Tetrahedron: *Asymmetry* 23 (2012) 53–59

Contents lists available at SciVerse ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Synthesis of Binol-based diphosphinites bearing chiral phospholane units and their application in asymmetric catalysis

Tim Hammerer [a], Laurent Weisgerber [a], Stefan Schenk [b], Othmar Stelzer [b,✠], Ulli Englert [c], Walter Leitner [a,*], Giancarlo Franciò [a,*]

[a] *Institut für Technische Chemie und Makromolekulare Chemie, RWTH Aachen University, Worringerweg 1, 52074 Aachen, Germany*
[b] *Fachbereich 9, Anorganische Chemie, Bergische Universität, Gaußstraße 20, 42097 Wuppertal, Germany*
[c] *Institut für Anorganische Chemie, RWTH Aachen University, Landoldtweg 1, 52074 Aachen, Germany*

ARTICLE INFO

Article history:
Received 9 November 2011
Accepted 13 December 2011

ABSTRACT

New diphosphinite ligands based on atropoisomeric diol backbones and (*R*,*R*)-2,5-dimethylphospholane moieties have been prepared and fully characterised. For each ligand structure, both diastereomers have been synthesised. These ligands are available through a straightforward procedure in good yields. The solid state structures of two diastereomeric ligands are reported. These ligands have been applied to Rh-catalysed asymmetric hydrogenations and hydroformylations of C=C bonds as well as in Ir-catalysed asymmetric hydrogenations of C=N bonds. Turnover frequencies in the range of 10,000 h^{-1} and enantioselectivities of up to 98% ee have been achieved. The different chirality elements within the ligands led to marked cooperative effect in catalysis. Interestingly, there is no general privileged diastereomeric structure but rather a matched diastereomer for each application.

1. Introduction

The fruitful development of transition metal catalysed asymmetric transformations over the last decades has been largely steered by the introduction of new chiral ligands.[1] Bidentate C_2-symmetric diphosphines are a prominent ligand class and structures such as DuPHOS and BINAP belong to the most efficient chiral ligands for many different metal-catalysed reactions.[2] In contrast, only a limited number of chiral diphosphinite ligands have been reported up to now despite their easy accessibility. Diphosphinites based on cyclic[3,4] and spirocyclic diols,[5] as well as on sugar and pinene derivatives[6] have been used in Rh-,[3,6a,c,7] Ru-[8] and Ir-catalysed asymmetric hydrogenations,[9] Ru-catalysed Diels–Alder reactions,[10] Ni-catalysed asymmetric hydrocyanations,[11] Pd-catalysed asymmetric allylic alkylations[12] and Rh-catalysed asymmetric hydroformylation,[13] leading to moderate to good enantioselectivities. Within the class of diphosphinites, BINAPO and its derivatives probably define the most versatile lead structure[7b,8,9c,13b,14] and these ligands have led to remarkable results e.g. in the asymmetric hydrogenations.[7b,9c,14] All diphosphinites reported to date bear achiral bisaryl phosphine groups directly attached to the oxygen atoms (Fig. 1).

The structural variety of the R_2P moieties in diphosphinites is, in principle, only limited by the availability of the corresponding chlorophosphine moiety Cl-PR_2. In 2007, Börner et al. described a very efficient synthetic route to enantiomerically pure 1-chloro-2,5-dimethylphospholane starting from the corresponding (2*R*,5*R*)-1-trimethylsilyl-2,5-dimethylphospholane (Scheme 1).[15]

This versatile building block was used in the synthesis of phospholane,*N*-[15] and phosphine,phospholane-ligands.[16] Following our longstanding interest in new ligand structures,[17] we wished to integrate the two successful structural motifs of an atropoisomeric diol backbone and a chiral phospholane unit in new C_2-symmetric diphosphinite ligands (DiolPhos) (Scheme 2).[18] This approach allows us to explore different chiral elements within the ligand structure, thus capitalising on cooperative effects in catalysis.[19] Herein we report the synthesis and characterisation of DiolPhos ligands and their application in different transition metal catalysed asymmetric transformations.

2. Results and discussion

2.1. Synthesis and structure

Starting from (2*R*,5*R*)-1-chloro-2,5-dimethylphospholane **1**,[15] the synthesis of the targeted diphosphinites is very straightforward. The highly reactive compound **1** undergoes smooth condensation with an alcohol in the presence of an organic base under mild conditions.[18] This synthetic approach can be adapted readily to diols. As diols, (R_a)- and (S_a)-Binol (Binol = 2,2′-dihydroxy-1,1′-binaphthyl) as well as the related partially hydrogenated compounds (R_a)- and (S_a)-H_8-Binol[20] (H_8-Binol = 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol) were used. The corresponding ligands **L1**–**L4** could be synthesised in good yields (74–86%) using NEt_3 as

* Corresponding authors.
E-mail addresses: francio@itmc.rwth-aachen.de (G. Franciò), leitner@itmc.rwth. aachen.de (W. Leitner).
✠ Deceased.

0957-4166/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2011.12.011

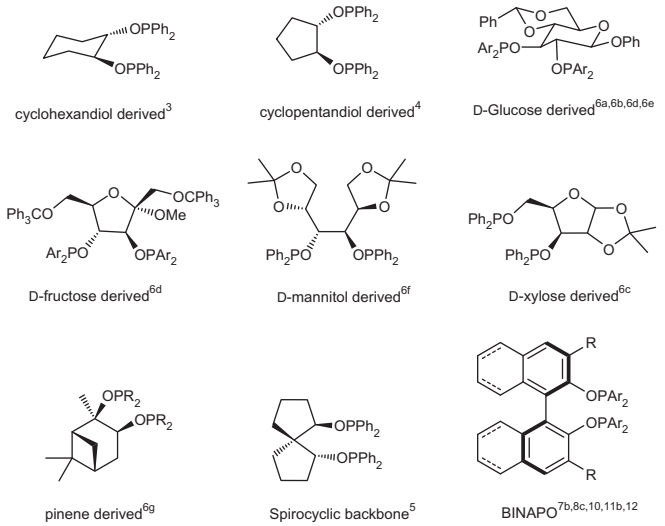
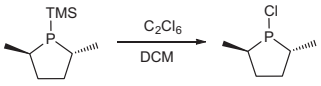


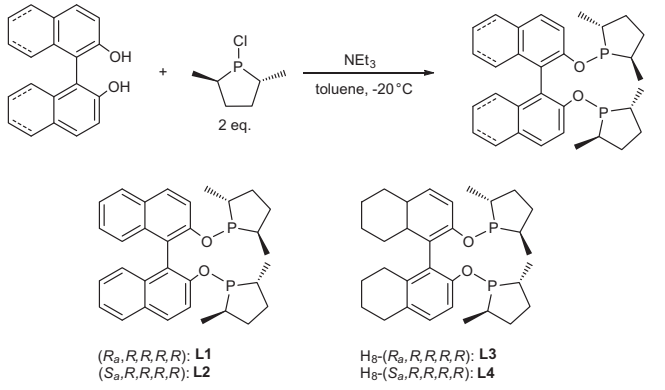
Figure 1. Examples of diphosphinite ligands.



