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Rhodium-catalyzed asymmetric olefin hydrogenation by easily accessible aniline- and pyridine-derived chiral phosphites

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ABSTRACT

An aniline- and two pyridine-derived (R)-BINOL-based *P,N*-containing phosphite ligands have been synthesized via a one-pot procedure. Treatment of the aniline-derived ligand with 1 equiv of $[Rh(COD)_2]BF_4$ yielded a mixture of a *P,N*-chelate complex and a biligated *P*-monodentate complex (exclusively obtained by treatment of the ligand with rhodium in a ratio of 2:1), while the pyridine analogues led to the corresponding *P,N*-bidentate complexes as unique species. For the first time, such phosphites were studied for rhodium-catalyzed enantioselective olefin hydrogenation. At room temperature, the aniline-derived ligand was found to be more active and selective compared to the pyridine analogues, which can probably be attributed to its different coordination mode and the formation of a biligated *P*-monodentate complex.

Transition metal asymmetric hydrogenation is a highly attractive strategy for gaining access to enantiomerically pure compounds in the development of pharmaceuticals, agrochemicals, fragrances, and fine chemicals, and thus the development of new chiral ligands, which provide high activity, selectivity, and stability remains an important challenge.[1,2] Hybrid chelating ligands, and in particular ligands bearing phosphorus and nitrogen donors as the most abundant hybrids, are of significant interest due to the improved catalytic activity of their transition metal complexes in a variety of homogeneously catalyzed reactions,[3] and also in the development of new reactions.[4] Chiral *P,N*-ligands, which bear 'soft' and 'hard' donors and obvious electronic asymmetry, are the most widely used heterodentate ligands for asymmetric induction,[5,6] and they have also been used successfully to introduce, in one step, two or more stereogenic centers into a prochiral substrate.[7]

Phosphite ligands are easily prepared from readily available alcohols, they are less sensitive to air than phosphines, and they usually display high enantioselectivities. Thus they constitute an extremely attractive class of chiral ligands for asymmetric catalysis.[8] The first highly enantioselective Rh-catalyzed hydrogenation using chiral monophosphite ligands was reported in 2000 by Reetz,[9] and this was elaborated in further studies.[8,10] Extensive investigations by Reetz showed that the efficacy of BINOL-based monophosphites in Rh-catalyzed asymmetric hydrogenation was due to two important features: (a) two monodentate ligands are attached to the metal in the transition state of the hydrogenation, and (b) the catalytic system obeys the lock-and-key mechanism.[11] Reetz also developed a new approach to combinatorial homogeneous transition metal catalysis by the use of mixtures of chiral monodentate ligands, which not only form homocombinations, but also heterocombinations.[12] High enantioselectivity can also be achieved by using mixtures comprising a BINOL-derived *P*-ligand in combination with an achiral *P*-compound.[13]

Significant attention has also been focused on bidentate *P,N*-phosphites. The synthesis of the first *P,N*-phosphite ligand and its rhodium complex was reported in 1993 by Gavrilov,[14] but the major contribution for the design of these systems for asymmetric catalysis was started in 1997 by Pfaltz.[15] Since then, impressive progress in the field has been made, and applications of *P,N*-phosphites in asymmetric catalysis include Rh-catalyzed hydroformylation,[16] Rh-catalyzed hydrosilylation–oxidation,[16b,17] Rh-catalyzed hydroboration–oxidation,[16c,18] Ni-catalyzed hydrovinylation,[19] Ni-catalyzed 1,2-addition reactions to aldehydes,[20] Pd-catalyzed allylic substitution,[15b,16c,17b,c,21–25] Pd-catalyzed Heck reaction,[26] and Cu-catalyzed 1,4-addition reactions to enones.[15a,22,27] Rh-, Ir-, and even Pd-catalyzed asymmetric hydrogenation has also successfully been achieved using *P,N*-phosphites, in which the nitrogen atom is part of an oxazoline[16c,21a,b,28] (with the first example being a TADDOL-based phosphite-oxazoline),[21] oxazole,[29] thiazole,[29] or ferrocenylimino[24g,30] moiety.

