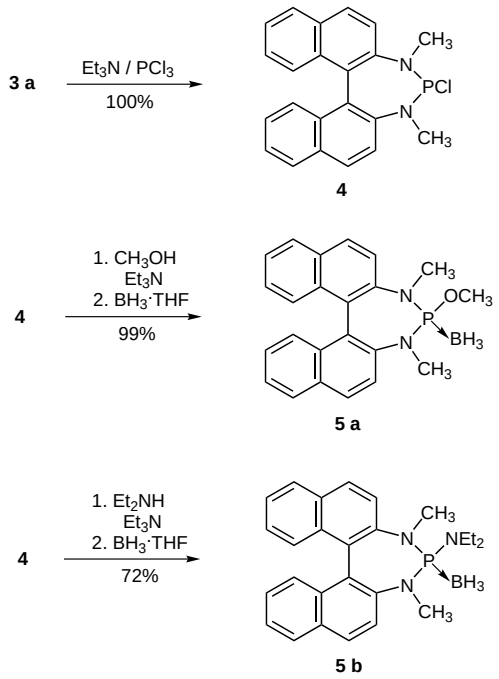


3 a R = CH_3
b R = C_6H_5
c R = 2,4,6 - $(CH_3)_3C_6H_2$

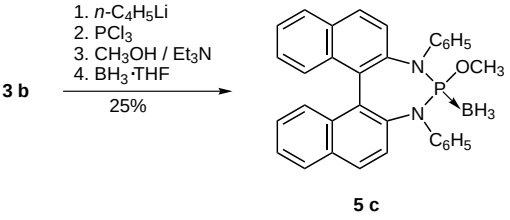
Scheme 1 Synthesis of methyl- and aryl-substituted dinaphthyldiamines **3a** (reductive amination using CH_2O–$NaCNBH_4$) and **3b**,**c** (amination of arylbromides using the Buchwald–Hartwig procedure)

Ring-closing reaction of **3b** with PCl_3 in the presence of Et_3N readily provided the sensitive chloride **4** in quantitative yield. This key compound was then used in the introduction of alkoxy and amino groups, the products being isolated and purified as the BH_3-adducts **5a**,**b**, respectively. Compound **5b** can be prepared even more conveniently by treating **3a** with $(Et_2N)_2PCl$ and protecting with BH_3 (72% overall yield) (Scheme 2).

Unfortunately, these reactions failed to proceed smoothly with the aryl substituted derivatives **3b**,**c**, possibly due to steric effects. Therefore, more forcing conditions had to be applied, specifically double deprotonation using *n*-bu-



Scheme 2 Preparation of BH_3-protected diazaphospholidines

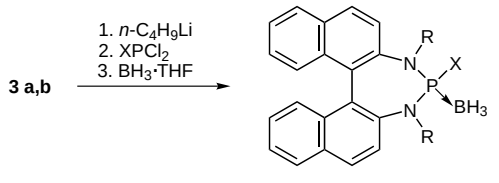


Scheme 3 Synthesis of **5c**

tyllithium followed by phosphorylation, as in the case of **5c** (25% yield) (Scheme 3).

Along similar lines further derivatives **5d**–**g** were prepared and isolated in pure form (Scheme 4). However, upon subjecting the mesityl-derivative **3c** to the reaction conditions, mixtures of inseparable products were obtained. The synthesis of P-ligands based on **3c** was therefore not pursued.

All compounds **5d**–**g** were characterized by NMR spectroscopy and mass spectrometry (MS), and in two cases



5 **d** R = C_6H_5; X = CH_3 (84%)
e R = C_6H_5; X = $CH(CH_3)_2$ (70%)
f R = C_6H_5; X = *c*-C_6H_{11} (50%)
g R = C_6H_5; X = $C(CH_3)_3$ (53%)

Scheme 4 Synthesis of **5e**–**g**

(**5b** and **5c**) suitable crystals were grown for X-ray crystallographic analyses. Figures 2 and 3 show that chiral seven-membered P-heterocycles are indeed involved,[11] the degree of puckering depending on the nature of R. In **5c** all the N atoms are almost planar (R = C_6H_5, max. r.m.s. deviation 0.028 Å), whereas in **5b** N1 lies 0.330 Å out of its coordination plane.

