Articles

A New Reagent for Chiral Recognition Containing a Five-Membered Palladacycle with a σ(Pd-$C_{sp^2,ferrocene}$) Bond

Concepción López,* Ramón Bosque, and Daniel Sainz

Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028-Barcelona, Spain

Xavier Solans and Mercé Font-Bardía

Departament de Cristal.lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, 08028-Barcelona, Spain

Received February 10, 1997[⊗]

The chiral recognition of β-hydroxyphosphines and the discrimination of (±)-bis(diphenylphosphino)-1,1′-binaphthyl can be easily achieved using the bis(cyclopalladated) complex (R_P,S_C,S_C,R_P)-(+)-[Pd{[(η^5-C_5H_3)CH(CH_3)N(CH_3)$_2$]Fe(η^5-C_5H_5)}(μ-Cl)]$_2$ **(1)**.

Introduction

An important area of organometallic chemistry is that concerning cyclopalladated compounds.[1] Over the last few years the interest in compounds of this kind has increased exponentially due to their novel applications.[2−6] For instance, cyclopalladated complexes provide new methods for the regio- and stereoselective syntheses of organic and organometallic compounds.[2] Several examples of metallomesogens containing palladacyclic units have also been described,[3] and in addition, some articles dealing with the antitumoral activity of such derivatives have also been published.[4] Furthermore, recent studies have shown that optically active cyclopalladated compounds derived from N-donor ligands containing a chiral carbon such as the amines (*R* or *S*)-(α-methylbenzyl)amines and (α-methylnaphthyl)amines and their substituted derivatives or the imine *(R)*-C_6H_5-CH(CH_3)N=CH(C_6H_3-2,5-Cl_2) (Chart 1) are valuable reagents not only for the determination of enantiomeric excesses of chiral phosphines, amines, or arsines but also for the resolution of chiral substrates.[6]

On the other hand, and although it is well-known that ferrocene derivatives are useful substrates in asymmetric synthesis,[7] as far as we know none of the articles dealing with the applications of cyclopalladated compounds for the resolution and/or determination of enantiomeric excesses of the chiral amines, phosphines, or arsines described so far involve the use of cyclopalladated compounds containing ferrocenyl units. We have recently reported that ortho palladation of (S_C)-[(η^5-C_5H_5)Fe{(η^5-C_5H_4)CH(CH_3)N(CH_3)$_2$}] is diastereoselective,[8] producing exclusively the enantiomerically pure dimeric compound (R_P,S_C,S_C,R_P)-(+)-[Pd{[(η^5-C_5H_3)CH-(CH_3)N(CH_3)$_2$]Fe(η^5-C_5H_5)}(μ-Cl)]$_2$ **(1)**, and it seemed

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

(1) (a) Newkome, R. G.; Pucket, W. E.; Gupta, V. C.; Kiefer, E. *Chem. Rev.* **1986**, *86*, 451. (b) Omae, I. *Coord. Chem. Rev.* **1988**, *83*, 137. (c) Dunina, V. V.; Zalewskaya, O. A.; Potatov, V. M. *Russ. Chem. Rev. (Engl. Transl.)* **1988**, *57*, 250. (d) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.

(2) Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 567 and references therein.

(3) Espinet, P.; Esteruelas, M. A.; Oro, L. A.; Serrano, J. L.; Sola, E. *Coord. Chem. Rev.* **1992**, *15*, 215 and references therein.

(4) (a) Navarro-Ranninger, C.; López Solera, J.; Pérez, J. M.; Massaguer, J. M.; Alonso, C. *Appl. Organomet. Chem.* **1993**, *7*, 57. (b) Higgius, J. *J. Inorg. Biochem.* **1993**, *49*, 149.

(5) (a) Bose, A.; Saha, C. H. *J. Mol. Catal.* **1989**, *49*, 271. Santra, P. K.; Saha, C. H. *J. Mol. Catal.* **1987**, *39*, 279. (b) Wakatsuki, Y.; Yamazaki, H.; Gutsch, P. A.; Southanan, M.; Kutal, C. *J. Am. Chem. Soc.* **1985**, *107*, 8153. (c) Maestry, M.; Sandrini, D.; Balzani, V.; von Zelewsky, A. *Helv. Chim. Acta* **1988**, *71*, 134. (d) Cornioley-Deschel, C.; Ward, T.; von Zelewsky, A. *Helv. Chim. Acta* **1988**, *71*, 130.

