Resolution of Secondary Phosphanes Chiral at Phosphorus by Means of Palladium Metallacycles

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The synthesis of new epimeric compounds [PdCl(C–N){(±)-PHPhR}] (C–N = (*R*)-$C_{10}H_6CHMeNH_2$ and (*R*)-$C_6H_4CHMeNH_2$, R = Me and $PhCH_2$) containing chiral secondary phosphanes is reported. Some of these diastereomers can be separated by column chromatography; subsequent reaction of these complexes with 1,2-bis(diphenylphosphanyl)-ethane (dppe) affords the free phosphanes PHBzPh and PHMePh. The configurational stability of the secondary phosphanes resolved has also been studied.

Introduction

Due to the reactivity of their P−H bonds, secondary phosphanes are versatile synthons for the preparation of chiral mono- and bidentate ligands[1] but only one secondary phosphane chiral at phosphorus has been resolved to date. Six consecutive recrystallizations from acetonitrile in the presence of sodium acetylacetonate afforded the [R_P-(1*R*,2*S*,5*R*)] diastereomer of menthylmesitylphosphane in 94% optical purity.[2] The low configurational stability of P-chiral secondary phosphanes has been explained by acid-catalyzed racemization, in which the protonation of secondary phosphanes affords achiral phosphonium ions with two enantiotopic protons that can be removed at identical rates. Wild et al. have shown by ^{31}P NMR experiments that the H/D exchange between PHMePh and PDEtPh is negligible in highly purified acetonitrile in the presence of sodium acetylacetonate as a proton scavenger, showing that the resolution of secondary phosphanes may be feasible under mildly basic conditions.[3] When the phosphane is attached to metal ions, a borane or chalcogens by means of the lone pair the racemization does not occur and some diastereomers containing coordinated secondary phosphanes have been separated.[3,4] However, with the exception of the remarkable results described by Wild et al. with menthylmesitylphosphane,[2] recovery of the free optically pure ligand has not been accomplished.

Here we report the synthesis and separation of some diastereomers of compounds [$PdCl(C_{10}H_6CHMeNH_2)$-(PHPhR)] (R = Me and $PhCH_2$) and the isolation of the free secondary phosphanes by the action of 1,2-bis(diphenylphosphanyl)ethane (dppe) on these cyclopalladated derivatives. The configurational stability of the secondary phosphanes resolved and the isotopic exchange between these ligands and D_2O has also been studied.

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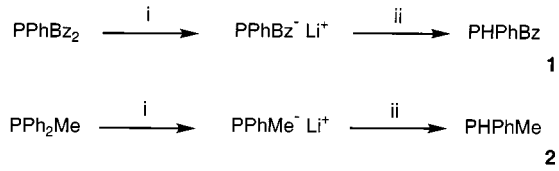
Results and Discussion

(±)-Benzylphenylphosphane was synthesized by reaction of dibenzylphenylphosphane and lithium metal in tetrahydrofuran under a dry nitrogen atmosphere. After 16 h of stirring at room temperature complete cleavage of one of the CH_2−P bonds of the starting phosphane was accomplished, with formation of the benzylphenylphosphide anion. The ^{31}P NMR spectrum, under nitrogen, clearly illustrated the formation of this anion ($\delta = -37.1$) and was used to monitor the progress of the reaction. Subsequent addition of H_2O gave the secondary phosphane (±)-**1** in THF solution (Scheme 1). When methyldiphenylphosphane and lithium metal reacted in the same conditions complete cleavage of one of the Ph−P bonds of the starting phosphane was accomplished, with formation of the methylphenylphosphide anion ($\delta_P = -77.3$). Subsequent addition of H_2O gave (±)-methylphenylphosphane **(2)** in THF solution. It should be noted that these secondary phosphanes are air sensitive and careful workup under nitrogen is needed to obtain them in the free form. The separation of some diastereomers containing PHMePh or PHBzPh coordinated to iron[4b] or platinum[3][4c] has been reported but, to the best of our knowledge, these phosphanes have not been obtained in free form, optically pure.