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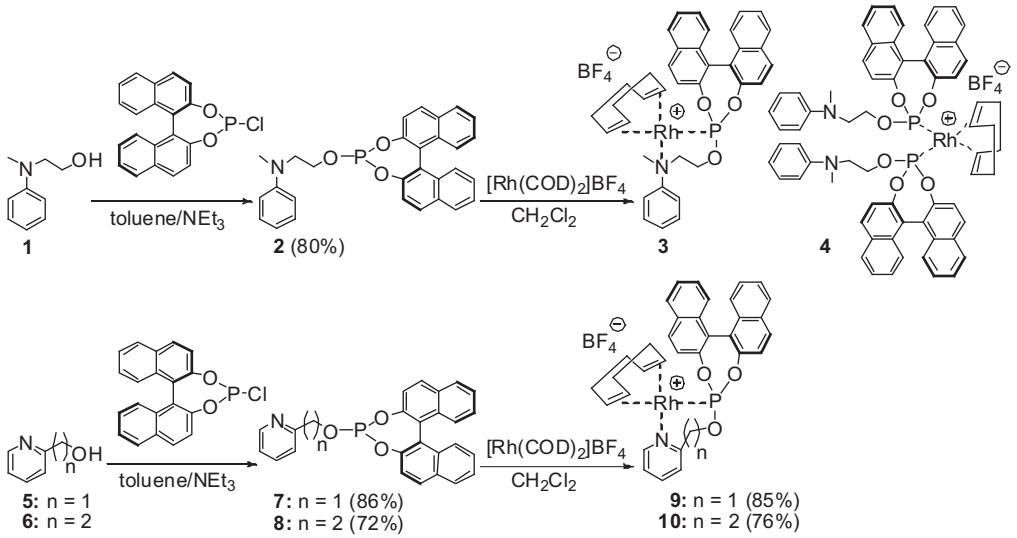
We have previously reported a number of *P*,*N*-containing ligands derived from a substituted aniline moiety for transition-metal homogeneous catalysis.[31] Herein, we report the synthesis of a new aniline-derived phosphite ligand and its coordination chemistry with rhodium. The ligand was evaluated in the Rh-catalyzed asymmetric hydrogenation of prochiral olefins as the first study concerning the application of *P*,*N*-containing phosphites with the nitrogen atom being part of an aniline moiety for asymmetric hydrogenation. An analogous *N*-phenyldiethanolamine-derived tridentate *P*,*N*,*P*-diphosphite, reported by us, resulted in low enantioselectivities (ee <29%) in asymmetric hydrogenation.[31h] For comparison purposes, we also synthesized two analogous pyridine-derived *P*,*N*-phosphites with sp^2-hybridised nitrogen atoms and their rhodium complexes. The ligands were tested in the hydrogenation reaction under identical conditions to the aniline analogue. Other pyridine-derived *P*,*N*-phosphites have not been evaluated for asymmetric hydrogenation to date. The synthesis of the (*S*)-BINOL analogue of one of the pyridine-derived ligands has previously been reported by Faraone, and evaluated in Pd-catalyzed allylic alkylation, but unfortunately, the reaction led to a racemic mixture attributed to the presence of different configurational isomers of the intermediate palladium complexes.[23]

The *P*,*N*-phosphite ligands **2**, **7**,[23] and **8**, based on the (*R*)-BINOL moiety, possessing chirality close to the phosphorus atom and also a rigid structure imposed by the binaphthyl group, were synthesized easily via a one-pot route by treatment of [(*R*)-(1,1′-binaphthalene-2,2′-diyl)]chlorophosphite with one equivalent of [*N*-(2-hydroxyethyl)-*N*-methyl]-aniline (**1**),[31a] 2-(hydroxymethyl)-pyridine (**5**), and 2-(2-hydroxyethyl)-pyridine (**6**), respectively, in toluene/triethylamine (Scheme 1).[32] The phosphite phosphorus atom displayed a singlet in the ^{31}P NMR spectra of **2**, **7**, and **8** at δ 140.39, 136.05, and 139.37, respectively, and the measured accurate masses corresponded exactly to the proposed formulas $[M+H]^+$: $C_{29}H_{25}NO_3P$, $C_{26}H_{19}NO_3P$, and $C_{27}H_{21}NO_3P$, respectively.

The ligands **2**, **7**, and **8** were treated with one equiv of $[Rh(COD)_2]BF_4$ in dichloromethane, and the coordination mode in the resulting complexes was investigated by NMR (^{1}H, ^{13}C, ^{31}P, COSY, HSQC, HMBC, DOSY) and ESI-MS experiments (Scheme 1).[33] It is known that a P,N-type donor ligand can act as a chelating bidentate ligand, a monodentate *P*-ligand, or a bridging ligand in dimeric species, and also a dynamic equilibrium could take place between the monomeric rhodium chelate complex and the dimer.[8c,16b,24b,34,35] The absence of a singlet assigned to the phosphite phosphorus atom of the free ligands in the ^{31}P NMR spectra of the reaction products indicated that all the ligands are bound to the metal, at least via the phosphorus atom. In addition, the absence of a $[L_2Rh_2(COD)_2]^+$ ion in the ESI-MS suggests the absence of binuclear rhodium species.

