# Enantioselective Catalysis; Part 93:[1] Optically Active Expanded Phosphanes Derived from 1,2-Bisphosphanobenzene and Amides and Esters of Acrylic Acid

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Three new expanded phosphanes were synthesized by reaction of 1,2-bisphosphanobenzene with optically active derivatives of acrylic acid: (*R*)-(+)-*N*-methyl-*N*-(1-phenethyl)acrylamide, (1*S*,2*R*,5*S*)-(+)-menthyl acrylate and (1*S*)-*endo*-(−)-bornyl acrylate. The three phosphanes with $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ as in situ catalysts, as well as the isolated complexes $[Rh(PP)(COD)]PF_6$, where PP and COD denote a phosphane and 1,5-cyclooctadiene, respectively, were tested in several enantioselective catalytic reactions.

The addition of the P–H group to olefinic double bonds to afford organophosphanes can be either base or acid catalyzed (ionic mechanism) or free-radical or UV-radiation initiated (radical mechanism). The reaction can also be accomplished thermally but only in the case of olefins bearing strongly activating groups.[2]

In the present work, we report the synthesis of new optically active organophosphanes by addition of the P–H groups of 1,2-bisphosphanobenzene to the following derivatives of acrylic acid: (*R*)-(+)-*N*-methyl-*N*-(1-phenethyl)acrylamide, (1*S*,2*R*,5*S*)-(+)-menthyl acrylate and (1*S*)-*endo*-(−)-bornyl acrylate (Figure 1). Two different synthetic methods were tested for this purpose: the addition in the presence of a strong base and the addition at elevated temperatures without any catalyst. Both methods have been frequently used in the P–H addition to olefins possessing strongly activating groups.[3–7]

For the synthesis by the ionic mechanism, the best results were obtained in THF with potassium *tert*-butoxide, a base which has proved to be very effective as a catalyst for this kind of reaction.[8–14] Potassium hydroxide, which has successfully catalyzed a similar system,[6] gave much less satisfactory results. By the base-catalyzed reaction of 1,2-bisphosphanobenzene and a slight excess of (*R*)-(+)-*N*-methyl-*N*-(1-phenethyl)acrylamide at room temperature, the corresponding compound **1** was obtained in good yield (Scheme 1). This dialkylphosphane was easily separated from the excess amide by chromatography. The same reaction did not work for the acrylic esters. Using a slight excess of acrylic ester, products arising from four, five and even six additions could be detected by mass spectroscopy (peaks at $m/z = 982.7$ and 1193.1 in the case of menthyl acrylate, and at $m/z = 974.6$, 1182.6 and 1391.7 in the case of bornyl acrylate). Even with stoichiometric amounts of acrylate, products containing three and five acrylate groups in addition to the expected product with four groups were observed. These results can be explained taking into account the high reactivity of the activated acrylic esters for the base catalyzed Michael addition.[15] Figure 2 depicts the proposed structure for the product arising from five additions. Similar results were reported for the reaction of phosphane with ethyl acrylate initiated by α,α-azobisisobutyronitrile (AIBN)[16] but surprisingly not for the potassium hydroxide catalyzed addition of phenylphosphane to methyl acrylate.[6]