Scheme 1. i) Li, THF, room temperature, 16 h; ii) THF, room temperature, 10 min

The versatility of *ortho*-palladated derivatives of optically active N-donor ligands as resolving agents for Lewis bases has been convincingly demonstrated.[5] The optically pure cyclopalladated dinuclear compounds **3** and **4** were obtained from the optically active amines as reported.[6] Reaction of these dimers with the secondary phosphanes (±)-

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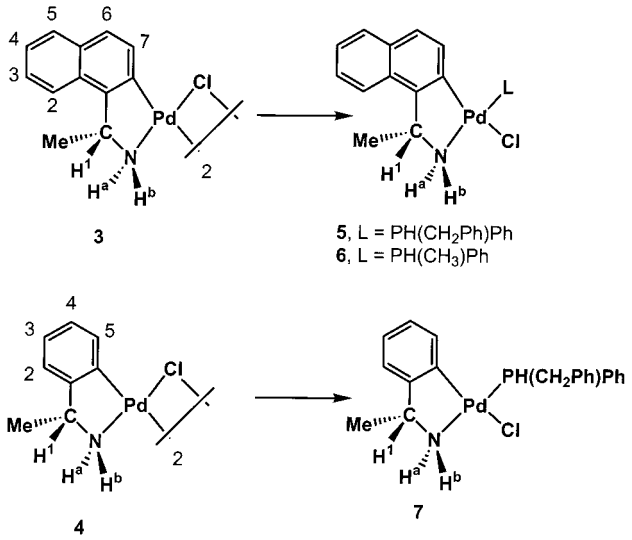
PHPhR afforded the mononuclear compounds [PdCl(C−N)(PHPhR)] (**5**, **6** and **7**), as a 1:1 mixture of the diastereomers (R_C,R_P) and (R_C,S_P) (Scheme 2). All the new organometallic compounds obtained were characterized by elemental analysis and IR, ^{1}H and ^{31}P NMR spectroscopy. In some cases, 2D NMR experiments (COSY and NOESY) were carried out to complete the characterization. The high-field shift of the aromatic protons of the palladated ring in the mononuclear derivatives, due to the aromatic rings of phosphanes, indicates the *cis* disposition of the phosphorus relative to the metallated carbon atom and the chemical shift in the ^{31}P NMR spectra confirms this arrangement.[7]

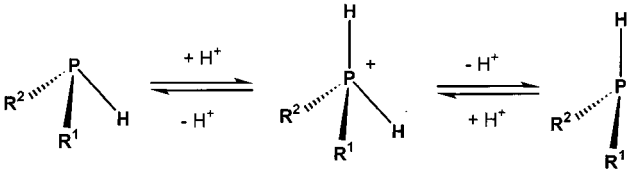


Scheme 2. L, 20 °C, $CHCl_3$ for **5** and **6** and THF for **7**

All attempts to separate the diastereomers of compounds **5**, **6** and **7** by recrystallization and all attempts to separate the diastereomers of **7** by column chromatography were unsuccessful. In contrast, the elution of compounds **5** and **6**, which contain the metallated (*R*)-(+)-1-(1-naphthyl)ethylamine, in a SiO_2 column (see Experimental Section) allowed the separation of the first diastereomer eluted **5′** and **6′**, in 45 and 63% yield, respectively (22.5 and 31.5% with respect to the total Pd), with a *de* higher than 95% in both cases [the superscripts (′) and (′′) indicate the first and the second diastereomer eluted in the column]. These results are consistent with previous reports since naphthyl adducts generally provide greater enantiomeric discrimination than their phenyl counterparts. It has been proposed that this is due to the fact that the methyl substituent of the chiral carbon atom adopts an axial disposition to avoid the unfavorable interaction with H^2 in the naphthyl adducts (see Scheme 2), and, in consequence, the five-membered metallacycle has a locked asymmetric envelope conformation. In contrast the methyl group is either axial or equatorial and this metallacycle adopts different conformations in 1-phenylethylamine derivatives.[8] The NOESY spectra of compounds **5** and **6** show that H^1 has strong negative off-diagonal peaks with H^2 and H^b and, in contrast, the methyl protons of the chiral carbon atom present only strong NOE interactions with H^a and H^1. These data confirm the axial disposition of this methyl group and the equatorial disposition of H^1 in both complexes.[9]

When a stoichiometric amount of 1,2-bis(diphenylphosphanyl)ethane was added to an ether solution of the optically pure cyclopalladated derivatives **5′** and **6′** the quantitative precipitation of the ionic compound [Pd(C−N)(dppe)]Cl took place and solutions of the enantiopure free phosphanes PHBzPh and PHMePh (^{31}P NMR : $\delta = -41.0$ or -71.7, respectively) in diethyl ether were obtained. No racemization of benzylphenylphosphane was observed when this ligand was stored in solution for 20 minutes, as verified by ^{31}P NMR spectroscopy, which showed the quantitative regeneration of the starting material **5′** from the dinuclear cyclopalladated derivative **3** and the corresponding free ligand. Three hours later significant racemization of the free phosphane was observed. In contrast, when this experiment was carried out with methylphenylphosphane, the formation of a ca. 1:1 mixture of diastereomers of **6** was observed in less than five minutes. The high configurational stability of PHBzPh is remarkable; it should be noted that an acetonitrile solution of menthylmesitylphosphane, the only secondary phosphane resolved until now, led to immediate epimerization at phosphorus in the absence of sodium acetylacetonate.[2]