Scheme 1. Synthesis of chiral (2*R*,5*R*)-1-chloro-2,5-dimethylphospholane.

the base (Scheme 2). Analytically pure ligands were obtained upon recrystallisation from acetonitrile **L1** and **L2** or upon filtration over basic alumina **L3** and **L4**.

Ligands **L1**–**4** include two distinct elements of chirality, the axial chirality from the backbone and four stereogenic carbon centres, two from each phospholane moiety. Their $^{31}P\{^{1}H\}$ NMR spectra show one singlet in the typical range for phosphinites (Table 2).



Scheme 2. Synthesis of DiolPhos ligands.

Table 1
Comparison of principal crystallographic data for **L1** and **L2** and BINAPO

Ligand	**L1**	**L2**	BINAPO[10]
Crystal system	Tetragonal	Tetragonal	Monoclinic
Space group	$P4_32_12$	$P4_12_12$	$I2$
P,P distance	7.114 Å (major conformer)	5.284 Å	6.190 Å
Torsion angle	114.5°	117.7°	91.6°

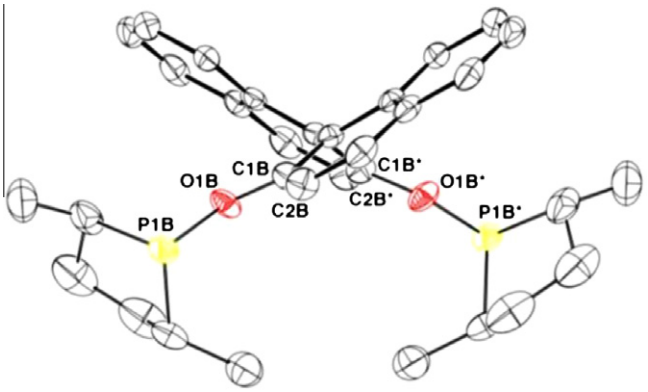


Figure 2. ORTEP representation of **L1** (50% probability, major conformer. Hydrogen atoms are omitted for clarity).

Table 2
^{31}P NMR chemical shifts and coupling constants of **L1**–**4** and the corresponding [Rh(COD)**L**]BF_4.complexes

Ligand	Free ligand	[Rh(COD)**L**]BF_4		$\Delta\delta$ ^{31}P (ppm)
	δ ^{31}P (ppm)	δ ^{31}P (ppm)	J_{PRh} (Hz)	
L1	159.4	162.6	161.7	3.2
L2	159.6	175.0	170.6	15.4
L3	153.8	160.5	161.1	6.7
L4	155.6	178.8	160.3	23.2

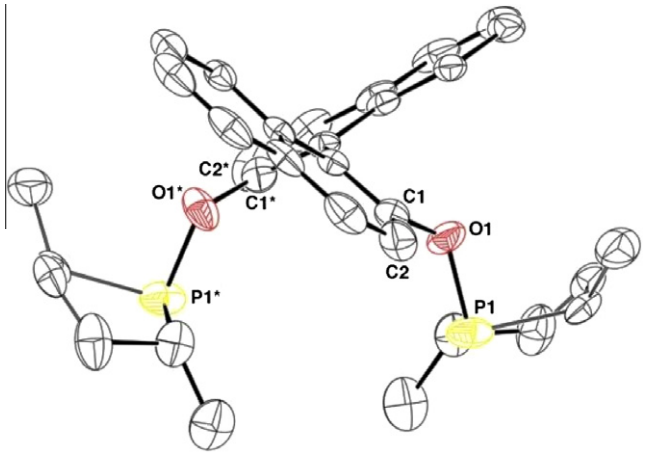
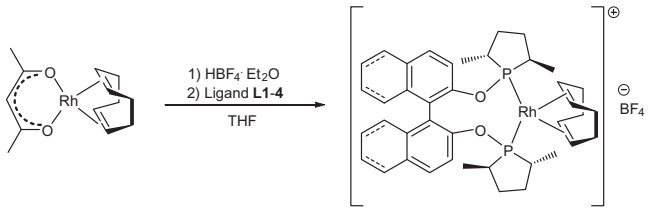


Figure 3. ORTEP representation of **L2** (50% probability, hydrogen atoms are omitted for clarity).

The ^{1}H and ^{13}C NMR spectra are fully in line with the structural motifs and confirm the C_2-symmetric structure in solution at room temperature.[21]

Ligands **L1** and **L2** could be recrystallised from acetonitrile to give colourless needles, which were suitable for X-ray diffraction. Both compounds adopt C_2-symmetry in the solid state. In **L1**, the torsion angle of the binaphthyl backbone is very large with a value of 114.5°, much larger than that reported for BINAPO (91.6°).[10] This minimises the steric repulsion between the phospholane moieties (Fig. 2). In the solid, the binaphthyl backbone is well-ordered, whereas the phospholane substituents adopt two alternative conformations of slightly different geometry. The phosphorus atoms are almost coplanar with the corresponding naphthyl moieties with a deviation from the least-squares plane passing through the aromatic rings of 0.26 and 0.34 Å for the major and the minor conformers, respectively. The lone pairs of the phospholane units



Scheme 3. Synthesis of [Rh(COD)**L**]BF_4 complexes.

point in opposite directions in an antiperiplanar arrangement. The through space distance between the two phosphorus atoms is 7.114 Å for the major and 6.419 Å for the minor conformer. The latter value is very close to that found for BINAPO (6.190 Å, Table 1).

In ligand **L2**, the phosphorus atoms are significantly bent out of the least-squares plane defined by the corresponding naphthyl units (0.91 Å) and point towards the twofold axis (Fig. 3). As a consequence, the phosphorus atoms are much closer to each other when compared with **L1** and BINAPO and the through space distance amounts to 5.284 Å. The lone pairs of the phospholane units are again in an antiperiplanar arrangement. The torsion angle of the binaphthyl backbone has a value of 117.7° and is even larger than in **L1**.

The cationic rhodium complexes of all four ligands could be obtained from [Rh(COD)acac] (COD = 1,5-cyclooctadiene; acac = acetylacetonate). Protonation of the anionic ligand acac with HBF_4 followed by the addition of the corresponding diphosphinite resulted in the desired complexes in good yields between 70% and 82% (Scheme 3).

