An Approach to the Synthesis of Platinum Complexes Containing Chiral Monodentate Phosphines with Simultaneous Regeneration of the Resolving Agent

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Summary: Elution of compounds [PdCl{3-ClC$_6$H$_3$-CH=NCH(Me)Ph}{trans-2-PPh$_2$(CyOH)}] ***5a*** *and [PdX{C$_6$H$_4$CH(Me)NH$_2$}{Ph$_2$PCH(OMe)Ph}]* ***6b****, containing the racemic phosphines as ligands, through a SiO$_2$ column allows the separation of the two diastereoisomers. Optically active coordination complexes trans-[PtCl$_2${Ph$_2$PCH(OMe)Ph}$_2$] and trans-[PtCl$_2${Ph$_2$PCH(OMe)Ph}(PPh$_3$)], have been obtained by ligand transfer reactions between* ***6b*** *and PtCl$_2$ or trans-[PtCl(μ-Cl)(PPh$_3$)]$_2$, respectively. The dinuclear cyclopalladated resolving agent can be separated from the platinum compounds and used in a new resolution process.*

The resolution of racemic phosphines is an area of considerable current interest because chiral phosphines[1] are extensively used in a wide range of enantioselective transition-metal catalytic processes.[2] Cyclopalladated complexes have been successfully used for the resolution of bidentate P−E ligands, (E = P, N, As, S...)[3] and monodentate phosphines,[4] through recrystallization or column chromatography purification of the diastereomeric transition metal complexes [PdX(C−N)L] or [Pd(C−N)L$_2$]$^+$ and subsequent decoordination of the phosphine. Unfortunately, nearly all the examples described so far for the separation of phosphine ligands using these methods result in palladacycle degradation. Only very recently a sequence of reactions has been described that allows the regeneration of the resolving agent.[4e]

As a rule, the separation of the diastereoisomers containing cyclopalladated units is based on the solubility difference. In only a few cases the separation has been accomplished by column chromatography. Yoneda *et al.*[5] have described the resolution of palladium complexes containing a Pd−C*(sp^3) bond by column chromatography (150 cm high), and recently Dunina *et al.*[4d] have described the purification of two diastereoisomers containing *tert*-butylmethylphenylphosphine by using several flash columns.

In this paper we describe the resolution of functionalized monodentate phosphines using a single column chromatography of the corresponding diastereomeric cyclopalladated derivatives [PdCl(C−N)L] and the synthesis of optically active platinum coordination compounds with simultaneous regeneration of the resolution agent.

Results and Discussion

The homochiral complexes (*R*)-[PdX{3-ClC$_6$H$_3$CH=NCH(Me)Ph}]$_2$ (X = Cl or Br) and (*R*)-[PdX{C$_6$H$_4$CH(Me)NH$_2$}]$_2$ (X = Cl or Br) were obtained from the corresponding optically active imine or amine, by reaction with palladium acetate and subsequent treatment with LiX of the acetato dimer compounds.[6] Reaction of dimers **2** and **3** with the monodentate phosphines L afforded the mononuclear derivatives [PdX(C-N)L], L = PPh$_3$, *trans*-2-PPh$_2$(CyOH) or Ph$_2$PCH(OMe)Ph (see Scheme 1).[7]

All the new compounds obtained were characterized by elemental analysis, IR spectra, and ^{1}H and ^{31}P NMR spectra. In some cases, COSY experiments were undertaken to complete the NMR studies. The crystal structure of **4a** has been determined (Figure 1) and crystallographic data are listed in Table 1.

The crystal structure consists of discrete molecules separated by van der Waals distances. Bond distances

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(2) For recent reviews on asymmetric catalysis, see: (a) *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH Publishers: Weinheim, 1993. (b) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; John Wiley and Sons: New York, 1994.