The complexity of the ^{1}H spectrum of the aniline-derived rhodium complex in CD_2Cl_2 provided evidence that the reaction of **2** with $[Rh(COD)_2]BF_4$ in a ratio of 1:1 is not selective, and that two main products were present in solution. Indeed, in addition to the $[(\mathbf{2})Rh(COD)]^+$ ion (complex **3**) in the ESI-MS, the $[(\mathbf{2})_2Rh(COD)]^+$ ion (complex **4**), in which two ligands are attached to rhodium, was also present. A chromatographic separation was not attempted due to the instability of the complexes. In the ^{1}H NMR spectrum, the NMe protons appear as two signals: (i) at δ 3.17, which is shifted to a lower field compared to the free ligand (δ 2.85), corresponding to a species with Rh–N coordination (*P*,*N*-chelate complex **3**); (ii) at δ 2.92, almost at the same position as that of the free ligand, indicating the formation of a species with the nitrogen atom being uncoordinated (biligated *P*-monodentate complex **4**). In accordance with the integrated intensities of these two peaks (3:5), the two species **3** and **4** are present in dichloromethane in a molar ratio of 1.2:1. The ^{31}P NMR spectrum in CD_2Cl_2 showed a doublet at δ 126.50 (J_{RhP} = 262.6 Hz) assigned to complex **3**, and another doublet of a higher intensity at δ 123.27 (J_{RhP} = 258.6 Hz) assigned to complex **4** (see below). The above-mentioned spectroscopic consideration for the formation of complexes **3** and **4** is strongly supported by the spectral data of the reaction product resulting from treatment of ligand **2** with $[Rh(COD)_2]BF_4$ in a ratio of 2:1. The reaction was now selective yielding only complex **4** as indicated by the $[(\mathbf{2})_2Rh(COD)]^+$ ion in the ESI-MS. DOSY spectroscopy also indicated the presence of one major component. In addition, the ^{31}P NMR spectrum of **4** in CD_2Cl_2 showed a unique doublet at δ 123.35 with a Rh–P coupling constant of 258.4 Hz. In the ^{1}H NMR spectrum, the NMe protons appear as one signal at δ 2.92, almost at the same position as that of the free ligand, indicating the absence of Rh–N coordination. The integrated intensities of the ligand **2** protons (NMe, CH_2O, CH_2N, and aromatics) compared to the 1,5-cyclooctadiene ligand (COD-*CH* and -*CH*$_2$) protons provide clear evidence that the ratio of **2**/COD in the metal complex **4** is equal to 2:1. The COD ligand is part of complex **4** with the COD-*CH* protons at δ 5.88 and 4.40 in the ^{1}H NMR spectrum, and the COD-*C*H carbons at δ 109.58–109.41 in the ^{13}C NMR spectrum of **4**.

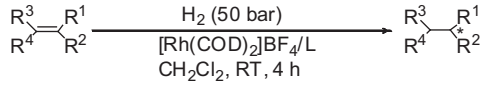


Scheme 1. Synthesis of aniline- and pyridine-derived chiral phosphite ligands and their rhodium complexes.

On the other hand, the pyridine-derived ligands **7** and **8**, upon treatment with 1 equiv of $[Rh(COD)_2]BF_4$, yielded only one species, **9** and **10**, respectively, the measured accurate masses of which suggest the formulas $[LRh(COD)]^+$: $C_{34}H_{30}NO_3PRh$, and $C_{35}H_{32}NO_3PRh$, respectively. DOSY spectroscopy also indicated the presence of one major component. In the NMR data of these complexes, the CH_2 protons and carbons were shifted downfield compared to the free ligands. The α-proton of the pyridine ring in complexes **9** and **10** was shifted to a lower field by 0.2–0.3 ppm and the corresponding carbon (α-py *C*H) downfield by 2.1–4.1 ppm compared to the free ligands as a strong evidence for the Rh–N coordination. The COD ligand is a part of these complexes as shown by ^1H and ^{13}C NMR spectroscopy with the COD-CH situated *trans* to P as well as *trans* to N; four signals were observed in the ^{13}C NMR spectra for the COD-*C*H group, and four signals for the COD-*C*H_2 carbons (see NMR data in Ref. 33). The ^{31}P NMR spectra of **9** and **10** in CD_2Cl_2 showed a doublet at δ 134.02 and 124.21 with a Rh–P coupling constant of 255.5 and 252.8 Hz, respectively, indicating the formation of rhodium chelate *P*,*N*-phosphite complexes as unique species. A doublet was also observed in the ^{31}P NMR spectra of **9** and **10** in other polar and non-polar solvents such as CD_3OD, $CDCl_3$, and acetone-d_6. A mononuclear *P*,*N*-bidentate complex has also been reported for the (*S*)-BINOL analogue of ligand **7** with palladium.[23] The resonance in the ^{31}P NMR spectrum of the pyridine-derived seven-membered chelate complex **10** is shifted to higher field compared to that of the analogous six-membered chelate complex **9** as a result of the decreased ring strain; it is also characterized by a decrease in the Rh–P coupling.[36]

