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Stereochemical Control of Chirally Flexible Phosphepines

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The barriers to interconversion of the two enantiomeric atropisomers of 6-methoxy-6,7-dihydro-5*H*-dibenzo[*c*,*e*]-phosphepine and that of the diastereomeric forms of 6-(–)-menthoxy-6,7-dihydro-3*H*-dibenzo[*c*,*e*]phosphepine were determined by NMR spectroscopical methods to be 19.3 and 18.5 kcal mol^{-1}, respectively, at 298 K. The ratio of the atropisomers was shown to depend on the group bound to phosphorus. Only complexes with two homochiral ligands bound to the each metal center were obtained upon reaction with $[Rh(COD)_2]^+$ BF_4^-. The Rh complexes catalyzed the hydrogenation of α-acetamidocinnamate. The major isomer of 6-(–)-menthoxy-6,7-dihydro-5*H*-dibenzo[*c*,*e*]phosphepine was found to exhibit higher activity but to afford a product with lower *ee* than its diastereomer.

Introduction

A variety of axially chiral ligands containing 2,2′-disubstituted binaphthyl units form highly enantioselective catalysts with a wide range of metal centers.[1] By replacing the binaphthyl unit by a 2,2′-disubstituted biphenyl group lacking substituents in the 6 and 6′ positions, stereochemically dynamic (tropos)[2] ligands are usually obtained. Although resolution under normal conditions is not permitted because of the lack of configurational stablility, the presence of a proximal chiral motif may result in different stabilities of the two isomers and occasionally in the presence of only one atropisomer. Thus, a chiral enantiopure ligand bound to a metal center in turn linked to a tropos ligand may induce a preferred twist of the configurationally flexible ligand. This phenomenon was first studied by Vallée[3] and further explored by Mikami and Noyori with the use of 2,2′-bis(diarylphosphanyl)biphenyl (BIPHEP) derivatives.[4] In a different approach, atropisomerism was induced in chiral ligands composed of a stereochemically dynamic part, most commonly a 2,2′-biphenol derivative, and a substituent with a stereogenic element.[5]

8,9-Dihydro-7*H*-dinaphtho[2,1-*c*:1′,2′-*e*]phosphepine (**A**) derivatives, first prepared by Gladiali[6] and subsequently explored by Steltzer,[7] have recently found numerous applications in asymmetric catalysis.[8] The corresponding stereochemically dynamic biphenyl derivative (**B**, X = P–R) has, however, been rarely studied or applied in catalytic reactions.[9] We used this flexible unit as well as its nitrogen analogue in the synthesis of ligands with pseudo-C_2 and pseudo-C_s symmetry, and the latter was later used as a component of phosphoramidite ligands.[10] However, other bridged *o*,*o*′-linked biphenyls have been the subject of extensive conformational studies. A three-atom bridged biphenyl, **B**, with X = $C(CO_2Et)_2$ was early resolved and found to be configurationally stable in the crystalline state, but found to lose half of its activity within 80 min in solution.[11] The barriers to conformational inversion for 5,7-dihydrodibenz[*c*,*e*]oxepin (**B**, X = O) and 5,7-dihydrodibenzo[*c*,*e*]thiepin (**B**, X = S) were determined by variable temperature NMR studies to be 9.2 kcal mol^{-1} at 189 K and 16.1 kcal mol^{-1} at 315 K, respectively.[12] 6,7-Dihydro-5*H*-dibenz[*c*,*e*]azepines (**B**, X = NR) were prepared earlier,[13] and the barrier to inversion was determined to be 13.4 kcal mol^{-1} for a quarternary ammonium bromide (Figure 1).[14]

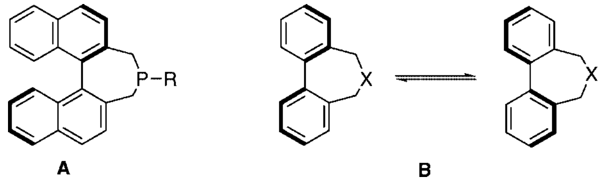

Figure 1. Stereochemically rigid 8,9-dihydro-7*H*-dinaphtho[2,1-*c*:1′,2′-*e*]phosphepine (**A**) and flexible bridged biphenyl analogues (**B**).

The barrier to rotation of 6,7-dihydro-5*H*-dibenzo[*c*,*e*]-phosphepines has, however, so far not been reported in spite of its versatility as a chirally flexible structural motif in asymmetric catalysis. Prompted by our previous studies of chirally flexible ligands incorporating bridged biphenyl units and by the usefulness of this particular structural unit in ligand design, we have now determined the barrier to configurational change and studied the effect of chiral substituents on the atropisomerism of 6,7-dihydro-5*H*-di-

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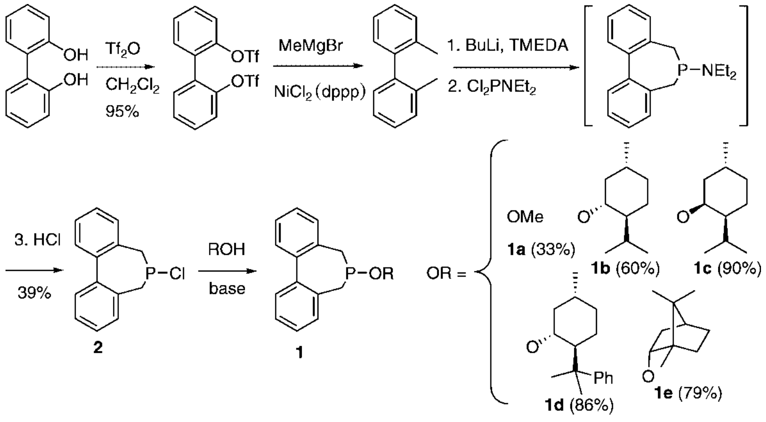
benzo[*c*,*e*]phosphepines and the possibility to induce a preferred twist by a neighboring stereogenic center.

