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Optically active cyclopalladated compounds containing P-chiral ligands. Restricted rotation around the Pd–P bond

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Dedicated to Professor Rafael Uson on the occasion of his 75th birthday

Abstract

The synthesis of the optically active complexes [PdCl($C_{10}H_6$CHMeNMe$_2$)L] (L = PPh_3, PBn_2Ph, PHBnPh and PBnCyPh) and the resolution of the secondary phosphine PHBnPh is reported. The study of the NMR data of these mononuclear compounds shows that in some of these complexes the rotation around the Pd–P bond is restricted. A relationship between the δ values of the aromatic proton adjacent to the Pd–C bond and the conformation of the Pd–phosphine fragment can be found and NMR data permit the assignment of the absolute configuration of the phosphine in [PdCl($C_{10}H_6$CHMeNMe$_2$)(PBnCyPh)]. Several molecular mechanics geometry optimizations were performed using the MMFF94 force field to estimate the height of the energy barrier corresponding to the rotation of the phosphine ligands around the Pd–P bond. These calculations show the rotation around the Pd–P bond to be restricted, if the phosphine contains at least one benzylic group, and agree with the results obtained in solution by means of mono- and bi-dimensional NMR. © 2001 Published by Elsevier Science B.V.

Keywords: P-chiral; Palladium; Metallacycles; Restricted rotation; Resolution

1. Introduction

Enantiomerically pure cyclopalladated compounds are of great interest as a consequence of their useful applications in many areas including the determination of enantiomeric excess [1] and absolute configuration of chiral compounds [2], the asymmetric synthesis of optically active organic molecules [3], and the optical resolution of Lewis bases [4]. *ortho*-Palladated derivatives of the tertiary amines *N*,*N*-dimethyl-1-(1-naphthyl)ethylamine and *N*,*N*-dimethyl-α-methylbenzylamine have been used in nearly all the stereochemical applications of such compounds. Only in the last few years, however, has the application of some new cyclometallated compounds in these fields been explored [1b,c,5]. In this paper we describe the reaction between (R_C)-[PdCl($C_{10}H_6$CHMeNMe$_2$)]$_2$, the chiral cyclopalladated compound most extensively used for the resolution of Lewis bases, and monodentate phosphines to afford the mononuclear derivatives [PdCl($C_{10}H_6$CHMeNMe$_2$)L], L = PPh_3, PBn_2Ph, PHBnPh and PBnCyPh. The study of the NMR data of these compounds shows the existence of a relationship between the δ values of the aromatic proton adjacent to the Pd–C bond and the conformation of the Pd–phosphine fragment in these complexes and permits the assignment of the absolute configuration of the phosphine in [PdCl($C_{10}H_6$CHMeNMe$_2$)(PBnCyPh)].

Due to the reactivity of their P–H bonds, secondary phosphines are versatile synthons for the preparation of chiral mono- and bidentate ligands [6]. However, as a consequence of their low configurational stability, only two secondary phosphine chiral at phosphorus have been resolved to date [7]. The low configurational stability of P-chiral secondary phosphines has been explained by the acid catalyzed racemization, where the protonation of secondary phosphines affords achiral phosphonium ions, with two enantiotopic protons that can be removed at identical rates. When the phosphine is attached to metal ions, borane or chalcogens by means of the lone pair, the racemization does not occur

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and some diastereomers containing coordinated secondary phosphines have been separated [8,9]. In a very few cases [7], however, the recovery of the free optically pure ligand has been accomplished. Here, we report the synthesis and separation of the two diastereomers of compound (R_C,R_P)- and (R_C,S_P)-[PdCl($C_{10}H_6$CHMeNMe$_2$)(PHBnPh)], and the isolation of the free secondary optically pure phosphine, by the action of 1,2-bis(diphenylphosphino)ethane (dppe) on this cyclopalladated derivative.