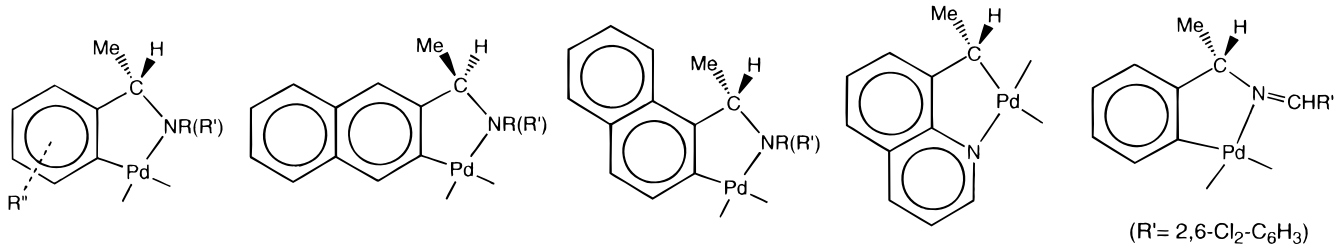
(6) (a) Doyle, R. J.; Salem, E, G.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **1995**, 1867. (b) Vicente, J.; Saura-Llamas, I.; Palin, M. G.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1995**, 2535. (c) Vicente, J.; Saura-Llamas, I.; de Arellano, M. C. R. *J. Chem. Soc., Dalton Trans.* **1995**, 2529. (d) Loh, S. K.; Mok, K. F.; Leung, P. H.; White, A. J.; Williams, D. J. *Tetrahedron: Asymmetry* **1996**, *7*,46. (e) Berens, U.; Brown, J. M.; Long, J. M.; Selke, R. *Tetrahedron: Asymmetry* **1996**, *7*, 285. (f) García-Ruano, J. L.; González, A. M.; Barcena, A. I.; Camazon, M. J.; Navarro-Ranninger, C. *Tetrahedron: Asymmetry* **1996**, *7*, 139. (g) Leung, P. H.; Loh, S. K.; Mok, K. F.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1996**, 591. (h) Albert, J.; Granell, J.; Sainz, D.; Font-Bardía, M.; Solans, X. *Tetrahedron: Asymmetry* **1995**, *6*, 325. (i) Tani, N. K.; Brown, L. D.; Ahmed, J.; Ibers, J. A.; Yokota, M.; Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 7876. (j) Roberts, N. K.; Wild, S. W. *J. Am. Chem. Soc.* **1979**, *100*, 6254. (k) Roberts, N. K.; Wild, S. B. *J. Chem. Soc., Dalton Trans.* **1979**, 2015. (l) Allen, D. G.; Mclaughlin, G. M.; Robertson, G. B.; Steffer, W. L.; Salem, G.; Wild, S. B. *Inorg. Chem.* **1982**, *21*, 1007. (m) Salem, G.; Wild, S. B. *Inorg. Chem.* **1983**, *22*, 4049. (n) Chooi, T. S. A.; Hor, S. Y. M.; Leung, P. H.; Mok, K. F. *Inorg. Chem.* **1992**, *31*, 1494. (o) Gabbitas, N.; Salem, G.; Sterns, M.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **1993**, 3271. (p) Ramsdem, J. A.; Brown, J. M.; Hursthouse, H. B.; Karalulov, A. I. *Tetrahedron: Asymmetry* **1994**, *5*, 2033. (q) Chooi, S. Y. M.; Leung, P. H.; Lim, C. C.; Mok, K. F.; Quek, G. H.; Sim, K.Y.; Tam, M. K. *Tetrahedron: Asymmetry* **1992**, *3*, 529−532. (r) Chooi, S. Y. M.; Siah, S. Y.; Leung, P. H.; Mok, K. F. *Inorg. Chem.* **1993**, *32*, 4812. (s) Lim, C. C.; Leung, P. H.; Mok, K. F.; Sim, K. Y. *Tetrahedron: Asymmetry* **1994**, *5*, 1983. (t) Otsuka, S.; Nakamura, A.; Kano, T.; Tani, K. *J. Am. Chem. Soc.* **1971**, *93*, 4301. (u) Valk, J. M.; Claridge, T. D. W.; Brown, J. M.; Hibbs, D.; Hursthouse, M. B. *Tetrahedron: Asymmetry* **1995**, *6*, 2597. (v) Dunina,V. V.; Golovan, E. B.; Buyerich, A. V. *Tetrahedron: Asymmetry* **1995**, *6*, 2731. (x) Dunina, V. V.; Golovan, E. B. *Tetrahedron: Asymmetry* **1995**, *6*, 2747.