Results and Discussion

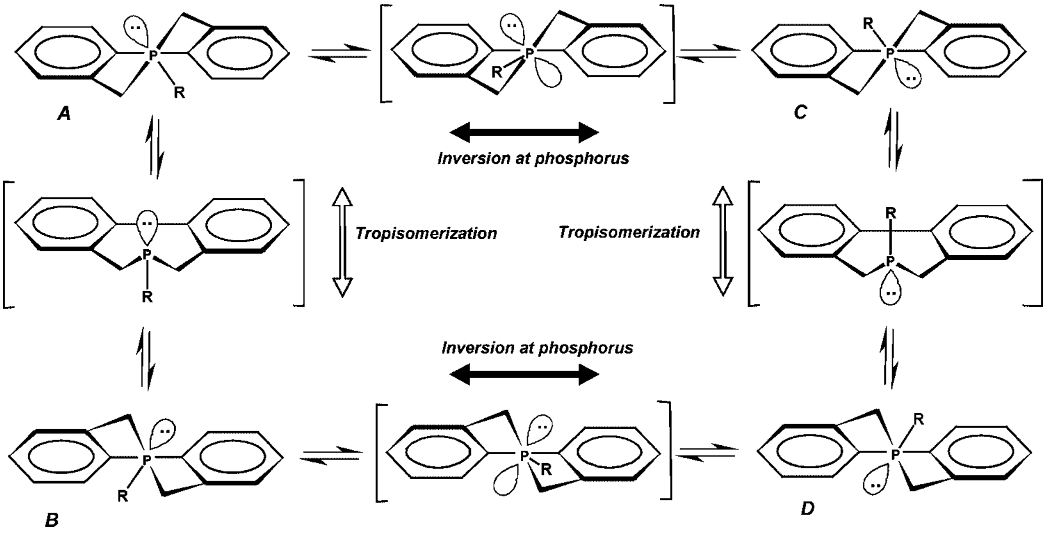
Preparation of Ligands

Ligands with the general structure **1** were prepared by reaction of 6-chloro-6,7-dihydro-5*H*-dibenzo[*c*,*e*]phosphepine (**2**), obtained from 2,2′-dihydroxybiphenyl in analogy to the procedure described for 8-chloro-8,9-dihydro-7*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine,[15] with achiral and chiral alcohols, as described in Scheme 1. Thus, reaction with methanol in the presence of triethylamine produced **1a** in a moderate yield (33%). Reaction with L-(–)-menthol resulted in some chlorinated product when performed in the same way, but afforded **1b** (60%) in the presence of butyllithium. (+)-Neomenthol, (–)-8-phenylmenthol, and (–)-borneol reacted analogously to give **1c** (90%), **1d** (86%), and **1e** (79%), respectively.

The stereochemical properties of compounds **1a**–**e** were studied by NMR spectroscopy. The phosphorus atom is not a stereogenic center and therefore pyramidal inversion at phosphorus does not affect the chirality of the molecules. In **1a**, H^A–H^D and H^B–H^C are interchanged through tropoinversion, whereas H^A–H^B and H^C–H^D are interchanged by pyramidal inversion at phosphorus (Figure 2 and Scheme 2). Except for **1a**, two signals were observed in the ^{31}P NMR spectra of the ligands, which demonstrates that interconversion between the two diastereomers is slow on the NMR time scale. The four methylene protons are inequivalent; this gives rise to four signals in the ^1H NMR spectrum of **1a**, and consequently a total of eight signals from the diastereomeric mixtures **1b**–**e**. This demonstrates that both pyramidal inversion at phosphorus and atropisomerization are slow, which is in accordance with our expectations. The four methylene protons labeled A, B, C, and D in **1a** (Figure 2) resonate at δ = 2.97 (H^A, $J_{H,H}$ = 11.9 Hz, $J_{P,H}$ = 14.9 Hz), 2.82 (H^B, $J_{H,H}$ = 15.0 Hz), 2.51 (H^C, $J_{H,H}$ = 11.9 Hz), and 2.34 (H^D, $J_{H,H}$ = 15.0 Hz, $J_{P,H}$ = 18.7 Hz) ppm, respectively. From the H–H coupling constants it was



Scheme 1.



Scheme 2.

concluded that A and C, as well as B and D, are geminal protons (Figure 2). In each compound, coupling to phosphorus was observed only for two of the methylene protons. From the NOESY spectrum, H^A and H^B were found to be the protons aligned with the phenyl groups, whereas H^B and H^C showed cross peaks with the methoxy group. The assignment is consistent with the dependence of the dihedral angle on the phosphorus proton coupling constants.[16] It is worth noting that cross peaks due to the tropoisomerization can be observed between H^A–H^D and H^C–H^B.

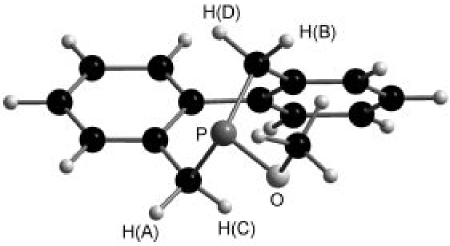


Figure 2. Conformational view of **2**.

The ratio between the two diastereomers was determined from their ^{31}P NMR spectra. It was found to be somewhat dependent on the structure of the alcohol part of the ligands, but did not exceed 1.43:1, as observed for **1d** (Table 1). The low diastereomeric ratios contrast those of (5*R*,7*R*)-5,7-dimethyl-6,7-dihydro-5*H*-dibenz[*c*,*e*]azepine[17] and a phosphoramidite composed of 6,6′-binaphthol and 6,7-dihydro-5*H*-dibenz[*c*,*e*]azepine,[10] which exist as single diastereomers, but which have the stereogenic centers situated closer to the biphenyl part of the molecules.

Table 1. Diastereomeric ratios of atropisomers of **1b**–**e**.

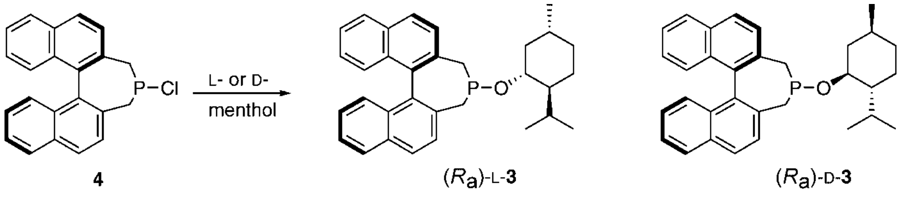
Ligand	Ratio (R_a*:S_a*)
1b	1:1.02 [(R_a)-L:(S_a)-L]
1c	1:1.26
1d	1:1.43
1e	1:1.12

In order to allow assignment of the absolute configuration of the two diastereomers of menthol containing ligands **1b**, the rigid analogues (R_a)-L-**3** and (R_a)-D-**3** were prepared from 8-chloro-8,9-dihydro-7*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine (**4**) in 36 and 39% yields, respectively, by a route analogous to that used for compounds **1b**–**e** (Scheme 3).

Representative ^{1}H NMR spectroscopic values for the two diastereomers of **1b** and the two rigid ligands are given in Table 2. The most characteristic signals are those originating from H^8 (methine proton in the isopropyl group). The chemical shift of this proton is affected by the proximity of the aromatic ring. Studies of molecular models suggest that H^8 is situated above an aromatic ring in the (R_a)-L and (S_a)-D isomers and should thus be shifted to higher field in these compounds, in accordance with what was observed for (R_a)-L-**3**. In this compound no coupling was observed between H^8 and H^2, which suggests that there is restricted rotation of the isopropyl group and a ca. 90° H–C–C–H dihedral angle. From these observations, **1b** was assigned the (S_a)-L configuration and consequently **1b′** is the (R_a)-L isomer. Comparison of the ^{31}P NMR signals of (R_a)-L-**3** and (R_a)-D-**3** with those of the two diastereomers of **1b** allowed assignments of the latter signals.