Secondary phosphanes are difficult to obtain in an optically active form due to acid-catalyzed racemization, which involves the formation of an achiral phosphonium salt (see Scheme 3). In order to evaluate the tendency to protonation of the secondary phosphanes **1** and **2**, we analyzed the H/D exchange between the free phosphanes and D_2O in an NMR tube. A few drops of D_2O were added to THF solutions of the free secondary phosphanes **1** and **2** and ^{31}P NMR spectra were recorded (Figure 1). These spectra show that after 15 minutes a significant amount of PDMePh was formed, and after six hours PDMePh was the major compound. In contrast only a small amount of PDBzPh was formed after six hours. These findings suggest that the high configurational stability of PHBzPh is related to its stability against acid-catalyzed racemization, although the contribution to the racemization of other mechanisms cannot be ruled out.



Scheme 3. Acid-catalyzed racemization

The free secondary phosphanes described here are readily oxidizable and should be stored under nitrogen, although when coordinated to palladium (compounds **5** and **6**) they can be handled in air and are stable for several months. In consequence, these naphthyl cyclopalladated derivatives can also be used to store the phosphanes and to obtain them in free form when needed by reaction with dppe.

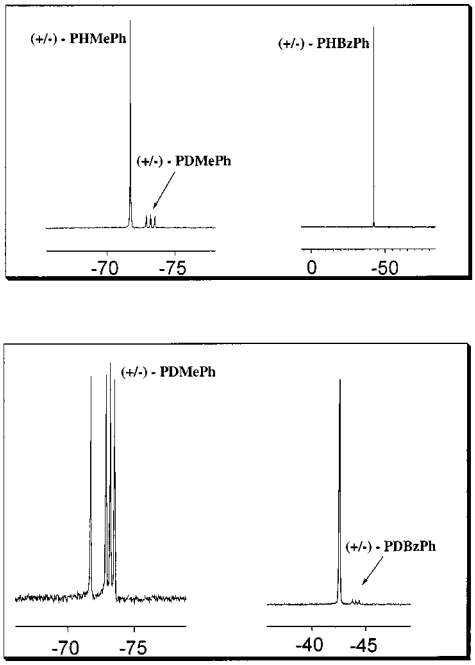


Figure 1. $^{31}P\{^{1}H\}$ NMR spectrum in THF solution of the free secondary phosphanes **1** and **2**: (a) five minutes after the addition of D_2O; (b) after six hours

Experimental Section

^{1}H NMR at 200 MHz or 500 MHz, and $^{31}P\{^{1}H\}$ at 101.26 MHz spectra were recorded on Varian Gemini 200, Varian VXR 500 and Bruker DRX 250 spectrometers, respectively. 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 $CDCl_3$ for ^{1}H NMR and THF or $CHCl_3$ for ^{31}P NMR. 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 phosphanes were carried out using Schlenk techniques under a nitrogen atmosphere. All solvents were dried and degassed by standard methods. Tetrahydrofuran and diethyl ether were distilled over sodium/benzophenone, under nitrogen, before use. All chemicals were of commercial grade and used as received. Cyclopalladated compounds **3** and **4**, and $PPhBz_2$ were prepared according to procedures described elsewhere.[6,10]

Synthesis of [PdCl{(*R*)−$C_{10}H_6CHMeNH_2$}{(±)-PHBzPh}] (5): Small pieces of lithium (86.0 mg, 12.4 mmol) were added to a solution of dibenzylphenylphosphane (1.5 g, 5.2 mmol) in THF (40 mL) and the reaction mixture was stirred for 16 hours at 20 °C. The unreacted lithium was removed by decantation, and then 0.5 mL of water was added and the mixture stirred for a further 10 min. The resulting solution was dried over anhydrous Na_2SO_4 and filtered off to obtain a THF solution of (±)-PHBzPh [^{31}P NMR (101.26 MHz, $CDCl_3$): δ = −41.0 (d, J_{H-P} = 205 Hz)]. This solution was slowly added to a suspension formed by 0.24 mmol of the corresponding cyclopalladated dimer **3** in $CHCl_3$ (30 mL) until complete dissolution of the precipitate. The resulting solution was concentrated in vacuo and the solid obtained was eluted by SiO_2 column chromatography with $CHCl_3$/acetone (100:4) as eluent. Compound **5** [ca. 1:1 mixture of the diastereomers (R_C,R_P) and (R_C,S_P)] was isolated as a yellow solid. The yield of the process was 65% (160 mg) relative to the cyclopalladated compound **3**. − $C_{25}H_{25}ClNPPd$ (512.31): calcd. C 58.61, H 4.91, N 2.73; found C 58.7, H 4.8, N 2.5. − ^{31}P NMR (101.26 MHz, $CDCl_3$): δ = 26.9 (d, J_{H-P} = 362 Hz), 25.2 (d, J_{H-P} = 367 Hz).