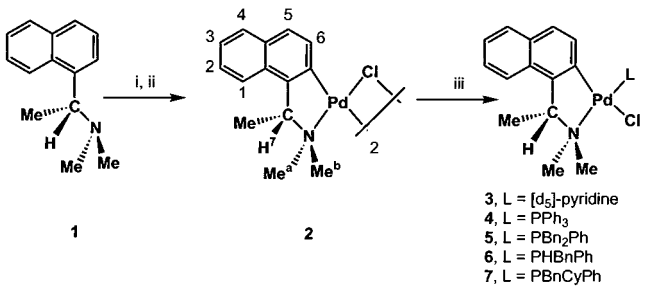
2. Results and discussion

2.1. Synthesis of the compounds

(R_C)-[PdCl($C_{10}H_6$CHMeNMe$_2$)]$_2$ was obtained by reaction between the tertiary amine and palladium acetate in acetic acid for 4 h at 60 °C [10]. Subsequent treatment of the reaction residue with LiCl in ethanol afforded, after purification by SiO_2 column chromatography, the corresponding chloro-bridged cyclopalladated dimer **2** in 80% yield. The ^{1}H-NMR spectrum of **2** was recorded in the presence of an excess of deuterated pyridine, which affords the mononuclear derivative (R_C)-[PdCl($C_{10}H_6$CHMeNMe$_2$)(py-d_5)]. The aromatic proton adjacent to the Pd–C bond appears high-field shifted at $\delta = 6.21$. This is due to the pyridine ring and shows that this ligand is located in *cis* position relative to the palladated carbon [11].

Reaction of dimers **2** with the phosphines PPh_3 and PBn_2Ph afforded the mononuclear complexes (R_C)-[PdCl(C–N)L] (**4**, L = PPh_3; **5**, L = PBn_2Ph). When this reaction was performed with the racemic PHBnPh or with the coordination compound dichlorobis[(±)-benzylcyclohexylphenylphosphine]nickel(II), the mononuclear complexes [PdCl(C–N)L] were obtained as a 1:1 mixture of diastereomers (R_C,R_P)- and (R_C,S_P)-**6** and (R_C,R_P)- and (R_C,S_P)-**7** (see Scheme 1).

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.



Scheme 1. (i) $Pd(AcO)_2$/AcOH, 60 °C, 4 h; (ii) LiCl, acetone, room temperature, 30 min; (iii) L, $CHCl_3$ or THF, room temperature.

NMR data of the new complexes show the *cis* disposition of phosphorus relative to the metallated carbon. This arrangement is very usual in cyclopalladated derivatives [11,12] and it is explained by the destabilizing effect of two soft ligands in mutual *trans* positions [13]. Recently, the term *transphobia* has been proposed to describe the difficulty of coordinating mutually *trans* phosphine and aryl ligands in palladium complexes [14].

Cyclopalladated naphthyl adducts generally provide greater enantiomeric discrimination than their phenyl counterparts. This may be due to the fact that the methyl substituent of the chiral carbon atom adopts an axial disposition to avoid the unfavorable interaction with H^1 in the naphthyl adducts (see Scheme 1) and, in consequence, the five-membered metallacycle has a locked asymmetric envelop conformation [15]. The NOESY spectra of all the mononuclear complexes show that H^7 has a strong negative off-diagonal peaks with H^1 and Me^b. On the other hand, the methyl protons of the chiral carbon atom present strong NOE interaction only with Me^a and H^7. These data confirm the axial disposition of this methyl group and the equatorial disposition of H^7 in compounds **4**–**7** [16].

2.2. Separation of diastereomers

Satisfactory separation of diastereomers **7**, containing the P-chiral tertiary phosphine, was not accomplished and only partially enriched mixtures were obtained by column chromatography. Better results were obtained with diastereomers **6**, which contain the P-chiral secondary phosphine. The elution of these diastereomers in a SiO_2 column (see Section 3) allowed the separation of the first diastereomer eluted **6′**, in 55% yield, with a *d.e.* higher than 95% {the superscripts (′) and (″) indicate the first and the second diastereomer eluted in the column, respectively}. When a stoichiometric amount of 1,2-bis(diphenylphosphino)ethane was added to a solution of the optically pure cyclopalladated derivatives **6′** in diethylether, the quantitative precipitation of the ionic compound [Pd(C–N)(dppe)]Cl took place and a solution of enantiopure free phosphine PHBnPh (RMN ^{31}P: $\delta = -41.0$, d, $J_{H-P} = 205$ Hz) was obtained. No racemization of benzylphenylphosphine was observed when this ligand was stored in solution for 20 min, as verified by ^{31}P-NMR spectroscopy, which showed the quantitative regeneration of the starting material **6′** from the dinuclear cyclopalladated derivative **2** and the corresponding free ligand. Three hours later significant racemization of the free phosphine was observed. The high configurational stability of PHBnPh is remarkable given that an acetonitrile solution of menthylmesitylphosphine led to immediate epimerization at phosphorus in the absence of sodium acetylacetonate [7a].