Determination of Rotational Barrier

The tropoisomerization barriers for compounds **1a** and **1b** were determined by dynamic NMR spectroscopy. The large chemical shift difference between the two phosphorus signals in **1b** served an excellent possibility to determine the activation parameters of the exchange by NMR spectroscopy in a relatively large temperature region. The two different dynamic processes, pyramidal inversion at the phosphorus atom and flipping of the phenyl rings are illustrated in Scheme 2. Because the phosphorus center is not a stereogenic center, pyramidal inversion does not change the chirality of the molecules and the increase in the line width of the phosphorus signals at higher temperatures is due to flipping of the phenyl rings, which results in the exchange of the isomers. However, the temperature-dependent proton decoupled phosphorus spectra for compound **1b** showed that the exchange rate was not fast enough to affect the line width significantly. An increase in the temperature from 20 to 80 °C resulted in only an approximate 10 Hz change in the line widths of the signals. Therefore, in order to increase the accuracy of the determination of the kinetic parameters, the rate constants for the exchange process between the diastereomers at different temperatures were measured by one-dimensional inversion-transfer experiments.[18] The linear regression of the temperature dependence of the rate constant (Eyring plot) resulted in the following activation parameters: $\Delta H^{\ddagger} = 90.8 \pm 1.9\ \text{kJ mol}^{-1}$ ($21.7\ \text{kcal mol}^{-1}$) and $\Delta S^{\ddagger} = 44.5 \pm 6.4\ \text{J mol}^{-1}\text{K}^{-1}$ (errors were estimated from the least-squares fit method). By using these values, a Gibbs free energy of activation, $77.5\ \text{kJ mol}^{-1}$ ($18.5\ \text{kcal mol}^{-1}$), could be calculated at 298 K for the flipping process for **1b**. This barrier is considerably higher than those found for the



Scheme 3.

Table 2. Selected ^{1}H NMR spectroscopic chemical shift data (in [ppm]) for **1b**, **1b′**, (R_a)-L-**3**, and (R_a)-D-**3**.

Compound	H^1	H_A	H_B	H_C	H_D	H_{6e}	H^8
1b	3.44 (dq)	2.90 (dd)	2.74 (d)	2.58 (d)	2.37 (dd)	2.03 (br. d)	2.24 (dsept)
1b′	3.42 (dq)	2.87 (dd)	2.71 (d)	2.54 (d)	2.36 (dd)	1.97 (br. d)	1.90 (dsept)
(R_a)-D-**3**	3.46 (dq)	3.08 (dd)	2.90 (d)	2.61 (d)	2.44 (dd)	2.06 (br. d)	2.33 (dsept)
(R_a)-L-**3**	3.40 (dq)	3.02 (dd)	2.80 (d)	2.48 (d)	2.34 (dd)	2.03 (br. d)	1.81 (sept)

O and S analogues,[12] but too low to permit isolation of the isomers at room temperature.[19]

In the case of **1a**, only the ^{1}H NMR spectrum can be used to determine the activation barrier for the enantiomers. In this case also, one-dimensional inversion-transfer experiments were run by inverting the corresponding proton signals. The analysis of the temperature dependence of the rate constants resulted in approximately the same activation parameters as for **1b**: $\Delta H^{\ddagger} = 95.5 \pm 2.3\ \text{kJ mol}^{-1}$ (22.8 kcal mol^{-1}), $\Delta S^{\ddagger} = 49.8 \pm 7.5\ \text{J mol}^{-1}\text{K}^{-1}$, and a Gibbs free energy of activation at 298 K, 80.6 kJ mol^{-1} (19.3 kcal mol^{-1}).

Metal Complexes

In order to study the influence of complexation to a metal ion on the ratio of the two diastereomeric rotamers of **1b**–**e**, Rh^I complexes of the ligands were prepared by using [Rh(COD)$_2$]$^+$ BF$_4^-$. Upon mixing ligand **1b** and the Rh precursor in a ratio of 2:1, ^{31}P NMR signals originating from the free ligand disappeared and were replaced by two sets of doublets ($J_{\text{Rh,P}}$ = 170 Hz, proton decoupled). No P–P couplings were observed. Upon addition of excess ligand, signals originating from the free ligand were observed in addition to those of the complexes. This behavior is consistent with the formation of two homochiral 2:1 complexes;[20] an equilibrating mixture of complexed and free ligands would lead to a gradual change in chemical shift upon addition of excess ligand, and formation of a mixture of homo- and heterochiral complexes would give rise to additional signals and increased splitting due to P–P couplings.

The ^{31}P NMR spectra of the analogous complexes obtained from (R_a)-L-**3** and (R_a)-D-**3** each showed one doublet. Comparison of these spectra with that of **1b** allowed the assignment of the two isomers of the latter complex. The major complex was found to contain the (S_a)-L-**1b** isomer.

The same type of self assembly of homochiral isomers was also observed for complexes of the remaining ligands **1c**–**e**, where each 1:2 mixture of [Rh(COD)$_2$]$^+$ BF$_4^-$ and ligand exhibited only two sets of doublets. In the same way as for the free ligands, the ratio between the two doublets was found to depend on the structure of the alcohol part of the ligand (Table 3). The highest ratio, 1.94:1, was again observed for **1d**. The ^{31}P NMR signals from one of the isomers were always broader than those from the other diastereomer. The broadening is probably a result of conformational changes in the alcohol part of the ligands. Upon lowering the temperature, the line width gradually increased.

Table 3.Diastereomeric ratios of Rh^I complexes **1b**–**e**.

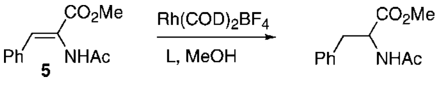
Complex	Ratio (R_a*):(S_a*)
Rh**1b**	1:1.45 [(R_a)-L:(S_a)-L]
Rh**1c**	1:1.08
Rh**1d**	1:1.94
Rh**1e**	1:1.12

In order to test whether self assembly of equal structures is a more general phenomenon for this type of ligands, equimolar amounts of [Rh(COD)$_2$]$^+$ BF$_4^-$, **1b**, and **1c** were mixed. The ^{31}P NMR spectrum of the mixture showed signals from the 1:2 Rh complexes of **1b** and **1c**, but no additional signals, which demonstrates that mixed complexes were not formed. This is in sharp contrast to the situation involving phosphites or phosphoramidites derived from biphenol or binaphthol, which form mixtures of homo- and heterocomplexes with Rh^I, and where the heterocomplex/homocomplex ratios usually exceed the statistical values.[21]

Reaction of ligands **1b**–**e** with [Ir(COD)$_2$]$^+$ BF$_4$ led to similar situations, although singlets were observed in place of doublets.

Rh-Catalyzed Hydrogenations

Replacement of binaphthyl groups by biphenyl groups in chiral ligands leads to simpler ligand preparation and allows the use of less expensive starting materials. In addition, and what is even more important, a chirally flexible ligand may adopt different configurations in different situations, and may even adapt its configuration to the reacting substrate. In order to compare the behavior of a flexible 6,7-dihydro-5*H*-dibenzo[*c*,*e*]phosphepine ligand to that of its rigid analogues, the ligands were tested in a catalytic reaction. Rh-catalyzed hydrogenation of α-acetamidocinnamate (**5**) was selected as a suitable model reaction to study the influence of atropisomerism in ligands **1b**–**e** on their catalytic properties (Scheme 4).



Scheme 4.

