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# Synthesis and resolution of a new P-chiral hydroxy phosphine

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**Abstract**

The synthesis of the functionalized P-chiral phosphine BzPhP{CH(OH)Ph}and its resolution by palladium metallacycles is reported. The cyclopalladated compound containing the primary amine 1-(1-naphthyl)ethylamine has been shown to be a better resolving agent for this phosphine than the corresponding metallacycle containing the tertiary amine *N*,*N*-dimethyl-1-(1-naphthyl)ethylamine © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Hydroxyphosphines; P-chiral; Metallacycles; Resolution; Palladium

## 1. Introduction

Spectacular progress has been made in the field of asymmetric catalysis by using homogeneous catalysts based on transition metal complexes modified by chiral ligands. Thus, chiral phosphines have become very important in asymmetric catalysis [1]. Among the great number of chiral phosphines developed for application in asymmetric catalysis, examples of monodentate ligands possessing a stereogenic phosphorus atom are rare, even though metal complexes featuring marked asymmetry near the catalytic center are considered to be excellent optical inducers [2]. In addition, it has been shown that active functional groups (such as hydroxy or amino group) situated properly can enhance the stereo-discriminating ability of a metal catalyst as a consequence of attractive interactions (e.g. by hydrogen bonding) of the functional group with suitable reagents [3]. We describe here the synthesis of the functionalized phosphine BzPhP{CH(OH)Ph} containing two stereogenic centers, the phosphorus and the hydroxy-substituted carbon atom, and its resolution by palladium metallacycles, derived from 1-(1-naphthyl)ethylamines.

## 2. Discussion and results

(±)-Benzylphenylphoshine [4] was synthesized by reaction of dibenzylphenylphosphine and lithium metal in tetrahydrofuran under a dry nitrogen atmosphere. After 16 h of stirring at room temperature (r.t.) complete cleavage of one of the $CH_2$–P bonds of the starting phosphine was accomplished, with formation of the phenylbenzylphosphide anion. The $^{31}$P-NMR spectrum, under nitrogen, illustrated clearly the formation of this anion ($\delta = -37.1$ ppm) [5]. Subsequent addition of $H_2O$ gave the secondary phosphine (±)-**1** in THF solution (Scheme 1). The reaction between the secondary phosphine PHBzPh and benzaldehyde afforded the functionalized phosphine BzPhP{CH(OH)Ph} (**2**), containing two stereogenic centers, the phosphorus and one carbon atom, as a 1:1 mixture of diastereomers.

The versatility of *ortho*-palladated derivatives of optically active N-donor ligands as resolving agents for Lewis bases has been demonstrated convincingly. Cyclopalladated derivatives of the tertiary amines *N*,*N*-dimethyl-1-(1-naphthyl)ethylamine and *N*,*N*-dimethyl-α-methylbenzylamine have been used widely for the resolution of bidentate and monodentate ligands [6], and recently the application of some new cyclometallated compounds in this field have been explored [7]. The optically pure cyclopalladated dinuclear compounds **3** were obtained from the optically active

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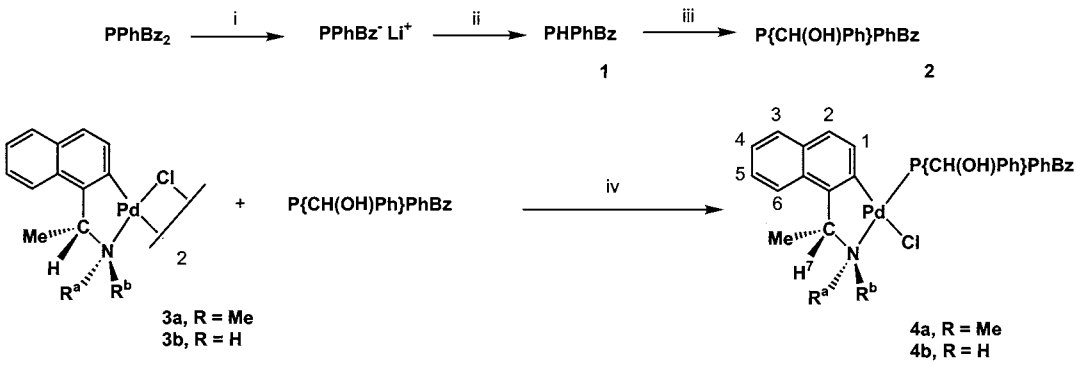


Scheme 1. (i) Li, THF, r.t., 16h. (ii) $H_2O$, THF, r.t., 10 min: PhCHO, 30 min. (iii) $CHCl_3$, r.t., 45 min, under nitrogen.

