# Unsymmetrical Bidentate Ligands Bearing Chiral Phosphetane Units

A. Marinetti,*[+] V. Kruger, B. Couëtoux

Laboratoire Hétéroélements et Coordination, UMR CNRS 1499, Ecole Polytechnique, F-91128 Palaiseau Cedex, France

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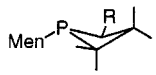
**Abstract:** Bidentate ligands containing a $PPh_2$ group and a P-chiral phosphetane moiety have been prepared from the optically pure P-menthyl substituted phosphetane oxide **4**. The $PPh_2$ group is introduced at a distance of three, four or five bonds from the other phosphorus atom by methodologies involving the corresponding hydroxy-substituted phosphetanes.

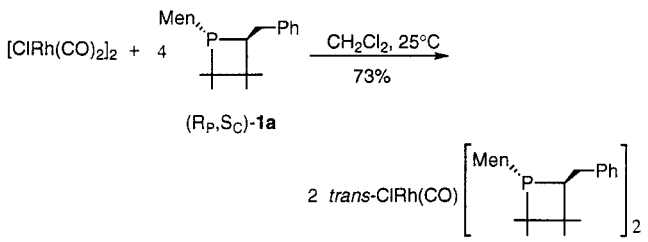
**Key words:** electron-rich chiral phosphines, P-chiral phosphetanes, *p*-menthylphosphetanes, phosphetane oxides, hydroxy phosphetanes, borane complexes, catalytic hydrogenation

Exploratory studies of the potential of phosphetanes as chiral ligands in organometallic catalysis have appeared recently. They have been mainly concerned with the easily accessible P-menthyl substituted species **1**.[1]



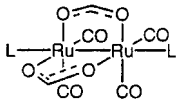
**1** Men = *l*-menthyl

These electron-rich, rather hindered phosphines are good ligands for palladium and their use as chiral auxiliaries in Pd-catalyzed olefin hydrosilylation[2] and allylic substitution reactions[3] has been reported. However, their behavior towards other catalytically useful transition metals, such as rhodium or ruthenium, is more difficult to predict. Thus, the rhodium complex *cis*-$[(COD)RhL_2]^+PF_6^-$ (L = **1a**) is an unstable compound,[2] while the very stable *trans*-complex **2** is easily obtained at room temperature according to Scheme 1.




**Scheme 1**

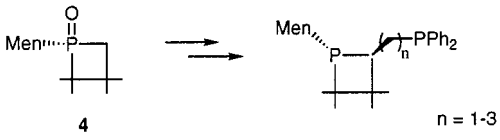
Slightly unpredictable reactivity is also observed toward ruthenium complexes: under the usual reaction conditions,[4,5] phosphetane **1a** failed to give the expected (*p*-cymene)$RuCl_2$•(**1a**) and (2-methylallyl)$_2$Ru•(**1a**)$_2$ by replacement of a chloride ligand from the dimeric complex $[(p\text{-cymene})RuCl_2]_2$ or the 1,5-cyclooctadiene (COD) ligand from (2-methylallyl)$_2$Ru(COD), respectively. Nevertheless, the bimetallic derivative **3** has been easily obtained through standard procedures.[6]




**3** L = **1a**

These few examples suggest that an increase in sterical hindrance and/or electron density at the metal center strongly affects the stability of the phosphetane–rhodium or ruthenium bonds. This imposes limitations upon the use of these phosphetanes as ligands in several common catalytic processes. Thus, increased stability in their complexes is required and should be attained by incorporating phosphetanes into chelating species.

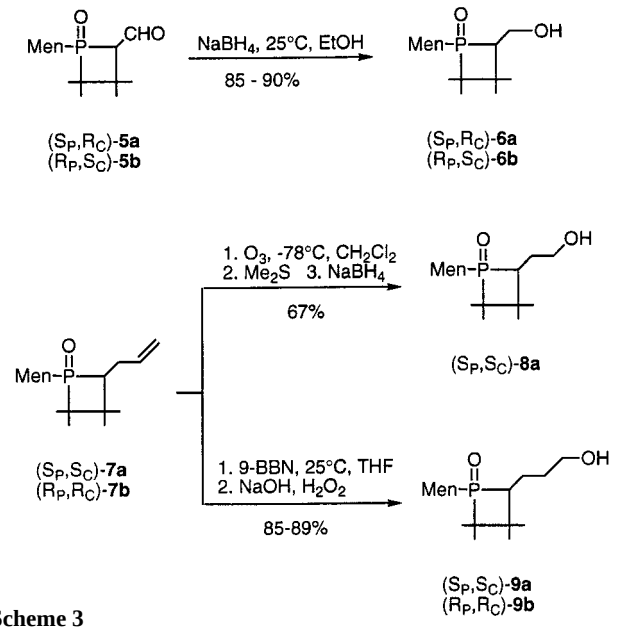
In this paper, we demonstrate a number of pathways which allow optically pure 1-menthyl-2,2,3,3-tetramethylphosphetane oxide **(4)** to be transformed into unsymmetrical bidentate ligands, while retaining the four-membered ring structure (Scheme 2). The second coordinating group is a $PPh_2$ unit located at a distance of three, four or five bonds from the phosphetane phosphorus atom.