Hydrogenations using a catalyst prepared from a 1:2 mixture of [Rh(COD)$_2$]$^+$ BF$_4^-$ and ligand (R_a)-L-**3** or (R_a)-D-**3** in methanol at 1 atm were followed over time. It was found that (R_a)-L-**3**, which provided the product with highest enantioselectivity, was approximately three times less reactive than (R_a)-D-**3**. Reaction using (R_a)-L-**3** resulted in full conversion to a product with 63% *ee* of the (*S*)-isomer within one hour, and the isomer (R_a)-D-**3** was found to afford full conversion to the same product with 48% *ee* within 30 min (68% conversion after 15 min). These results show that the absolute configuration of the product is determined by the naphthyl part of the ligand. Assuming the ratio of atropisomers in the catalytically active complex is the same as that found in the rhodium complexes of **1b** (1.45:1), and taking into account the different reactivities of the two complexes, assumed to be equal to those of (R_a)-D-**3** and (R_a)-L-**3**, respectively, the (*R*)-product with an *ee* of 27% was expected from a catalytic reaction employing **1b** as ligand, provided that the biphenyl ligands lead to the same levels of enantioselectivity as the binaphthyl analogues. The expected product was indeed observed, but with an *ee* of 41%, which is close to the value expected from the pure (S_a)-L isomer, which is the pseudoenantiomer of (R_a)-D-**3**. The major diastereomer is evidently more active but less selective than the minor one. This is in contrast to other cases where tropodiastereomeric mixtures have been employed in hydrogenations, where the most active isomer also leads to higher selectivity.[4a,5b]

Use of remaining ligands **1** (Table 4) in the same catalytic reaction led to low conversion and/or selectivity. This shows that the nature of the group attached to phosphorus has a large effect on the result of the catalytic reaction. 8-Amino-8,9-dihydro-7*H*-dinaphthophosphepines, that is, analogues of **3** having the alcohol part of the ligands replaced by amino groups, have indeed previously been shown to exhibit higher selectivity in hydrogenations of α-acetamidocinnamate.[15]

Table 4. Hydrogenations of **5** catalyzed by Rh^I complexes of ligands **1** and **3**.[a]

Entry	Ligand	Time [h]	Conversion [%]	ee [%]
1	**1b**	2	100	41 (*R*)
2	**1c**	20	0	–
3	**1d**	2	23	21 (*S*)
4	**1e**	1	100	0
5	(R_a)-L-**3**	1	100	63 (*S*)
6	(R_a)-D-**3**	0.5	100	48 (*S*)

[a] 25 °C, 1 atm, MeOH.

Conclusions

The barrier to tropoisomerization in phosphepine ligands based on 2,2′-dihydroxybiphenyl with achiral or chiral alkoxy groups bound to phosphorus is too low to allow isolation of the tropoisomers, but high enough to permit observation of diastereomers by NMR spectroscopy at ambient temperature. The ratio of diastereomers varies with the group bound to phosphorus, although the preference for one of the diastereomers is low. Rh^I complexes containing only homochiral ligands were formed, and upon mixing $[Rh(COD)_2]^+$ BF_4^- and two ligands containing different alkoxy groups, only complexes containing two identical ligands were obtained. The Rh complexes catalyzed the hydrogenation of α-acetamidocinnamate. The diastereomer with lowest selectivity was found to be more reactive than that affording the product with higher enantioselectivity.

Experimental Section

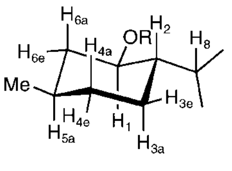
General: ^{1}H-, ^{13}C-, and ^{31}P NMR spectra were recorded at 500, 125, and 202 MHz, respectively. The ^{1}H- and ^{13}C NMR chemical shifts are reported relative to $CHCl_3$, and the ^{31}P NMR chemical shifts are reported relative to H_3PO_3 (external). The line widths of the proton decoupled phosphorus signals were determined by fitting a Lorentzian curve to the experimental signal with the use of the standard Bruker software. Selective inversion of the proton signals for **1a** and the proton decoupled phosphorus signals for **1b** in the inversion-transfer experiments were performed with Gaussian pulses.

All operations were performed under a nitrogen atmosphere. (*R*)-2,2′-Dimethylbinaphthyl was prepared according to a literature procedure, by coupling of the bistriflate of 2,2′-dihydroxybinaphthyl, obtained by reaction of 2,2′-dihydroxybinaphthyl with triflic anhydride, with MeMgBr and catalyzed by $NiCl_2$(dppp).[8a] An analogous procedure was used for the preparation of 2,2′-dimethylbiphenyl.[22]

6-Chloro-6,7-dihydro-5*H*-dibenzo[*c*,*e*]phosphepine (2): *n*BuLi (2.02 M in hexane, 33.26 mL, 67.2 mmol) was added dropwise to a stirred solution of 2,2′-dimethylbiphenyl (5.10 g, 28.0 mmol) and TMEDA (10.30 mL, 68.2 mmol) in Et_2O (30 mL) at 0 °C. The resulting mixture was stirred for 20 h at room temperature. The bislithium salt of 2,2′-dimethylbiphenyl was obtained as a yellow solid (7.24 g, 17.0 mmol) after filtration and evaporation of the solvent under vacuum. The salt was suspended in hexane (40 mL) and a solution of dichloro(diethylamino)phosphane[23] (3.35 g, 19.2 mmol) in hexane (20 mL) was added whilst stirring at 0 °C. Stirring was continued for 2.5 h at 65 °C followed by 18 h at room temperature. Hexane was evaporated under vacuum and PhMe (40 mL) was added. The precipitates formed were filtered off and, after washing with PhMe (20 mL), were discarded. PhMe was evaporated under vacuum. Cyclohexane (100 mL) was added and HCl gas was passed through the solution for 2.5 h at 30 °C. The solids formed were filtered off and the solvent evaporated under vacuum to yield product **2** (2.66 g, 39%) as an oil which slowly crystallized in the freezer. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44–7.18 (m, 8 H), 3.30–3.15 (br. m, 1 H), 3.00–2.76 (br. m, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.8, 140.2, 133.0, 129.8, 129.3, 129.0, 128.0, 127.6, 127.1, 38.3 (d, $J_{P,C}$ = 30.1 Hz), 36.4 (d, $J_{P,C}$ = 35.4 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 112.7 ppm. MS (EI, 70 eV): *m*/*z* (%) = 246/248 (100/32) $[M]^+$, 211 (26), 179 (47), 165 (67), 152 (10), 104 (8), 89 (4.6), 76 (5.2).