Ligands **2**, **7**, and **8** were tested in the rhodium-catalyzed asymmetric hydrogenation of methyl (*Z*)-α-acetamidocinnamate (**11**), methyl (*Z*)-α-acetamidoacrylate (**12**), *N*-(1-phenylvinyl)acetamide (**13**), and dimethyl itaconate (**14**) (Scheme 2).[37] In the standard procedure, the ligand was treated in situ with 1 equiv of $[Rh(COD)_2]BF_4$, and reduction was performed with 50 bar hydrogen pressure for 4 h at room temperature with a substrate to rhodium molar ratio of 100:1. Optimization of the most suitable solvent was performed with ligand **2** for the hydrogenation of the α-dehydroamino acid derivative **12** and dimethyl itaconate (**14**) (Table 1). Four solvents were chosen for this reaction under identical conditions: dichloromethane, toluene, tetrahydrofuran, and 2,2,2-trifluoroethanol. Dichloromethane led to an almost quantitative conversion and the highest ee (82% for **12** and 65% for **14**; entries 1 and 5) compared to the other solvents, while toluene was the least suitable solvent (entries 2 and 6).

Since dichloromethane was found to be the most efficient solvent, further investigation concerning hydrogenation of the four chosen prochiral olefins by all the ligands was performed using this solvent under the same reaction conditions by treating in situ the ligand with 1 equiv of $[Rh(COD)_2]BF_4$, yielding the products with *S* configuration, with the exception of dimethyl itaconate, the hydrogenation product of which had the *R* configuration (Table 2). The aniline-derived ligand **2** led to almost quantitative conversions for all substrates with enantiomeric excesses in the range of 65–84%. Hydrogenation of **11**, **12**, and **14** was also performed using the rhodium complex **4** (**2**:Rh ratio = 2:1) as the catalyst, which gave analogous or slightly better results compared to ligand **2** mixed in situ with 1 equiv of $[Rh(COD)_2]BF_4$. Complex **4** led to almost quantitative conversions with ees up to 89%. The pyridine analogues **7** and **8** gave lower conversions and ees compared to ligand **2** in most experiments, and with the exception of dimethyl itaconate, ligand **8** was more active and selective than the analogous ligand **7**.



11: R^1 = COOMe, R^2 = NHAc, R^3 = H, R^4 = Ph
12: R^1 = COOMe, R^2 = NHAc, R^3 = R^4 = H
13: R^1 = NHAc, R^2 = Ph, R^3 = R^4 = H
14: R^1 = COOMe, R^2 = CH_2COOMe, R^3 = R^4 = H

Scheme 2. Asymmetric hydrogenation of prochiral olefins.

Table 1
Hydrogenation of (*Z*)-α-acetamidoacrylate (**12**) and dimethyl itaconate (**14**) catalyzed by $[Rh(COD)_2]BF_4$/**2** (1:1). Optimization of the solvent

Entry	Solvent	Conversion (%)	ee (%) (Conf.)
Substrate ***12***			
1	CH_2Cl_2	>99	82 (*S*)
2	$PhCH_3$	3	[a]
3	THF	>99	76 (*S*)
4	CF_3CH_2OH	20	75 (*S*)
Substrate ***14***			
5	CH_2Cl_2	>99	65 (*R*)
6	$PhCH_3$	18	7 (*R*)
7	THF	>99	4 (*R*)
8	CF_3CH_2OH	>99	16 (*R*)

[a] The ee was 97% but this is of no value due to the extremely low conversion.