**Scheme 2**

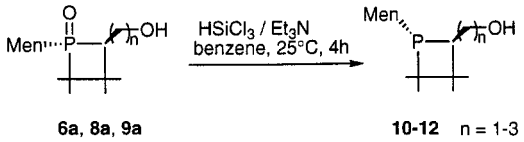
Usually, $PPh_2$ moieties are introduced into chiral substrates by the reaction of lithium diphenylphosphide with the mesylates of chiral alcohols. This approach has been adopted here. Phosphetane oxides bearing an hydroxyl function are easily accessible from the $\alpha$-formyl and $\alpha$-allyl phosphetane oxides **5** and **7** (Scheme 3), which are in turn obtained from **4** according to published procedures.[2,3]

In the first two examples of Scheme 3, the OH group is formed by sodium borohydride reduction of a formyl functionality. For the synthesis of **8a** the olefinic double bond of **7a** was cleaved by ozonolysis and the intermediate ozonide reduced with $Me_2S$ to the corresponding aldehyde which was then conveniently reduced in situ. Compound **7a** was also used as the precursor for **9**, which was obtained in good yield after a highly regioselective 9-BBN[7] hydroboration and subsequent oxidation with $H_2O_2$.



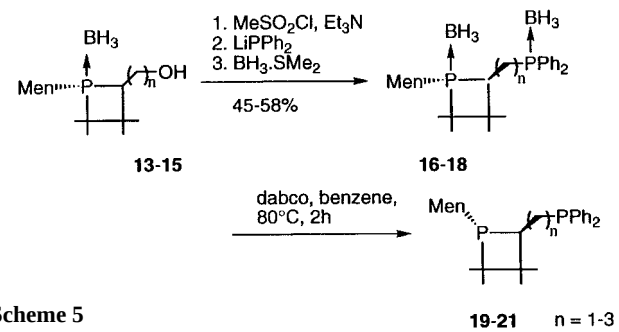

**Scheme 3**

The optimal procedure for the synthesis of the bidentate species involves reduction of the phosphetane oxides **6**, **8** and **9** and complexation of the corresponding phosphetanes **10–12** with $BH_3$. Successive mesylation of the hydroxyl function, substitution with lithium diphenylphosphide and addition of borane gave the bidentate ligands as their bis(borane) complexes (Scheme 4 and 5). This reaction sequence was applied to the representative $S_P$ configured phosphetane oxides **6a**, **8a** and **9a**.




**Scheme 4**

Reduction of the phosphetane oxides with trichlorosilane/triethylamine takes place stereospecifically, with assumed retention of the phosphorus stereochemistry.[8] The most convenient workup procedure involves the direct addition of $BH_3$•$SMe_2$ to the crude product from Scheme 4, but the phosphetanes **10–12** have nonetheless been isolated and fully characterized. The hydroxy-phosphetanes borane complexes **13–15** were isolated and treated successively




**Scheme 5**

with mesyl chloride/$Et_3N$ and $LiPPh_2$ under the usual experimental conditions. The $PPh_2$ group of the final product was complexed with $BH_3$ in situ to prevent oxidation during the purification process.

The borane protecting group was displaced from compounds **16–18** by treatment with 1,4-diazabicyclo[2.2.2]octane (DABCO)[9] in toluene at 80°C. Quantitative yields of the corresponding diphosphines **19–21** were obtained after filtration of the reaction mixture on a short alumina column (cyclohexane/$Et_2O$, 99:1).

Selected NMR data for the trivalent phosphetanes **10–12**, their borane complexes **13–15** and the diphosphine-bis(borane) complexes **16–18** are reported in the Table. Additional NMR data for **18** and selected data for **19–21** are given in the experimental section.