Separation of Diastereomers 5: The 1:1 mixture of the diastereomers (R_C,R_P)- and (R_C,S_P)-**5** (100 mg) was carefully eluted at room temperature on an SiO_2 column (30 × 400 mm, 50 g SiO_2) with $CHCl_3$/acetone (100:2) as eluent. Fractions of 15 mL were collected, concentrated in vacuo and checked by ^{1}H NMR spectroscopy. The fractions were selected using the aromatic or the methylic proton signals. The first diastereomer eluted, **5′**, was obtained in 45% yield (22.5 mg), with a *de* higher than 95%, and the second diastereomer, **5′′**, was obtained in 38% yield (19 mg), with 52% diastereomeric purity.

5′: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88 (m, 2 H, H_{ar}), 7.67 (d, J_{HH} = 7.5 Hz, 1 H, H_{ar}), 7.59 (d, J_{HH} = 8.0 Hz, 1 H, H_{ar}), 7.47 (m, 1 H, H_{ar}), 7.40−7.30 (m, 5 H, H_{ar}), 7.19−7.12 (m, 5 H, H_{ar}), 6.97 (t, J_{HH} = 9.0 Hz, 1 H, H^7), 5.23 (sextuplet, J_{HH} = 5.5 Hz, 1 H, H^1), 5.02 (dt, J_{HH} = 6 Hz, J_{PH} = 367 Hz, 1 H, *H*P), 4.04 (br s, 1 H, H_a), 3.92 (m, 1 H, CH_2P), 3.63 (m, 1 H, CH_2P), 3.46 (br s, 1 H, H_b), 1.84 (d, $^{3}J_{HH}$ = 6.5 Hz, 3 H, *Me*). − ^{31}P NMR ($CDCl_3$): δ = 25.2 (d, J_{H-P} = 367 Hz). − $[\alpha]_D^{20}$ = +62.4 (*c* = 204 mg/100 mL, in $CHCl_3$).

5′′: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72−7.60 (m, 4 H, H_{ar}), 7.40−7.13 (m, 10 H, H_{ar}), 6.85 (m, 2 H, H^6, H^7), 4.91 (dt, J_{HH} = 5.6 Hz, J_{PH} = 362 Hz, 1 H, *H*P), 5.25 (q, J_{HH} = 5.8 Hz, 1 H, H^1), 4.71 (br s, 1 H, H_a), 3.57 (m, 3 H, CH_2P, H_b), 1.82 (d, $^{3}J_{HH}$ = 6.2 Hz, 3 H, *Me*). − ^{31}P NMR ($CDCl_3$): δ = 26.9 (d, J_{H-P} = 362 Hz).

[PdCl{(*R*)-$C_6H_4CHMeNH_2$}{(±)-PHBzPh}] (7): To a suspension of **4** in THF (30 mL) as starting material, the synthesis of **7** was analogous to the preparation of **5**. Compound **7** [ca. 1:1 mixture of the diastereomers (R_C,R_P) and (R_C,S_P)] was isolated as a yellow solid. The yield of the process was 30% (70 mg).

7: $C_{21}H_{23}ClNPPd$ (462.25): calcd. C 54.57, H 5.02, N 3.03; found C 54.4, H 5.2, N 3.2. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.90−7.70 (m, 4 H, H_{ar}), 7.50−7.30 (m, 6 H, H_{ar}), 7.20−7.10 (m, 10 H, H_{ar}), 6.95−6.85, (m, 8 H, H_{ar}), 5.05 (d, J_{HP} = 360 Hz, 2 H, *HP*), 4.10−3.50 (m, 6 H, *NH*, CH_2), 3.30 (br m, 2 H, *NH*), 1.67 (d, J_{HH} = 6.5 Hz, 3 H, *Me*), 1.60 (d, J_{HH} = 6.5 Hz, 3 H, *Me*). − ^{31}P NMR (101.26 MHz, $CDCl_3$): δ = 29.4 (d, J_{HP} = 360 Hz), 27.7 (d, J_{HP} = 362 Hz).