The complexes were purified by recrystallisation from dichloromethane/diethylether. They all display a doublet in the ^{31}P {^1H} NMR with coupling constants J_{PRh} in the expected range for a phosphinite rhodium coupling. The coordination shifts range from $\Delta\delta$ = 3–23 ppm, although all ligands lead to nine membered rings at rhodium (Table 2).

2.2. Rh-Catalysed asymmetric C=C-hydrogenation

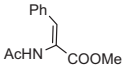
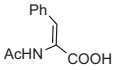
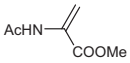
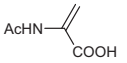
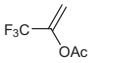
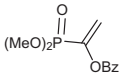
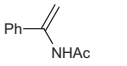
Dimethyl itaconate was chosen as benchmark substrate for the optimisation of the reaction conditions in the Rh-catalysed asymmetric hydrogenation reaction (Table 3). The first series of experiments were conducted using [Rh(COD)**L1**]BF_4 as the catalyst. The choice of the solvent showed a pronounced influence on the outcome of the reaction. While low conversion and enantioselectivity were achieved in MeOH (entry 1), full conversion and significantly higher enantioselectivites were obtained in aprotic solvents (entries 2–4). We identified CH_2Cl_2 as the solvent of choice leading to an enantioselectivity of 98% (*S*) ee (entry 4). Only a minor increase in the ee at the expense of conversion was observed when decreasing the hydrogen pressure from 10 to 1 bar (entry 5); increasing the pressure to 50 bar led to a slight decrease in the enantioselectivity (entry 6). To benchmark the catalyst activity, an experiment at a high substrate/catalyst ratio of 10,000 was carried out. After one hour, almost full conversion was attained corresponding to a remarkable TOF_{av} of 9920 h^{-1}.

Table 3
Rh-catalysed asymmetric hydrogenation of dimethyl itaconate[a]

Entry	Ligand	Solvent	pH_2 [bar]	Conv. (%)	TOF_{av} (h^{-1})	ee (%)
1	**L1**	MeOH	10	10	100	37.9 (*S*)
2	**L1**	EtOAc	10	>99	⩾1000	84.6 (*S*)
3	**L1**	THF	10	>99	⩾1000	90.7 (*S*)
4	**L1**	CH_2Cl_2	10	>99	⩾1000	98.0 (*S*)
5	**L1**	CH_2Cl_2	1	55	550	98.2 (*S*)
6	**L1**	CH_2Cl_2	50	>99	⩾1000	95.6 (*S*)
7[b]	**L1**	CH_2Cl_2	10	99.2	9920	96.3 (*S*)
8	**L2**	CH_2Cl_2	10	>99	⩾1000	65.0 (*R*)
9	**L3**	CH_2Cl_2	10	86	860	91.3 (*S*)
10	**L4**	CH_2Cl_2	10	75	750	71.0 (*R*)

[a] Sub = 1.5 mmol, CH_2Cl_2 = 2 mL, *t* = 1 h, rt, Sub/Cat = 1000.
[b] Sub/Cat = 10,000.

Table 4
Asymmetric hydrogenation of prochiral olefins with [Rh(COD)**L1**]BF_4[a]

Entry	Substrate	Conv. (%)	TOF_{av} (h^{-1})	ee (%)
1		>99	⩾1000	74 (*R*)
2[b]		>99	⩾1000	20 (*R*)
3		>99	⩾1000	84 (*R*)
4[b]		71	710	21 (*R*)
5		33	333	67 (*R*)
6[c]		>99	⩾41	59 (*R*)
7		>99	⩾1000	17 (*R*)

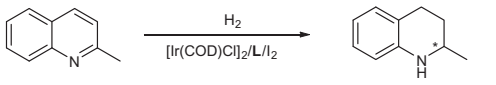
[a] Sub = 1.5 mmol, CH_2Cl_2 = 2 mL, *t* = 1 h, rt, pH_2 = 10 bar, Sub/Cat = 1000.
[b] In MeOH.
[c] 24 h.

Next, ligands **L2–4** were tested under these optimised conditions. Catalyst [Rh(COD)**L2**]BF_4 led to the preferential formation of the opposite product enantiomer with a significantly lower enantioselectivity of 65% (*R*) ee. These results indicate that the chiral information of the backbone has a dominant effect and the *all*-(*R*) ligand **L1** is the matched diastereomer for this reaction. The same trend, albeit less pronounced, was found for the diastereomeric pair **L3** and **L4** based on H_8-Binol. While [Rh(COD)**L3**]BF_4 resulted in an enantioselectivity of 91% ee for the (*S*)-product, the catalyst bearing **L4** led preferentially to the (*R*)-product with a reduced enantioselectivity of 71% ee. Next, the substrate scope of the best performing catalyst based on **L1** was evaluated and a range of differently functionalised olefins were included (Table 4). The hydrogenation of dehydroamino acid methylesters led to full conversion and good enantioselectivities (entries 1 and 3), while poor results were obtained in the hydrogenation of the corresponding free acids (entries 2 and 4). The latter two reactions had to be carried out in MeOH because of the solubility constraints of these substrates; this may partially account for the low enantioselectivities (cf. Table 3, entry 1). Enantioselectivities of 67% and 59% were achieved in the hydrogenation of 1-(trifluoromethyl)vinylacetate and 1-(dimethoxyphosphoryl)vinyl benzoate, respectively (entries 5 and 6). Only poor enantioselectivity was observed in the hydrogenation of *N*-(1-phenylvinyl)acetamide (entry 7).

2.3. Ir-Catalysed asymmetric C=N-hydrogenation

Ligands **L1–4** were also applied in the Ir-catalysed asymmetric hydrogenation of 2-substituted quinolines under reaction conditions adapted from the literature.[17a] The catalysts were formed in situ and iodine was added as an activator. The *all*-(*R*) configured DiolPhos ligand **L1** led again to the best results in this series. The (*S*)-product was obtained with all ligands with various degrees of selectivities while the chiral elements within the ligands exhibited pronounced cooperative effects only in the case of **L1** giving rise to good catalyst performances. In the presence of **L1**, 2-methylquino-

line was hydrogenated with 41% conversion and a good enantioselectivity of 75% ee in favour of the (*S*)-enantiomer (Scheme 4). With ligand **L2** a conversion of only 21% and a poor enantioselectivity of 25% ee towards the same enantiomer were achieved. Since diphosphinite H_8-BINAP[9b,9c] is superior than BINAPO in this application, it was surprising that the catalyst formed with the *all*-(*R*) H_8-Binol-based ligand **L3** gave a much poorer set of results in comparison to **L1**, and both low activity and enantioselectivity were obtained. Similar to **L2**, **L4** also did not result in a suitable catalyst for this transformation.