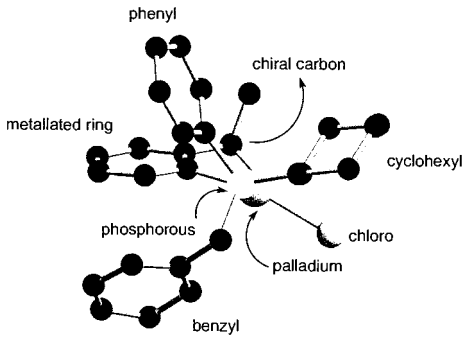


Fig. 1. Structure of the compound (R_C,S_P)-[PdCl($C_6H_4CHMeNMe_2$)-(PBnCyPh)].

It should be noted that the results reported here, combined with previous work of our group [5a,7c], show that compound **2**, (R_C)-[PdCl($C_{10}H_6CHMeNMe_2$)]$_2$, is a better resolution agent for secondary phosphine PHBnPh than the analogous cyclopalladated derivative of the primary amine (R_C)-[PdCl($C_{10}H_6CHMeNH_2$)]$_2$. However, this latter compound is a better resolution agent for the tertiary phosphine PBnCyPh. In conclusion, it is not easy to predict the best resolution agent that can be used for a specific chiral ligand and it is important to have a wide range of resolution agents to use in every case.

2.3. Restricted rotation around the Pd–P bond

The signal of the aromatic proton adjacent to the Pd–C bond (H^6) in the NMR spectra of complexes [PdX(C–N)L] is strongly dependent on the ligand in *cis* position and appears high-field shifted if this ligand has aryl substituents. Statistical considerations lead to a prediction that the sequence triarylphosphines < diarylphosphines < monoarylphosphines should be followed for the δ values of H^6, in compounds with free rotation around Pd–P bonds. Recently, it has been shown that the rotation around the Pd–P bond is restricted in the cyclopalladated complexes containing the monodentate P-chiral ligands *tert*-butylphenyl(4-bromophenyl)phosphine [5f] and benzylisopropylphenylphosphine [17]. It has also been shown that it is possible to assign the absolute configuration of these monodentate phosphines by NMR techniques using the homochiral palladacycle as a reference point.

In the proton NMR spectra of diastereomers **7**, the signal assigned to H^6 appears at $\delta = 5.44$ in **7′** and at $\delta = 6.46$ in **7″**. Following the same model used to assign the absolute configuration of benzylisopropylphenylphosphine in the two diastereomers (R_C,R_P)- and (R_C,S_P)-PdCl($C_{10}H_6CHMeNH_2$)(PBn^{i}PrPh)] [17] it is possible to explain the great difference of δ values in the diastereomers **7** and it is even possible to assign the absolute configuration of the phosphine in these complexes. The δ values in the NMR spectra of the two diastereomers of **7** can be explained assuming that, in both diastereomers, the rotation around Pd–P in these complexes is restricted and that the benzyl group of the phosphine is widely separated from the metallacycle and is located on the opposite side of the coordination plane in relation to the methyl group of the chiral carbon atom [18]. Thus, the most significant difference between these diastereomers is the relative position of the cyclohexyl and phenyl groups. In one diastereomer, the phenyl group is nearer to the metallated ring. Consequently, the signal assigned to H^6 appears at higher fields than in the other diastereomer, where the cyclohexyl group is near the metallacycle (Fig. 1 shows the structure of the compound (R_C,S_P)-[PdCl($C_6H_4CHMeNMe_2$)(PBnCyPh)], see Ref. [5a]). The NOESY spectra also confirmed this, because there was a NOE interaction between H^6 and the *ortho*-aromatic proton of the phenyl group of the phosphine ($\delta = 7.30$ ppm) in diastereomer **7′** and, in contrast, there was NOE interaction between H^6 and one aliphatic proton of the cyclohexyl group ($\delta = 2.20$ ppm) in the diastereomer **7″**. In conclusion, **7′**, the first diastereomer eluted, has the absolute configuration (R_C,S_P) and **7″** is the (R_C,R_P)-diastereomer. The addition of dppe to a partially enriched mixture of the diastereomers **7** and the subsequent reaction of the free phosphine formed with the cyclopalladated compound (R_C)-[PdCl($C_6H_4CHMeNMe_2$)Cl]$_2$ permitted the determination of the absolute configuration of the phosphine on each of the diastereomers by ^{31}P- or ^1H-NMR [5a] and confirmed the assignment.