(7) (a) Togni, A., Hayashi, T., Eds. *Ferrocenes: Homogeneous Catalysis, Organic Chemistry and Materials Science*; VCH: Weinheim, Germany, 1995. (b) Sokolov, V. I. *Chirality and Optical Activity in Organometallic Compounds*; Gordon and Beach: London, 1991.

(8) López, C.; Bosque, R.; Solans, X.; Font-Bardía, M. *Tetrahedron: Asymmetry* **1996**, *9*, 2527.

S0276-7333(97)00098-8 CCC: $14.00

Chart 1



interesting to test whether this substrate could also be useful for the separation of chiral phosphines. In this paper we report the reactions of **1** with racemic mixtures of monodentate chiral β-hydroxyphosphines L* (*trans*-2-(diphenylphosphino)cyclohexanol, L_1; or *trans*-2-(diphenylphosphino)-1-methyl-4-isopropenylcyclohexanol, L_2) or with the diphosphine (±)-bis(diphenylphosphino)-1,1′-binaphthyl (hereafter referred to as (±)-binap).

Results and Discussion

The bis(μ-chloro) cyclopalladated complex (R_P,S_C, S_C,R_P)-(+)-[Pd{[(η^5-C_5H_3)CH(CH_3)N(CH_3)$_2$]Fe(η^5-C_5H_5)}-(μ-Cl)]$_2$ **(1)**[8] reacts at room temperature with racemic mixtures of the phosphines L_1 and L_2[9] in a 1:2 molar ratio, producing equimolar mixtures of (±)-[Pd{[(η^5-C_5H_3)CH(CH_3)N(CH_3)$_2$]Fe(η^5-C_5H_5)}]Cl{L*}] (L = L_1 **(2)**, L_2 **(3)**) (Scheme 1).

In both cases, ^{1}H NMR spectra showed two sets of signals in a 1:1 ratio and two singlets (1:1) were also detected in the ^{31}P NMR spectra, thus indicating an excellent diastereomeric peak separation. Concentration of the solutions to dryness in a rotary evaporator allowed the isolation of **2** and **3**. Compounds **2b** and **3a** were isolated as pure materials by fractional crystallization of the solutions of **2** and **3**, respectively, in CH_2Cl_2−CH_3OH mixtures (1:1), as the more insoluble components. ^{1}H NMR spectra of the solids obtained through evaporation of the mother liquors obtained after the removal of **2a** and **3a** revealed that they were enriched in the other isomer in the molar ratios 20:80 (for **2a:2b**) and 23:77 (for **3a:3b**).

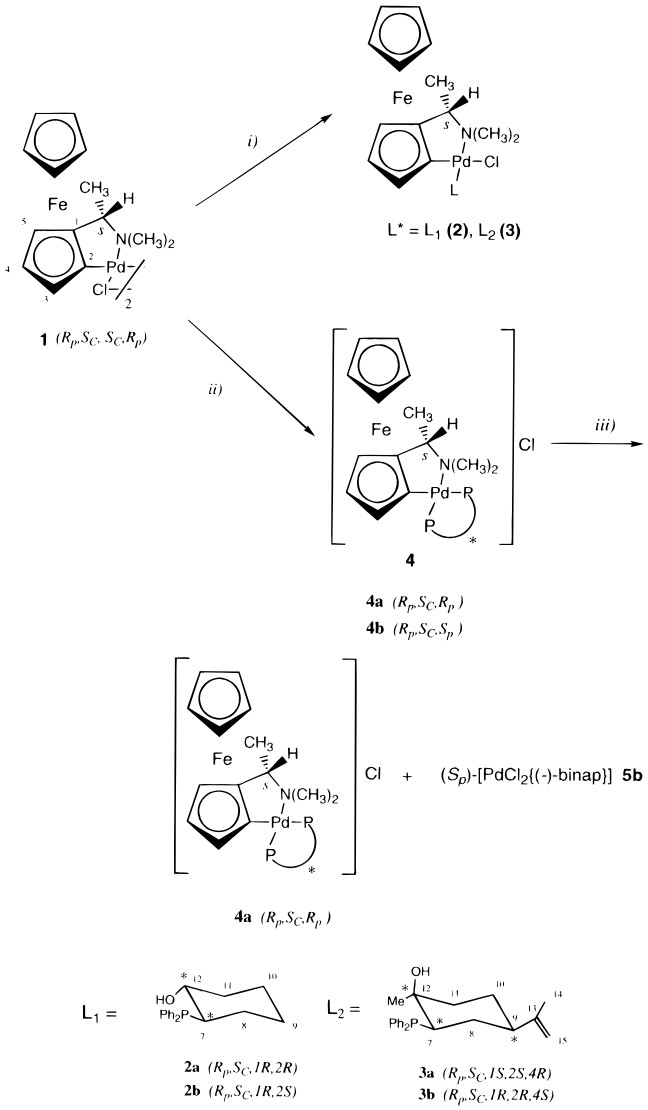
The absolute configuration of **2b** has been determined unambiguously by X-ray diffraction (see below), while the absolute configuration of the phosphines in **3a** and **3b** has been tentatively assigned by comparison between their NMR data and those of the analogous [Pd{(C_6H_4)C(CH_3)HN=CH(C_6H_3-2,6-Cl_2)Cl{L_2}], previously reported.[6h]