(3) For recent references in this subject see: (a) Alcock, N. W.; Brown, J. M.; Hulmes, D. I. *Tetrahedron: Asymmetry* **1993**, *4*, 743. (b) Choi, S. Y. M.; Siah, S.; Leung, P; Mok, K. F. *Inorg. Chem.* **1993**, *32*, 4812. (c) Gabbitas, N.; Salem, G.; Sterns, M.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **1993**, 3271. (d) Aw, B.; Leung, P. *Tetrahedron: Asymmetry* **1994**, *5*, 1167. (e) Ramsden, J. A.; Brown, J. M.; Hursthouse, M. B.; Karaulov, A. I. *Tetrahedron: Asymmetry* **1994**, *5*, 2033. (f) Doyle, R. J.; Salem, G.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **1995**, 1867. (g) Leitch, J.; Salem, G.; Hockless, D. C. R. *J. Chem. Soc., Dalton Trans.* **1995**, 649.

(4) (a) Tani, K. J.; Brown, L. D.; Ahmed, J.; Ibers, J. A.; Yokota, M.; Nakamura, A.; Otsuka, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 7876. (b) Gladiali, S.; Dore, A.; Fabbri, D.; De Lucchi, O.; Manassero, M. *Tetrahedron: Asymmetry* **1994**, *5*, 511. (c) Pabel, M.; Willis, A. C.; Wild, S. B. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1835. (d) Pabel, M.; Willis, A. C.; Wild, S. B. *Tetrahedron: Asymmetry* **1995**, *6*, 2369. (e) Dunina, V. V.; Golovan, F. B.; Gulyukina, N. S.; Buyevich, A. V. *Tetrahedron: Asymmetry* **1995**, *6*, 2731. (f) Dunina, V. V.; Golovan, F. B. *Tetrahedron: Asymmetry* **1995**, *6*, 2747. (g) Pabel, M.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1996**, *35*, 1244.

(5) Yoneda, A.; Hakushi, T.; Newkome, G. R.; Fronczek, F. R. *Organometallics* **1994**, 4912.

(6) Cyclopalladated dinuclear compound **3b** has been previously prepared by reaction of [PdCl$_2${C$_6$H$_5$CH(Me)NH$_2$}$_2$] with AgClO$_4$: Vicente, J.; Saura-Llamas, I.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1993**, 3619.

(7) For the synthesis of phosphines *trans*-PPh$_2$(2-OHC$_6$H$_{10}$) and Ph$_2$PCH(OMe)Ph, see Muller, G.; Sainz, D. *J. Organomet. Chem.* **1995**, *495*, 103 and Oehme, H.; Leissring, E. *Tetrahedron* **1981**, *37*, 753, respectively.

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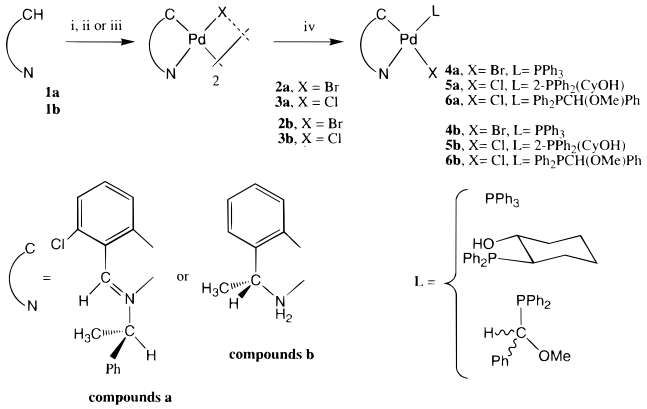
Scheme 1[a]



[a] (i) $Pd(AcO)_2$/AcOH, 60 °C, 4 h; (ii) LiBr/EtOH, room temperature, 30 min; (iii) LiCl/EtOH, room temperature, 30 min; (iv) L, $CHCl_3$, room temperature, 30 min.