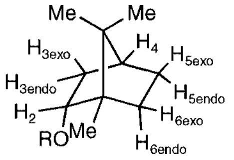
1a: MeOH (16 µL, 395 µmol) was added to a solution of 6-chloro-6,7-dihydro-5*H*-dibenzo[*c*,*e*]phosphepine (**2**, 50 mg, 202 µmol) and NEt_3 (84 µL, 603 µmol) in THF (1.5 mL) at –30 °C. The mixture was stirred at room temperature for 2 h and then filtered through a small plug of celite. The solvent was evaporated and the crude product was filtered through a column (0.5 × 6 cm) with neutral alumina (activated at 220 °C overnight) and CH_2Cl_2 (3.0 mL) as the eluent. The product (**1a**, 16 mg, 33%) was obtained as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.2–7.0 (m, 8 H), 3.47 (d, $J_{P,H}$ = 13.2 Hz, 3 H), 2.97 (dd, $J_{H,H}$ = 11.9 Hz, $J_{P,H}$ = 14.9 Hz, 1 H), 2.82 (d, $J_{H,H}$ = 15.0 Hz, 1 H), 2.51 (d, $J_{H,H}$ = 11.9 Hz, 1 H), 2.34 (dd, $J_{H,H}$ = 15.0 Hz, $J_{P,H}$ = 18.7 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.7 (d, $J_{P,C}$ = 2.6 Hz), 140.2, 134.8 (d, $J_{P,C}$ = 1.5 Hz), 133.6, 129.3, 129.2 (d, $J_{P,C}$ = 1.6 Hz), 129.1, 129.0, 127.5, 127.3 (d, $J_{P,C}$ = 1.5 Hz), 127.1 (d, $J_{P,C}$ = 2.0 Hz), 126.5, 56.2 (d, $J_{P,C}$ = 16.8 Hz), 36.2 (d, $J_{P,C}$ = 23.5 Hz), 36.1 (d, $J_{P,C}$ = 24.8 Hz) ppm. ^{31}P NMR (202 MHz, CDCl$_3$): δ = 152.2 ppm. MS (EI, 70 eV): *m*/*z* (%) = 242 (100) [M]$^+$, 227 (3), 212 (90), 197 (68), 178 (47), 165 (61), 152 (10).

1b: *n*BuLi (2.02 M in hexane, 110 µL, 220 µmol) was added to a solution of (–)-menthol (34.4 mg, 220 µmol) in THF (1 mL) at –78 °C, and the mixture was stirred at –78 °C for 20 min . A solution of 6-chloro-6,7-dihydro-5*H*-dibenzo[*c*,*e*]phosphepine (**2**, 50.0 mg, 202 µmol) in THF (1 mL) was then added dropwise at –78 °C, and the mixture was stirred at the same temperature for 5 min followed by 3 h at 0 °C. The solvent was evaporated, and the crude product was filtered through a column (0.5 × 6 cm) with neutral alumina (activated at 220 °C overnight) and hexane/CH$_2$Cl$_2$, 2:1 (3.0 mL) as the eluent. The product (**1b**, 45 mg, 60%, colorless oil) was obtained as a mixture of two diastereomers. ^{1}H NMR (500 MHz, CDCl$_3$) (mixture of two diastereomers): δ = 7.25–7.0 (m, 2 × 8 H), 3.44 (app. dq, $J_{H,H}$ = 10.2, 10.2, 5.9 Hz, $J_{P,H}$ = 10.2 Hz, 1 H, H$_1$), 3.42 (app. dq, $J_{H,H}$ = 10.4, 10.4, 4.3 Hz, $J_{P,H}$ = 10.4 Hz, 1 H, H$_1$), 2.90 (dd, $J_{H,H}$ = 12.0 Hz, $J_{P,H}$ = 14.4 Hz, 1 H), 2.87 (dd, $J_{H,H}$ = 12.1 Hz, $J_{P,H}$ = 14.6 Hz, 1 H), 2.74 (d, $J_{H,H}$ = 14.8 Hz, 1 H), 2.71 (d, $J_{H,H}$ = 14.7 Hz, 1 H), 2.58 (d, $J_{H,H}$ = 11.9 Hz, 1 H), 2.54 (d, $J_{H,H}$ = 11.9 Hz, 1 H), 2.37 (dd, $J_{H,H}$ = 14.8 Hz, $J_{P,H}$ = 19.2 Hz, 1 H), 2.36 (dd, $J_{H,H}$ = 14.8 Hz, $J_{P,H}$ = 18.2 Hz, 1 H), 2.24 (dsept, $J_{H,H}$ = 7.0, 2.7 Hz, 1 H, H$_8$), 2.03 (br. d, $J_{H,H}$ = 12 Hz, 1 H, H$_{6e}$), 1.97 (br. d, $J_{H,H}$ = 12 Hz, 1 H, H$_{6e}$), 1.90 (dsept, $J_{H,H}$ = 7.0, 2.7 Hz, 1 H, H$_8$), 1.58–1.48 (m, 2 × 2 H, H$_{3e}$, H$_{4e}$), 1.39–1.28 (m, 2 × 1 H, H$_{5a}$), 1.20–1.08 (m, 2 × 1 H, H$_2$), 1.03 (q, $J_{H,H}$ = 11.5 Hz, 2 × 1 H), 0.9–0.7 (m hidden under signals for Me groups, 2 × 2 H), 0.88 (d, $J_{H,H}$ = 6.6 Hz, 3 H), 0.87 (d, $J_{H,H}$ = 7.1 Hz, 3 H), 0.81 (d, $J_{H,H}$ = 6.6 Hz, 3 H), 0.80 (d, $J_{H,H}$ = 7.0 Hz, 3 H), 0.75 (d, $J_{H,H}$ = 7.1 Hz, 3 H), 0.69 (d, $J_{H,H}$ = 7.0 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 140.8 (d, $J_{P,C}$ = 2.3 Hz), 140.7 (d, $J_{P,C}$ = 2.2 Hz), 140.4, 140.3, 135.1, 134.2 (d, $J_{P,C}$ = 5.2 Hz), 129.4, 129.3, 129.2, 129.1, 129.0, 128.9 (d, $J_{P,C}$ = 2.9 Hz), 128.8, 127.5, 127.4, 127.2 (d, $J_{P,C}$ = 3.6 Hz), 126.9, 126.3, 126.2, 80.7 (d, $J_{P,C}$ = 17.4 Hz), 80.5 (d, $J_{P,C}$ = 16.9 Hz), 48.9 (d, $J_{P,C}$ = 5.7 Hz), 48.7 (d, $J_{P,C}$ = 5.7 Hz), 44.1 (d, $J_{P,C}$ = 2.8 Hz), 43.6 (d, $J_{P,C}$ = 4.5 Hz), 38.7 (d, $J_{P,C}$ = 27.0 Hz), 37.9 (d, $J_{P,C}$ = 19.0 Hz), 37.1 (d, $J_{P,C}$ = 25.4 Hz), 36.6 (d, $J_{P,C}$ = 17.5 Hz), 34.3, 31.8, 31.7, 25.5, 25.4, 23.0, 22.9, 22.3, 22.2, 21.0, 20.9, 15.9 ppm. ^{31}P NMR (202 MHz, CDCl$_3$): δ = 146.2 [(R_a)-L-isomer], 142.1 [(S_a)-L-isomer] ppm. MS (EI, 70 eV): *m*/*z* (%) = 366 (1.0) [M]$^+$, 228 (100), 209 (4.0), 197 (0.6), 178 (14), 165 (23), 152 (1.9), 138 (2.5), 95 (9).