More interesting are the results obtained in the reaction of **1** with a racemic mixture of (*R* and *S*)-bis-(diphenylphosphino)-1,1′-binaphthyl in a 1:1 molar ratio. The ^{31}P NMR spectra of the reaction mixture, recorded immediately after mixing at 298 K, showed a singlet due to the free ligand and two pairs of (1:1) doublets, which differed in the coupling constants and the line broadening (Figure 1A), consistent with the formation of complexes **4**.

However, the structure and pattern of these spectra changed over time. For instance, after 2 days at *ca.* 288 K the ^{31}P NMR spectra (Figure 1B) showed that, although the pair of narrower doublets remained unchanged, the intensity of the other pair decreased substantially and an additional, intense singlet at *ca.* 28.9 ppm appeared. After 4 days the intensity ratio between the singlet at *ca.* 28.9 ppm and the doublets (Figure 1C) increased considerably, and two tiny doublets at *ca.* 32.13 and 17.74 ppm were also detected in the ^{31}P NMR spectrum.

These observations suggested that a chemical reaction involving one of the isomers of complex **4** was taking place. According to the literature, the reaction of cyclopalladated compounds with bidentate phosphines, such as bis(diphenylphosphino)ethane (dppe) or bis-

Scheme 1[a]



[a] (*i*) L*, L_1 = *trans*-2-(diphenylphosphino)cyclohexanol or L_2 = *trans*-2-(diphenylphosphino)-1-methyl-4-isopropenylcyclohexanol, $CDCl_3$. (*ii*) (±)-binap, $CDCl_3$. (*iii*) SiO_2, column chromatography.

(9) Muller, G.; Sainz, D. *J. Organomet. Chem.* **1995**, *495*, 103.