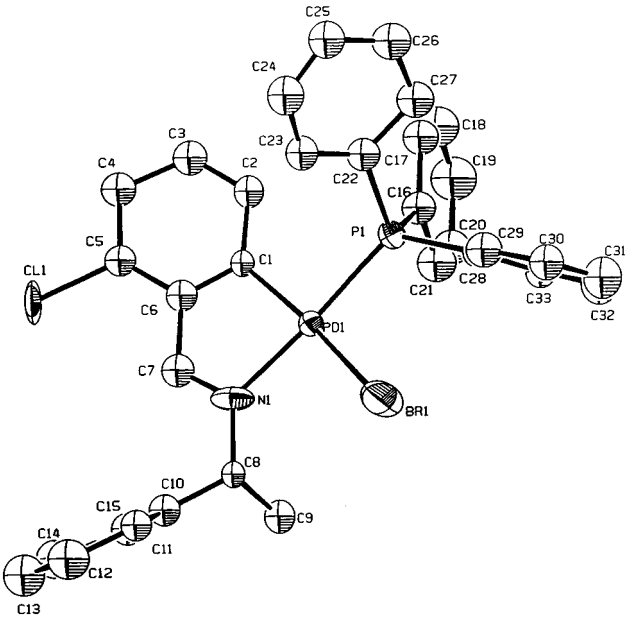


Figure 1. Crystal structure of **4a**: selected bond lenghts [Å] and angles [deg]: Pd(1)−Br(1) 2.469(2), Pd(1)−P(1) 2.251(4), Pd−N(1) 2.12(1), Pd(1)−C(1) 2.03(1), N(1)−C(7) 1.28(2), N(1)−C(8) 1.48(2), Br(1)−Pd(1)−P(1) 92.5(1), Br(1)−Pd(1)−N(1) 93.5(3), P(1)−Pd(1)−C(1) 93.5(4), N(1)−Pd(1)−C(1) 80.4(5).

and angles are similar to those reported for related metallacycles,[8] the absolute configuration of the imine ligand is *R* and the iminic nitrogen and the phosphine molecule adopt a *trans* arrangement.

The elution of compounds **5a** and **6b** (containing the racemic phosphines as ligands) in a SiO_2 column, using chloroform−methanol (100/1 and 100/0.3, respectively) as an eluent, allowed the separation of the two diastereoisomers (see experimental procedure). The diastereomeric ratios were determined by ^{1}H NMR spectroscopy (500 MHz), at room temperature, using the integral intensities ratio of signals of methyl, methoxy, or methinic protons, or by ^{31}P NMR spectroscopy (101.26 MHz) at 240 K.

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Table 1. Crystallographic Data

A. Crystal Data	
empirical formula	$PdC_{33}H_{28}BrClNP$
formula weight	691.32
crystal color, habit	yellow, irregular
crystal dimensions (mm)	0.290 × 0.200 × 0.350
crystal system	orthorombic
no. reflections used for unit cell determination (2θ range) (deg)	25 (12.5−15.0)
ω scan peak width at half-height	0.22
lattice parameters	
a (Å)	10.266(2)
b (Å)	28.021(9)
c (Å)	10.009(2)
V (Å^3)	2879(2)Å^3
space group	$P2_12_12_1$ (No. 19)
Z	4
D_{calc} (g/cm^3)	1.595
F_{000}	1384
$\mu_{(Mo\ K\alpha)}$ (cm^{-1})	21.81
B. Intensity Measurements	
diffractometer	Rigaku AFC6S
radiation	Mo Kα (λ = 0.71069 Å)
temperature (°C)	17
take-off angle (deg)	6.0
detector aperture (mm)	6.0 horizontal 6.0 vertical
crystal to detector distance (mm)	285
scan type	ω
scan rate (deg/min)	4.0 (in omega) (3 rescans)
scan width (deg)	0.94 + 0.30 tan θ
$2\theta_{max}$ (deg)	50.1
no. of reflections measured	total: 2606
corrections	Lorentz-polarization absorption (trans. factors: 0.88−1.00) decay (−2.70% decline)
C. Structure Solution and Refinement	
structure solution	Patterson method
refinement	full-matrix least-squares
function minimized	$\sum w(\|F_o\| - \|F_c\|)^2$
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
p-factor	0.03
anomalous dispersion	all non-hydrogen atoms
no. observations ($I > 3.00\sigma(I)$)	1818
no. variables	178
reflection /parameter ratio	10.21
residuals: *R*; R_w	0.054; 0.069
goodness of fit indicator	2.81
max. shift/error in final cycle	0.38
maximum peak in final diff map (e/Å^3)	1.25
minimum peak in final diff map (e/Å^3)	−0.68