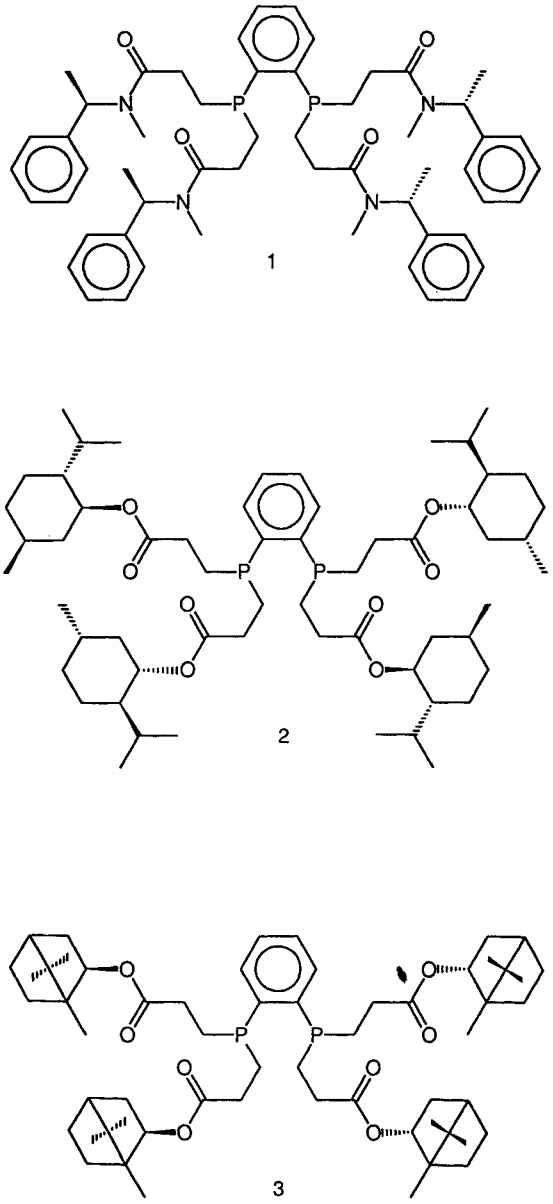
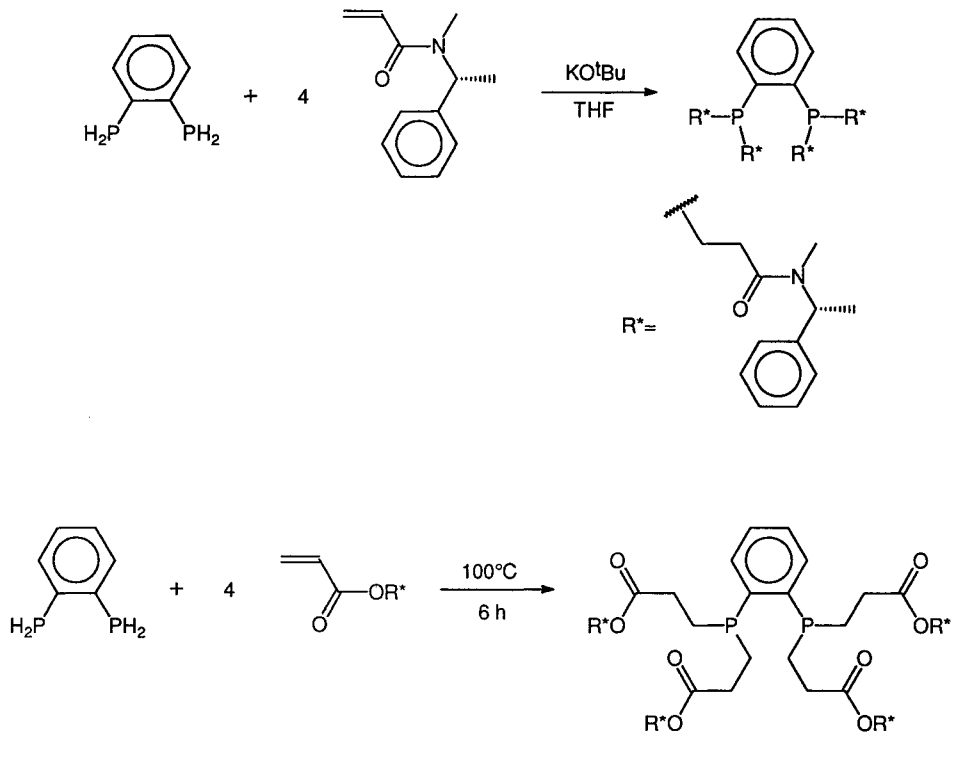