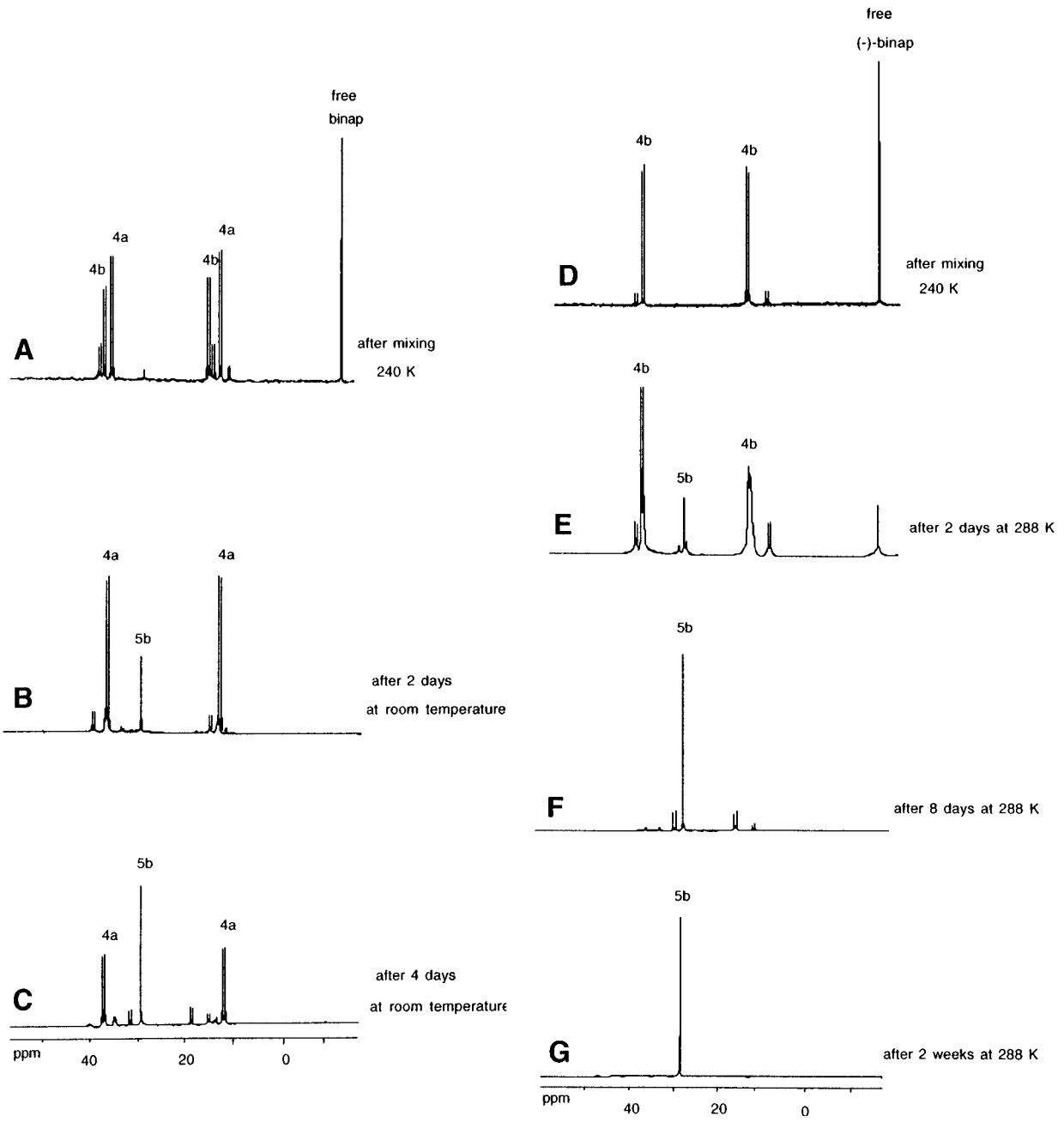


Figure 1. Changes detected in the ^{31}P NMR spectra during the reaction of **1** with (±)-binap (**A**−**C**) or with (−)-binap (**D**−**G**). In each case the spectrum was recorded under the experimental conditions indicated on the right-hand side of each plot.

(diphenylphosphino)methane (dppm) can produce two different kinds of derivatives: (a) monomeric compounds of general formula [Pd(C−N)(P−P)]Cl or (b) polynuclear species such as $[Pd_2(C-N)_2(\mu\text{-}P-P)Cl_2]$ or $[Pd_2(C-N)_2(\mu\text{-}P-P)(\mu\text{-}Cl)]Cl$.[10] The former compounds exhibit two doublets in the ^{31}P NMR spectra, while only one singlet (in the range *ca.* 27−36 ppm) is usually observed for the polynuclear derivatives. Consequently, the signal observed at *ca.* 28.9 ppm in the reaction of **1** with (+)-binap could be ascribed in principle to either polynuclear species or coordination compounds, such as *cis*-[Pd(P−P)Cl_2], which may be formed by decomposition. The use of SiO_2-column chromatography allowed us to separate the two major components of the mixture: a violet solid and a yellow solid. The elemental analyses of the violet solid, as well as its NMR data, were consistent with those expected for compounds **4**, while the ^1H NMR spectrum of the yellow solid revealed that it did not contain the ferrocenyl group; in addition, the elemental analyses of this material were consistent with those expected for *cis*-[$PdCl_2$(binap)] **(5)**. This suggests that one of the isomers of **4** decomposed in the course of the reaction. In order to elucidate the absolute configuration of compounds **4** and to find out which of the isomers of binap was responsible for the changes detected in the NMR, compound **1** was treated separately with each one of the isomers of the diphosphine.

When (+)-binap was added to a $CDCl_3$ solution of **1**,

(10) (a) Vila, J. M.; Gayoso, M.; Pereira, T.; Rodríguez, C.; Ortigueira, J. M.; Fernández, J. J.; López-Torres, M. *J. Organomet. Chem.* **1994**, *479*, 37. (b) Vila, J. M.; Gayoso, M.; Fernández, J. J.; Ortigueira, J. M.; Suarez, A. *Polyhedron* **1990**, *9*, 2741. (c) Dehand, J.; Pfeffer, M.; Zinsius, M. *Inorg. Chim. Acta* **1975**, *13*, 229.