amines as reported [8]. Reaction of dimers **3** with the phosphine afforded the mononuclear diastereomers [Pd-Cl(C–N)(BzPhP{CH(OH)Ph})], compounds **4**, as a mixture 1:1:1:1 of diastereomers. All the new organometallic compounds obtained were characterized by elemental analysis, IR spectra, and $^1$H- and $^{31}$P-NMR spectra. In some cases, 2D-NMR experiments and positive FAB-mass spectra, were carried out to complete the characterization. The high-field shift of the aromatic protons of the palladated ring in **4**, due to the aromatic rings of the phosphine, indicates the *cis* disposition of the phosphorus relative to the metallated carbon atom and the chemical shift of the phosphorus confirms this arrangement [9]. This arrangement is usual in cyclopalladated compounds containing phosphines [10].

### 2.1. Resolution of the phosphine

The 1:1:1:1 mixture of **4a** diastereomers (400 mg) was eluted carefully in a $SiO_2$ column with chloroform–acetone (100:4) as eluent. The first and second diastereomers **4a**′ and **4a**″ were eluted as a mixture in 70% yield (140 mg). The third diastereomer separated **4a**‴ was obtained in 30% yield (30 mg), with a *d.e.* higher than 95%, and the last diastereomer eluted **4a**⁗ was not obtained in a pure form {the superscripts (′), (″), (‴) and (⁗) indicate the first, the second, the third and the forth diastereomer eluted in the column, respectively}. Nevertheless, better results were obtained with **4b**. The 1:1:1:1 mixture of **4b** diastereomers (400 mg) was eluted carefully, in a $SiO_2$ column with chloroform–acetone (100:3) as eluent. The first diastereomer eluted **4b**′ was separated in 30% yield (30 mg), with a *d.e.* higher than 95%. And the last, **4b**⁗ was obtained in 60% yield (60 mg), with a *d.e.* higher than 95%. The second and third diastereomers eluted **4b**″ and **4b**‴ were obtained as a mixture in 40% yield (80 mg). Recrystallization of this mixture of diastereomers from a saturated solution of diethylether at 20°C afforded **4b**‴ with a *d.e.* higher than 95%.

The efficiency of cyclopalladated compounds derived from 1-(1-naphthyl)ethylamine as resolving agents has been related to the locked asymmetric envelop conformation of the metallacycle, due to the fact that the methyl substituent of the chiral carbon atom adopts an axial disposition to avoid the unfavorable interaction with $H^6$ (see Scheme 1). [11] The NOESY spectra of compounds **4** showed that the methinic proton of the chiral carbon atom $H^7$ had strong negative off-diagonal peaks with $H^6$ and $H^b$ and, in contrast, the methyl protons of the chiral carbon atom presented only strong NOE interaction with $H^a$ and $H^7$. These data confirmed the axial disposition of this methyl group and the equatorial disposition of $H^7$ in this complexes [12].

The aromatic proton in *ortho* position in relation to the metal atom is very high field shifted in **4a**⁗ ($\delta = 5.79$ ppm) and appears at higher fields compared to their $PPh_3$ analog ($\delta = 6.60$ ppm). This fact shows that the rotation around Pd–P is rather restricted and that rotamers with the nearly orthogonal orientation of two aromatic rings of the phosphine with respect to the metallated ring are predominant in this diastereomer. Analogous results have been found for cyclopalladated compounds containing monodentate phosphines such as $P(Bu^t)(C_6H_5)(4\text{-}BrC_6H_4)$ [7c].

The NOESY spectra of diastereomers **4b**′ and **4b**⁗ showed that only one of the signals of the $CH_2$ protons presented strong NOE interaction with the metallated ring proton $H^1$, suggesting a restricted rotation around the $CH_2$–P bond.

The action of 1,2-bisdiphenylphosphinoethane (dppe) on the optically pure cyclopalladated derivatives **4** led to the free phosphine BzPhP{CH(OH)Ph}. No racemization of the phosphine was observed and the displacement proceeded with retention of the configuration at phosphorus as verified by the quantitative regeneration of the same starting material **4** (optically pure) from the free ligand and the corresponding dinuclear cyclopalladated derivative **3**.

In conclusion a new functionalized phosphine BzPhP{CH(OH)Ph}, containing two stereogenic cen-

ters, has been prepared and resolved. It has also been shown that the cyclopalladated compound of the primary amine 1-(1-naphthyl)ethylamine is a better resolving agent for this ligand than the corresponding metallacycle containing the tertiary amine *N*,*N*-dimethyl-1-(1-naphthyl)ethylamine.