Table 2
Rhodium-catalyzed asymmetric hydrogenation of prochiral olefins by aniline- and pyridine-derived phosphites

Entry	Substrate	Conversion (%)	ee (%) (Conf.)
Ligand ***2***[a] (*Complex* ***4***)[b]			
1	**11**	>99 (>99)	70 (*S*) [74 (*S*)]
2	**12**	>99 (>99)	82 (*S*) [89 (*S*)]
3	**13**	>99	84 (*S*)
4	**14**	>99 (>99)	65 (*R*) [74 (*R*)]
Ligand ***7***[a]			
5	**11**	6	29 (*S*)
6	**12**	69	41 (*S*)
7	**13**	>99	8 (*S*)
8	**14**	>99	70 (*R*)
Ligand ***8***[a]			
9	**11**	32	40 (*S*)
10	**12**	84	83 (*S*)
11	**13**	>99	11 (*S*)
12	**14**	34	55 (*R*)

[a] The ligand was treated in situ with $[Rh(COD)_2]BF_4$ (L:Rh ratio = 1:1).
[b] Hydrogenation was performed by complex **4** (L:Rh ratio = 2:1).

In summary, we have prepared an aniline- and two pyridine-derived (*R*)-BINOL-based phosphite ligands synthesized in only one step using cheap and very easily accessible reagents. Complexation of the aniline-derived ligand with rhodium in a ratio of 1:1 is not selective, yielding a mixture of a *P*,*N*-bidentate chelate complex and a complex in which two ligands are bound to the metal via the phosphorus atoms with the nitrogen atoms being uncoordinated. The latter species is obtained exclusively by treatment of the ligand with rhodium in a ratio of 2:1. On the other hand, the pyridine-derived analogues led to the corresponding *P*,*N*-bidentate chelate complexes as unique species, using a ligand to rhodium ratio of 1:1. The ligands mixed in situ with $[Rh(COD)_2)]BF_4$ in a ratio of 1:1, were utilized for the rhodium-catalyzed asymmetric hydrogenation of α-dehydroamino acid derivatives, *N*-(1-phenylvinyl)acetamide, and dimethyl itaconate at room temperature. The aniline-derived ligand was found to be more active and selective compared to the pyridine analogues, leading to almost quantitative conversions and ees up to 84%. This could be attributed to its different coordination mode with rhodium, yielding a mixture of two main complexes, a *P*,*N*-chelate complex with a certain degree

of rigidity necessary for the chirality in catalysis, and another complex, possibly more beneficial, being absent in the pyridine analogues, in which two ligands are attached to the metal in a *P*-monodentate fashion, in accordance with the previously reported justification for the efficacy of BINOL-based monophosphites.[11] Indeed, in some control experiments, the aniline-derived biligated *P*-monodentate complex displayed analogous or slightly better enantioselectivities (ees up to 89%) compared to the same aniline-derived ligand treated in situ with the rhodium precursor in a ratio of 1:1, yielding a mixture of the two above-mentioned complexes. However, since the aniline-derived *P,N*-chelate complex could not be isolated in order to establish its catalytic activity and selectivity, and in addition, the activity and selectivity of the biligated *P*-monodentate complex was not considerably higher compared to the mixture of both complexes, other causes which render the aniline-derived ligand more beneficial in asymmetric hydrogenation compared to the pyridine analogues could not be excluded. Although a number of other known chiral ligands display a higher selectivity, this first study on the application of *P,N*-containing phosphites with the nitrogen atom being part of an aniline or a pyridine moiety in asymmetric hydrogenation, provide important information on the catalytic activity of these systems, and should be considered as a complementary study on the application of *P,N*-containing phosphites in asymmetric hydrogenation.

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A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.11.023. These data include MOL files and InChiKeys of the most important compounds described in this article.