(11) Ozawa, F.; Kubo, A.; Matsumoto, Y.; Hayashi, T.; Nishioka, E.; Yanagi, K. Moriguchi, K. *Organometallics* **1993**, *12*, 4188.

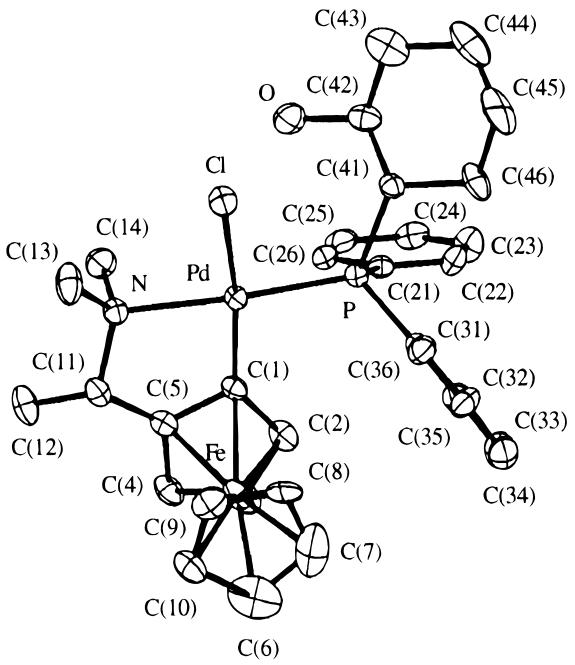


Figure 2. Molecular structure and atom-numbering scheme for compound **2a**. Selected bond distances (in Å): Pd−C(1), 1.977(5); Pd−N, 2.217(5); Pd−P, 2.266(2); Pd−Cl, 2.4267(14). Selected bond lengths (in degrees): C(1)−Pd−N, 80.7(2); C(1)−Pd−P, 93.3(2); N−Pd−Cl, 92.64(13); P−Pd−Cl, 95.5(5).

the solution turned violet immediately, and compound **4a** was isolated as a pure material by evaporation to dryness. In addition, no significant change was detected in either the ^{1}H or the ^{31}P NMR spectra of the reaction mixture after more than 3 weeks.

However, NMR studies revealed that the reaction of **1** with (−)-binap was more complex. When the ^{31}P NMR spectrum of the red reaction mixture was recorded at 240 K immediately after mixing, two narrow doublets and a singlet (at −15.0 ppm) (Figure 1D) appeared, which are attributed to compound **4b** and the free (−)-binap, respectively. These findings suggested that the reaction between **1** and (−)-binap was slow at this temperature. On this basis, the reaction mixture was then stored at *ca.* 288 K for 2 days; after this period the ^{31}P NMR spectrum (Figure 1E) showed (a) a substantial broadening and decrease in the intensities of the two doublets, (b) the presence of an additional singlet at *ca.* 28.9 ppm, and (c) a pair of tiny doublets at *ca.* 32.13 and 17.74 ppm, thus suggesting that a reaction involving compound **4b** was taking place. After 8 days at *ca.* 288 K, the solution was brownish and the substantial change in the relative intensities of the singlet and the two pairs of doublets was much more evident (Figure 1F). These observations indicate that **4a** is more stable in solution than **4b**, which decomposes easily. In addition, comparison of the spectra shown in Figure 1D−F suggests that the degradation of **4b** may occur through the formation of a pentacoordinated intermediate, with a weak Pd−N bond, which may be responsible for the two additional doublets detected at *ca.* 32.13 and 17.74 ppm that disappeared completely if the reaction mixture was stored at 288 K for 2 weeks (Figure 1G), while only the signal due to complex **5b** appears in the ^{31}P NMR spectrum. The formation of such an intermediate has been postulated for related compounds of general formula [M(C−N)X(PR_3)$_2$] (with M = Pd, Pt, X = Cl, Br, I, and R = alkyl, phenyl).[12]