In compound **5**, which contains the PBn_2Ph ligand, the signal assigned to H^6 appeared high-field shifted in relation to **4**, which contains the PPh_3 ligand. This fact suggests that the rotation around the Pd–P bond is rather restricted in **5** and that conformations where the phenyl group of the phosphine is near the metallated ring have an important contribution. The NOE spectrum showed that H^6 has NOE interaction with the *ortho*-aromatic protons of the phenyl group of the phosphine ($\delta = 7.42$ ppm). Besides this, a NOE interaction was observed between H^6 and only one of the four CH_2P protons of the phosphine ($\delta = 3.40$ ppm), in agreement with the restricted rotation around the Pd–P bond in this complex.

Finally, the δ values of H^6 are very similar in the two diastereomers of **6**, which contain the PHBnPh ligand, and are low-field shifted in relation to **4**, suggesting that conformations in which the H atom of the phosphine is near the metallated ring have an important contribution. In agreement, the NOE spectra show that H^6 have only NOE interaction with the H–P proton in these complexes.

In order to estimate the height of the energy barrier corresponding to the rotation of the phosphine ligand

around the Pd–P bond, a coordinated driving study was undertaken, based on the molecular mechanics methodology. The phosphorus–palladium bond was rotated in nine-degree steps, while the remaining set of geometric parameters was optimized. The results obtained are shown in Fig. 2. This figure shows that the higher values of energy are found when one of the groups R of the phosphine lies within the coordination plane eclipsing the metallated carbon atom (θ values of 30, 150 and 270°). The height of the rotation barrier, taken as the difference between the minimum and the maximum energy systems, is 17.4 and 16.3 kcal mol^{-1} for Pd–PBn$_2$Ph and Pd–PBnCyPh bonds in compounds **5** and **7**, respectively. This value is too high to allow a free rotation of the phosphine at room temperature. In compound **6**, which contains the secondary phosphine coordinated, the rotation barrier for the Pd–P bond is 12.8 kcal mol^{-1}, a higher value than is expected for a secondary phosphine. The sterical hindrance between the CH_2Ph protons and the naphthyl group seems to be one of the main factors for the high rotational barrier in all these compounds. This has been confirmed by the calculations performed on compound **4**, which contains coordinated PPh_3. The rotational barrier for the Pd–P bond in this complex is 9.5 kcal mol^{-1}, showing that there is almost free rotation around the Pd–P bond in the PPh_3 derivative. In conclusion, the calculations show that the Pd–P bond is rather restricted, if the phosphine contains at least one benzylic group, and agree with the results obtained in solution by means of mono- and bi-dimensional NMR.