**Figure 1**

To avoid this multiaddition, the reaction was carried out thermally in the absence of any catalyst. Good yields of **2** and **3** were obtained on heating the phosphane for six hours at 100 °C in the presence of an excess of the acrylic acid derivative (Scheme 1). The products were separated from the excess acrylate by removing the volatile acrylic




**Scheme 1**

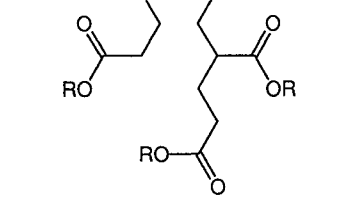


**Figure 2**

esters at 100 °C in high vacuum. No reaction was observed on stirring the reactants at room temperature for 24 hours. This thermal method is also applicable for the synthesis of phosphane **1**.

The optically active phosphanes **2** and **3** are colorless, extremely viscous oils, whereas **1** could be obtained as a white solid. Though they are dialkylaryl phosphanes, **2** and **3** are relatively resistant to air oxidation. Phosphane **1**, on the other hand, oxidizes slowly upon exposure to air.

The $^{31}P\{^1H\}$ NMR spectra of **2** and **3** consist of only one singlet, as expected. As a result of the *E*/*Z* isomerism in the four amide groups, the phosphorus signal of **1** appears as a multiplet and the $^1H$ and $^{13}C$ NMR spectra of this compound are complicated.

The phosphanes **2** and **3** react with $AgPF_6$ and 0.5 equiv of $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ to afford the yellow orange salts $[Rh(PP)(COD)]PF_6$ (PP = **2**, **3** and COD = 1,5-cyclooctadiene). Higher temperatures resulted in a mixture of products with a considerable loss of COD, probably due to partial formation of $[Rh(PP)_2]^+$, a phenomenon also observed for other strongly chelating diphosphanes.[17]

In the solid state these rhodium complexes are stable in air over long periods. The $^{31}P\{^1H\}$ NMR signals of these salts appear as doublets at $\delta = 57.6$ ($J_{Rh-P} = 151.5$ Hz) for $[Rh(\mathbf{2})(COD)]PF_6$ and at $\delta = 57.0$ ($J_{Rh-P} = 143.7$ Hz) for $[Rh(\mathbf{3})(COD)]PF_6$.

The reaction performed under the same conditions with phosphane **1** afforded mixtures of complexes containing no COD. The presence of a strong band in the IR spectrum at $\nu = 1580\ cm^{-1}$, in addition to the normal amide carbonyl band at $\nu = 1640\ cm^{-1}$, suggests a possible coordination of one or more of the amide groups to the metal.

The group of Hayashi achieved high enantiomeric excesses in asymmetric allylations with phosphane ligands possessing the chiral groups at relatively large distances from the phosphorus.[18,19] Our group has been working for some time on the synthesis of the so-called expanded phosphanes, ligands designed to exhibit long range effects through the assembly of chiral and nonchiral layers around the phosphorus atoms of strongly chelating cores.[20,21] Compounds **1**, **2** and **3**, which can be described as expanded phosphanes, were tested, using methods described in the literature,[22-26] in some catalytic enantioselective reactions: the Rh-catalyzed hydrogenation of (*Z*)-(α)-acetamidocinnamic acid, the Rh-catalyzed hydrosilylation of acetophenone and the Pd-catalyzed allylation of 1,5-dimethylbarbituric acid.

For the hydrogenation, in situ catalysts as well as the isolated rhodium complexes were tested. In all cases 100% hydrogenation was achieved at 20 bar $H_2$ in methanol after one week. The degree of reaction and the chemical yield of the hydrosilylated product were after 10 days, respectively: 74 and 54% for **1**; 64 and 55% for **2**; 91 and 68% for **3**. However, the optical inductions were disappointingly low for both reactions: 1.5 (**1**), 8.6 (**2**) and 2.2% ee (**3**) in the hydrogenation and 1.8 (**1**), 6.4 (**2**) and 1.0% ee (**3**) in the hydrosilylation. A possible explanation for these results may be the lack of rigidity of the four chiral "arms".