L1 41 % cv 75 % *ee* (*S*)
L2 21 % cv 25 % *ee* (*S*)
L3 21 % cv 12 % *ee* (*S*)
L4 18 % cv 5 % *ee* (*S*)

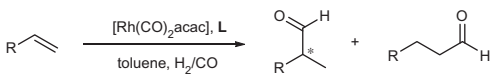
Scheme 4. Iridium-catalysed asymmetric hydrogenation of 2-methylquinoline.

2.4. Rh-Catalysed asymmetric hydroformylation

The DiolPhos ligands **L1** and **L2** were tested in the asymmetric hydroformylation of styrene as well as vinylacetate (Table 5). In the hydroformylation of styrene, **L1** led to good regioselectivity b:l = 84:16, but almost racemic branched aldehydes (entry 1). Ligand **L2** resulted in lower regioselectivity, but an enantioselectivity of 40% ee, independent from the syngas pressure (entries 2 and 3). Using vinylacetate as a substrate, an excellent regioselectivity of 96:4 with a moderate enantioselectivity of 33% ee could be achieved with **L2**.

The hydroformylation results were in good agreement with those obtained with related diphosphinite ligands.[13b] In particular, Bakos et al. reported that electron rich P-donor groups at the Binol-backbone lead to high regioselectivities, but at the expense of activity.[13b] In addition to the electronic effects, the present ligand systems exhibited strong cooperative interactions of the atropoisomeric and the carbon centred elements of chirality as revealed for the diastereomeric **L1** and **L2** pair. In accordance with other diastereomeric ligand systems,[22] the matched diastereomer for the hydroformylation has the opposite relative configurations compared to the hydrogenation reactions.

Table 5
Rhodium-catalysed asymmetric hydroformylation[a]



Entry	Ligand	R	pH_2/CO [bar]	Conv.[a] (%)	b:l[b]	ee[c] (%)
1	**L1**	Ph	20	58	84:16	4 (*S*)
2	**L2**	Ph	20	22	73:27	40 (*R*)
3	**L2**	Ph	50	19	75:25	40 (*R*)
4	**L2**	AcO	20	25	96:4	33 (*R*)

[a] Sub = 2.0 mmol, toluene = 1 mL, **L**/[Rh] = 4, H_2/CO 1:1, *t* = 18 h, *T* = 60 °C.
[b] Determined by ^{1}H NMR.
[c] Determined by chiral GC.

3. Conclusions

In conclusion, new diphosphinite ligands including an atropoisomeric diol backbone and chiral phospholane moieties have been synthesised and fully characterised. Moreover, the structures in the solid state of two diastereomeric ligands have been determined via X-ray diffractometry. The ligands display C_2-symmetry in solution as well as in the solid state. Positive synergistic effects of the different chirality elements were evident for the *all*-(*R*) ligand **L1** based on the Binol backbone. This ligand gave promising results in the Rh-catalysed olefin hydrogenation with excellent activities and with good enantioselectivities up to 98% ee for a wide range of substrates. Lower activities were obtained in the Ir-catalysed hydrogenation of 2-methylquinoline with a good enantioselectivity of 75% ee. Ligand **L2** turned out to be the matched diastereomer for the asymmetric hydroformylation of styrene and vinyl acetate, leading to good to excellent regioselectivities of 75:25 and 96:4, respectively, at moderate enantioselectivities of up to 40% ee.

In general, these results indicate that the use of chiral R_2P moieties provides an additional element in the toolbox of diphosphinite ligands. The cooperative effects between the dominating chiral information of the diol backbone and the tuning influence of the chirality at the donor unit offer a hitherto neglected control factor for the development of new structures in this readily accessible class of ligands.

4. Experimental

4.1. 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. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded with Bruker AV 300 and AV 400 spectrometers. The operating frequencies of these spectrometers for NMR measurements are 300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P with the AV 300 spectrometer and 400.1 MHz for ^{1}H, 100 MHz for ^{13}C and 162 MHz for ^{31}P with the AV 400 spectrometer. For ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, the chemical shifts (δ) are given in ppm with use of the residual solvent signals as internal standards. For ^{31}P NMR spectroscopy, the chemical shift values (δ) are given in ppm relative to 85% phosphoric acid as the external standard. The multiplicities of the signals were assigned by assuming spectra of first order. The coupling constants (*J*) are given in Hertz. For the description of the multiplicity of the signals the following symbols are used: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. The signals were assigned on the basis of two-dimensional NMR spectra (^{31}P–^{1}H HMBC, ^{1}H–^{1}H COSY, ^{13}C–^{1}H HMBC, ^{13}C–^{1}H HSQC). Mass spectra were recorded on a Varian 1200L Quadrupole GC–MS, Finnigan MAT 8200 (MS and HRMS-EI) or a Bruker FTICR-Apex III spectrometer (HRMS-ESI). High-resolution MS measurements were performed with a Finnigan-MAT 95 spectrometer (EI, 70 eV). The mass of the molecule ion is given. Optical rotations were measured on a Jasco P-1020 polarimeter. The concentrations used for measuring specific rotations are given as g/100 mL. Dichloromethane, toluene and pentane were dried over alumina with a solvent purification system from Innovative Technology. THF, Et_2O, MeOH and acetonitrile were distilled and then dried over molecular sieves. All other organic solvents were purged with argon for 2 h prior to use. Deuterated solvents were degassed through freeze–pump–thaw cycles and stored over molecular sieves. The following substances have been synthesised according to literature procedures: (2*R*,5*R*)-1-chloro-2,5-dimethylphospholane,[15] (R_a)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol.[20] All other chemicals were purchased from Sigma–Aldrich, Acros or Alfa Aesar and used as received.