## 3. Experimental

$^1$H-NMR at 200 and 500 MHz, and $^{31}$P{$^1$H} at 101.26 MHz spectra were recorded, respectively, on Varian Gemini 200, Varian VXR 500 and Bruker DRX 250 spectrometers. Chemical shifts (in ppm) were measured relative to $SiMe_4$ for $^1$H and to 85% $H_3PO_4$ for $^{31}$P. The solvents used were $CDCl_3$ in $^1$H and THF or $CHCl_3$ in $^{31}$P. Microanalyses were performed at the Institut de Química Bio-Orgànica de Barcelona and the Serveis Científico-Tècnics de la Universitat de Barcelona. The optical rotations of the complexes were determined at 20°C using a Perkin–Elmer 241-MC polarimeter. Infrared spectra were recorded as KBr disks on a Nicolet 520 FT-IR spectrometer.

Materials and Synthesis. All the reactions involving free phosphines were carried out using Schlenk techniques under nitrogen atmosphere. All solvents were dried and degassed by standard methods. Tetrahydrofuran was distilled over sodium–benzophenone, under nitrogen, before use. All chemicals were of commercial grade and used as received. Cyclopalladated compounds **3a** and **3b**, and $PPhBz_2$ were prepared according to procedures described elsewhere [8,13]. BzPhP{CH(OH)Ph} was prepared following the procedure described for related monohydroxyphosphines [14].

### 3.1. Synthesis of (±)-PHBzPh and BzPhP{CH(OH)Ph}

Small pieces of lithium (0.086 g, 12.4 mmol) were added to a solution of dibenzylphenylphosphine (1.5 g, 5.17 mmol) in THF (40 ml) and the reaction mixture was stirred for 16 h at 20°C. The excess of lithium was removed by decantation, and then 0.5 ml of water was added and the mixture was stirred for 10 min. The resulting solution was dried over anhydrous $Na_2SO_4$ and filtered off and the filtrate was concentred in vacuo to obtain (±)-PHBzPh in 90% yield. $^{31}$P-NMR (101.26 MHz, THF): $\delta = -41.0$ (d, $J_{H-P} = 205$ Hz).

A mixture of 2.5 mmol (500 mg) of secondary phosphine PHBzPh and 3.0 mmol (265.3 mg) of benzaldehyde was stirred for 30 min at 0°C to obtain BzPhP{CH(OH)Ph} (1:1 mixture of diastereomers) in 90% yield as an oily material, easy oxidable. $^{31}$P{$^1$H}-NMR (101.26 MHz, THF): $\delta = 1.4$ s and 1.1 s.

### 3.2. Synthesis of **4a**

A mixture of compound **3a** (0.25 mmol, 170 mg) and the hydroxyphosphine **2** (0.25 mmol, 76.6 mg) in THF (30 ml) was stirred for 30 min at r.t. and then filtered. The filtrate was concentred in vacuo and the solid was recrystallized from acetone to obtain the 1:1:1:1 mixture of **4a** diastereomers, as a yellow solid in 75% yield.

#### 3.2.1. Characterization data for **4a**

Anal. (%) Calc. for $C_{34}H_{35}NOClPPd$: C: 63.17, H: 5.46, N: 2.17. Found: C, 63.2; H, 5.3; N, 2.2. $^{31}$P{$^1$H}-NMR (101.26 MHz, $CDCl_3$): $\delta = 52.6$ s, 51.5 s, 41.5 s and 41.4 s.

#### 3.2.2. Separation of **4a** diastereomers

The 1:1:1:1 mixture of **4a** diastereomers (400 mg) was eluted carefully at r.t., in a $SiO_2$ column (30 × 400 mm, 30 g $SiO_2$) with chloroform–acetone (100:4) as eluent. The eluted solution was collected in fractions of 15 ml, concentrated in vacuo and checked by $^{31}$P{$^1$H}-NMR spectroscopy (101.26 MHz). The first and second diastereomers eluted **4a**′ and **4a**″ were obtained as a mixture in 70% yield (140 mg). The third diastereomer eluted **4a**‴ was obtained in 30% yield (30 mg), with a *d.e.* higher than 95%. The last diastereomer eluted **4a**⁗ was not obtained in a pure form.