Phosphane **1** is the only ligand which gave optically active allylated products (3% ee) in the reaction of allyl acetate with 1,5-dimethylbarbituric acid, a system for which the maximum enantiomeric excess achieved up to now is 12.9%.[26]

All reactions were performed under nitrogen by using standard Schlenk techniques. Solvents were purified and dried by standard procedures. 1,2-Bisphosphanobenzene,[27] (*R*)-(+)-*N*-methyl-*N*-(1-phenethyl)acrylamide,[28,29] (1*S*,2*R*,5*S*)-(+)-menthyl acrylate,[30] (1*S*)-*endo*-(−)-bornyl acrylate[31] and $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$[32] were prepared as described in the literature.

$^1H$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ on a Bruker ARX 400 instrument ($T = 21\,°C$) using TMS as internal standard ($^1H$ and $^{13}C$) or $H_3PO_4$ as external standard ($^{31}P$). LI-SIMS (matrix = 3-nitrobenzylalcohol) and FD mass spectra were recorded on a Finnigan Mat 95 spectrometer using $CH_2Cl_2$ as solvent. IR spectra were recorded on a Beckman IR 4240 instrument in the form of KBr pellets (solid products) or films between NaCl windows (oils). The optical rotations were measured on a Perkin-Elmer polarimeter 241.

Compounds **1**–**3**, [Rh(**2**)(COD)]$PF_6$ and [Rh(**3**)(COD)]$PF_6$ gave C,H analysis ± 0.21%, except [Rh(**3**)(COD)]$PF_6$, C − 0.55%.

**1,2-Bis(bis{2-[(+)-*N*-methyl-*N*-(1-phenylethyl)aminocarbonyl]-ethyl})phosphanobenzene (1):**
A solution of (*R*)-(+)-*N*-methyl-*N*-(1-phenethyl)acrylamide (2.40 g, 12.7 mmol) in THF (20 mL) was added dropwise to a solution of 1,2-bisphosphanobenzene (0.40 g, 2.81 mmol) and KOBu-*t* (63 mg, 0.56 mmol). The initial yellow color of the solution faded during the addition. The colorless solution was stirred for 2 h and the solvent was removed. The yellowish-oil residue was chromatographed (silica gel; EtOAc/hexane, 2:1) to give the acrylamide. Then, EtOAc was used to elute the phosphane **1**. After removing the solvent, **1** was obtained as a white, air-sensitive solid. Yield: 2.32 g (92% yield). $[\alpha]_D^{25} = +135.5°$ ($c = 1.0$, $CH_2Cl_2$).
MS (LI-SIMS): $m/z = 899.7$ ($MH^+$).
IR (KBr): $\nu = 1640\,cm^{-1}$ (C=O).
$^{31}P\{^1H\}$ NMR ($CDCl_3/H_3PO_4$): $\delta = -33.04$ (m).
$^1H$ NMR ($CDCl_3$/TMS): $\delta = 7.6$–$7.1$ (24H, m, ArH), 6.01 (2.8H, m, CHN), 5.02 (1.2H, m, CHN), 2.62 (3.6H, m, $CH_3N$), 2.54 (8.4H, m, $CH_3N$), 2.49 (8H, m, $CH_2$), 2.17 (8H, m, $CH_2$), 1.50 (3.6H, m, $CH_3C$), 1.43 (8.4H, m, $CH_3C$).
$^{13}C\{^1H\}$ NMR ($CDCl_3$/TMS): $\delta = 172.2$ (br s, C=O), 143.6 (br s, $C_{arom}P$), 140.6, 140.2 ($C_{arom}CH$), 130.2, 129.3, 128.6, 128.4, 127.4, 127.2, 127.1, 126.3, ($C_{arom}$), 54.4, 50.4 (*C*HPh), 30.3, 29.7 ($CH_2$), 29.3, 28.0 ($CH_3N$), 22.8, 22.4 ($CH_2$), 15.5 ($CH_3CH$).