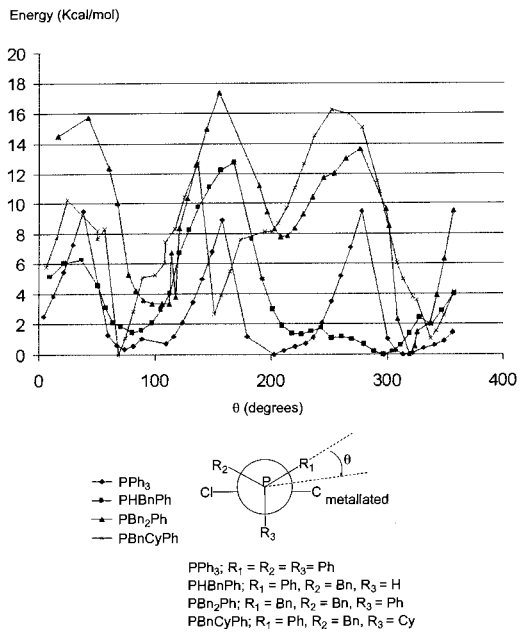


Fig. 2. Energy of [PdCl(C–N)L] (L = PPh_3, PHBnPh, PBn_2Ph and PBnCyPh) derivatives.

3. Experimental

^{1}H-NMR at 200 MHz were recorded in a Varian Gemini 200 spectrometer and ^{1}H-NMR at 500 MHz, ^{13}C at 75.42 and ^{31}P{^{1}H} at 101.26 MHz were recorded, respectively, in a Varian VXR 500, a Varian 300 and a 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. Microanalyses were performed at the Institut de Química Bio-Orgànica de Barcelona and the Serveis Científico-Tècnics de la Universitat de Barcelona. Infrared spectra were recorded as KBr disks in a Nicolet 520 FTIR spectrometer. The optical rotations of the complexes (c = g/100 ml, in $CHCl_3$) were determined at 20 °C using a Perkin–Elmer 241-MC polarimeter. Mass spectra were recorded in a Fisons VG-Quattro spectrometer. The samples were introduced in a matrix of 2-nitrobenzylalcohol for FAB analysis and then subjected to bombardment with cesium atoms.

3.1. 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 and toluene were distilled over sodium-benzophenone, under nitrogen, before use. All chemicals were of commercial grade and used as received. PBnCyPh and PHBnPh were prepared according to procedures described elsewhere [5a,7c]. The cyclopalladation of (*R*)-*N*,*N*-dimethyl-1-(1-naphthyl)ethylamine has been previously reported [10].

3.1.1. Cyclometallation of (R)-N,N-dimethyl-1-(1-naphthyl)ethylamine with palladium acetate in acetic acid

Palladium acetate (2.23 mmol, 500 mg) was added to (*R*)-*N*,*N*-dimethyl-1-(1-naphthyl)ethylamine (2.23 mmol, 440 mg) in AcOH (30 ml) and the reaction mixture was stirred for 4 h at 60 °C, under nitrogen. The resulting solution was concentrated to dryness in vacuo. The residue obtained was dissolved in Me_2CO (20 ml) and was treated with an excess of LiCl (3.5 mmol, 150 mg) for 30 min at room temperature (r.t.). Water (50 ml) was added to the resulting solution and the mixture was stirred for 5 min. The precipitate formed was filtered, washed with ether and purified by column chromatography over SiO_2, with $CHCl_3$–Me_2CO (100:1) as eluent to obtain **2** in 80% yield (605 mg). Characterization data: **2** + [d_5]-pyridine, RMN-^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 7.71$ (d, 1H, aromatic, $J_{HH} = 7.8$ Hz); 7.62 (d, 1H, aromatic, $J_{HH} = 7.2$ Hz), 7.42–7.28 (m, 3H, aromatic); 6.21 (d, 1H, H^6, $J_{HH} = 8.4$ Hz); 4.20 (q, 1H, H^7, $J_{HH} = 6.6$ Hz); 2.90 (s, 6H, Me^a, Me^b), 1.92 (d, 3H, MeCH, $J_{HH} = 6.6$ Hz).