As a first attempt to explain these results, molecular models of compounds **4** were built up and their manipulations revealed that, in **4b**, one of the phenyl rings is in a close vicinity to the C_5H_5 ring and, in addition, there is also strong steric hindrance between one of the methyl groups bound to the nitrogen and one of the phenyl rings of the other "PPh_2" fragment. Such an arrangement of groups decreases the stability of the complex and could be responsible for the weakening of the Pd−N bond. This finding suggests that the arrangement of ligands around the palladium in **1** is so crowded that it hinders the stabilization of compound **4b**, and consequently, the instability of **4b** in solution could arise from the steric effects produced by the (−)-binap coordinated to the palladium. This suggests that, in compound **1**, steric effects are strong enough as to enable the chiral discrimination of the bulky (±)-binap. This finding appears to be especially interesting, since complex **1** may also enable the chiral discrimination of related atropisomeric susbtrates containing heteroatoms with good donor abilities, through a simple procedure based on the cleavage of the two chloro bridges. Current work in this field is now under way.

Description of the Crystal Structure of Compound 2a. The molecular structure and the atom-labeling scheme for compound **2a** are presented in Figure 2 together with a selection of bond distances and angles. Final atomic coordinates for non-hydrogen atoms are given in the Supporting Information.

The structure consists of discrete molecules of *(R_P,S_C,1*R*,2*R*)*-[Pd{[(η^5-C_5H_3)CH(CH_3)N(CH_3)$_2$]Fe(η^5-C_5H_5)}Cl{L_1}] separated by van der Waals forces (Figure 2). The palladium atom is in a distorted-square-planar environment, since it is bound to the P, Cl, N and C(1) atoms of the ferrocenyl moiety. The deviations from the mean plane (Å) are as follows: P, 0.210; Cl, −0.168; N, 0.244; C(1), −0.242; Pd, −0.044 Å. The Pd−ligand distances are similar to those reported for analogous five-membered palladocycles.[12] The angles between adjacent atoms in the coordination sphere lie in the range 80.7(2)−95.5(2)°, and the smallest of these angles is that between the coordinated atoms of the chelate ligand.

The metallacycle has an envelope-like conformation with the nitrogen out of the plane defined by the remaining atoms. The P−Pd−N bond angle is 164.22(13)°, thus confirming the *trans* arrangement of the phosphine ligand and the nitrogen. The cyclohexyl ring of the phosphine ligand has a chair conformation with the atoms C(41) and C(44) lying respectively above and below the plane defined by C(42), C(43), C(45), and C(46).

The Fe−C_{ring} and C−C_{ring} bond distances of the ferrocenyl moiety are consistent with those reported for this type of compound.[13] The two pentagonal rings are planar and nearly parallel (tilt angle 2.7°), and their

(12) (a) Cross, R. J.; Tennent, N. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1444. (b) Anderson, G. K.; Cross, R. J.; Leaman, S. A.; Robertson, F. J.; Rycroft, D. S.; Rocamora, M. *J. Organomet. Chem.* **1990**, *388*, 221. (c) Granell, J.; Sainz, D.; Sales, J.; Solans, X.; Font-Bardía, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1785. (d) Albert, J.; Granell, J.; Luque, A.; Minguez, J.; Moragas, R.; Font-Bardía, M.; Solans, X. *J. Organomet. Chem.* **1996**, *522*, 87.

(13) Allen, T. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146.

conformation is intermediate between those expected for the ideal eclipsed or staggered conformation (twist angle 18.5(3)°).

Experimental Section

Elemental analyses (C, H, and N) were carried out at the Serveis Cientifico-Técnics de la Universitat de Barcelona. Infrared spectra were obtained with a Nicolet 520-FTIR spectrophotometer using KBr pellets. Routine ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded at *ca.* 20 °C on a Bruker 250-DXR instrument using $CDCl_3$ (99.8%) and $Si(CH_3)_4$ as solvent and internal standard, respectively. The ^{1}H NMR of complex **2a** was recorded with a Varian 500 MHz instrument. The optical rotations of the complexes in CH_2Cl_2 were determined at 20 °C using a Perkin-Elmer 241C polarimeter. Compound **1** was prepared as described previously.[8]