The action of dppe on the optically active cyclopalladated derivatives **5a** and **6b** permits us to obtain the free phosphines (RMN ^{31}P: $\delta = -7.6$ and -0.5 for *trans*-2-PPh_2(CyOH) and Ph_2PCH(OMe)Ph, respectively),[9] but the cyclopalladated compound [Pd(C−N)(dppe)]X formed does not permit an easy regeneration of the resolving agent. Furthermore, careful workup is needed to obtain the air sensitive phosphine *trans*-Ph_2PCH(OMe)Ph in the free state. The ^{31}P NMR spectrum obtained when the cyclopalladated compound $[Pd(2\text{-}\{Z\text{-}(R)\text{-}CHMeN{=}CH\text{-}2',6'\text{-}Cl_2C_6H_3\}C_6H_4)Cl]_2$ is added to the solution containing the free phosphine *trans*-2-PPh_2(CyOH), shows that the absolute configuration of the phosphine is 1*S*,2*S* in the first eluted diastereoisomer (δ = 41.8 ppm).[10]

(9) A signal at δ = 25.5, corresponding to the phosphine oxide, is also observed when the reaction is carried on **6b**.

The lability of the palladium−phosphorous bond in cyclopalladated derivatives,[4d] and the fact that the main objective of the resolution of phosphine ligands is the synthesis of coordination compounds (that can be useful reagents for enantioselective catalysis), prompted us to study ligand transfer reactions between optically active **5a** and **6b** and some platinum compounds like $PtCl_2$ or *trans*-$[PtCl(\mu\text{-}Cl)(PPh_3)]_2$ (in the molar ratio 2/1). When these reactions were performed with the imine derivative **5a**, the formation of mixtures of platinum coordination compounds was observed. But when the reactions were performed with the amine derivative **6b**, the coordination platinum complexes *trans*-$[PtCl_2\{Ph_2PCH(OMe)Ph\}_2]$ **7** and *trans*-$[PtCl_2\{Ph_2PCH(OMe)Ph\}(PPh_3)]$ **8** were cleanly obtained from $PtCl_2$ and *trans*-$[PtCl(\mu\text{-}Cl)(PPh_3)]_2$, respectively.[11] Moreover, the dinuclear cyclopalladated resolving agent **3b** can be separated from the platinum compounds and used in a new resolution process.[12] It should be noted that platinum complexes $[PtCl_2(PR_3)_2]$ or $[PtCl_2(P\text{-}P)]$, in the presence of $SnCl_2$, are useful catalysts in the asymmetric hydroformylation of olefins.[13]

In conclusion, despite the low chemical yield of the separation of the diastereoisomers, the process presented is a useful approach to the subject of the phosphine resolution because it allows, for the first time, the synthesis of optically active platinum complexes and the regeneration of the resolving agent in one step. Furthermore, this sequence of reactions permits the synthesis of the platinum coordination compounds without the isolation of the free phosphine, thus preventing the racemization or decomposition of this ligand.[14] The extension of this process to new cyclopalladated derivatives and to new racemic ligands is currently under way.

Experimental Section

^1H NMR spectra at 200 MHz and 500 MHz, and $^{31}P\{^1H\}$ spectra at 101.26 MHz, 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 ^1H and to 85% H_3PO_4 for ^{31}P. The solvents used were $CDCl_3$ in ^1H and $CHCl_3$ 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.

Crystallographic Studies. A crystal (0.29 × 0.2 × 0.35 mm), obtained by slow evaporation (at room temperature ca 20 °C) of a saturated $CHCl_3$ solution layered with MeOH, was selected and mounted on Rigaku AFC6s diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($12.5 \le \theta \le 15°$) and refined by the least squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using ω-scan technique. Reflections having $I \ge 3\sigma(I)$ were used for structure resolution. All calculations for data reduction and structure solution and refinement were carried out using the TEXSAN software system.[15] The palladium and bromine atoms were located by Patterson synthesis, and the remaining non-hydrogen atoms were found by the DIRDIF method[16] and refined by full-matrix least-squares method. Hydrogen atoms were included in idealized positions. The final R factor was 0.054, ($R_w = 0.069$)-$wR = 0.134$. The maximum and minimum peaks in the final difference synthesis were 1.25 eÅ^{-3} and −0.68 eÅ^{-3}, respectively. Crystal parameters, data collection details, and results of the refinements are summarized in Table 1.