$^1$H-NMR data (500 MHz, $CDCl_3$) for **4a**‴: $\delta = 8.08$ (t, 2H, $J_{HH} = 7.2$ Hz, *Ar*), 7.91–6.92 (m, 16H, *Ar*), 6.55 (d, 1H, $J_{HH} = 8.4$ Hz, *Ar*), 6.25 (d, 1H, $J_{HH} = 8.4$ Hz, $H^2$), 5.72 (dd., 1H, $J_{HH} = 7.0$ Hz, $J_{HP} = 1.5$ Hz, *H*COH), 5.66–5.52 (m., 2H, H$^1$ and *H*OCH), 4.33–4.17 (m., 1H, *H*CMe), 4.08–3.96 (m, 1H, $H_2$CP), 3.72 (m, 1H, $H_2$CP), 3.10–2.93 (d, $J_{HH} = 3.4$ Hz, 3H, $Me_b$N), 2.78–2.63 (d, $J_{HH} = 1.6$ Hz, 3H, $Me_a$N), 1.92 (d, $J_{HH} = 6.1$ Hz, 3H, $H_3$CH). $^{31}$P{$^1$H}-NMR (101.26 MHz, $CDCl_3$): $\delta = 51.5$ s. $[\alpha]_D^{20} = -38.92$ deg cm$^2$ g$^{-1}$, c = 6.0 mg ml$^{-1}$.

$^1$H-NMR data (500 MHz, $CDCl_3$) for the mixture of **4a**′ and **4a**″: $\delta = 7.62$–$6.95$ (m, 38 H, *Ar*), 6.92–6.81 (m, 4H, *Ar*), 6.72–6.64 (m, 1H), 6.18–6.10 (m., 1H), 5.97–5.86 (m., 2H), 4.35–4.02 (m., 2H, *H*CMe), 3.52–3.31 (m., 4H, $H_2$CP), 2.87 (d, $J_{HH} = 3.4$Hz, 3H, $Me_b$N), 2.78 (d, $J_{HH} = 3.2$ Hz, 3H, $Me_b$N), 2.67 (d, $J_{HH} = 1.6$ Hz, 3H, $Me_a$N), 2.60 (d, $J_{HH} = 1.4$ Hz, 3H, $Me_a$N), 1.52 (d., 3H, $J_{HH} = 6.2$ Hz, $H_3$CH)), 1.21 (d., 3H, $J_{HH} = 6.6$ Hz, $H_3$CH). $^{31}$P{$^1$H}-NMR (101.26 MHz, $CDCl_3$): $\delta = 41.5$ s and 41.4 s.

### 3.3. Synthesis of **4b**

A mixture of compound **3b** (0.25 mmol, 156 mg) and the hydroxyphosphine **2** ( 0.25 mmol, 76.6 mg) in THF (30 ml) was stirred for 30 min at r.t. and then filtered. The filtrate was concentred in vacuo and the solid formed was purified by column chromatography over

$SiO_2$, with chloroform–acetone (100:7) as eluent to obtain the 1:1:1:1 mixture of **4b** diastereomers, as yellow solid in 70% yield.

*3.3.1. Characterization data for **4b***

Anal. (%) Calc. for $C_{32}H_{31}NOClPPd$: C: 62.15, H: 5.05, N: 2.26. Found: C, 62.5; H, 5.0; N, 2.1. $^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$): $\delta = 46.6$ s, 45.6 s, 41.9 s, 39.5 s. MS-Positive FAB: 582 $[(M–Cl)^+]$

*3.3.2. Separation of **4b** diastereomers*

The 1:1:1:1 mixture of **4b** diastereomers (400 mg) was eluted carefully at r.t., in a $SiO_2$ column (30 × 400 mm, 30 g $SiO_2$) with chloroform–acetone (100:3) as eluent. The eluted solution was collected in fractions of 15 ml, concentrated in vacuo and checked by $^{31}P\{^1H\}$-NMR spectroscopy (101.26 MHz). The first diastereomer eluted **4b′** was obtained in 30% yield (30 mg), with a *d.e.* higher than 95%. And the last diastereomer eluted **4b′′′′** was obtained in 60% yield (60 mg), with a *d.e.* higher than 95%. The second and third diastereomers eluted **4b′′** and **4b′′′** were obtained as a mixture in 40% yield. The recrystallization of this mixture of diastereomers from a saturated solution of diethylether at 20°C afforded **4b′′′** with a *d.e.* higher than 95%.