**1,2-Bis{bis-2-[(+)-menthoxycarbonyl]ethyl}phosphanobenzene (2) and 1,2-Bis{bis-2-(−)-*endo*-bornyloxycarbonyl]ethyl}phosphanobenzene (3):**
A mixture of 1,2-bisphosphanobenzene (426.2 mg, 3 mmol) and acrylate [3.16 g, 15 mmol of (1*S*,2*R*,5*S*)-(+)-menthyl acrylate; or 3.13 g, 15 mmol of (1*S*)-(−)-*endo*-bornyl acrylate] was heated for 6 h at 100 °C. In order to separate the product from the excess acrylate, the mixture was maintained at 100 °C in high vacuum over 10 h. The yields were nearly quantitative.

*Phosphane* (**2**):
$[\alpha]_D^{25} = +62.7°$ ($c = 1.0$, $CH_2Cl_2$).
MS (FD): $m/z = 982.8$ ($M^{+\cdot}$).
IR (neat): $\nu = 1730\,cm^{-1}$ (C=O).
$^{31}P\{^1H\}$ NMR ($CDCl_3/H_3PO_4$): $\delta = -33.55$ (s).
$^1H$ NMR ($CDCl_3$/TMS): $\delta = 7.48$ (2H, m, $H_{arom}$), 7.38 (2H, m, $H_{arom}$), 4.67 (4H, td, $J = 10.9$, 4.4 Hz, HCO menthyl), 2.34 (8H, m, $CH_2$), 2.06 (8H, m, $CH_2$), 1.95 (4H, m, menthyl), 1.66 (4H, m, menthyl), 1.46 (4H, m, menthyl), 1.35 (4H, t, $J = 11.6$ Hz, menthyl), 1.04 (4H, qd, $J = 13.1$, 2.8 Hz, menthyl), 1.00–1.81 (8H, m, menthyl), 0.89 (12H, dd, $J = 6.5$, 2.4 Hz, $CH_3$ menthyl), 0.88 (12H, dd, $J = 7.0$, 2.7 Hz, $CH_3$ menthyl), 0.74 (12H, dd, $J = 6.9$, 1.9 Hz, $CH_3$ menthyl).
$^{13}C\{^1H\}$ NMR ($CDCl_3$/TMS): $\delta = 172.7$ (td, $J = 7.3$, 3.5 Hz, C=O), 143.0 (t, $J = 8.3$ Hz, $C_{arom}P$), 130.0, 129.4 ($CH_{arom}$), 74.3 (CHO menthyl), 46.9 (*C*HPr-*i* menthyl), 40.8 (d, $J = 2.6$ Hz, OCH*C*H$_2$CMe), 34.2 (CHMe*C*H$_2$CH$_2$ menthyl), 31.3 (CH$_2$*C*HMe menthyl), 30.9 (td, $J = 8.5$, 5.5 Hz, $CH_2$), 26.2 [*C*H(CH$_3$)$_2$ menthyl), 23.4 (d, $J = 2.15$ Hz, CHMeCH$_2$*C*H$_2$ menthyl), 22.3 (t, $J = 4.0$ Hz, $CH_2$), 22.0 (*C*H$_3$CHCH$_2$CH menthyl), 20.7 (*C*H$_3$ *i*-Pr menthyl), 16.3 (d, $J = 2.4$ Hz, *C*H$_3$ *i*-Pr menthyl).