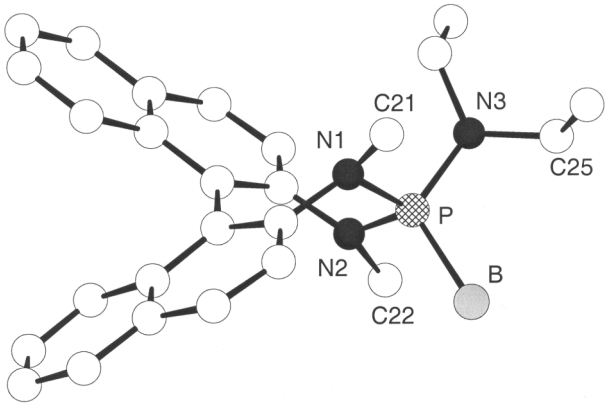


Figure 2 Crystal structure of **5b**: selected distances (Å), angles and torsion angles (°): P–N1 1.696(2), P–N2 1.685(2), P–N3 1.655(2), N1–P–N2 100.4(1), N1–P–N3 104.0(1), N2–P–N3 111.9(1), B–P–N1–C21 71(1), B–P–N2–C22 –49(1), B–P–N3–C25 –2(1).

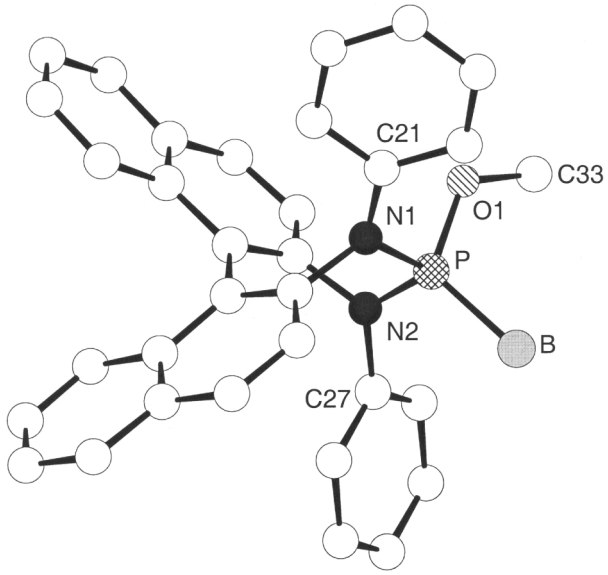
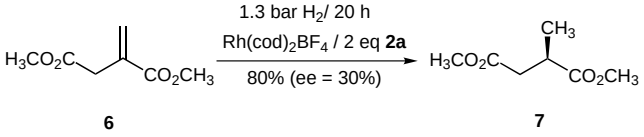


Figure 3 Crystal structure of **5c**: selected distances (Å), angles and torsion angles (°): P–N1 1.680(1), P–N2 1.650(2), P–O 1.589(1), N1–P–N2 102.7(1), N1–P–O1 97.8(1), N2–P–O1 107.7(1), B–P–N1–C21 87(1), B–P–N2–C27 –1(1), B–P–O1–C33 42(1).

The final step in the synthetic sequence called for deprotection of the P-function, which in other cases is known to proceed best with DABCO.[12] However, in the present cases the reaction generally failed to occur cleanly. Therefore, Et_2NH was used, which resulted in smooth deprotection and concomitant generation of the desired ligands **2a**–**g** in essentially pure form as shown by NMR analyses. Since chromatography of the compounds for an-

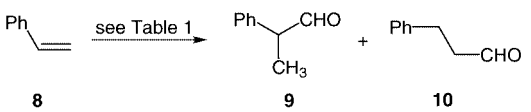
alytical purposes led to excessive decomposition, the ligands were used directly in various transition metal catalyzed reactions.