The chiral unsymmetrical diphosphines **19–21** containing the phosphetane moiety and a $PPh_2$ group have the potential to undergo chelation to transition metals. To confirm this behaviour, compounds **19–21** were allowed to react with $[(COD)_2Rh]PF_6$ and the formation of the chelated rhodium complexes $[(COD)Rh(L)]PF_6$ was observed by $^{31}P$ NMR spectroscopy: L = **19**: $\delta$ = 105.0 ($J_{P\text{-}Rh}$ = 137 Hz, $J_{P\text{-}P}$ = 0) and 78.5 ($J_{P\text{-}Rh}$ = 151 Hz); L = **20**: $\delta$ = 58.2 ($J_{P\text{-}Rh}$ = 134 Hz, $^2J_{P\text{-}P}$ = 43 Hz) and 11.9 ($J_{P\text{-}Rh}$ = 146 Hz); L = **21**: $\delta$ = 71.2 ($J_{P\text{-}Rh}$ = 133 Hz, $^2J_{P\text{-}P}$ = 38 Hz) and 6.3 ($J_{P\text{-}Rh}$ = 156 Hz). Both the chemical shifts and coupling constants are consistent with chelate ring formation. For example, the low-field shifts and small P-P coupling constants expected for five-membered chelate rings[10] were observed with L = **19**.

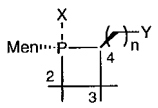
These rhodium complexes were employed to catalyze the hydrogenation of a standard substrate, *trans*-$\alpha$-acetamidocinnamic acid. Unlike monodentate phosphetanes, the bidentate ligands **19–21** gave reasonably active catalysts. The levels of enantioselectivity peak under non-optimized reaction conditions at about 75% ee (*S*-enantiomer), which was obtained with ligand ($R_P$,$R_C$)-**19**. When complexed to rhodium, ligand ($R_P$,$R_C$)-**19** forms a 5-membered metallacycle which is fused to the 4-membered cyclic phosphetane unit. The very restricted conformational freedom of this bicyclic structure probably contributes to its control of stereochemistry.

Obviously, the catalytic hydrogenation reaction under consideration and the enantioselectivities attained in this paper are of only academic interest at present. However, our intention in this work has been to show that appropriate elaboration of the phosphetane scaffold should allow the properties of these ligands to be matched to the requirements of any given catalytic reaction. More meaningful applications of the bidentate ligands described here should be possible when taking advantage of the electronic and steric dissymmetry of their two phosphorus atoms.

Finally, it should be noted that the intermediate hydroxy-phosphetanes **10–12** themselves are potentially versatile functional ligands for enantioselective catalysis.[11]

**Table.** Selected NMR data for compounds **10–18**;[a] $\delta$, $J$ (Hz)

| Assignments of spectra | X = lone electron pair, Y = OH[b] | | | X = $BH_3$ Y = OH[c] | | | X = $BH_3$ Y = $Ph_2P(BH_3)$ [c] | | |
|---|---|---|---|---|---|---|---|---|---|
| | **10** n = 1 | **11** n = 2 | **12** n = 3 | **13** n = 1 | **14** n = 2 | **15** n = 3 | **16** n = 1 | **17** n = 2 | **18** n = 3 |
| $^{31}$P NMR | 19.6 | 29.3 | 29.5 | 51.7 | 55.5 | 54.8 | 58.0, 16.0 | 58.6, 16.9 | 57.0, 15.8 |
| $^{13}$C NMR:[d] | | | | | | | | | |
| C-2 | 42.0 (4.8) | 42.4 (4.7) | 42.5 (4.7) | 40.5 (35.2) | 40.4 (35.2) | 40.3 (36.3) | 39.6 (35.1) | 40.2 (35.3) | 40.1 (36.3) |
| C-3 | 36.3 (2.7) | 36.7 (2.9) | 36.4 | 42.8 (5.8) | 43.2 (4.8) | 43.4 (4.5) | 43.3 (4.5) | 43.4 (5.0) | 43.1 (4.6) |
| PCH-4 | 42.1 | 36.1 | 39.8 | 42.5 (34.9) | 36.7 (36.6) | 40.8 (37.0) | 34.6 (37.4) | 42.0 (36.2, 12.3) | 40.7 (36.9) |
| PCH-3' (menthyl) | 36.5 (29.0) | 36.5 (30.8) | 36.5 (30.8) | 37.0 (15.5) | 36.9 (16.1) | 37.1 (15.0) | 37.6 (14.1) | 36.5 (15.1) | 36.6 (15.1) |
| $CH_2Y$ | 63.4 (27.3) | 62.2 (10.4) | 62.8 | 59.6 (2.7) | 61.7 (10.5) | 63.0 | 22.8 (33.5) | 25.6 (36.4, 7.9) | 26.0 (37.6) |
| $(CH_2)_n$ | – | 34.3 (16.9) | 27.3 (18.2) | – | 28.8 | 22.7 | – | 18.9 | 23.0 (10.2) |
| | – | – | 33.2 (8.9) | – | – | 32.8 (10.2) | – | – | 27.5 (14.4) |
| $^1$H NMR:[e] | | | | | | | | | |
| $CH_2OH$ | $3.56_{AB}$ $3.77_{AB}$ (11.1) | 3.43 (t, 6.8) | 3.35 (t, 6.3) | 3.8–4.0 | 3.55 (t, 6.7) | 3.63 (t, 6.2) | | | |