*Phosphane* (**3**):
$[\alpha]_D^{25} = -36.8°$ ($c = 1.0$, $CH_2Cl_2$).
MS (FD): $m/z = 974.6$ ($M^{+\cdot}$).
IR (neat): $\nu = 1730\,cm^{-1}$ (C=O).
$^{31}P\{^1H\}$ NMR ($CDCl_3/H_3PO_4$): $\delta = -33.63$ (s).
$^1H$ NMR ($CDCl_3$/TMS): $\delta = 7.42$ (2H, m, $H_{arom}$), 7.33 (2H, m, $H_{arom}$), 4.80 (4H, dm, $J = 9.9$ Hz, HCO bornyl), 2.31 (8H, m, $CH_2$), 2.25 (4H, m, bornyl), 2.02 (8H, m, $CH_2$), 1.83 (4H, m, bornyl), 1.66 (4H, m, bornyl), 1.59 (4H, m, bornyl), 1.17 (4H, m, bornyl), 0.87 (4H, dd, $J = 13.9$, 3.2 Hz, bornyl), 0.82 (12H, s, $CH_3$ bornyl), 0.79 (12H, s, $CH_3$ bornyl), 0.74 (12H, d, $J = 3.3$ Hz, $CH_3$ bornyl).
$^{13}C\{^1H\}$ NMR ($CDCl_3$/TMS): $\delta = 173.3$ (t, $J = 7.1$ Hz, C=O), 142.9 (t, $J = 8.2$ Hz, $C_{arom}P$), 129.9, 129.4 ($CH_{arom}$), 80.0 (d, $J = 2.2$ Hz, CHO bornyl), 48.6 (d, $J = 1.2$ Hz, OC*C*Me bornyl), 47.7 (*C*Me$_2$ bornyl), 44.7 (CH$_2$*C*HCH$_2$ bornyl), 36.6 (d, $J = 4.0$ Hz, *C*H$_2$CHO bornyl), 30.8 (t, $J = 8.1$ Hz, $CH_2$), 27.9 (OCHCH$_2$*C*HCH$_2$ bornyl), 27.0 (OCHCMe*C*H$_2$ bornyl), 22.3 (d, $J = 3.2$ Hz, $CH_2$), 19.6 (*anti*-*C*H$_3$CCH$_3$ bornyl), 18.7 (*syn*-*C*H$_3$CCH$_3$ bornyl), 13.4 (OCHC*C*H$_3$ bornyl).

**[Rh(PP)(COD)]$PF_6$, (PP = 2, 3):**
$AgPF_6$ (51.3 mg, 0.203 mmol) was added to a solution of $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ (50.0 mg, 0.101 mmol) in THF (10 mL). The mixture was cooled to − 78 °C and a solution of **2** (199.4 mg, 0.203 mmol) or **3** (197.8 mg, 0.203 mmol) in THF (20 mL) was added with a Pasteur pipette. After stirring for 1 h, the mixture was allowed to

warm to r.t. and was filtered. The solvent was removed and the residue was dissolved in $CH_2Cl_2$ (1 mL). On addition of pentane (40 mL) a dark yellow solid precipitated.

*[Rh(2)(COD)]$PF_6$:*

Yield: 220.0 mg (81%); mp = 143–145°C (dec).

IR (KBr): $\nu = 1730\,cm^{-1}$ (C=O).

$^{31}P\{^1H\}$ NMR ($CDCl_3/H_3PO_4$): $\delta = 57.62$ (d, $J = 151.5$ Hz), −143.67 (sept. $J = 713.0$ Hz, $PF_6$).

*[Rh(3)(COD)]$PF_6$:*

Yield: 198.3 mg (73%); mp = 128–131°C (dec).

IR (KBr): $\nu = 1730\,cm^{-1}$ (C=O).

$^{31}P\{^1H\}$ NMR ($CDCl_3/H_3PO_4$): $\delta = 57.03$ (d, $J = 151.4$ Hz), −143.68 (sept. $J = 713.2$ Hz, $PF_6$).

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