4.2. Preparation of ligands L1–L4

4.2.1. (R_a)-2,2′-Bis((2*R*,5*R*)-2,5-dimethylphospholan-1-yloxy)-1,1′-binaphthyl L1

A solution of (2*R*,5*R*)-1-chloro-2,5-dimethylphospholane (295 mg, 1.96 mmol), in toluene (3 ml) was added at −20 °C over 30 min through a syringe pump to a mixture of (*R*)-1,1′-binaphthyl-2,2′-diol (280.4 mg, 0.98 mmol) and triethylamine (300 μL, 2.16 mmol) in toluene (10 mL). The reaction mixture was stirred at −20 °C for 1 h and then at ambient temperature overnight. The reaction mixture was filtered through a PTFE membrane to remove the ammonium salt formed as a by-product. After evaporation of the solvent, a white solid formed, which was recrystallised from hot acetonitrile. (385.9 mg, 75%); ^{1}H NMR ($CDCl_3$): δ = 0.53–0.80 (m, 2H, CH_2); 0.67 (d, 6H, J_{HH} = 7.7, J_{PH} = 19.2; CH_3); 0.86 (d, 6H, J_{HH} = 6.9, J_{PH} = 11.4; CH_3); 0.89–1.01 (m, 2H, CH); 1.15–1.35 (m, 2H, CH); 1.35–1.59 (m, 2H, CH); 7.07–7.11 (m, 2H, Ar-H); 7.11–7.14 (m, 2H, Ar-H); 7.35–7.49 (m, 2H, CH); 7.69–7.82 (m, 4H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): δ = 12.91 (d, CH_3, J_{CP} = 3.03 Hz), 17.19 (d, CH_3, J_{CP} = 31.5 Hz), 34.92 (d, CH_2, J_{CP} = 3.36 Hz), 35.24 (d, CH_2, J_{CP} = 3.17 Hz), 40.16 (d, CH, J_{CP} = 13.2 Hz), 42.41 (d, CH, J_{CP} = 19.2 Hz), 119.96 (d, CH, J_{CP} = 15.4 Hz), 122.19 (d, C, $^3J_{CP}$ = 2.07 Hz), 123.73 (s, CH), 125.81 (s, CH), 126.12 (s, CH), 127.88 (s, CH), 129.09 (s, CH), 129.64 (s, CH), 134.25 (s, C), 153.36 (d, C, J_{CP} = 6.6 Hz) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 159.4 ppm; MS (CI, 80 eV): calculated: 514.6; found: 515.3 [M^+]; $[\alpha]_D^{20} = +186.8$ (*c* 0.732, CH_2Cl_2).

4.2.2. (S_a)-2,2′-Bis((2*R*,5*R*)-2,5-dimethylphospholan-1-yloxy)-1,1′-binaphthyl L2

The title compound was obtained by the procedure described above using (*S*)-1,1′-binaphthyl-2,2′-diol as the diol. The product is a white solid, which was recrystallised from hot acetonitrile (447.7 mg; 74%); ^{1}H NMR ($CDCl_3$): δ = 0.59 (dd, J_{HH} = 7.07 Hz, J_{PH} = 11.45 Hz, 6H, CH_3); 0.82–1.03 (m, 5H, CH, CH_2); 0.93 (dd, J_{HH} = 7.40 Hz, J_{PH} = 19.11 Hz, 6H, CH_3); 1.50–1.60 (m, 2H, CH); 1.63–1.74 (m, 5H, CH); 7.14–7.16 (m, 2H, Ar-H); 7.21–7.26 (m, 2H, Ar-H); 7.43 (dd, 2H, J_{HH} = 1.96 Hz, J_{PH} = 8.89 Hz, CH); 7.78 (dd, 4H, $^3J_{HH}$ = 8.5 Hz, J_{PH} = 21.23 Hz, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): δ = 12.9 (s, C); 17.5 (s, $C_{aliph.}$); 17.8 (s, C); 35.1 (d, CH_2, J_{CP} = 2.7 Hz); 35.5 (d, CH_2, J_{CP} = 2.7 Hz); 41.0 (d, CH, J_{CP} = 14.5 Hz); 42.7 (d, CH, J_{CP} = 20.0 Hz); 119.4 (d, J_{CP} = 15.6 Hz, CH); 122.9 (s, C); 124.2 (s, CH); 126.4 (s, CH); 126.7 (s, CH); 129.6 (s, CH); 130.3 (s, CH); 134.8 (s, CH); 134.3 (s, C); 153.8 (d, C, J_{CP} = 7.1 Hz) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 159.6 ppm; $[\alpha]_D^{20} = +14.6$ (*c* 0.772, CH_2Cl_2); MS (CI, 80 eV): calculated: 514.6; found: 515.3 [M^+].

4.2.3. (R_a)-2,2′-Bis((2*R*,5*R*)-2,5-dimethylphospholan-1-yloxy)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl L3

The title compound was obtained by the procedure described above using (R_a)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol (333 mg, 1.13 mmol) as the diol. The product was obtained as a colourless solid after filtration over basic alumina which can be used without further purification. (428.6 mg, 81%); ^{1}H NMR ($CDCl_3$): δ = 0.82 (dd, J_{HH} = 7.00 Hz, J_{PH} = 11.41 Hz, 6H, CH_3); 0.90–1.05 (dd, J_{HH} = 7.71 Hz, J_{PH} = 18.82 Hz, 6H, CH_3); 0.96–1.05 (m, 1H, CH); 1.24–1.33 (m, 2H, CH_2); 1.39–1.83 (m, 14H, CH_2, CH); 1.86–1.99 (m, 2H, CH_2); 2.00–2.13(m, 2H, CH_2); 2.20–2.31 (m, 2H, CH_2); 2.61–2.69 (m, 4H, CH_2); 6.78 (d, J_{HH} = 8.20 Hz, 2H, Ar-H); 6.87 (d, J_{HH} = 8.30 Hz, 2H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): δ = 12.7 (s, CH_3); 17.4 (s, CH_3); 17.7 (s, CH_2) 23.4 (d, $^2J_{CP}$ = 2,7 Hz, CH_2); 27.6 (s, CH_2); 29.6 (s, CH_2); 35.2 (d, J_{CP} = 2.8 Hz, CH_2); 35.5 (d, J_{CP} = 2.6 Hz, CH_2); 40.4 (d, J_{CP} = 12.9 Hz, CH); 42.4 (d, J_{CP} = 19.4 Hz, CH); 114.4 (d, J_{CP} = 16.7 Hz, C); 128.2 (s, C); 128.4 (s, C); 130.2 (s, C); 136.6 (s, C); 152.6 (d, J_{CP} = 7.3 Hz, C) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 153.8 ppm; HRMS (EI, 80 eV): calculated: 522.28111; found: 522.28181; $[\alpha]_D^{20} = +121.3$ (*c* 1.033, CH_2Cl_2).

4.2.4. (S_a)-2,2′-Bis((2*R*,5*R*)-2,5-dimethylphospholan-1-yloxy)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl L4

The title compound was obtained by the procedure described above using (S_a)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol (376 mg, 1.27 mmol) as the diol. The product was obtained after filtration over basic alumina as a colourless solid. (449.5 mg; 86%).