Thus far only a few exploratory experiments to assess the P-compounds **2** as ligands in transition metal catalyzed reactions have been performed. In all cases the *S*-form was used. Upon treating $Rh(cod)_2BF_4$ (cod = 1,5-cyclooctadiene) with two equivalents of a P-ligand **2** and using the Rh-complexes $RhL_2(cod)BF_4$ as catalysts in the in situ hydrogenation of itaconic acid dimethyl ester (**6**) under standard conditions[1–5] (**6**: Rh = 1000:1; 1.3 bar H_2; 20 h; CH_2Cl_2 as solvent) (Scheme 5), it became clear that the catalyst systems are considerably less active than the previously described Rh-catalysts using BINOL-based phosphites,[1] phosphonites[2,3] or phosphoramidites.[4] Acceptable conversion under these conditions was only achieved with ligands **2a** (80%, **7** having an ee of 30% in favor of the *R*-product **7**). The other ligands led to substrate conversions of only 2–10%. Higher catalyst to substrate ratios and higher pressures still need to be studied in order to make a final assessment.



Scheme 5 Rh-catalyzed hydrogenation of **6**

In the case of the Rh-catalyzed hydroformylation of styrene (**8**) (Scheme 6), a different picture evolved. Although not all of the ligands were tested, initial experiments using **2a**–**d**, turned out to be promising (Table 1). Ligand **2d** seems to be the most active, leading to a nearly quantitative conversion at room temperature and only 25 bar H_2/CO (Table 1, entry 7). The regioselectivity in favor of the branched isomer (**9**:**10** = 80:20) and the ee-value of 31% [in favor of (*S*)-**9**] are remarkable for a monodentate ligand in asymmetric hydroformylation, but certainly far below the standard set by Takaya and Nozaki using their bidentate MOP-ligand.[13] However, due to the modular nature of the diazaphospholidines described in the present paper, further ligand tuning can be expected to be straightforward. Moreover, the concept of using mixtures of two different P-ligands[6] recently introduced by us can now be extended to include the new chiral monodentate ligands prepared in the present study.



Scheme 6 Rh-catalyzed hydroformylation of **8**

Thus, starting from commercially available 1,1′-binaphthyl-2,2′-diamine (**1**), we have prepared a number of novel diazaphospholidines **2a**–**g**. They constitute a new class of chiral monodentate P-ligands. Characterization by NMR spectroscopy and mass spectrometry has been performed in all cases, and two representative ligands were analyzed by X-ray crystallography. Some of the preliminary experiments applying these ligands in asymmetric transition metal-catalyzed reactions are promising, as for example, in enantioselective hydroformylation. It remains to be seen if the modular nature of these compounds can be exploited so that further ligand tuning will lead to efficient catalyst systems. Moreover, other types of transition metal catalyzed reactions need to be tested with the ligands described here, either in pure form or in mixtures.

Table 1 Rh-Catalyzed Hydroformylation of Styrene (**8**)[a]

Entry	Ligand	Rh-salt	H_2/CO (bar)	Temp. (°C)	Conv. (%)[b]	**9**:**10**[b]	ee (%)[b,c]
1	**2a**	$Rh(acac)(CO)_2$	50	60	100	80: 20	24
2	**2a**	$Rh(cod)_2BF_4$	50	60	100	87: 13	5
3	**2b**	$Rh(acac)(CO)_2$	50	60	100	78: 22	37
4	**2b**	$Rh(cod)_2BF_4$	50	60	93	86: 14	10
5	**2c**	$Rh(acac)(CO)_2$	50	60	100	87: 13	18
6	**2c**	$Rh(cod)_2BF_4$	50	60	100	84: 16	20
7	**2d**	$Rh(acac)(CO)_2$	25	25	98	80: 20	31

[a] Rh:substrate = 1:400; 20 h; H_2:CO = 1:1; toluene as solvent.
[b] Determined by GC.
[c] Determined by GC following oxidation to the acid.

All reactions were carried out in anhyd flasks under an atmosphere of argon. 1,1′-Binaphthyl-2,2′-diamine (**1**) was purchased from Fluka (Switzerland) in enantiomerically pure *S*-form. NMR spectra were recorded on 300 and 400 MHz instruments (Bruker, Germany).

(*S*)-*N*,*N*′-Bis(2,4,6-trimethylphenyl)dinaphthyldiamine (3c)

The mixture of (*S*)-1,1′-binaphthyl-2,2′-diamine [(*S*)-**1**] (284 mg, 1.0 mmol), 2-bromomesitylene (0.33 mL, 436 mg, 2.2 mmol), $Pd_2(dba)_3$ (22 mg, 0.04 mmol Pd), (±)-BINAP (25 mg, 0.04 mmol) and sodium *tert*-butoxide (270 mg, 2.8 mmol) was suspended in anhyd *o*-xylene (8 mL) and stirred at 150 °C for 24 h. To the dark brown reaction mixture was added H_2O (20 mL) and the mixture was extracted with *tert*-butyl methyl ether (3 × 30 mL). The combined organic phases were washed with H_2O, then with brine and dried ($MgSO_4$). Evaporation of the solvents gave an orange oil (ca. 700 mg), which was purified by chromatography (SiO_2; hexane–EtOAc, 20:1).