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32. *Ligand* ***2***: A solution of [*N*-(2-hydroxyethyl)-*N*-methyl]aniline (**1**)[31a] (0.51 g, 3.38 mmol) and Et_3N (2.4 mL) in toluene (8 mL) was added dropwise to a solution of [(*R*)-(1,1′-binaphthalene-2,2′-diyl)]chlorophosphite (1.19 g, 3.39 mmol) in toluene (15 mL) at 0 °C. The reaction mixture was stirred at this temperature for 2 h, then the temperature was increased slowly to room temperature and the mixture was stirred overnight. The reaction mixture was filtered through Celite, and dried under vacuum at 70 °C to yield **2** as a white solid (1.26 g, 2.71 mmol, 80%), mp 107–108 °C. $[\alpha]_D^{20}$ −383.3 (*c* 0.84, $CHCl_3$). ^1H NMR ($CDCl_3$, 599.8 MHz): δ 7.89 (d, ^3J = 9.0 Hz, 1H, Ar), 7.84 (d, ^3J = 8.4 Hz, 1H, Ar), 7.81 (d, ^3J = 7.8 Hz, 1H, Ar), 7.73 (d, ^3J = 8.4 Hz, 1H, Ar), 7.40–7.09 (m, 10H, Ar), 6.63 (t, ^3J = 7.2 Hz, 1H, Ar), 6.55 (d, ^3J = 8.1 Hz, 2H, Ar), 4.00–3.95 (m, 1H, CH_2N), 3.83–3.78 (m, 1H, CH_2N), 3.48–3.38 (m, 2H, CH_2O), 2.85 (s, 3H, NCH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 148.82–112.19 (Ar), 62.4 (d, $^3J_{CP}$ = 3.5 Hz, CH_2N), 53.2 (d, $^2J_{CP}$ = 3.9 Hz, CH_2O), 39.06 (s, NCH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 242.8 MHz): δ 140.39. HRMS (ESI$^+$): calcd for $C_{29}H_{25}NO_3P$ $[M+H]^+$ 466.1567, found 466.1572.
Ligand ***7***[23] was synthesized as described for **2** by the reaction of 2-(hydroxymethyl)-pyridine (**5**) (0.18 g, 1.65 mmol) and [(*R*)-(1,1′-binaphthalene-2,2′-diyl)]chlorophosphite (0.58 g, 1.65 mmol) in toluene (12 mL)/Et_3N (1.2 mL). Compound **7** was obtained as a white solid (0.60 g, 1.42 mmol, 86%), mp 120 °C. $[\alpha]_D^{20}$ −435.0 (*c* 0.70, $CDCl_3$). ^1H NMR ($CDCl_3$, 599.8 MHz): δ 8.42 (d, ^3J = 4.7 Hz, 1H, α-py *CH*), 7.91–7.77 (m, 4H, Ar), 7.63–7.57 (m, 1H, Ar), 7.46–6.86 (m, 10H, Ar), 5.06–4.99 (m, 1H, CH_2O), 4.84–4.77 (m, 1H, CH_2O); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 157.21 (d, $^3J_{CP}$ = 4.3 Hz, α-py *C*), 149.01 (α-py *CH*), 148.57–121.09 (Ar), 66.88 (d, $^2J_{CP}$ = 4.7 Hz, CH_2O); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 136.05. HRMS (ESI$^+$): calcd for $C_{26}H_{19}NO_3P$ $[M+H]^+$ 424.1097, found 424.1088.
Ligand ***8*** was synthesized by the reaction of 2-(2-hydroxyethyl)-pyridine (**6**) (0.18 g, 1.46 mmol) and [(*R*)-(1,1′-binaphthalene-2,2′-diyl)]chlorophosphite (0.50 g, 1.43 mmol) in toluene (12 mL)/Et_3N (1.0 mL). Compound **8** was obtained as a white solid (0.45 g, 1.03 mmol, 72%), mp 59 °C (dec.). $[\alpha]_D^{20}$ −414.8 (*c* 0.98, $CHCl_3$). ^1H NMR ($CDCl_3$, 300.1 MHz): δ 8.46 (d, ^3J = 4.2 Hz, 1H, α-py *CH*), 7.91–7.80 (m, 4H, Ar), 7.56–7.50 (m, 1H, Ar), 7.40–7.11 (m, 10H, Ar), 4.34–4.24 (m, 1H, CH_2O), 4.17–4.07 (m, 1H, CH_2O), 3.04 (t, ^3J = 6.3 Hz, 2H, CH_2–py); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 157.89 (α-py *C*), 149.33 (α-py *CH*), 148.56–121.58 (Ar), 64.20 (d, $^2J_{CP}$ = 7.4 Hz, CH_2O), 39.67 (d, $^3J_{CP}$ = 4.2 Hz, CH_2–py); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 139.37. HRMS (ESI$^+$): calcd for $C_{27}H_{21}NO_3P$ $[M+H]^+$ 438.1254, found 438.1233.