Synthesis of [PdCl{(*R*)-$C_{10}H_6CHMeNH_2$}{(±)-PHMePh}], 6: Small pieces of lithium (37.0 mg, 5.37 mmol) were added to a solution of methyldiphenylphosphane (0.5 mL, 2.68 mmol) in THF (20 mL) and the reaction mixture was stirred for 16 hours at 20 °C. The unreacted lithium was removed by decantation, and then 0.5 mL of water was added and the mixture stirred for a further 10 min. The resulting solution was dried over anhydrous Na_2SO_4 and filtered to obtain a THF solution of (±)-PHMePh [^{31}P NMR (101.26 MHz, $CDCl_3$): δ = −71.7 (d, J_{H-P} = 203 Hz)]. This solution was slowly added to a suspension formed of **3** (150.0 mg, 0.24 mmol) in 30 mL of $CHCl_3$ until dissolution of the precipitate. The resulting solution was concentrated in vacuo and the solid obtained was eluted by SiO_2 column chromatography with $CHCl_3$/methanol (100:3) as eluent. Compound **6** [ca. 1:1 mixture of the diastereomers (R_C,R_P) and (R_C,S_P)] was isolated as a yellow solid

in 75% yield (160 mg). – $C_{19}H_{21}ClNPPd$ (436.21): calcd. C 52.31, H 4.85, N 3.21; found C 51.3, H 4.8, N 3.1. – ^{31}P NMR ($CDCl_3$): δ = −0.8 (d, J_{H-P} = 360 Hz); −1.2 (d, J_{H-P} = 364 Hz).

Separation of Diastereomers 6.: The 1:1 mixture of the diastereomers (R_C,R_P)- and (R_C,S_P)-**6** (100 mg) was carefully eluted at room temperature on a SiO_2 column (30 × 400 mm, 30 g SiO_2) with $CHCl_3$/acetone (100:6) as eluent. Fractions of 15 mL were collected, concentrated in vacuo and checked by ^1H NMR spectroscopy. The fractions were selected using the aromatic or the methylic proton signals. The first diastereomer eluted, **6′**, was obtained in 63% yield (31.5 mg), with a *de* higher than 95%, and the second diastereomer, **6′′**, was obtained in 15% yield (7.5 mg), with 86% diastereomeric purity.

6′: ^1H NMR ($CDCl_3$): δ = 8.00 (m, 2 H, H_{ar}), 7.70 (d, J_{HH} = 6.0 Hz, 1 H, H_{ar}), 7.63 (d, J_{HH} = 8.0 Hz, 1 H, H_{ar}), 7.49−7.32 (m, 7 H, H_{ar}), 7.07 (t, J_{HH} = 8.5 Hz, 1 H, H^7), 5.28 (dq, J_{HH} = 6.0 Hz, J_{HP} = 364 Hz, 1 H, *HP*), 5.26 (sextuplet, J_{HH} = 5.5 Hz, 1 H, H^1), 4.10 (br s, 1 H, H_a), 3.46 (br s, 1 H, H_b), 1.99 (dd, J_{HH} = 6.0 Hz, J_{PH} = 11.5 Hz, 3 H, *Me*P), 1.88 (d, $^3J_{HH}$ = 6.5 Hz, 3 H, *Me*). – ^{31}P NMR ($CDCl_3$): δ = −1.2 (d, J_{H-P} = 364 Hz).

6′′: ^1H NMR ($CDCl_3$): δ = 7.75−7.60 (m, 4 H, H_{ar}), 7.43−7.20 (m, 7 H, H_{ar}), 5.07 (dq, J_{HH} = 6.0 Hz, J_{HP} = 360 Hz, 1 H, *HP*), 5.28 (sextuplet, J_{HH} = 6.2 Hz, 1 H, H^1), 4.93 (br s, 1 H, H_a), 3.45 (br s, 1 H, H_b), 1.84 (d, $^3J_{HH}$ = 6.5 Hz, 3 H, *Me*), 1.50 (dd, J_{HH} = 6.1 Hz, J_{HP} = 11.4 Hz, 3 H, *MeP*). – ^{31}P NMR ($CDCl_3$): δ = −0.8 (d, J_{H-P} = 360 Hz).

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