^{1}H NMR ($CDCl_3$): δ = 0.93 (dd, J_{HH} = 7.00 Hz, J_{HP} = 18.33 Hz, 6H, CH_3); 0.98 (dd, J_{HH} = 7.71 Hz, J_{HP} = 26.61 Hz, 6H, CH_3); 1.21–1.34 (m, 3H, CH_2, CH); 1.51–1.79 (m, 15H, CH_2, CH); 1.81–1.92 (m, 2H, CH_2); 1.98–2.11 (m, 2H, CH_2); 2.22–2.33 (m, 2H, CH_2); 2.60–2.70 (m, 4H, CH_2) 6.87 (d, J_{HH} = 8.31 Hz, 2H, Ar-H); 6.96 (d, J_{HH} = 8.20 Hz, 2H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): δ = 12.9 (s, CH_3); 17.4 (s, CH_3); 17.7 (s, CH_2); 23.4 (d, J_{CP} = 3.4 Hz, CH_2); 27.5 (s, CH_2); 29.6 (s, CH_2); 35.2 (d, J_{CP} = 2.8 Hz, CH_2); 35.5 (d, J_{CP} = 2.8 Hz, CH_2); 40.5 (d, J_{CP} = 12.6 Hz, CH); 42.3 (d, J_{CP} = 20.3 Hz, CH); 114.4 (d, J_{CP} = 15.9 Hz, C); 128.5 (s, C); 129.4 (s, C); 130.4 (s, C); 130.5 (s, C); 136.8 (s, C) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 155.6 ppm; HRMS (EI, 80 eV): calculated: 522.28111; found: 522.28142; $[\alpha]_D^{20} = +36.9$ (*c* 1.065, CH_2Cl_2).

4.3. Preparation of rhodium complexes

4.3.1. [Rh(cycloocta-1,5-diene)L1]BF_4

At first, $HBF_4{\cdot}Et_2O$ (0.120 mmol, 51 μL) was added to a solution of (acetylacetonato)-(1,5-cyclooctadiene)-rhodium (I) (37.6 mg, 0.120 mmol) in dry THF (3 mL). The solution was stirred for 10 min at ambient temperature, then a solution of **L1** (63.3 mg, 0.120 mmol) in THF (3 mL) was added dropwise. During the addition, the colour of the solution turned from yellow to orange. After stirring for 60 min, the solvent was removed under reduced pressure. The orange residue was dissolved in CH_2Cl_2 (1 mL) and the resulting solution added dropwise to Et_2O (25 mL), whereupon a yellow precipitate was formed. The mother liquor was removed and the remaining yellow solid was washed with Et_2O (3 × 5 mL) and dried under reduced pressure (79.0 mg; 81%); ^{1}H NMR (CD_2Cl_2): δ = 0.02 (dd, J_{HH} = 6.70 Hz, J_{HP} = 13.16 Hz, 6H, CH_3); 1.46 (dd, J_{HH} = 7.45 Hz, J_{PH} = 16.93 Hz, 9H, CH_3, CH); 1.58–1.79 (m, 4H, CH); 1.93–2.07 (m, 2H, CH); 2.19–2.42 (m, 8H, CH); 2.42–2.53 (m, 2H, CH); 2.82–2.96 (m, 2H, CH); 5.12–5.26 (m, 4H, CH); 7.104 (d, J_{HH} = 8.43 Hz, 2H, Ar-H); 7.31 (t, J_{HH} = 7.69 Hz, 2H, Ar-H); 7.42 (d, J_{HH} = 8.89 Hz, 2H, Ar-H); 7.55 (t, 2H, J_{HH} = 7.55 Hz, Ar-H); 7.98 (d, J_{HH} = 8.05 Hz, 2H, Ar-H); 8.10 (d, J_{HH} = 8.88 Hz, 2H, Ar-H) ppm; ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz): δ = 162.6 (d, J_{PRh} = 161.7 Hz) ppm; MS (ESI, pos): calculated: 725.6, found: 725.0.

4.3.2. [Rh(cycloocta-1,5-diene)L2]BF_4

The title compound was obtained by the procedure described above using $HBF_4{\cdot}Et_2O$ (0.077 mmol, 33 μL), (acetylacetonato)-(1,5-cyclooctadiene)-rhodium (I) (24.1 mg, 0.077 mmol) and **L2** (40.0 mg, 0.077 mmol); (47.4 mg; 75%); ^{1}H NMR (CD_2Cl_2): δ = 0.57 (dd, J_{HH} = 7.55 Hz, J_{HP} = 20.45 Hz, 6H, CH_3); 1.04–1.17 (m, 2H, CH); 1.62 (dd, J_{HH} = 6.62 Hz, J_{PH} = 13.88 Hz, 8H, CH_3, CH); 1.81–1.93 (m, 2H, CH); 1.93–2.14 (m, 6H, CH); 2.18–2.54 (m, 8H, CH); 4.64–4.73 (m, 2H, CH); 5.41–5.49 (m, 2H, CH); 7.07 (d, J_{HH} = 8.92 Hz, 2H, Ar-H); 7.28 (t, J_{HH} = 7.65 Hz, 2H, Ar-H); 7.42 (d, J_{HH} = 8.95 Hz, 2H, Ar-H); 7.47 (t, J_{HH} = 7.58 Hz, 2H, Ar-H); 7.97 (d, J_{HH} = 8.14 Hz, 2H, Ar-H); 8.08 (d, J_{HH} = 8.94 Hz, 2H, Ar-H) ppm; ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 175.0 (d, J_{PRh} = 170.6 Hz) ppm; MS (ESI, pos): calculated: 725.6, found: 725.0.

4.3.3. [Rh(cycloocta-1,5-diene)L3]BF_4

The title compound was obtained by the procedure described above using $HBF_4{\cdot}Et_2O$ (0.178 mmol, 71 μL), (acetylacetonato)-(1,5-cyclooctadiene)-rhodium (I) (54.7 mg, 0.178 mmol) and **L3** (1 equiv, 93.2 mg, 0.178 mmol); (105.4 mg; 72%); ^1H NMR (400 MHz, CD_2Cl_2): δ = 400 MHz, CD_2Cl_2): δ = 0.49 (dd, J_{HH} = 6.48 Hz, J_{HP} = 19.04 Hz, 6H, CH_3); 0.95–1.26 (m, 3H, CH, CH_2.); 1.35 (dd, J_{HH} = 7.52 Hz, J_{PH} = 23.93 Hz, 6H, CH_3); 1.91–2.55 (m, 6H, CH_2); 2.61–2.77 (m, 4H, CH_2); 5.06–5.14 (m, 2H, =CH–); 5.15–5.22 (m, 2H, =CH–); 6.81 (d, J_{HH} = 8.32 Hz, 2H, Ar-H); 7.08 (t, J_{HH} = 8.36 Hz, 2H, Ar-H); ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 160.5 (d, J_{PRh} = 161.1 Hz) ppm; MS (ESI, pos): calculated: 735.7, found: 735.0.