$^1H$-NMR data (500 MHz, $CDCl_3$) for **4b′**: $\delta = 7.55$ (m, 2H, *Ar*), 7.50 (m, 2H, *Ar*), 7.48 (d, $J_{HH} = 8.2$ Hz, 1H, $H^6$), 7.40–7.05 (m, 11H, *Ar*), 6.94–6.82 (m, 4H *Ar*), 6.50 (dd, $J_{PH} = 5.8$ Hz, $J_{HH} = 8.4$ Hz, 1H, $H^1$), 5.75 (d, $J_{PH} = 8.5$ Hz, 1H, *H*COH), 5.57 (m, 1H, *H*OCH), 4.97 (q, $J_{HH} = 5.0$ Hz, 1H, *H*CMe), 3.87 (br, 1H, $H_b$), 3.50 (t, $J_{HH} = J_{PH} = 14.8$ Hz, 1H, $H_2$CP), 3.23 (br, 1H, $H_a$), 3.02 (dd, $J_{HH} = 14.6$ Hz, $J_{PH} = 10.6$ Hz, 1H, $H_2$CP), 1.39 (d, $J_{HH} = 6.2$ Hz, 3H, $H_3$CH). $^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$): $\delta = 41.9$ s.

$^1H$-NMR data (500 MHz, $CDCl_3$) for **4b′′**: $\delta = 7.5$–7.4 (m, 4H, *Ar*), 7.32–7.01 (m, 14H, *Ar*), 6.8 (d, $J_{HH} = 8.0$ Hz, 2H, *Ar*), 6.47 (dd, $J_{HH} = 8.0$ Hz, $J_{PH} = 5.4$ Hz, 1H, $H^1$), 5.84 (br, 1H, *H*COH), 5.7 (br, 1H, *H*OCH), 5.13 (br q, $J_{HH} = 5.4$ Hz, 1H, *H*CMe), 4.09 (br, 1H, $H_b$), 3.46 (br, 1H, $H_a$), 3.29 (br, 2H, $H_2$CP), 1.6 (d, $J_{HH} = 6.2$ Hz, 3H, $H_3$CH). $^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$): $\delta = 39.5$ s

$^1H$-NMR data (500 MHz, $CDCl_3$) for **4b′′′**: $\delta = 7.85$–7.8 (m, 2H, *Ar*), 7.61 (d, $J_{HH} = 8.2$ Hz, 1H, $H^6$), 7.5 (d, $J_{HH} = 7.6$ Hz, 1H, *Ar*), 7.34–7.0 (m, 13H, *Ar*), 6.92–6.89 (m, 2H, *Ar*), 6.67 (d, $J_{HH} = 8.8$ Hz, 1H, $H^2$), 5.88 (dd, $J_{P–H} = 5.4$ Hz, $J_{HH} = 8.8$ Hz, 1H, $H^1$), 5.6 (br, 1H, *H*COH), 5.48 (br, 1H, *H*OCH), 5.22 (q, $J_{HH} = 5.4$ Hz, 1H, *H*CMe), 4.02 (br, 1H, $H_b$), 3.75 (m, 2H, $H_2$CP), 3.46 (br, 1H, $H_a$), 1.98(d, $J_{HH} = 6.6$ Hz, 3H, $H_3$CH). $^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$): $\delta = 45.6$ s.

$^1H$-NMR data (500 MHz, $CDCl_3$) for **4b′′′′**: $\delta = 7.68$ (d, $J_{HH} = 8.0$ Hz, 2H, *Ar*), 7.51 (d, $J_{HH} = 8.0$ Hz, 1H, $H^6$), 7.40 (d, $J_{HH} = 8.0$ Hz, 1H, $H^3$), 7.26 (t, $J_{HH} = 8.0$ Hz, 1H, $H^5$), 7.18–7.11 (m, 7H, *Ar*), 7.09–6,97 (m, 5H, *Ar*), 6.86 (d, $J_{HH} = 7.5$ Hz, 2H, *Ar*), 6.55 (d, $J_{HH} = 8.5$ Hz, 1H, $H^2$), 5,85 (dd, $J_{PH} = 10.5$ Hz, $J_{HH} = 3.0$ Hz, 1H, *H*COH), 5.79 (dd, $J_{HH} = 9.0$ Hz, $J_{PH} = 5.5$ Hz, 1H, $H^1$), 5.28 (d, $J_{HH} = 2.5$ Hz, 1H, *H*OCH), 5,11 (q, $J_{HH} = 5.5$ Hz, 1H, *H*CMe), 3.9 (m, 2H, $H_2$CP and $H_b$), 3.5 (t, $J_{HH} = J_{HP} = 13.5$ Hz, 1H, $H_2$CP), 3.39 (br, 1H, $H_a$), 1.92 (d, $J_{H–H} = 6.5$ Hz, 3H, $H_3$CH) $^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$): $\delta = 46.6$ s. $[\alpha]_D^{20} = +66.62$ deg $cm^2\ g^{-1}$, $c = 10.1$ mg $ml^{-1}$.

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