[a] 


[b] Recorded in $C_6D_6$.
[c] Recorded in $CDCl_3$.
[d] $J_{H-P}$.
[e] $J_{H-H}$.

All reactions were carried out under $N_2$ in anhydrous solvents. NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13 MHz for $^1$H, 50.32 MHz for $^{13}$C and 81.01 MHz for $^{31}$P. Only selected NMR data are given in this section.

**ClRh(CO)[1a]$_2$ (2):**
Complex **2** was obtained from 0.10 g (0.28 mmol) of $[ClRh(CO)_2]_2$ and 0.20 g (0.56 mmol) of **1a** in 73% yield (0.33 g) after crystallization of the crude reaction mixture from pentane; yellow solid.
$^{31}$P NMR ($C_6D_6$) : $\delta$ = 74.5 ($^1J_{P\text{-}Rh}$ = 116 Hz).
$^{13}$C NMR ($C_6D_6$) : $\delta$ = 17.6, 22.9, 23.0, 24.1 ($CH_3$), 24.9 (t, $J_{C\text{-}P}$ = 7.9 Hz, $CH_3$), 25.3 (t, $J_{P\text{-}C}$ = 5.2 Hz, $CH_2$), 30.5 (CH), 34.1 (t, $J_{P\text{-}C}$ = 4.4 Hz, CH), 34.7 ($CH_2$), 35.9 ($CH_2$), 36.2 ($CH_2$), 43.2 (CH), 44.7 (C), 46 (br, C), 47.1 (CH), 48.8 (br, CH), 188.3 (dt, $^1J_{C\text{-}Rh}$ = 71.7 Hz, $^2J_{C\text{-}P}$ = 16.8 Hz, CO).
IR ($CH_2Cl_2$): $\nu$ = 1954 cm$^{-1}$ (C=O).
Anal. Calcd. for $C_{49}H_{78}ClOP_2Rh$: C, 66.62; H, 8.90. Found: C, 66.37; H, 8.85.

**Di-$\mu$-formatotetracarbonyl-bis(phosphetane)diruthenium (3):**
$Ru_3(CO)_{12}$ (0.15 g) was added to formic acid (6 mL) and the reaction mixture was refluxed for 20 h. The mixture was then evaporated to dryness to afford a yellow solid which was taken up in $Et_2O$. Phosphetane **1a** (0.22 g, 0.62 mmol) was added to the resulting suspension at r.t. and an immediate gas evolution was observed. The solution was concentrated and hexane was added to precipitate the final product (0.24 g, 69%); yellow solid; mp 182 °C; $[\alpha]_D$ –64 ($c$ = 0.2, $CHCl_3$).
$^{31}$P NMR ($C_6D_6$) : $\delta$ = 53.6.
$^1$H NMR ($C_6D_6$) (selected data): $\delta$ = 0.64 ($CH_3$), 0.84 [d, $^3J_{H\text{-}H}$ = 6.5 Hz, CH($CH_3$)$_2$], 0.91 (d, $^3J_{H\text{-}H}$ = 5.8 Hz, CH$CH_3$), 1.08 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, CH($CH_3$)$_2$], 1.16 (t, $J_{H\text{-}P}$ = 5.5 Hz, $CH_3$), 1.36 (t, $J_{H\text{-}P}$ = 9.0 Hz, $CH_3$), 1.58 ($CH_3$), 8.22 (OCHO).
$^{13}$C NMR ($C_6D_6$) : $\delta$ = 142.8 (t, $J_{P\text{-}C}$ = 5.8 Hz, OCHO), 206.86 and 206.80 (CO).
IR ($CHCl_3$): $\nu$ = 2020 s, 1974 m, 1945 s cm$^{-1}$.
Anal. Calcd. for $C_{54}H_{80}O_8P_2Ru_2$: C, 57.84; H, 7.19. Found: C, 57.78; H, 7.41.