3.1.2. Synthesis of [PdCl($C_{10}H_6CHMeNMe_2$)(PPh_3)] (4)

A stirred suspension of **2** (0.15 mmol, 100 mg) in Me_2CO (30 ml) was treated with PPh_3 (0.3 mmol, 80 mg) for 30 min at r.t. and then filtered. The filtrate was concentrated in vacuo and the solid obtained after addition of ether was recrystallized from $CHCl_3$–ether to obtain compound **4** in 90% yield (160 mg). Characterization data: $^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$): $\delta = 40.8$ (s). Anal. Found: C, 63.6; H, 5.4; N, 2.2. Calc. for $C_{32}H_{31}ClNPPd$: C, 63.80; H, 5.19; N, 2.33%. $[\alpha]_D^{20} = -59.4°\ cm^{-2}\ g^{-1}$, $c = 0.5$. ^1H-NMR (200 MHz, $CDCl_3$): $\delta = 7.76$–7.66 (m, 6H, H^1, aromatic); 7.59–7.54 (d, 1H, H^4, $J_{HH} = 8.5$ Hz); 7.50–7.26 (m, 12H, aromatic); 6.84 (d, 1H, H^5, $J_{HH} = 8.5$ Hz); 6.55 (dd, 1H, H^6, $J_{HH} = 8.5$ Hz, $J_{HP} = 6.2$ Hz); 4.34 (q, 1H, H^7, $J_{HH} = 6.2$ Hz); 2.94 (d, 3H, Me^a, $J_{HH} = 3.2$ Hz); 2.72 (s, 3H, Me^b); 2.04 (d, 3H, $MeCH$, $J_{HH} = 6.2$ Hz).

3.1.3. Synthesis of [PdCl($C_{10}H_6CHMeNMe_2$)(PBn_2Ph)] (5)

A stirred suspension of **2** (0.44 mmol, 300 mg) in THF (30 ml) was treated with dibenzylphenylphosphine (0.88 mmol, 270 mg) for 2 h at r.t. under nitrogen. The resulting solution was concentrated in vacuo and the solid obtained was eluted by SiO_2 column chromatography with $CHCl_3$–Me_2CO (100:3.5) as eluent to obtain **5** in 30% yield (165 mg). Characterization data: $^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$): $\delta = 38.7$ (s). Anal. Found: C, 64.4; H, 5.6; N, 2.3. Calc. for $C_{34}H_{35}ClNPPd$: C, 64.77; H, 5.60; N, 2.22%. $[\alpha]_D^{20} = +20.2°\ cm^{-2}\ g^{-1}$, $c = 0.5$. MS-Positive FAB: 594 ($[M-Cl]^+$). ^1H-NMR (200 MHz, $CDCl_3$): $\delta = 7.60$–7.47 (m, 3H, H^1, *ortho*-$C_6H_5CH_2$); 7.42–7.26 (m, 6H, aromatic); 7.18–6.95 (m, 10H, *ortho*-$C_6H_5CH_2$, aromatic); 6.67 (d, 1H, H^5, $J_{HH} = 8.4$ Hz); 5.80 (dd, 1H, H^6, $J_{HH} = 8.2$ Hz, $J_{HP} = 6.0$ Hz); 4.23–4.06 (m, 2H, H^7, CH_2P); 3.89 (dd, 1H, CH_2P, $J_{HH} = 10.8$ Hz, $J_{HH} = 13.4$ Hz); 3.61 (t, 1H, CH_2P, $J_{HH} = J_{HP} = 12.4$ Hz); 3.40 (t, 1H, CH_2P, $J_{HH} = J_{HP} = 10.8$ Hz); 2.95 (d, 3H, Me^a, $J_{HP} = 3.6$ Hz); 2.62 (d, 3H, Me^b, $J_{HP} = 1.4$ Hz), 1.81 (d, 3H, $MeCH$, $J_{HH} = 6.4$ Hz).

3.1.4. Synthesis of [PdCl($C_{10}H_6CHMeNMe_2$)(PHBnPh)] (6)

A stirred suspension of **2** (0.44 mmol, 300 mg) in THF (30 ml) was treated with benzylphenylphosphine (0.88 mmol, 176 mg) for 30 min at r.t. under nitrogen. The resulting solution was concentrated in vacuo and the solid obtained was recrystallized from Me_2CO to obtain **6**, as a 1:1 mixture of diastereomers in 95% yield (450 mg). Characterization data: Anal. Found: C, 60.0; H, 5.5; N, 2.7. Calc. for $C_{27}H_{29}ClNPPd$: C, 60.02; H, 5.41; N, 2.59%.