33. *Reaction of* ***2*** *with [Rh(COD)$_2$]BF$_4$ in a ratio of 1:1:* A solution of ligand **2** (0.075 g, 0.16 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a dark red solution of $[Rh(COD)_2]BF_4$ (0.065 g, 0.16 mmol) in CH_2Cl_2 (2 mL) at 0 °C. The mixture was stirred at this temperature for 30 min, and then for an additional 2.5 h at room temperature. The resulting solution was evaporated under reduced pressure to 1 mL, and addition of hexane (10 mL) caused precipitation of a solid. The supernatant was decanted, the solid was washed with hexane and Et_2O, and dried under vacuum, yielding a mixture of rhodium complexes **3** and **4** in a molar ratio of 1.2:1 (0.090 g; 31% yield for **3** and 52% yield for **4**) as a yellow–orange solid, mp 199–204 °C (dec.). ^1H NMR (CD_2Cl_2, 300.1 MHz): δ 8.26–7.96, 7.62–7.51, 7.39–7.27, 7.13–7.07, 6.70–6.66 and 6.55–6.53 (m, 50H, Ar), 6.31–6.09, 6.02–5.96, 5.92–5.85, 5.33–5.32 and 4.38 (m, 11H, COD-*CH*), 4.31, 4.22–4.17, 4.10–4.08 and 3.96–3.92 (m, 6H, CH_2N), 3.80–3.48 (m, 6H, CH_2O), 3.17 (s, 3H, NCH_3), 2.92 (s, 5H, NCH_3), 2.35–2.16 and 2.03–1.90 (m, 22H, COD-CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 126.50 (d, J_{RhP} = 262.6 Hz) (**3**) and 123.27 (d, J_{RhP} = 258.6 Hz) (**4**). HRMS (ESI$^+$): calcd for $C_{37}H_{36}NO_3PRh$ $[M-BF_4]^+$ (**3**) 676.1482, found 676.1507; calcd for $C_{66}H_{60}N_2O_6P_2Rh$ $[M-BF_4]^+$ (**4**) 1141.2976, found 1141.3027.
Rh complex ***4*** was synthesized as described above by the reaction of ligand **2** (0.069 g, 0.15 mmol) and $[Rh(COD)_2]BF_4$ (0.030 g, 0.07 mmol) in CH_2Cl_2 (4 mL). Complex **4** was obtained as a yellow–orange solid (0.078 g, 0.06 mmol, 86%), mp 203–208 °C (dec.). ^1H NMR (CD_2Cl_2, 599.8 MHz): δ 8.16 (d, ^3J = 8.8 Hz, 2H, Ar), 8.09 (d, ^3J = 8.2 Hz, 2H, Ar), 7.95 (d, ^3J = 8.2 Hz, 2H, Ar), 7.82 (d, ^3J = 8.9 Hz, 2H, Ar), 7.66 (d, ^3J = 8.9 Hz, 2H, Ar), 7.59–7.52 (m, 4H, Ar), 7.36–7.27 (m, 8H, Ar), 7.21 (d, ^3J = 8.7 Hz, 2H, Ar), 7.11–7.08 (m, 4H, Ar), 6.68 (t, ^3J = 7.5 Hz, 2H, Ar), 6.54 (d, ^3J = 8.0 Hz, 4H, Ar), 5.88 (br s, 2H) and 4.40 (m, 2H) (COD-*CH*), 4.09 (m, 2H) and 3.94 (m, 2H) (CH_2N), 3.53–3.49 (m, 2H) and 3.46–3.41 (m, 2H) (CH_2O), 2.92 (s, 3H, NCH_3), 2.35–2.18 and 2.02–1.98 (2 × m, 8H, COD-CH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ 148.84–112.50 (Ar), 109.58–109.41 (m, COD-*CH*), 68.38–68.23 (m, CH_2N), 52.78–52.70 (m, CH_2O), 39.62 (NCH_3), 30.46 and 29.51 (COD-CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 123.35 (d, J_{RhP} = 258.4 Hz). HRMS (ESI$^+$): calcd. for $C_{66}H_{60}N_2O_6P_2Rh$ $[M-BF_4]^+$ 1141.2976, found 1141.2969.