**4-(Hydroxymethyl)phosphetane Oxides (6):**
A solution of the formylphosphetane **5a** (or **5b**) (0.30 g, 0.96 mmol) in EtOH was cooled to 0 °C. $NaBH_4$ (0.07 g) was then added and the reaction mixture was warmed to r.t. for about 1 h. After hydrolysis, extraction with $Et_2O$ and drying ($MgSO_4$), the product was crystallized from an $Et_2O$/hexane mixture.
($S_P$,$R_C$)-**6a**: yield 0.27 g (90%); colorless solid; $[\alpha]_D$ –52 ($c$ = 1, $CHCl_3$).
$^{31}$P NMR ($CDCl_3$) : $\delta$ = 73.4.
$^1$H NMR ($CDCl_3$) : $\delta$ = 2.44 (q, $J$ = 6.8 Hz, 1H), 3.4 (m, 1H), 3.96 (m, 2H, $CH_2OH$).
$^{13}$C NMR ($CDCl_3$) : $\delta$ = 40.2 ($^1J$ = 41.1 Hz, PCH), 40.9 ($^2J$ = 11.9 Hz, $CMe_2$), 49.0 ($^1J$ = 53.8 Hz, P$CMe_2$), 50.8 ($^1J$ = 50.5 Hz, PCH), 58.0 ($^2J$ = 4.1 Hz, $CH_2OH$).
MS: $m/z$ = 314 (M, 28%).
Anal. Calcd. for $C_{18}H_{35}O_2P$: C, 68.75; H, 11.22. Found: C, 68.09; H, 11.09.
($R_P$,$S_C$)-**6b**: yield 0.25 g (85%); $[\alpha]_D$ –41 ($c$ = 1, $CHCl_3$).
$^{31}$P NMR ($CDCl_3$): $\delta$ = 69.4.
$^1$H NMR ($CDCl_3$): $\delta$ = 2.53 (m, 1H), 2.8 (m, 1H), 3.9–4.0 (m, 2H, $CH_2OH$).
$^{13}$C NMR ($CDCl_3$): $\delta$ = 41.7 ($^2J$ = 12.4 Hz, $CMe_2$), 43.3 ($^1J$ = 40.1 Hz, PCH), 48.2 ($^1J$ = 57.1 Hz, P$CMe_2$), 52.8 ($^1J$ = 47.6 Hz, PCH), 58.6 ($CH_2OH$).

**($S_P$,$S_C$)-4-(2-Hydroxyethyl)phosphetane Oxide (8a):**
A stream of $O_3$ was passed through a cooled solution (–78 °C) of the 4-allylphosphetane oxide **7a** (1.0 g, 3 mmol) in $CH_2Cl_2$ (100 mL). The reaction was complete in about 0.5 h. Reduction of the intermediate ozonide with excess $Me_2S$ (10 mL) and $NaBH_4$ (0.26 g) took place between –78 and 25 °C. After hydrolysis, extraction with $CHCl_3$ and evaporation of the solvent, the residue was crystallized from hexane to afford ($S_P$,$S_C$)-**8a;** yield: 0.68 g (67%); colorless solid; mp 192 °C.
$^{31}$P NMR ($CDCl_3$): $\delta$ = 73.6.
$^1$H NMR ($CDCl_3$): $\delta$ = 2.34 (q, $J$ = 7.1 Hz, 1H), 3.5–3.7 (m, $CH_2OH$).
$^{13}$C NMR ($CDCl_3$): $\delta$ = 27.4 ($^2J$ = 5.6 Hz, PCH*C*H$_2$), 40.2 ($^1J$ = 40.8 Hz, PCH), 41.4 ($^2J$ = 11.7 Hz, *C*Me$_2$), 46.1 ($^1J$ = 52.0 Hz, PCH), 48.5 ($^1J$ = 54.1 Hz, P*C*Me$_2$), 61.3 ($^3J$ = 9.9 Hz, $CH_2OH$).
MS: $m/z$ = 328 (M, 20%).
Anal. Calcd. for $C_{19}H_{37}O_2P$: C, 69.48; H, 11.35. Found: C, 68.17; H, 11.02.