1c: This compound (67 mg, 90%) was prepared in the same way as **1b** from (+)-neomenthol (34.4 mg, 220 µmol) and **2**. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.35–7.08 (m, 2 × 8 H), 4.13 (br. s, 2 × 1 H, H$_1$), 2.97 (dd, $J_{H,H}$ = 12.0 Hz, $J_{P,H}$ = 14.4 Hz, 1 H), 2.92 (dd, $J_{H,H}$ = 11.8 Hz, $J_{P,H}$ = 15.3 Hz, 1 H), 2.81 (d, $J_{H,H}$ = 14.9 Hz, 1 H), 2.78 (d, $J_{H,H}$ = 14.9 Hz, 1 H), 2.64 (d, $J_{H,H}$ = 11.8 Hz, 1 H), 2.63 (d, $J_{H,H}$ = 12.0 Hz, 1 H), 2.47 (dd, $J_{H,H}$ = 14.9 Hz, $J_{P,H}$ = 19.8 Hz, 1 H), 2.46 (dd, $J_{H,H}$ = 14.9 Hz, $J_{P,H}$ = 18.8 Hz, 1 H), 2.02 (br. d, $J_{H,H}$ = 13.8 Hz, 1 H, H$_{6e}$), 1.91 (br. d, $J_{H,H}$ = 14.0 Hz, 1 H, H$_{6e}$), 1.88–1.80 (m, 1 H, H$_{5a}$), 1.75–1.53 (m, 2 × 2 H, H$_{3e}$ and H$_{4e}$), 1.55–1.45 (m, 1 H, H$_{5a}$), 1.39 (sept, $J_{H,H}$ = 6.7 Hz, 1 H, H$_8$), 1.37 (sept, $J_{H,H}$ = 6.7 Hz, 1 H, H$_8$), 1.24–1.16 (m, 2 × 1 H), 1.08 (ddd, $J_{H,H}$ = 14.0, 12.2, 2.0 Hz, 2 × 1 H, H$_{6a}$), 1.03 (d, $J_{H,H}$ = 6.6 Hz, 3 H), 0.96 (d, $J_{H,H}$ = 6.7 Hz, 3 H), 0.95 (d, $J_{H,H}$ = 6.8 Hz, 3 H), 0.91 (d, $J_{H,H}$ = 6.7 Hz, 3 H), 0.82 (d, $J_{H,H}$ = 6.7 Hz, 3 H), 0.79 (d, $J_{H,H}$ = 6.7 Hz, 3 H), 1.03–0.94 (m hidden under signals for Me groups, 2 × 1 H), 0.90–0.77 (m hidden under signals for Me groups, 2 × 1 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 140.8 (d, $J_{P,C}$ = 2.8 Hz), 140.7 (d, $J_{P,C}$ = 2.5 Hz), 140.3 (d, $J_{P,C}$ = 3.6 Hz), 135.4 (d, $J_{P,C}$ = 6.3 Hz), 134.5, 134.3, 129.8, 129.4, 129.3, 129.2, 129.1, 129.0 (d, $J_{P,C}$ = 2.9 Hz), 128.8, 128.7, 127.2 (d, $J_{P,C}$ = 2.0 Hz), 127.1, 126.8, 126.2, 126.1, 125.5, 76.8 (d, $J_{P,C}$ = 16 Hz), 76.4 (d, $J_{P,C}$ = 18 Hz), 48.5, 48.4, 41.9 (d, $J_{P,C}$ = 2.8 Hz), 41.7 (d, $J_{P,C}$ = 4.3 Hz), 38.7 (d, $J_{P,C}$ = 26 Hz), 38.3 (d, $J_{P,C}$ = 22 Hz), 37.0 (d, $J_{P,C}$ = 22 Hz), 36.8 (d, $J_{P,C}$ = 19 Hz), 35.1, 35.0, 29.7, 29.0, 28.7, 26.2, 25.8, 24.6, 24.5, 22.4, 22.3, 21.1, 21.0 (d, $J_{P,C}$ = 1.7 Hz), 20.9 ppm. ^{31}P NMR (202 MHz, CDCl$_3$): δ = 146.0, 142.6 ppm. MS (EI, 70 eV): *m*/*z* (%) = 366 (1.4) [M]$^+$, 228 (100), 178 (12), 165 (21), 138 (4.5), 95 (14).

1d: This compound (77 mg, 86%) was prepared in the same way as **1b** from (–)-8-phenylmenthol (51.8 mg, 220 µmol) and **2**. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.34–7.00 (m, 2 × 13 H), 3.77–3.65 (m, 2 × 1 H), 2.92 (d, $J_{H,H}$ = 14.7 Hz, 1 H), 2.89 (d, $J_{H,H}$ = 14.7 Hz, 1 H), 2.78 (dd, $J_{H,H}$ = 10.2 Hz, $J_{P,H}$ = 14.0 Hz, 1 H), 2.77 (dd, $J_{H,H}$ = 9.0 Hz, $J_{P,H}$ = 15.1 Hz, 1 H), 2.62 (d, $J_{H,H}$ = 11.7 Hz, 1 H), 2.43 (dd, $J_{H,H}$ = 15.0 Hz, $J_{P,H}$ = 20.7 Hz, 1 H), 2.37 (dd, $J_{H,H}$ = 14.7 Hz, $J_{P,H}$ = 18.9 Hz, 1 H), 2.35 (d, $J_{H,H}$ = 11.7 Hz, 1 H), 2.21 (br. d, $J_{H,H}$ = 12.0 Hz, 1 H), 2.00 (br. d, $J_{H,H}$ = 12.0 Hz, 1 H), 1.85–1.76 (m, 2 × 1 H), 1.54 (s, 3 H), 1.52–1.20 (m, 2 × 2 H), 1.36 (s, 3 H), 1.29 (s, 3 H), 1.23 (s, 3 H), 1.15 (q, $J_{H,H}$ = 11.5 Hz, 2 × 1 H), 0.99 (q, $J_{H,H}$ = 11.8 Hz, 2 × 1 H), 0.95–0.64 (m, 2 × 2 H), 0.94 (d, $J_{H,H}$ = 6.5 Hz, 3 H), 0.85 (d, $J_{H,H}$ = 6.5 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 151.5, 151.4, 140.8, 140.6, 140.5, 140.3, 135.0, 134.4, 134.1, 129.6, 129.3, 129.1, 129.0, 128.9 (d, $J_{P,C}$ = 3.8 Hz), 128.7, 128.0, 127.7, 127.3, 127.2, 127.1, 126.8, 126.3, 126.1, 125.9, 125.7, 125.1, 124.9, 81.3 (d, $J_{P,C}$ = 16.4 Hz), 81.0 (d, $J_{P,C}$ = 16.4 Hz), 52.3 (d, $J_{P,C}$ = 6.2 Hz), 52.1 (d, $J_{P,C}$ = 6.6 Hz), 45.3 (d, $J_{P,C}$ = 5.0 Hz), 45.0 (d, $J_{P,C}$ = 5.0 Hz), 40.6, 40.3, 38.9 (d, $J_{P,C}$ = 24.0 Hz), 38.4 (d, $J_{P,C}$ = 29.0 Hz), 36.0 (d, $J_{P,C}$ = 23.3 Hz), 35.9 (d, $J_{P,C}$ = 17.0 Hz), 34.6, 34.5, 31.7, 30.4, 29.1, 27.4, 27.2, 25.5, 24.8, 22.1, 22.0 ppm. ^{31}P NMR (202 MHz, CDCl$_3$): δ = 143.7, 141.6 ppm. MS (EI, 70 eV): *m*/*z* (%) = 442 (1.6) [M]$^+$, 305 (100), 228 (27), 178 (4.6), 165 (8).