3.1.5. Separation of diastereomers 6

Compound **6** (300 mg) (1:1 mixture of diastereomers) was carefully eluted at r.t., in a SiO_2 column (50 g SiO_2) with $CHCl_3$–Me_2CO (100:3) as eluent. The fractions eluted (15 ml) were concentrated in vacuo and checked by ^1H-NMR spectroscopy using the methinic proton signals at $\delta = 5.3$–5.0 ppm. The fractions of the first diastereomer eluted were recrystallized in Me_2CO to obtain **6′** in 55% yield (80 mg), with a *d.e.* higher than 95%. Characterization data: $^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$): $\delta = 25.2$ s. ^1H-NMR (500 MHz, $CDCl_3$): $\delta = 7.98$–7.94 (m, 2H, aromatic); 7.70 (m, 2H, H^1, aromatic); 7.65 (d, 1H, aromatic, $J_{HH} = 8.5$ Hz); 7.50 (td, 1H, aromatic, $J_{HH} = 7.5$ Hz, $J_{HH} = 2.0$ Hz); 7.42 (m, 2H, aromatic); 7.38 (td, 1H, aromatic, $J_{HH} = 7.75$ Hz, $J_{HH} = 1.5$ Hz); 7.32 (m, 2H, aromatic); 7.22–7.14 (m, 4H, *ortho*-$C_6H_5CH_2$, aromatic); 6.96 (dd, 1H, H^6, $J_{HH} = 9.7$ Hz, $J_{HP} = 8.7$ Hz); 5.00 (dt, 1H, HP, $J_{HH} = 7.0$ Hz, $J_{HP} = 367$ Hz); 4.28 (q, 1H, H^7, $J_{HH} = J_{HP} = 6.5$ Hz); 3.95 (ddd, 1H, CH_2P, $J_{HH} = 7.0$ Hz, $J_{HP} = 7.5$ Hz, $J_{HH} = 14.0$ Hz); 3.62 (td, 1H, CH_2P, $J_{HH} = 7.0$ Hz, $J_{HH} = 14.0$ Hz, $J_{HP} = 14.0$ Hz); 2.93 (d, 3H, Me^a, $J_{HP} = 3.5$ Hz); 2.66 (d, 3H, Me^b, $J_{HP} = 1.5$ Hz); 1.76 (d, 3H, MeCH, $J_{HH} = 6.5$ Hz). The second diastereomer eluted was obtained in 25% yield with 52% of diastereomeric purity. Characterization data: $^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$): $\delta = 28.6$ s. ^1H-NMR (200 MHz, $CDCl_3$): $\delta = 7.98$ (dd, 1H, aromatic); 7.82–7.64 (m, 5H, H^1, aromatic); 7.51–7.20 (m, 9H, *ortho*-$C_6H_5CH_2$, aromatic); 7.08 (t, 1H, H^6, $J_{HP} = J_{HH} = 9.2$ Hz); 5.22 (dt, 1H, HP, $J_{HP} = 363$ Hz; $J_{HH} = 6.6$ Hz); 4.31 (q, 1H, H^7, $J_{HH} = J_{HP} = 6.2$ Hz); 4.02 (ddd, 1H, CH_2P, $J_{HH} = 7.0$ Hz, $J_{HP} = 7.6$ Hz, $J_{HH} = 13.7$ Hz); 3.66 (td, 1H, CH_2P, $J_{HH} = 7.0$ Hz, $J_{HH} = 13.7$ Hz, $J_{HP} = 13.7$ Hz); 2.95 (d, 3H, Me^a, $J_{HP} = 3.2$ Hz); 2.70 (s, 3H, Me^b); 1.81 (d, 3H, $MeCH$, $J_{HH} = 6.2$ Hz).