**4-(3-Hydroxypropyl)phosphetane Oxides (9):**
A solution of **7a** (or **7b**) (2.3 g, 7.2 mmol) in THF was cooled to 0 °C and 9-BBN (0.5 M solution in THF, 30 mL) was added slowly. The reaction mixture was then warmed to r.t. After stirring for 3 h, the organoborane was oxidized at 0 °C by adding, successively MeOH (2 mL), 20% NaOH (1.4 mL) and 35% $H_2O_2$ (2.1 mL). The mixture was stirred at r.t. for 1 h, hydrolyzed with a $Na_2S_2O_5$ solution and extracted with $Et_2O$. The organic layer was separated and the aqueous layer was reextracted with $Et_2O$. After evaporation, the final product was purified by column chromatography on alumina with an $Et_2O$/MeOH gradient (up to 96:4) as eluent ($R_f$ 0.5).
($S_P$,$S_C$)-**9a**: yield 2.2 g (89%); colorless solid; mp 148 °C; $[\alpha]_D$ –45 ($c$ = 1, $CHCl_3$).
$^{31}$P NMR ($CDCl_3$): $\delta$ = 70.8.
$^1$H NMR ($CDCl_3$): $\delta$ = 2.20 (q, $J$ = 6.7 Hz, 1H), 3.63 (t, $J$ = 6.2 Hz, $CH_2OH$).
$^{13}$C NMR ($CDCl_3$): $\delta$ = 20.0 ($J$ = 5.7 Hz, $CH_2$), 32.6 ($J$ = 9.6 Hz, $CH_2$), 40.1 ($^1J$ = 40.0 Hz, PCH), 41.2 ($^2J$ = 13.4 Hz, *C*Me$_2$), 48.6 ($^1J$ = 54.0 Hz, P*C*Me$_2$), 49.2 ($^1J$ = 52.3 Hz, PCH), 62.4 ($CH_2OH$).
($R_P$,$R_C$)-**9b**: yield 2.1 g (85%).
$^{31}$P NMR ($CDCl_3$):$\delta$ = 68.1.
$^1$H NMR ($CDCl_3$):$\delta$ = 3.59 (t, $J$ = 6.1 Hz, $CH_2OH$).
$^{13}$C NMR ($CDCl_3$):$\delta$ = 19.9 ($J$ = 4.7 Hz, $CH_2$), 32.3 ($J$ = 11.3 Hz, $CH_2$), 42.0 ($^2J$ = 12.3 Hz, *C*Me$_2$), 44.0 ($^1J$ = 39.0 Hz, PCH), 47.8 ($^1J$ = 56.3 Hz, P*C*Me$_2$), 51.2 ($^1J$ = 49.2 Hz, PCH), 62.2 ($CH_2OH$).
MS: $m/z$ = 342 (M, 45%).
Anal. Calcd. for $C_{20}H_{39}O_2P$: C, 70.14; H, 11.48. Found: C, 70.01; H, 11.52.

**Reduction of Phosphetane Oxides 6a, 8a and 9a: ($R_P$,$S_C$)-12a; Typical Procedure (Scheme 4):**
Compound **9a** (2.2 g, 6.4 mmol) was dissolved in anhyd benzene (30 mL). $Et_3N$ (1.8 mL, 2 equiv) and $Cl_3SiH$ (1.3 mL, 2 equiv) were then added at 5 °C. The mixture was stirred at r.t. for about 4 h, cooled to 5 °C and hydrolyzed with 20% NaOH (10 mL). The organic layer was chromatographed directly, under argon, on a short alumina column with $Et_2O$ as eluent. Phosphetane ($R_P$,$S_C$)-**12a** was obtained in 95% yield (2.0 g) as a colorless solid. All reduction reactions are quantitative according to $^{31}$P NMR analysis of the reaction mixtures.
For the direct synthesis of the borane complexes **13–15**, the organic layers obtained from the reductions above were dried ($MgSO_4$), filtered, and treated with excess $BH_3$•$Me_2S$ (1.3 equiv). After evaporation, the residue was purified by chromatography on alumina using hexane/EtOAc (80:20) as eluent.