Yield: 490 mg (94%); colorless solid.

^{1}H NMR ($CDCl_3$): δ = 2.1 (s, 12 H, 4 CH_3), 2.27 (s, 6 H, 2 CH_3), 5.18 (br, s, 2 H, NH), 6.72 (d, *J* = 8.9 Hz, 2 H, Ar), 6.88 (s, 4 H, Ar), 7.16–7.32 (m, 4 H, Ar), 7.67–7.83 (m, 4 H, Ar).

^{13}C NMR: δ = 18.6, 20.9, 111.3, 114.3, 122.0, 124.2, 126.6, 128.0, 128.1, 129.1, 129.5, 134.0, 134.9, 135.7, 136.6, 143.3.

MS (EI): *m*/*z* = 520 [M^+], 386.

(*S*)-5a

A stirred mixture of diamine (*S*)-**3a** (146 mg, 0.467 mmol) and Et_3N (0.5 mL, 360 mg, 3.6 mmol) in CH_2Cl_2 (7 mL) in a Schlenk flask was treated with an Et_2O solution of PCl_3 (0.5 M; 1.05 mL, 0.525

mmol) dropwise at 0 °C. After stirring for 16 h, anhyd MeOH (25 μL, 20 mg, 0.6 mmol) was added and the mixture was stirred for 2 h. All volatiles were removed under reduced pressure and the resultant solid was suspended in toluene. A portion did not dissolve, and was filtered off by a pad of Celite® under argon. The yellowish orange filtrate was treated with a THF solution of BH_3·THF (1 M; 1 mL, 1 mmol) and the mixture stirred at r.t. for 2 h. All volatiles were removed and the resultant colorless solid was purified by chromatography (5 g neutral alumina; EtOAc).

Yield: 184 mg (99%); colorless solid.

^{1}H NMR ($CDCl_3$): δ = –0.2–1.4 (br, 3 H, BH_3), 2.9–3.1 (m, 6 H, 2 NCH_3), 3.62 (d, *J* = 11.5 Hz, 3 H, OCH_3), 7.0–8.1 (m, 12 H, Ar).

^{13}C NMR: δ = 35.3 (d, *J* = 8.4 Hz), 37.7 (d, *J* = 16.1 Hz), 53.1 (d, *J* = 4.2 Hz), 122–133 (Ar).

^{31}P NMR: δ = 134.9 (m).

MS (EI): *m*/*z* = 372 [$M^+ – BH_3$], 281.

(*S*)-5b

A 20 mL Schlenk flask equipped with a bubbler was charged with (*S*)-**3a** (152 mg, 0.487 mmol) in toluene (5 mL). After the addition of $ClP(NEt_2)_2$ (0.11 mL, 110 mg, 0.523 mmol) the mixture was stirred for 20 h at 90 °C. The light-yellow suspension was filtered through a pad of Celite® and the filtrate was treated with a THF solution of BH_3·THF (1 M; 1 mL, 1 mmol). After stirring for 3 h, all volatiles were removed and the resultant solid was purified by chromatography (25 g SiO_2; hexane–EtOAc, 20: 1) to provide **5b**. Crystallization for an X-ray structural analysis was performed in EtOAc.

Yield: 155 mg (72%); colorless solid.

^{1}H NMR ($CDCl_3$): δ = –0.2–1.3 (br, 3 H, BH_3), 1.05 (t, *J* = 7.0 Hz, 6 H, 2 CH_3), 2.8–3.1 (br, m, 4 H, 2 NCH_2), 3.00 (s, 3 H, NCH_3), 3.04 (s, 3 H, NCH_3), 6.95–8.00 (m, 12 H, Ar).

^{13}C NMR: δ = 13.9, 35.8 (d, *J* = 9.0 Hz), 36.2 (d, *J* = 14.2 Hz), 38.3, 122–133 (Ar).