Materials and Syntheses. All chemicals and solvents were commercial and used as received, except ethanol, chloroform, methanol, and acetone, which were dried over $CaCl_2$ and distilled before use. Phosphines *trans*-2-PPh_2(CyOH) and $Ph_2PCH(OMe)Ph$ were prepared as described.[7]

(*R*)-2-$ClC_6H_3CH{=}NCHMeC_6H_5$. A 5 mmol amount (0.705 g) of 2-chlorobenzaldehyde was treated with 5 mmol (0.605 g) of (*R*)-(+)-1-phenylethylamine in ethanol (30 mL) at reflux for 4 h and the resulting solution concentrated *in vacuo*. The oil obtained contains the imine **1a** (>95%) and was used without further purification. **1a**: ^1H: 8.80 [s, 1H, C*H*═N], 8.12 [m, 1H, aromatic], 7.60−7.20 [m, 8H, aromatic], 4.60 [q, ^3J(HH) = 6.6 Hz, 1H, C*H*Me], 1.60 [d, ^3J(HH) = 6.6 Hz, 3H, CH*Me*]. IR: ν_{max}/cm^{-1}1635 (C═N).

Synthesis of 2 and 3. A stirred suspension of $Pd(AcO)_2$ (2.2 mmol, 0.5 g) in acetic acid (25 mL) was treated with 2.2 mmol of the N-donor ligand (imine or amine) at 60 °C for 4 h and the resulting solution concentrated *in vacuo*. The reaction residue was treated with 4.4 mmol of LiBr or LiCl in ethanol (25 ml) and the suspension stirred at room temperature for 30 min. The resulting solution was concentrated *in vacuo*, and the solid obtained was purified by SiO_2 column chromatography. Compounds **2** and **3** were eluted with $CHCl_3$/MeOH (100/2) and isolated as yellow powders in yields of 50−70%, after concentration of the solvents and addition of ethanol (10 mL). **2a**: ^1H: 8.10 [s, 2H, C*H*═N], 7.50−6.95 [m, 16 H, aromatic], 5.40 [br m, 2H, C*H*Me], 1.80 [br m, 6H, CH*Me*]. Anal. Calcd (found) for $C_{30}H_{26}Br_2Cl_2N_2Pd_2$: C, 41.98 (42.2); H, 3.05 (3.3); N, 3.27 (3.3). **3a**: ^1H: 8.05 [s, 2H, C*H*═N], 7.50−6.95 [m, 16H, aromatic], 5.40 [br m, 2H, C*H*Me], 1.75 [br m, 6H, CH*Me*]. Anal. Calcd (found) for $C_{30}H_{26}Cl_4N_2Pd_2$: C, 46.84 (47.0); H, 3.40 (3.4); N, 3.64 (3.6). **2b**: ^1H: 7.40−6.70 [m, 8 H, aromatic], 4.35 [br m, 2H, C*H*Me], 4.05 [br m, 2H, N*H*], 3.20 [br m, 2H, N*H*], 1.60 [br m, 6H, CH*Me*]. Anal. Calcd (found) for $C_{16}H_{20}Br_2N_2Pd_2$: C, 31.34 (31.3); H, 3.29 (3.3); N, 4.57 (4.5). **3b**: ^1H: 7.40−6.70 [m, 8H, aromatic], 4.30 [br m, 2H, C*H*Me], 4.15 [br m, 2H, N*H*], 3.20 [br m, 2H, N*H*], 1.65 [br m, 6H, CH*Me*]. Anal. Calcd (found) for $C_{16}H_{20}Cl_2N_2Pd_2$: C, 36.67 (36.3); H, 3.85 (3.9); N, 5.35 (5.5).