**Diphosphine-bis(borane) Complexes 16–18: ($R_P$,$S_C$)-18; Typical Procedure (Scheme 5):**
Mesyl chloride (0.18 mL, 2.4 mmol) was added to a cooled solution (0 °C) of the phosphetane borane complex ($R_P$,$S_C$)-**15** (0.68 g, 2 mmol) and $Et_3N$ (0.33 mL) in $CH_2Cl_2$. The mixture was stirred for 18 h at r.t. and then hydrolyzed with aq $NH_4Cl$ solution. The organic layer was evaporated, the residue taken up in hexane/EtOAc (80:20) and filtered over a short alumina column to afford the desired mesylate as a colorless solid. The mesylate was dissolved in THF and cooled to –78 °C before addition of a THF solution of $Ph_2PLi$ (2 mmol, 0.5M). [A 0.5 M solution of lithium diphenylphosphide was prepared either by reacting $Ph_2PCl$ (0.78 mL, 4 mmol) with an excess lithium in THF (8 mL) at r.t. or by metallation of $Ph_2PH$ (0.37 g, 2 mmol) with BuLi in THF (40 mL) between –78 and 25 °C]. The reaction mixture was warmed to r.t., a few drops of $H_2O$ and $BH_3$•$Me_2S$ (0.2 mL, 2 mmol) were added successively at 0 °C. After hydrolysis and extraction with $Et_2O$, the final product was purified by chromatography on alumina with hexane/$Et_2O$ (95:5) as eluent and crystallized from hexane. The borane complex ($R_P$,$S_C$)-**18** was obtained in 47% yield (0.48 g) as a colorless solid.
$^1$H NMR ($CDCl_3$): $\delta$ = 0.76 (d, $^3J_{H-H}$ = 6.7 Hz, $CH_3$), 0.79 (d, $^3J_{H-H}$ = 6.9 Hz, $CH_3$), 0.90 (s, $CH_3$), 0.94 (d, $^3J_{H-H}$ = 6.7 Hz, $CH_3$), 1.05 (d, $^3J_{H-P}$ = 17.4 Hz, $CH_3$), 1.16 (s, $CH_3$), 1.22 (d, $^3J_{H-P}$ = 12.9 Hz, $CH_3$), 7.4-7.7 ($C_6H_5$).
$^{13}$C NMR ($CDCl_3$): $\delta$ = 17.3 ($CH_3$), 19.6 ($CH_3$), 21.4 ($CH_3$), 21.5 ($CH_3$), 22.4 ($CH_3$), 22.6 ($J$ = 4.4 Hz, $CH_3$), 24.5 ($J$ = 10.2 Hz, $CH_2$), 27.3 ($J$ = 15.6 Hz, $CH_3$), 30.5 ($J$ = 4.4 Hz, CH), 33.3 ($J$ = 10.4 Hz, CH), 34.0 ($CH_2$), 34.9 ($CH_2$), 41.6 (CH).

**Displacement of Diphosphines 19–21 from their Borane Complexes; General Procedure (Scheme 5):**
The phosphine-borane complex ($R_P$,$R_C$)-**16** (50 mg, 0.10 mmol) was heated with DABCO (23 mg, 0.20 mmol) in benzene at 80 °C for 2 h. Quantitative formation of the diphosphine ($R_P$,$R_C$)-**19** was observed by $^{31}$P NMR analysis of the reaction mixture. The final product was obtained in quantitative yield after chromatography on a short alumina column with cyclohexane/$Et_2O$ (99:1) as eluent.

($R_P$,$R_C$)-**19**: $[\alpha]_D$ –25 ($c$ = 1, $CH_2Cl_2$).
$^{31}$P NMR ($C_6D_6$): $\delta$ = 33.3 and –18.5 ($^3J_{P-P}$ = 23 Hz).
$^1$H NMR ($C_6D_6$) (selected data): $\delta$ = 0.71 (d, $^3J_{H-H}$ = 6.8 Hz, $CH_3$), 0.87 (d, $^3J_{H-H}$ = 6.4 Hz, $CH_3$), 0.97 (d, $^3J_{H-H}$ = 6.9 Hz, $CH_3$), 0.99 (s, $CH_3$), 0.98 (d, $^3J_{H-P}$ = 3.8 Hz, $CH_3$), 1.09 (d, $^3J_{H-P}$ = 15.4 Hz, $CH_3$), 1.14 (s, $CH_3$), 7.0–7.7 ($C_6H_5$).
$^{13}$C NMR ($C_6D_6$): $\delta$ = 16.6 ($CH_3$), 22.1 ($^2J$ = 10.7 Hz, $CH_3$), 22.5 ($CH_3$), 22.8 (2 $CH_3$), 23.9 ($^2J$ = 23.3 Hz, $CH_3$), 25.3 ($J$ = 9.5 Hz, $CH_2$), 26.6 (t, $J$ = 6.9 Hz, $CH_3$), 30.0 ($J$ = 13.4 Hz, CH), 31.0 (dd, $J$ = 36.6, 18.3 Hz, $PCH_2$), 33.9 ($J$ = 5.0 Hz, CH), 35.1 ($CH_2$), 35.9 ($J$= 9.2 Hz, CH-4), 36.2 (C-3), 36.7 ($J$ = 31.7 Hz, CH-3'), 37.4 ($CH_2$), 43.2 ($J$ = 3.8 Hz, C-2), 48.8 ($J$ = 22.1 Hz, CH), 126–140 ($C_6H_5$).
MS: $m/z$ = 466 (M, 9%), 243 ($PCHCH_2PPh_2$, 100%).
The same procedure applied to the borane complexes ($R_P$,$S_C$)-**17** and ($R_P$,$S_C$)-**18** afforded the diphosphines ($R_P$,$S_C$)-**20** and ($R_P$,$S_C$)-**21** respectively.