^{31}P NMR: δ = 121.5 (m).

MS (EI): *m*/*z* = 413 [$M^+ – BH_3$], 386, 281.

Crystal data for 5b

[$C_{26}H_{31}BN_3P$], from EtOAc, M_r = 427.32, crystal size: 0.07 × 0.10 × 0.19 mm; *a* = 7.7547(1), *b* = 8.0805(1), *c* = 35.8042(4) Å, *V* = 2243.56(5) Å^3, *T* = 100 K, orthorhombic, space group *P* $2_12_12_1$ (No. 19), *Z* = 4, ρ_{calcd} = 1.265 g cm^{-3}, Nonius KappaCCD diffractometer, λ($Mo_{Kα}$) = 0.71073 Å, μ = 0.14 mm^{-1}, 23107 measured and 8043 independent reflections (R_{int} = 0.053), 6683 with $I > 2\sigma(I)$, θ_{max} = 33.06°, T_{min} = 0.973, T_{max} = 0.989, direct methods (*SHELXS-97*) and least-squares refinement (*SHELXL-97*) on F_o^2, both programs from G. Sheldrick, University of Göttingen, H atoms riding, Flack parameter 0.10(9), Chebychev weights, R_1 = 0.058 [$I > 2\sigma(I)$], wR_2 = 0.126 (all data), $\Delta\rho_{max/min}$ = 0.462/–0.335 eÅ^{-3}. CCDC 213916.

(*S*)-5c

In a Schlenk flask an Et_2O solution of (*S*)-**3b** (10 mL; 436 mg, 1.0 mmol) was treated with a BuLi solution in hexane (1.6 M; 1.5 mL, 2.4 mmol) at –78 °C. The orange solution was stirred at r.t. for 20 min, cooled once again to –78 °C and then treated dropwise with a solution of PCl_3 in Et_2O (0.5 M; 2.5 mL, 1.25 mmol). The yellow solution was warmed to r.t., stirred for 16 h and then treated with anhyd MeOH (0.05 mL, 40 mg, 1.2 mmol). After 2 h all volatiles were removed under reduced pressure and the solid suspended in toluene (50 mL). The remaining solid was filtered off by a pad of Celite® under argon. The yellow–orange filtrate was treated with a THF solution of BH_3·THF (1 M; 2 mL, 2 mmol) and stirred at r.t. for 2 h. All volatiles were removed and the resultant colorless solid was purified by chromatography (SiO_2; hexane–EtOAc, 15:1) to provide (*S*)-**5c**. Crystallization for an X-ray structural analysis was performed in toluene–pentane.

Yield: 126 mg (25%); colorless solid.

^{1}H NMR ($CDCl_3$): δ = 0.0–1.5 (br, 3 H, BH_3), 3.48 (d, *J* = 11.1 Hz, 3 H, OCH_3), 6.8–8.1 (m, 22 H, Ar).

^{13}C NMR: δ = 54.2 (d, *J* = 9.0 Hz), 123–132 (Ar), 141.0 (d), 144.3 (d).

^{31}P NMR: δ = 120.3 (m).

MS (EI): *m*/*z* = = 496 [$M^+ – BH_3$], 343.

Crystal data for 5c

[$C_{33}H_{28}BN_2OP$], from toluene–pentane, M_r = 510.35, crystal size: 0.04 × 0.15 × 0.16 mm; *a* = 9.1778(1), *b* = 10.1788(1), *c* = 28.8611(3) Å, *V* = 2696.17(5) Å^3, *T* = 100 K, orthorhombic, space group *P* $2_12_12_1$ (No. 19), *Z* = 4, ρ_{calcd} = 1.257 g cm^{-3}, Nonius KappaCCD diffractometer, λ($Mo_{Kα}$) = 0.71073 Å, μ = 0.13 mm^{-1}, 49894 measured and 10319 independent reflections (R_{int} = 0.089), 8392 with $I > 2\sigma(I)$, θ_{max} = 33.20°, T_{min} = 0.981, T_{max} = 0.995, direct methods (*SHELXS-97*) and least-squares refinement (*SHELXL-97*) on F_o^2, both programs from G. Sheldrick, University of Göttingen, H atoms riding, Flack parameter -0.11(7), Chebychev weights, R_1 = 0.055 [$I > 2\sigma(I)$], wR_2 = 0.122 (all data), $\Delta\rho_{max/min}$ = 0.386/–0.391 eÅ^{-3}. CCDC 213917.