Synthesis of 4a and 4b. A suspension formed by 0.37 mmol of **2**, 0.74 mmol of PPh_3, and 20 mL of $CHCl_3$ was stirred at room temperature for 30 min and the resulting suspension or solution concentrated *in vacuo*. Addition of ether (10 mL) to the reaction residue produces the precipitation of compounds **4** as white or pale yellow powders in yields of 80%. **4a**: ^1H: 8.65 [d, 1H, J(HP) = 7.6 Hz, C*H*═N], 7.80−7.70 [m, 6H,

(10) Albert, J.; Granell, J.; Muller, G.; Sainz, D.; Font-Bardia, M.; Solans, X. *Tetrahedron: Asymmetry* **1995**, *6*, 325.

(11) The reaction between the free phosphine $Ph_2PCH(OMe)Ph$ and the platinum compound *trans*-$[PtCl(\mu\text{-}Cl)(PPh_3)]_2$, in a molar ratio 2/1, affords a complex mixture of coordination platinum compounds, but when the reaction was undertaken using the cyclopalladated derivative **6b**, as a source of the phosphine ligand, only the compound *trans*-$[PtCl_2\{Ph_2PCH(OMe)Ph\}(PPh_3)]$ was obtained. Probably the use of the palladium complex **6b**, as a phosphine source, assures a low concentration of this ligand in solution, that prevents the formation of the mixtures of coordination complexes.

(12) The intensity of the signals in the NMR spectrum of **7** shows that this reaction does not change the optical enrichment of the phosphine.

(13) (a) Parinello, G.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7122. (b) Kollar, L.; Consiglio, G.; Pino, P. *J. Organomet. Chem.* **1987**, *330*, 305. (c) Gómez, M.; Muller, G.; Sainz, D.; Sales, J. *Organometallics* **1991**, *10*, 4036. (d) Botteghi, C.; Paganelli, S.; Schionato, A.; Marchetti, M. *Chirality* **1991**, *3*, 355. (e) Agbossou, F.; Carpentier, J. F.; Mortreux, A. *Chem. Rev.* **1995**, *95*, 2485. (f) Scrivanti, A.; Beghetto, V.; Bastianini, A.; Matteoli, U.; Menchi, G. *Organometallics* **1996**, *15*, 4687.

(14) The functionalized phosphine $Ph_2PCH(OMe)Ph$ is readily oxidizable and should be stored under nitrogen but, when coordinated to palladium, this ligand becomes very stable and can be stored several months in air.

(15) TEXSAN: *Single-Crystal Structure Analysis Software*, version 5.0; Molecular Structure Corp.: The Woodlands, TX, 1989.

(16) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. N.; Gould, R. D.; van der Hark, T. E.; Prick, P. A. J.; Nordik, J. H.; Beurskens, G.; Partasarati, V. DIRDIF, an automatic procedure for phase extension and refinement of difference structure factors; Technical Report 1981/2, Crystallographic Laboratory Toernooiveld: Nijmegen, The Netherlands, 1981.

aromatic], 7.50−7.25 [m, 14 H, aromatic], 6.80 [d, *J*(HH) = 8.0 Hz, 1H, aromatic], 6.45−6.20 [m, 3H, aromatic and C*H*Me], 1.80 [d, *J*(HH) = 7.0 Hz, 1H, CH*Me*]. ^{31}P: 43.5, s. Anal. Calcd (found) for $C_{33}H_{28}BrClNPPd$: C, 57.33 (57.5); H, 4.08 (4.3); N, 2.03 (2.0). **4b**: ^{1}H: 7.80−7.70 [m, 6H, aromatic], 7.60−7.20 [m, 9H, aromatic], 7.00−6.80 [m, 2H, aromatic], 6.50−6.30 [m, 2H, aromatic], 4.60 [br m, 1H, C*H*Me], 4.15 [br m, 1H, N*H*], 3.55 [br m, 1H, N*H*], 1.75 [br m, 3H, CH*Me*]. ^{31}P: 42.3, s. Anal. Calcd (found) for $C_{26}H_{25}BrNPPd$: C, 54.90 (54.9); H, 4.43 (4.5); N, 2.46 (2.6).