4.3.4. [Rh(cycloocta-1,5-diene)L4]BF_4

The title compound was obtained by the procedure described above using $HBF_4{\cdot}Et_2O$ (0.108 mmol, 45 μL), (acetylacetonato)-(1,5-cyclooctadiene)-rhodium (I) (33.1 mg, 0.108 mmol) and **L4** (56.4 mg, 0.108 mmol); (61.3 mg; 70%); ^1H NMR (CD_2Cl_2): δ = 0.66–0.85 (m, 3H, CH_2, CH); 1.09 (dd, J_{HH} = 7.58 Hz, J_{HP} = 28.53 Hz, 6H, CH_3); 1.48 (dd, J_{HH} = 10.56 Hz, J_{PH} = 21.02 Hz, 6H, CH_3); 1.56–1.75 (m, 15H, CH_2, CH); 1.76–1.90 (m, 2H, CH_2); 1.92–2.09 (m, 2H, CH_2); 2.14–2.25 (m, 2H, CH_2); 2.70–2.84 (m, 2H, CH_2); 4.28–4.39 (m, 2H, =CH–); 5.45–5.54 (m, 2H, =CH–); 6.87 (d, J_{HH} = 8.53 Hz, 2H, Ar-H); 7.14 (d, J_{HH} = 8.28 Hz, 2H, Ar-H); ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 178.8 (d, J_{PRh} = 160.3 Hz) ppm; MS (ESI, pos): calculated: 735.7, found: 735.1.

4.4. General procedure for the asymmetric C=C-hydrogenation

A 10 mL stainless steel autoclave equipped with a glass inlet and a magnetic stirring bar was charged under an argon atmosphere with the substrate (1.5 mmol). The desired Rh complex (1.5 μmol) was added by syringe as a stock solution in CH_2Cl_2 or MeOH. The total amount of solvent was adjusted to 2 mL by the addition of the appropriate quantity of the same solvent and the autoclave was pressurised with hydrogen. The reaction mixture was stirred at room temperature for the desired reaction time (see Table 3 and 4) and then the pressure was carefully released. The conversion was determined by ^1H NMR spectroscopy of the concentrated reaction mixture. The ee value was determined by chiral GC or HPLC analysis after filtration through a plug of silica. The absolute configurations of the hydrogenation products were assigned by comparison of the sign of the specific rotation with those reported in the literature.

4.5. General procedure for the asymmetric C=N-hydrogenation

A 10 mL stainless steel autoclave equipped with a glass inlet and a magnetic stirring bar was charged under an argon atmosphere with the 2-methylquinoline (68 μL, 0.5 mmol) and iodine (3.17 mg, 0.025 mmol). A Schlenk-flask equipped with a magnetic stirring bar was charged with $[Ir(COD)Cl]_2$ (1.68 mg, 2.5 μmol) and the desired ligand (5.5 μmol) and toluene (2 mL). After 10 min of stirring, the resulting solution was transferred to the autoclave. The autoclave was pressurised with hydrogen (40 bar) and stirred at ambient temperature for 16 h. After carefully releasing the pressure, the conversion and ee values were determined via GC.

4.6. General procedure for the asymmetric hydroformylation

A 10 mL stainless steel autoclave equipped with a glass inlet and a magnetic stirring bar was charged under an argon atmosphere with $[Rh(CO)_2acac]$ (0.5 mL of a 4.0 mM) stock solution in toluene, 2.0 μmol) and the desired ligand (8.0 μmol) and stirred at ambient temperature for 30 min. Then, the substrate (2.0 mmol) was added via syringe and the autoclave was pressurised with the desired syngas pressure (H_2–CO 1:1). After the desired reaction time, the autoclave was cooled down to ambient temperature and the pressure carefully released. The conversion was determined by ^1H NMR spectroscopy of the concentrated reaction mixture. The ee value and l:b ratio were determined by chiral GC.

4.7. Single crystal X-ray diffraction

Data collection for **L1** and **L2** was done with Mo Kα radiation (INCOATEC microsource, multilayer optics, λ = 0.71073 Å) on a Bruker D8 goniometer with SMART CCD area detector; The SADABS[23] programme was used for absorption correction of **L2** and PLATON[24] was used for multi-scan absorption correction of **L1**. The structures were solved by direct methods (SHELXS-97)[25] and refined by full matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97).[25] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions and were refined using a riding model. In the case of **L1**, the electron density was interpreted as overlap of two slightly different conformations; similarity restraints were imposed to ensure physically and chemically reasonable displacement and geometry parameters. Supplementary crystallographic data for **L1** (CCDC-844768) and **L2** (CCDC-844769) can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

Acknowledgments

We like to thank Dr. Renat Kadyrov (Evonik) and W. C. Heraeus GmbH for a generous donation of (2*R*,5*R*)-1-trimethylsilyl-2,5-dimethyl-phospholane and precious metal complexes, respectively, Dr. Yutian Wang for the acquisition of X-ray intensity data, Dr. Beatrice Braun for solving the structure of ligand **L2**, Ms. Brigitte Pütz for the measurement of MS data, Ms. Julia Wurlitzer and Ms. Hannelore Eschmann for GC- and HPLC-measurements. The research leading to these results has received funding from the European Community's Seventh Framework Programm (FP7/2007-2013) under grant agreement No. 246461.