3.1.6. Synthesis of [PdCl($C_{10}H_6CHMeNMe_2$)(PBnCyPh)] (7)

A suspension formed by 0.32 mmol (200 mg) of **2**, 0.32 mmol (197 mg) of [$NiCl_2${PBnPh(*i*-Pr)}$_2$] and 30 ml of $CHCl_3$ was stirred at r.t. for 30 min and the resulting solution was concentrated in vacuo. The solid obtained was eluted by SiO_2 column chromatography with $CHCl_3$–Me_2CO (100:4) as eluent. Compound **7** (1:1 mixture of diastereomers) was isolated as a yellow solid in 85% yield (525 mg). Characterization data: Anal. Found: C, 63.4; H, 6.4; N, 2.3. Calc. for $C_{33}H_{39}ClNPPd$: C, 63.67; H, 6.31; N, 2.25%. MS-Positive FAB: 586 ($[M-Cl]^+$).

First diastereomer eluted, ($R_{C,}S_P$)-[PdCl($C_{10}H_6$-$CHMeNMe_2$)(PBnCyPh)] characterization data: $^{31}P\{^1H\}$-NMR (101.26 MHz, $CDCl_3$): $\delta = 49.6$ s. ^1H-NMR (500 MHz, $CDCl_3$): $\delta = 7.83$ (m, 2H, aromatic); 7.60 (d, 1H, H^1, $J_{HH} = 8.5$ Hz); 7.46–7.40 (m, 3H, aromatic, *ortho*-$C_6H_5CH_2$); 7.37–7.28 (m, 3H, aro-

matic); 7.22–7.17 (m, 2H, aromatic); 7.12 (t, 2H, aromatic, $J_{HH} = 7.5$ Hz); 7.06–7.02 (m, 1H, aromatic); 6.48 (d, 1H, H^5, $J_{HH} = 9.0$ Hz); 5.44 (dd, 1H, H^6, $J_{HH} = 9.0$ Hz, $J_{HP} = 5.5$ Hz); 4.21 (q, 1H, H^7, $J_{HH} = J_{HP} = 6.5$ Hz); 3.87–3.76 (m, 2H, CH_2P); 2.94 (d, 3H, Me^a, $J_{HP} = 3.5$ Hz); 2.91–2.64 (m, 2H, aliphatic); 2.57 (d, 3H, Me^b, $J_{HP} = 1.5$ Hz); 2.01 (d, 3H, MeCH, $J_{HH} = 6.5$ Hz); 1.96–0.55 (m, 9H, aliphatic).

Second diastereomer eluted, (R_C,R_P)-[PdCl($C_{10}H_6$-CHMeNMe$_2$)(PBnCyPh)] characterization data: ^{31}P{^{1}H}-NMR (101.26 MHz, $CDCl_3$): $\delta = 38.8$ s. ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 7.65$ (d, 1H, H^1, $J_{HH} = 8.5$ Hz); 7.57 (d, 1H, aromatic, $J_{HH} = 8.0$ Hz); 7.37–7.33 (m, 3H, aromatic); 7.30–7.26 (m, 2H, aromatic); 7.14 (t, 2H, aromatic, $J_{HH} = J_{HH} = 7.5$ Hz); 7.11–7.05 (m, 5H, *ortho*-$C_6H_5CH_2$, aromatic); 6.91 (d, 1H, H^5, $J_{HH} = 8.5$ Hz); 6.46 (dd, 1H, H^6, $J_{HH} = 8.5$ Hz, $J_{HP} = 5.0$ Hz); 4.27 (q, 1H, H^7, $J_{HH} = J_{HP} = 6.0$ Hz); 3.94 (m, 1H, CH_2P); 3.53 (m, 1H, CH_2P); 2.94 (d, 3H, Me^a, $J_{HP} = 3.5$ Hz); 2.64 (d, 3H, Me^b, $J_{HP} = 1.5$ Hz); 2.44–2.08 (m, 3H, aliphatic); 1.95 (d, 3H, MeCH, $J_{HH} = 6.5$ Hz); 1.84–1.19 (m, 8H, aliphatic).

3.2. Computational details

All the calculations were performed with the SPARTAN 5.1 suite of programs [19]. The molecular mechanics geometry optimizations were carried out using the MMFF94 force fields [20] with the parameters supplied by the program. Single point DFT calculations were done using the BP86 functional [21], with the numerical basis set labeled as DN* in the program, which includes polarization for all atoms except hydrogen.

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