Synthesis of 5a and 5b. A suspension formed by 0.37 mmol of **3**, 0.74 mmol of *trans*-2-PPh_2(CyOH), and 20 mL of $CHCl_3$ was stirred at room temperature for 30 min, and the resulting solution was concentrated *in vacuo*. Addition of ether (10 mL) to the reaction residue produces the precipitation of compounds **5** as pale yellow powders in a yield of 80−90%. **5a** (50/50): ^{1}H: 8.40 [d, *J*(HP) = 7.6 Hz, 1H, C*H*═N], 8.25 [d, *J*(HP) = 7.6 Hz, 1H, C*H*═N], 8.15−7.80 [m, 8H, aromatic], 7.70−7.20 [m, 22H, aromatic], 6.85 [d, *J*(HH) = 8.0 Hz, 1H, aromatic], 6.80 [d, *J*(HH) = 8.0 Hz, 1H, aromatic], 6.55 [t, *J*(HH) = 8.0 Hz, 1H, aromatic], 6.50 [t, *J*(HH) = 8.0 Hz, 1H, aromatic], 6.40 [t, *J*(HH) = 8.0 Hz, 2H, aromatic], 6.10 [m, 2H, C*H*Me], 3.20−2.80 [br m, aliphatic], 2.30−2.10 [br m, aliphatic], 1.90−1.45 [br m, aliphatic], 1.80 [d, *J*(HH) = 7.3 Hz, 6H, CH*Me*], 1.40−0.80 [br m, aliphatic]. ^{31}P: 44.4, s; 43.6, s. Anal. Calcd (found) for $C_{33}H_{34}Cl_2NOPPd$: C, 59.26 (59.7); H, 5.12 (5.2); N, 2.10 (2.1). **5b** (50/50): ^{1}H: 8.15−7.95 [m, 8H, aromatic], 7.65−7.45 [m, 12H, aromatic], 6.90−6.80 [m, 4H, aromatic], 6.45−6.30 [m, 4H, aromatic], 5.00 [br m, 1H, N*H*], 4.73 [br m, 1H, N*H*], 4.70 [br m, 2H, C*H*Me], 4.28 [br m, 1H, N*H*], 3.90 [br m, 1H, N*H*], 3.45−3.20 [br m, 1H, N*H*], 3.20−2.80 [br m, aliphatic], 2.00−1.90 [br m, aliphatic], 1.90−1.45 [br m, aliphatic], 1.80 [d, *J*(HH) = 6.4 Hz, 3H, CH*Me*], 1.63 [d, *J*(HH) = 6.4 Hz, 3H, CH*Me*], 1.25−1.0 [br m, aliphatic]. ^{31}P: 46.7, s; 45.5, s. Anal. Calcd (found) for $C_{26}H_{31}ClNOPPd$: C, 57.16 (57.4); H, 5.71 (5.8); N, 2.56 (2.4).

Synthesis of 6a and 6b. A suspension formed by 0.37 mmol of **3**, 0.74 mmol of $Ph_2PCH(OMe)Ph$, and 20 mL of $CHCl_3$ was stirred under nitrogen at room temperature for 30 min and the resulting solution concentrated *in vacuo*. The solid obtained was eluted by SiO_2 column chromatography with $CHCl_3$/MeOH (100/1) as eluent. Compounds **6** were isolated as yellow solids in a yield of 70−80%. **6a** (50/50): ^{1}H: 8.50 [d, *J*(HP) = 7.5 Hz, 1H, C*H*═N], 8.25 [d, *J*(HP) = 7.5 Hz, 1H, C*H*═N], 8.10−7.80 [m, 8H, aromatic], 7.70−7.20 [m, 32H, aromatic], 6.95 [m, 2H, aromatic], 6.75 [m, 4H, aromatic, *H*C(OMe)], 6.40 [m, 2H, C*H*Me], 6.10 [t, 2H, aromatic], 3.35 [s, 3H, O*Me*], 3.30 [s, 3H, O*Me*], 1.85 [d, *J*(HH) = 6.6 Hz, 3H, CH*Me*], 1.80 [d, *J*(HH) = 6.6 Hz, 3H, CH*Me*]. ^{31}P: 45.2, s; 44.9, s. Anal. Calcd (found) for $C_{35}H_{32}Cl_2NOPPd$: C, 60.84 (60.8); H, 4.67 (4.5); N, 2.03 (2.0). **6b** (50/50): ^{1}H: 8.25−8.00 [m, 4H, aromatic], 7.60−7.30 [m, 10H, aromatic], 7.25−7.00 [m, 16H, aromatic], 6.70−6.60 [m, 4H, aromatic], 6.40−6.30 [m, 6H, aromatic and *H*C(OMe)], 4.45 [br m, 1H, C*H*Me], 4.40 [br m, 1H, C*H*Me], 4.00 [br m, 1H, N*H*], 3.90 [br m, 1H, N*H*], 3.45−3.20 [br m, 2H, N*H*], 3.35 [s, 3H, O*Me*], 3.30 [s, 3H, O*Me*], 1.70 [d, *J*(HH) = 6.6 Hz, 3H, CH*Me*], 1.65 [d, *J*(HH) = 6.6 Hz, 3H, CH*Me*]. ^{31}P: 46.3, s; 44.8, s. Anal. Calcd (found) for $C_{28}H_{29}ClNOPPd$: C, 59.17 (58.9); H, 5.13 (5.1); N, 2.46 (2.4).