References

1. Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H. *Comprehensive Asymmetric Catalysis*; Springer: Berlin, 2001; Ojima, I. *Catalytic Asymmetric Synthesis*, 2nd ed.; Wiley-VCH: Weinheim, 2000.
2. Börner, A. *Phosphorus Ligands in Asymmetric Catalysis*; Wiley-VCH: Weinheim, 2008.
3. Tanaka, M.; Ogata, I. *J. Chem. Soc., Chem. Commun.* **1975**, 735a.
4. Hayashi, T.; Tanaka, M.; Ogata, I. *Tetrahedron Lett.* **1977**, *18*, 295–296.
5. (a) Chan, A. S. C.; Hu, W.; Pai, C.-C.; Lau, C.-P.; Jiang, Y.; Mi, A.; Yan, M.; Sun, J.; Lou, R.; Deng, J. *J. Am. Chem. Soc.* **1997**, *119*, 9570–9571; (b) Zhu, G.; Zhang, X. *J. Org. Chem.* **1998**, *63*, 3133–3136.
6. (a) Cullen, W. R.; Sugi, Y. *Tetrahedron Lett.* **1978**, *19*, 1635–1636; (b) Selke, R. *React. Kinet. Catal. Lett.* **1979**, *10*, 135–138; (c) Jackson, R.; Thompson, D. J. *J. Organomet. Chem.* **1978**, *159*, C29–C31; (d) RajanBabu, T. V.; Ayers, T. A.; Halliday, G. A.; You, K. K.; Calabrese, J. C. *J. Org. Chem.* **1997**, *62*, 6012–6028; (e) RajanBabu, T. V.; Ayers, T. A.; Casalnuovo, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 4101–4102; (f) Chen, Y.; Li, X.; Tong, S.-K.; Choi, M. C. K.; Chan, A. S. C. *Tetrahedron Lett.* **1999**, *40*, 957–960; (g) Hobuß, D.; Hasenjäger, J.; Driessen-Hölscher, B.; Baro, A.; Axenov, K. V.; Laschat, S.; Frey, W. *Inorg. Chim. Acta* **2011**, *374*, 94–103.
7. (a) Grubbs, R. H.; DeVries, R. A. *Tetrahedron Lett.* **1977**, *22*, 1879–1880; (b) Tararov, V. I.; Kadyrov, R.; Riermeier, T. H.; Holz, J.; Börner, A. *Tetrahedron: Asymmetry* **1999**, *10*, 4009–4015; (c) Gergely, I.; Hegedüs, C.; Monsees, A.; Riermeier, T.; Bakos, J. *Tetrahedron Lett.* **2003**, *44*, 9025–9028; (d) Shi, C.; Chien, C.-W.; Ojima, I. *Chem. Asian J.* **2011**, *6*, 674–680.
8. (a) Guo, R.; Elpelt, C.; Chen, X.; Song, D.; Morris, R. H. *Chem. Commun.* **2005**, 3050–3052; (b) Guo, R.; Chen, X.; Elpelt, C.; Song, D.; Morris, R. H. *Org. Lett.* **2005**, *7*, 1757–1759.
9. (a) Tang, W.; Xu, L.; Fan, Q. H.; Wang, J.; Fan, B.; Zhou, Z.; Lam, K. H.; Chan, A. S. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 9135–9138; (b) Tang, W.-J.; Zhu, S.-F.; Xu, L.-J.; Zhou, Q.-L.; Fan, Q.-H.; Zhou, H.-F.; Lam, K.; Chan, A. S. C. *Chem. Commun.*

2007, 613–615; (c) Kim, H.; Lam, L.; Xu, L.; Feng, Q.-H.; Fan, F. L.; Lam, W.-H.; Chan, A. S. C. *Adv. Synth. Catal.* **2005**, *347*, 1755–1758.
10. Alezra, V. R.; Bernardinelli, G. R.; Corminboeuf, C. M.; Frey, U.; Kündig, E. P.; Merbach, A. E.; Saudan, C. M.; Viton, F.; Weber, J. *J. Am. Chem. Soc.* **2004**, *126*, 4843–4853.
11. (a) RajanBabu, T. V.; Casalnuovo, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6265–6266; (b) Casalnuovo, A. L.; RajanBabu, T. V.; Ayers, T. A.; Warren, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9869–9882.
12. (a) Nomura, N.; Mermet-Bouvier, Y. C.; RajanBabu, T. V. *Synlett* **1996**, 745–746; (b) Clyne, D. S.; Mermet-Bouvier, Y. C.; Nomura, N.; RajanBabu, T. V. *J. Org. Chem.* **1999**, *64*, 7601–7611; (c) Nishimata, T.; Yamaguchi, K.; Mori, M. *Tetrahedron Lett.* **1999**, *40*, 5713–5716.
13. (a) RajanBabu, T. V.; Ayers, T. A. *Tetrahedron Lett.* **1994**, *35*, 4295–4298; (b) Hegedüs, C.; Madarász, J.; Gergely, I.; Szöllosy, Á.; Monsees, A.; Riermeier, T.; Bakos, J. *Tetrahedron: Asymmetry* **2004**, *15*, 2507–2513.
14. (a) Zhang, F.-Y.; Kwok, W. H.; Chan, A. S. C. *Tetrahedron: Asymmetry* **2001**, *12*, 2337–2342; (b) Zhou, Y.-G.; Tang, W.; Wang, W.-B.; Li, W.; Zhang, X. *J. Am. Chem. Soc.* **2002**, *124*, 4952–4953; (c) Zhou, Y.-G.; Zhang, X. *Chem. Commun.* **2002**, 1124–1125.
15. Holz, J.; Monsees, A.; Kadyrov, R.; Börner, A. *Synlett* **2007**, 599–602.
16. Kadyrov, R.; Koenigs, R. M.; Brinkmann, C.; Voigtlaender, D.; Rueping, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 7556–7559; *Angew. Chem.* **2009**, *121*, 7693–7696.
17. (a) Eggenstein, M.; Thomas, A.; Theuerkauf, J.; Franciò, G.; Leitner, W. *Adv. Synth. Catal.* **2009**, *351*, 725–732; (b) Barta, K.; Hölscher, M.; Franciò, G.; Leitner, W. *Eur. J. Org. Chem.* **2009**, 4102–4116; (c) Lassauque, N.; Franciò, G.; Leitner, W. *Adv. Synth. Catal.* **2009**, *351*, 3133–3138; (d) Diez-Holz, C. J.; Böing, C.; Franciò, G.; Hölscher, M.; Leitner, W. *Eur. J. Org. Chem.* **2007**, 2995–3002.
18. Galland, A.; Paris, J. M.; Schlama, T.; Guillot, R.; Fiaud, J.-C.; Toffano, M. *Eur. J. Org. Chem.* **2007**, 863–873.
19. Burk, M. J.; Pizzano, A.; Martin, J. A.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **2000**, *19*, 250–260.
20. Korostylev, A.; Tararov, V. I.; Fischer, C.; Monsees, A.; Börner, A. *J. Org. Chem.* **2004**, *69*, 3220–3221.
21. Steric constraints and hindered rotation can prevent ligands from adopting C_2-symmetric conformations in the solid state and even in solution: see e.g. Hölscher, M.; Franciò, G.; Leitner, W. *Organometallics* **2004**, *23*, 5606–5617.
22. Franciò, G.; Faraone, F.; Leitner, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 1428–1430, *Angew. Chem.* **2000**, *112*, 1486–1488.
23. Sheldrick, G. M. University of Göttingen, 1996.
24. Spek, A. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
25. Sheldrick, G. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.