Rh Complex ***9*** was prepared by the reaction of ligand **7** (0.056 g, 0.13 mmol) and $[Rh(COD)_2]BF_4$ (0.054 g, 0.13 mmol) in CH_2Cl_2 (3 mL). Complex **9** was obtained as an orange solid (0.079 g, 0.11 mmol, 85%), m.p. 215 °C (dec.). ^1H NMR (CD_2Cl_2, 300.1 MHz): δ 8.65 (d, ^3J = 5.4 Hz, 1H, α-py *CH*), 8.15 (d, ^3J = 9.0 Hz, 1H, Ar), 8.00–7.97 (m, 3H, Ar), 7.91 (d, ^3J = 8.1 Hz, 1H, Ar), 7.69–7.60 (m, 3H, Ar), 7.48–7.40 (m, 3H, Ar), 7.29–7.23 (m, 4H, Ar), 6.02–5.94 (m, 1H, CH_2O), 5.61–5.50 (m, 2H, COD-*CH trans* to P), 5.28–5.16 (m, 1H, CH_2O), 4.41–4.39 (m, 1H) and 3.40–3.36 (m, 1H) (COD-*CH trans* to N), 2.69–2.58, 2.50–2.38, 2.30–2.11 and 2.08–1.89 (4 × m, 8H, COD-CH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ 155.03 (d, $^3J_{CP}$ = 5.1 Hz, α-py *C*), 153.15 (α-py *CH*), 147.21–120.79 (Ar), 118.18 (dd, $^1J_{CRh}$ = 14.6 Hz, $^2J_{CP}$ = 5.5 Hz) and 115.74 (dd, $^1J_{CRh}$ = 11.8 Hz, $^2J_{CP}$ = 4.8 Hz) (COD-*CH trans* to P), 81.53 (d, $^1J_{CRh}$ = 11.7 Hz) and 78.95 (d, $^1J_{CRh}$ = 10.3 Hz) (COD-*CH trans* to N), 71.42 (d, $^2J_{CP}$ = 10.4 Hz, CH_2O), 35.15 (d, $^2J_{CRh}$ = 3.2 Hz), 30.59, 29.23 and 26.32 (COD-CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 134.02 (d, J_{RhP} = 255.5 Hz). HRMS (ESI$^+$): calcd for $C_{34}H_{30}NO_3PRh$ $[M-BF_4]^+$ 634.1013, found 634.1006.
Rh Complex ***10*** was synthesized by the reaction of ligand **8** (0.050 g, 0.11 mmol) and $[Rh(COD)_2]BF_4$ (0.046 g, 0.11 mmol) in CH_2Cl_2 (3 mL). Complex **10** was obtained as an orange solid (0.062 g, 0.12 mmol, 76%), mp 230 °C (dec.). ^1H NMR (CD_2Cl_2, 300.1 MHz): δ 8.78 (d, ^3J = 5.7 Hz, 1H, α-py *CH*), 8.30 (d, ^3J = 8.7 Hz, 1H, Ar), 8.09–7.89 (m, 5H, Ar), 7.66–7.28 (m, 9H, Ar), 5.45 (m, 1H, COD-*CH trans* to P), 5.32–5.18 (m, 2H, COD-*CH trans* to P, and CH_2–py), 5.11–5.07 (m, 1H, CH_2O), 4.47–4.34 (m, 2H, CH_2O and COD-*CH trans* to N), 3.68 (dd, J = 14.1 Hz, J = 3.9 Hz, 1H, CH_2–py), 3.18–3.13 (m, 1H, COD-*CH trans* to N), 2.79–2.65, 2.51–2.46, 2.35–2.22 and 2.10–1.97 (4 × m, 8H, COD-CH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ 159.29 (α-py *C*), 151.44 (α-py *CH*), 147.14–120.63 (Ar), 115.82 (dd, $^1J_{CRh}$ = 15.3 Hz, $^2J_{CP}$ = 5.7 Hz) and 112.09 (dd, $^1J_{CRh}$ = 12.4 Hz, $^2J_{CP}$ = 5.1 Hz) (COD-*CH trans* to P), 80.31 (d, $^1J_{CRh}$ = 11.3 Hz) and 79.58 (d, $^1J_{CRh}$ = 11.5 Hz) (COD-*CH trans* to N), 66.65 (CH_2O), 41.31 (d, $^3J_{CP}$ = 8.2 Hz, CH_2–py), 34.60 (d, $^2J_{CRh}$ = 2.3 Hz), 30.75, 29.71 and 26.72 (COD-CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 124.21 (d, J_{RhP} = 252.8 Hz). HRMS (ESI$^+$): calcd for $C_{35}H_{32}NO_3PRh$ $[M-BF_4]^+$ 648.1169, found 648.1152.

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36. Borns, S.; Kadyrov, R.; Heller, D.; Baumann, W.; Spannenberg, A.; Kempe, R.; Holz, J.; Börner, A. *Eur. J. Inorg. Chem.* **1998**, 1291–1295.
37. In a typical experiment, a solution of the prochiral olefin (0.1 mmol), the ligand (0.001 mmol) and $[Rh(COD)_2]BF_4$ (0.001 mmol) in CH_2Cl_2 (0.3 mL) was prepared under a nitrogen atmosphere in a glove box and then transferred into an autoclave, which was then closed and pressurized with H_2 (50 bar). After 4 h at room temperature, the pressure was carefully released, hexane (2 mL) was added and the mixture was filtered through silica (hexane/EtOAc = 1:1). All solvents were removed under vacuum, the conversions were determined by achiral GC, and the ee values and configurations were determined by chiral GC or HPLC by comparison with the retention times of known enantiomers.