1e: This compound (81 mg, 79%) was prepared in the same way as **1b** from (–)-borneol (33.9 mg, 220 µmol) and **2**.^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.35–7.10 (m, 2 × 8 H), 4.05 (ddd, $J_{H,H}$ = 10.1, 3.2 Hz, $J_{P,H}$ = 10.1 Hz, 1 H, H$_2$), 4.04 (ddd, $J_{H,H}$ = 10.1, 3.2 Hz, $J_{P,H}$ = 10.1 Hz, 1 H, H$_2$), 3.02 (dd, $J_{H,H}$ = 11.2 Hz, $J_{P,H}$ = 11.6 Hz, 1 H), 2.99 (dd, $J_{H,H}$ = 11.2 Hz, $J_{P,H}$ = 11.6 Hz, 1 H), 2.87 (d, $J_{H,H}$ = 14.6 Hz, 1 H), 2.85 (d, $J_{H,H}$ = 14.6 Hz, 1 H), 2.66 (d, $J_{H,H}$ = 11.6 Hz, 1 H), 2.64 (d, $J_{H,H}$ = 11.6 Hz, 1 H), 2.45 (dd, $J_{H,H}$ = 14.6 Hz, $J_{P,H}$ = 19.6 Hz, 1 H), 2.44 (dd, $J_{H,H}$ = 14.6 Hz, $J_{P,H}$ = 19.4 Hz, 1 H), 2.29 (dddd, $J_{H,H}$ = 13.2, 10.1, 4.6, 3.4 Hz, 1 H, H$_{3exo}$), 2.23 (dddd, $J_{H,H}$ = 13.3, 10.1, 4.7, 3.4 Hz, 1 H, H$_{3exo}$), 1.98–1.91 (m, 1 H, H$_{6exo}$), 1.86 (ddd, $J_{H,H}$ = 12.7, 9.4, 4.5 Hz, 1 H, H$_{6exo}$), 1.74–1.62 (m, 2 × 1 H, H$_{5exo}$), 1.65 (dd, $J_{H,H}$ = 4.7, 4.7 Hz, 1 H, H$_4$), 1.60 (dd, $J_{H,H}$ = 4.6, 4.6 Hz, 1 H, H$_4$), 1.24–1.10 (m, 2 × 2 H, H$_{5endo}$ and H$_{6endo}$), 1.15 (dd, $J_{H,H}$ = 13.3, 3.2 Hz, 1 H,

H_{3endo}), 0.97 (dd, $J_{H,H}$ = 13.2, 3.2 Hz, 1 H, H_{3endo}), 0.93 (s, 3 H), 0.86 (s, 2 × 3 H), 0.85 (s, 3 H), 0.84 (s, 3 H), 0.81 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.7 (br), 140.6 (br), 140.4, 140.3, 135.4 (d, $J_{P,C}$ = 4.7 Hz), 134.2 (d, $J_{P,C}$ = 13.8 Hz), 129.8, 129.4, 129.3, 129.2, 129.1, 129.0 (d, $J_{P,C}$ = 2.0 Hz), 128.9 (d, $J_{P,C}$ = 2.9 Hz), 128.8, 127.3, 127.2, 127.1, 126.9, 126.1 (d, $J_{P,C}$ = 3.4 Hz) 125.5, 85.4 (d, $J_{P,C}$ = 16.5 Hz), 85.1 (d, $J_{P,C}$ = 15.3 Hz), 50.0 (d, $J_{P,C}$ = 5 Hz), 49.8 (d, $J_{P,C}$ = 5 Hz), 47.7, 47.6, 45.2, 45.1, 38.3 (d, $J_{P,C}$ = 3 Hz), 38.2 (d, $J_{P,C}$ = 3 Hz), 37.8 (d, $J_{P,C}$ = 28 Hz), 37.4 (d, $J_{P,C}$ = 20 Hz), 37.0 (d, $J_{P,C}$ = 26 Hz), 36.7 (d, $J_{P,C}$ = 19 Hz), 28.3, 28.1, 26.6, 26.5, 20.0, 19.9, 18.9, 18.8, 13.9, 13.5 ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 146.4, 145.6 ppm. MS (EI, 70 eV): *m*/*z* (%) = 364 (5.1) [M]$^+$, 228 (100), 178 (11), 165 (14), 137 (6), 121 (8), 93 (12).