Compounds (*S*)-5d–g; General Procedure

In a Schlenk flask a solution of (*S*)-**3a** or (*S*)-**3b** (0.6 mmol) in Et_2O (7 mL) was treated with a hexane solution of BuLi (1.6 M; 0.9 mL, 1.44 mmol) at –78 °C. After stirring at r.t. for 20 min, the solution was cooled once more to –78 °C and then treated with the appropriate $RPCl_2$ (0.72 mmol). The suspension was stirred at r.t. for 24 h and then treated with a THF solution of BH_3·THF (1 M; 1 mL, 1 mmol) at r.t. After 2 h all volatiles were removed and the solid material was purified by chromatography (SiO_2; hexane–EtOAc, 3:1).

(*S*)-5d

Yield: 160 mg (84%).

^{1}H NMR ($CDCl_3$): δ = –0.1–1.6 (br, 3 H, BH_3), 1.65 (d, *J* = 7.3 Hz, 3 H, CH_3), 6.7–8.1 (m, 22 H, Ar).

^{13}C NMR: δ = 16.2 (d, *J* = 39.0 Hz), 125–133 (Ar), 140–145 (Ar).

^{31}P NMR: δ = 120.4 (m).

MS (EI): *m*/*z* = 480 [$M^+ – BH_3$], 465.

(*S*)-5e

Yield: 184 mg (70%).

^{1}H NMR ($CDCl_3$): δ = 0.1–1.4 (br, 3 H, BH_3), 0.53 (dd, *J* = 7.2, 12.6 Hz, 3 H, CH_3), 1.48 (dd, *J* = 7.2, 18.7 Hz, 3 H, CH_3), 2.51 (m, 1 H, PCH), 6.7–8.0 (m, 22 H, Ar).

^{13}C NMR: δ = 16.1 (d, *J* = 6.6 Hz), 17.1 (d, *J* = 4.0 Hz), 29.8 (d, *J* = 36.6 Hz), 125–133 (Ar), 141–146 (Ar).

^{31}P NMR: δ = 131.1 (m).

MS (EI): *m*/*z* = 508 [$M^+ – BH_3$], 465.

(*S*)-5f

Yield: 142 mg (50%).

^{1}H NMR ($CDCl_3$): δ = 0.1–1.5 (br, 3 H, BH_3), 0.5–2.45 (m, 11 H, *c*-C_6H_{11}), 6.7–8.0 (m, 22 H, Ar).

^{31}P NMR: δ = 128.3 (m).

MS (EI): *m*/*z* = 548 [$M^+ – BH_3$], 465.

(*S*)-5g
Yield: 141 mg (53%).

^{1}H NMR ($CDCl_3$): δ = 0.3–1.5 (br, 3 H, BH_3), 1.07 (d, *J* = 14.3 Hz, 9 H, 3 CH_3), 6.7–8.0 (m, 22 H, Ar).

^{13}C NMR: δ = 27.8, 38.0 (d, *J* = 31.5 Hz), 122–135 (Ar), 142–145 (Ar).

^{31}P NMR: δ = 139.0 (m).

MS (EI): *m*/*z* = 522 [$M^+ - BH_3$], 465.

Deprotection of Ligands; General Procedure
Removal of BH_3 from the P-ligands is best performed by treatment with a large excess (> 10 equiv) of diethylamine at 75 °C overnight without a solvent. Excess diethylamine and amine–borane adduct were removed under reduced pressure (< 0.02 bar) at 45 °C for 3–4 h. Since the resulting P-ligands cannot be chromatographed without extensive degradation, they were used as such in catalysis. Characteristic NMR data could be obtained routinely.

(*S*)-2a
^{1}H NMR ($CDCl_3$): δ = 2.85 (d, *J* = 9.7 Hz, 3 H, NCH_3), 3.00 (d, *J* = 13.8 Hz, 3 H, NCH_3), 3.25 (d, *J* = 9.5 Hz, 3 H, OCH_3), 6.9–7.9 (m, 12 H, Ar).