Separation of 5a Diastereoisomers. Compound **5a** was carefully eluted at room temperature, in a SiO_2 column (30 × 400 mm, 40 g of SiO_2) with $CHCl_3$−MeOH (100/1) as eluent. The first band eluted was collected in fractions of 25 mL, concentrated *in vacuo*, and checked by ^{1}H NMR spectroscopy. The fractions of the optical pure compound (by 200 MHz ^{1}H NMR spectroscopy) were selected using the methinic or the methylic proton signals. From 200 mg of **5a** (50/50), 20 mg were obtained with a de higher than 95%.

Separation of 6b Diastereoisomers. Compound **6b** was carefully eluted at room temperature, in a SiO_2 column (30 × 400 mm, 40 g of SiO_2) with $CHCl_3$−MeOH (100/0.3) as eluent. The first band eluted was collected in fractions of 25 mL, concentrated *in vacuo*, and checked by ^{1}H NMR spectroscopy. The fractions of the optical purity desired were selected using the methoxy proton signals. From 200 mg of **6b** (50/50) can be isolated 25 mg of the same compound in de higher than 95%.

Synthesis of 7. A suspension formed by 0.14 mmol (0.08 g) of **6b** (de 95%) was treated with 0.14 mmol (0.036 g) of $PtCl_2$, in 20 mL of acetone−methanol (85−15) at reflux for 1.30 h. The resulting solution was concentrated to dryness *in vacuo*, 5 mL of methanol was added to the solid formed, and the mixture was stirred for 5 min. The insoluble residue formed was characterized as compound **7**. The methanolic solution was concentrated *in vacuo* to dryness to recover **3b**. The yield of the process is 60%. **7**: ^{31}P: 23.4 [d, *J*(P−Pt) = 2570 Hz], 23.5 [d, *J*(P−Pt) = 2570 Hz]; Anal. Calcd (found) for $C_{40}H_{38}Cl_2O_2P_2Pt$: C, 54.67 (54.4); H, 4.36 (4.2).

Synthesis of 8. A suspension formed by 0.14 mmol (0.08 g) of **6b** (de 95%) was treated with 0.14 mmol (0.156 g) of *trans*-$[PtCl(\mu\text{-}Cl)(PPh_3)]_2$, in 20 mL of acetone−methanol (85−15) at reflux for 1.30 h. The resulting solution was concentrated to dryness *in vacuo*, 5 mL of methanol was added to the solid obtained, and the mixture was stirred at room temperature for 5 min. The insoluble residue formed was characterized as compound **8**. The methanolic solution was concentrated *in vacuo* to dryness to recover **3b**. The yield of the process is 70%. **8**: ^{31}P: 23.2 and 18.5 [AB quartet, *J*(P−Pt) = 2570 Hz, *J*(P−Pt) = 2621 Hz, *J*(P−P) = 478 Hz.]. Anal. Calcd (found) for $C_{38}H_{34}Cl_2OP_2Pt$: C, 54.69 (54.7); H, 4.08 (4.0).

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Supporting Information Available: Full details of the X-ray structure of **4a**, including tables listing positional parameters, all bond lengths and angles, and isotropic and anisotropic displacement parameters (13 pages). Ordering information is given on any current masthead page.

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