($R_P$,$S_C$)-**20**:
$^{31}$P NMR ($CDCl_3$): $\delta$ = 29.2 and –17.2.
$^1$H NMR ($CDCl_3$) (selected data): $\delta$ = 0.78 (d, $^3J_{H-H}$ = 6.9 Hz, $CH_3$), 0.94 (s, $CH_3$), 0.94 (d, $^3J_{H-H}$ = 6.9 Hz, $CH_3$), 1.00 (d, $^3J_{H-H}$ = 6.2 Hz, $CH_3$), 1.14 (d, $^3J_{H-P}$ = 14.9 Hz, $CH_3$), 1.24 (d, $^3J_{H-P}$ = 5.1 Hz, $CH_3$), 1.29 (s, $CH_3$), 7.2 ($C_6H_5$).
$^{13}$C NMR ($CDCl_3$) (selected data): $\delta$ = 33.9 ($J$ = 18.4, $CH_2$), 36.4 ($J$ = 2.9 Hz, CH-4), 36.7 ($J$ = 4.5 Hz, C-3), 36.0 ($J$ = 29.0, CH-3'), 42.2 ($J$ = 4.6 Hz, C-2), 44.5 ($J$ = 10.7, $CH_2$), 48.6 ($J$ = 21.6 Hz, CH-4).

($R_P$,$S_C$)-**21**:
$^{31}$P NMR ($CDCl_3$): $\delta$ = 30.2 and –16.0.
$^1$H NMR ($C_6D_6$) (selected data): $\delta$ = 0.77 (d, $^3J_{H-H}$ = 6.7 Hz, $CH_3$), 0.78 (s, $CH_3$), 0.94 (d, $^3J_{H-H}$ = 6.4 Hz, $CH_3$), 0.99 (d, $^3J_{H-H}$ = 6.8 Hz, $CH_3$), 1.09 (d, $^3J_{H-P}$ = 15.0 Hz, $CH_3$), 1.12 (d, $^3J_{H-P}$ = 4.9 Hz, $CH_3$), 1.18 (s, $CH_3$), 7.1–7.5 ($C_6H_5$).

$^{13}$C NMR ($C_6D_6$): $\delta$ = 26.6 (dd, $J$ = 16.0, 9.4 Hz, $CH_2$), 29.0 ($J$ = 12.9, $CH_2$), 32.9 (dd, $J$ = 12.5, 18.0 Hz, $CH_2$), 36.3 (C-3), 36.5 ($J$ = 31.5, CH-3'), 39.8 (CH-4), 42.5 ($J$ = 5.3 Hz, C-2), 48.9 ($J$ = 22.1 Hz, CH-4').

**Catalytic Hydrogenation Reactions:**

The hydrogenation reaction with the rhodium complex of ($R_P$,$R_C$)-**19** is given as a representative example. The phosphine-borane complex ($R_P$,$R_C$)-**16** (10 mg, 0.02 mmol) was reacted with DABCO (4.5 mg, 0.02 mmol) in toluene at 70°C for about 3 h, after which time the rhodium complex [$(COD)_2$Rh]$PF_6$ (1 equiv, 10 mg) was added. Quantitative formation of the diphosphine ($R_P$,$R_C$)-**19** and the corresponding rhodium complex were confirmed by $^{31}$P NMR spectroscopy of the crude reaction mixtures.

Analogous procedures starting from ($R_P$,$S_C$)-**17** and ($R_P$,$S_C$)-**18** afforded the rhodium complexes of phosphetanes **20** and **21**, respectively, which were used in situ for catalytic hydrogenation reactions. Small amounts of byproducts were observed in the reaction mixture obtained from **15**.

Hydrogenation of the $\alpha$-acetamidocinnamic acid (2 mmol) was performed in MeOH (20 mL), under 3 bars of $H_2$ at r.t. Published procedures were used to remove the catalyst and to isolate the final product; optical yields were calculated from the $[\alpha]_D$ values {$[\alpha]_D$ +47.4 ($c$ = 2, EtOH) for (*S*)-*N*-acetylphenylalanine}.[12]

✣ Present address: Laboratoire de Synthèse Sélective Organique et Produits Naturels, UMR CNRS 7573, Ecole Nationale Supérieure de Chimie de Paris, 11, rue Pierre et Marie Curie, F-75231 Paris Cedex 05, France.

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