^{13}C NMR: δ = 33.9 (d, *J* = 26.2 Hz), 36.8 (d, *J* = 44.5 Hz), 49.5, 120–144 (Ar).

^{31}P NMR: δ = 165.9 (m).

(*S*)-2b
^{31}P NMR: δ = 149.0 (m).

(*S*)-2c
^{1}H NMR ($CDCl_3$): δ = 3.14 (d, *J* = 10.0 Hz, 3 H, OCH_3), 6.7–7.9 (m, 22 H, Ar).

^{13}C NMR: δ = 51.6 (d, *J* = 2.7 Hz), 123–147 (Ar).

^{31}P NMR: δ = 147.9 (m).

(*S*)-2d
^{1}H NMR ($CDCl_3$): δ = 1.22 (d, *J* = 9.2 Hz, 3 H, CH_3), 6.5–8.0 (m, 22 H, Ar).

^{13}C NMR: δ = 16.5 (d, *J* = 24.8 Hz), 116–147 (Ar).

^{31}P NMR: δ = 135.0 (m).

(*S*)-2e
^{1}H NMR ($CDCl_3$): δ = 0.59 (dd, *J* = 7.2 Hz, 11.6 Hz, 3 H, CH_3), 0.82 (dd, *J* = 7.2, 14.5 Hz, 3 H, CH_3), 1.92–2.08 (m, 1 H, PCH), 6.5–8.0 (m, 22 H, Ar).

^{13}C NMR: δ = 15.6 (d, *J* = 10.7 Hz), 16.4 (d, *J* = 15.4 Hz), 30.3 (d, *J* = 26.0 Hz), 125–133 (Ar), 141–146 (Ar).

^{31}P NMR: δ = 150.5 (m).

(*S*)-2f
^{1}H NMR ($CDCl_3$): δ = 0.7–1.9 (m, 11 H, *c*-C_6H_{11}), 6.5–8.0 (m, 22 H, Ar).

^{31}P NMR: δ = 148.8 (m).

(*S*)-2g
^{1}H NMR ($CDCl_3$): δ = 0.65 (d, *J* = 11.9 Hz, 9 H, 3 CH_3), 6.6–8.0 (m, 22 H, Ar).

^{13}C NMR: δ = 27.8, 36.9 (d, *J* = 32.2 Hz), 118–150 (Ar).

^{31}P NMR: δ = 160.4 (m).

Hydrogenation of 6; General Procedure
A 25 mL Schlenk flask was charged with a CH_2Cl_2 stock solution of $Rh(cod)_2BF_4$ (2 mM; 0.5 mL, 0.001 mmol), additional CH_2Cl_2 (7.3 mL), a CH_2Cl_2 solution of a chiral P-ligand **2** (10 mM; 0.2 mL, 0.002 mmol) and a CH_2Cl_2 solution of **6** (0.5 M; 2 mL, 1.0 mmol) at r.t. The argon gas was evacuated until bubbles could be observed in the solution, then H_2 gas was introduced until 1 bar was reached. The evacuation/introduction cycle was carried out three times, then the H_2 pressure was adjusted to 1.3 bar. The mixture was stirred at r.t. for 20 h. Conversion and the ee were determined by GC.

Hydroformylation of 8; General Procedure
A 4 mL reaction vessel equipped with a rubber septum was charged with a toluene solution of a rhodium precursor $[Rh(acac)(CO)_2$ or $Rh(cod)_2BF_4]$ (2 mM; 1.25 mL, 0.025 mmol) and a toluene solution of a monodentate P-ligand **2** (10 mM; 0.75 mL, 0.0075 mmol) under argon. After stirring for 1 h at r.t., styrene (**6**) (0.115 mL, 104 mg, 1.0 mmol) was added together with a few drops of dodecane as an internal standard for GC analysis following hydroformylation. The rubber septum was pierced with a short needle and the flask was placed in a stainless steel autoclave under argon. Syngas (H_2/CO, 1:1) was then introduced at the desired pressure, and the reaction carried out with stirring at the desired temperature for 20 h (Table 1). Conversion and regioselectivity were determined by GC. In order to determine the ee-value, oxidation by CrO_3 to the corresponding acid according to a literature procedure[13] was performed followed by GC analysis.

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