(*R*$_a$)-L-3 and (*R*$_a$)-D-3: *n*BuLi (2.19 M in hexane, 72 µL, 158 µmol) was added to a solution of L-(–)- or D-(+)-menthol (24.6 mg, 158 µmol) in THF (1 mL) at –78 °C, and the mixture was stirred at –78 °C for 20 min. A solution of (*R*)-8-chloro-8,9-dihydro-7*H*-dinaphtho[1,2-*c*:2′,1′-*e*]phosphepine (**4**, 50.0 mg, 145 µmol) in THF (1 mL) was added dropwise at –78 °C, and the mixture was stirred at the same temperature for 5 min followed by 1.5 h at 0 °C. The solvent was evaporated, and the crude product was filtered through a column (0.5 × 6 cm) with neutral alumina (activated at 220 °C overnight) and hexane/CH_2Cl_2, 2:1 (3.0 mL) as the eluent. After evaporation of the solvent, the ligands were obtained as colorless oils. (*R*$_a$)-L-**3**: Yield: 24 mg (36%). $[\alpha]_D^{25}$ = +45.2 (c 0.25, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.83–7.70 (m, 4 H), 7.44–7.36 (m, 1 H), 7.32–7.23 (m, 3 H), 7.18–7.06 (m, 3 H), 6.92 (d, $J_{H,H}$ = 8.3 Hz, 1 H), 3.40 (app. dq, $J_{H,H}$ = 10.3, 10.3, 4.0 Hz, $J_{P,H}$ = 10.3 Hz, 1 H, H_1), 3.02 (dd, $J_{H,H}$ = 12.0 Hz, $J_{P,H}$ = 15.3 Hz, 1 H), 2.80 (d, $J_{H,H}$ = 14.5 Hz, 1 H), 2.48 (d, $J_{H,H}$ = 11.6 Hz, 1 H), 2.34 (dd, $J_{H,H}$ = 14.7 Hz, $J_{P,H}$ = 18.3 Hz, 1 H), 2.05 (br. d, $J_{H,H}$ = 12 Hz, 1 H, H_{6e}), 1.81 (sept, $J_{H,H}$ = 6.8 Hz, 1 H, H_8), 1.55 (br. d, $J_{H,H}$ = 13 Hz, 1 H, H_{3e} or H_{4e}), 1.48 (br. d, $J_{H,H}$ = 13 Hz, 1 H, H_{3e} or H_{4e}), 1.38–1.29 (m, 1 H, H_{5a}), 1.07–0.96 (m, 1 H, H_2), 0.88–0.65 (m, 3 H, H_{3a}, H_{4a}, and H_{6a}), 0.88 (d, $J_{H,H}$ = 6.6 Hz, 3 H), 0.70 (d, $J_{H,H}$ = 6.9 Hz, 3 H), 0.65 (d, $J_{H,H}$ = 6.9 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 135.1, 134.3, 134.1, 133.7, 133.2, 132.8, 132.7, 132.4, 132.3, 132.2, 132.0, 128.7, 128.4, 128.2, 127.8, 127.6, 127.4, 126.9, 126.6, 126.1, 125.8, 125.7, 125.6, 124.9, 124.8, 124.6, 80.9 (d, $J_{P,C}$ = 17.1 Hz), 48.9 (d, $J_{P,C}$ = 6.0 Hz), 44.1 (d, $J_{P,C}$ = 3.2 Hz), 39.3 (d, $J_{P,C}$ = 29.5 Hz), 37.5 (d, $J_{P,C}$ = 19.5 Hz), 34.3, 31.8, 25.4, 23.0, 22.3, 20.9, 15.8 ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 149.7 ppm. MS (EI, 70 eV): *m*/*z* (%) = 466 (16) [M]$^+$, 328 (100), 311 (2.5), 138 (30). (*R*$_a$)-D-**3**: Yield: 26 mg (39%). $[\alpha]_D^{25}$ = +51.6 (c 0.25, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92–7.81 (m, 4 H), 7.54–7.48 (m, 1 H), 7.41–7.34 (m, 3 H), 7.25–7.17 (m, 3 H), 7.03 (d, $J_{H,H}$ = 8.3 Hz, 1 H), 3.46 (app. dq, $J_{H,H}$ = 10.6, 10.6, 4.5 Hz, $J_{P,H}$ = 10.6 Hz, 1 H, H_1), 3.08 (dd, $J_{H,H}$ = 11.7 Hz, $J_{P,H}$ = 15.9 Hz, 1 H), 2.90 (d, $J_{H,H}$ = 14.6 Hz, 1 H), 2.61 (d, $J_{H,H}$ = 11.7 Hz, 1 H), 2.44 (dd, $J_{H,H}$ = 14.7 Hz, $J_{P,H}$ = 19.6 Hz, 1 H), 2.33 (dsept, $J_{H,H}$ = 7.1, 2.8 Hz, 1 H, H_8), 2.03 (br. d, $J_{H,H}$ = 12 Hz, 1 H, H_{6e}), 1.64–1.58 (m, 2 H, H_{3e} and H_{4e}), 1.42–1.35 (m, 1 H, H_{5a}), 1.31–1.17 (m, 1 H, H_2), 0.98–0.73 (m, 3 H, H_{3a}, H_{4a}, and H_{6a}), 0.96 (d, $J_{H,H}$ = 7.1 Hz, 3 H), 0.89 (d, $J_{H,H}$ = 7.0 Hz, 3 H), 0.88 (d, $J_{H,H}$ = 6.5 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 135.1, 134.3, 134.0, 133.6, 133.5, 133.3, 133.0, 132.8, 132.7, 132.4, 132.3, 132.2, 132.1, 128.7, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.5, 127.4, 126.9, 126.7, 126.3, 126.1, 125.8, 125.7, 125.6, 125.0, 124.9, 124.7, 80.4 (d, $J_{P,C}$ = 16.7 Hz), 48.8 (d, $J_{P,C}$ = 6.0 Hz), 43.5 (d, $J_{P,C}$ = 5.1 Hz), 38.9 (d, $J_{P,C}$ = 21.4 Hz), 37.6 (d, $J_{P,C}$ = 27.5 Hz), 34.3, 31.7, 25.5, 22.9, 22.2, 21.1, 15.9 ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 145.2 ppm. MS (EI, 70 eV): *m*/*z* (%) = 466 (9) [M]$^+$, 328 (100), 311 (2.9), 265 (12), 138 (1.3).

Typical Procedure for the Preparation of Complexes for NMR Studies: 1b (3.0 mg, 7.4 µmol) in $CDCl_3$ (0.3 mL) and $Rh(COD)_2BF_4$ (5.4 mg, 14.8 µmol) were mixed in an NMR tube, which was sealed, and the NMR experiment run. Rh(**1b**)$_2$(COD)BF_4: ^{31}P NMR (202 MHz, $CDCl_3$): δ = 140.6 (d, $J_{Rh,P}$ = 170 Hz), 137.5 (d, $J_{Rh,P}$ = 170 Hz) ppm. Rh(**1c**)$_2$(COD)BF_4: ^{31}P NMR (202 MHz, $CDCl_3$): δ = 141.0 (d, $J_{Rh,P}$ = 170 Hz), 136.4 (d, $J_{Rh,P}$ = 170 Hz) ppm. Rh(**1d**)$_2$(COD)BF_4: ^{31}P NMR (202 MHz, $CDCl_3$): δ = 135.8 (d, $J_{Rh,P}$ = 171 Hz), 134.5 (d, $J_{Rh,P}$ = 171 Hz) ppm. Rh(**1e**)$_2$(COD)BF_4: ^{31}P NMR (202 MHz, $CDCl_3$): δ = 144.9 (d, $J_{Rh,P}$ = 171 Hz), 143.9 (d, $J_{Rh,P}$ = 171 Hz) ppm. Rh[(*R*$_a$)-L-**3**)]$_2$(COD)BF_4: ^{31}P NMR (202 MHz, $CDCl_3$): δ = 130.6 (d, $J_{Rh,P}$ = 170 Hz) ppm. Rh[(*R*$_a$)-D-**3**)]$_2$(COD)BF_4: ^{31}P NMR (202 MHz, $CDCl_3$): δ = 135.1 (d, $J_{Rh,P}$ = 174 Hz) ppm.

General Procedure for the Rh-Catalyzed Hydrogenation of *N*-Acetyldehydrophenylalanine Methyl Ester: $Rh(COD)_2BF_4$ (2.0 mg, 5 µmol, 1 mol-%), the ligand (10 µmol, 2 mol-%) and *N*-acetyldehydrophenylalanine methyl ester (110 mg, 0.5 mmol) were dissolved in dry MeOH (5 mL) in a dry flask under a nitrogen atmosphere and stirred for 15 min. The mixture was transferred with a syringe to a Schlenk tube filled with hydrogen. After stirring for the given reaction time under an atmospheric pressure (1 bar) of hydrogen, the solvent was removed under reduced pressure, and the crude product was filtered through a short silica gel plug with diethyl ether. Conversions were determined by ^{1}H NMR spectroscopy. The enantiomeric excess was determined by HPLC [CHIRALCEL OD-H (46 × 250 mm), flow rate = 0.5 mL/min, hexane/2-propanol (9:1), UV detector at 212 nm, $t_R(R)$ = 20.1 min, $t_R(S)$ = 26.6 min].

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