Preparation of the Compounds. *(R_P,S_C,1*R*,2*R*)*-(+)-[Pd{[(η^5-C_5H_3)CH(CH_3)N(CH_3)$_2$]Fe(η^5-C_5H_5)}Cl{L_1}] (2a; L_1 = *trans*-2-(Diphenylphosphino)cyclohexanol). A 50 mg (6.28×10^{-2} mmol) amount of **1** was suspended in 1 mL of $CDCl_3$, and then 14.4×10^{-2} mmol of the racemic mixture of the phosphine *trans*-2-(diphenylphosphino)cyclohexanol (L_1) was added. The reaction mixture was stirred for 2 days. After this period the solution was concentrated to dryness on a rotary evaporator and the gummy residue was treated with *n*-hexane and this solution stirred at room temperature. The orange solid formed, which consisted of a mixture (50%) of the isomers **2a** and **2b**, was filtered out and air-dried (yield 88%). The solid material was then dissolved in the minimum amount of CH_2Cl_2 and this solution layered with CH_3OH. Slow evaporation of the solution at room temperature gave complex **2a** as the most insoluble product (yield 40%), and the filtrate was enriched in the other isomer in the molar ratio **2a**:**2b** = 20:80. Anal. Calcd (found) for $C_{32}H_{39}NPPdClFeO$: C, 56.33 (56.3); H, 5.71 (5.8); N, 2.05 (2.1). *Characterization data*[14] for **2a** are as follows. ^{1}H NMR data (in ppm): ferrocenyl moiety protons 3.77 [5H, s, C_5H_5], 2.98 [1H, s, H^3], 4.00 [1H, s, H^4], 3.73 [1H, s, H^5], 2.98 [3H, s, N(CH_3)], 3.12 [3H, s, N(CH_3)], 1.20 [3H, d, CH_3], and 4.19 [1H, m, >CH−]; phosphine protons 7.48 [2H, d, $H^{2'}$ (Ph)], 7.51 [2H, d, $H^{6'}$(Ph)], 7.81−8.06 [6H, m, $H^{3'}$, $H^{4'}$ and $H^{5'}$(Ph)], 2.51 [1H, m, H^7], 1.10 [1H, m, H^{8b}], 1.73 [2H, m , H^{8a} and H^{10a}], 1.59 [1H, m, H^{9a}], 1.31 [2H, m, H^{9b} and H^{10b}], 1.90 [2H, m, H^{11a}], 1.46 [1H, m, H^{11b}], and 3.26 [1H, m, H^{12}]. ^{13}C NMR (in ppm): ferrocenyl moiety 60.49 [C_5H_5], 95.29 [d, C^1], 100.31 [d, C^2], 73.93 [C^3], 67.04 [C^4], 69.00 [C^5], 49.05 and 47.80 [N(CH_3)], 13.65 [CH_3] and 64.80 [>CH−]; phosphine fragment 137.36 [d, $C^{1'}$ (Ph)], 134.92 [d, $C^{2'}$ (Ph)], 128.58 [d, $C^{3'}$ (Ph)], 129.01 [d, $C^{4'}$ (Ph)], 127.9 [d, $C^{5'}$ (Ph)], 132.22 [d, $C^{6'}$ (Ph)], 42.7 [d, C^7], 26.68 [C^8], 25.34 [C^9], 24.39 [C^{10}], 35.39 [d, C^{11}], and 71.05 [d, C^{12}]. ^{31}P NMR (in ppm): 44.16. $[\alpha]_{20\ °C}$ (0.01 g/100 mL) = +20.7°. Data for **2b** are as follows. ^{1}H NMR data (in ppm): ferrocenyl moiety protons 3.48 [5H, s, C_5H_5], 3.15 [1H, s, H^3], 4.01 [1H, s, H^4], 3.71 [1H, s, H^5], 2.69 [3H, s, N(CH_3)], 3.20 [3H, s, N(CH_3)], 1.20 [3H, d, CH_3], and 4.04 [1H, m, >CH−]; phosphine protons 7.59 [2H, d, $H^{2'}$ (Ph)], 7.61 [2H, , $H^{6'}$ (Ph)], 7.78−8.10 [6H, m, $H^{3'}$, $H^{4'}$, and $H^{5'}$(Ph)], 2.34 [1H, m, H^7], 0.95 [1H, m, H^{8b}], 1.75 [2H, m, H^{8a} and H^{10a}], 1.63 [1H, m , H^{9a}], 1.29 [2H, m, H^{9b} and H^{10b}], 2.03 [1H, m, H^{11a}], 1.40 [1H, m, H^{11b}], and 3.30 [1H, m, H^{12}]. ^{13}C NMR (in ppm): ferrocenyl moiety 60.49 [C_5H_5], 94.50 [d, C^1], 99.80 [d, C^2], 73.29 [C^3], 66.82 [C^4], 68.63 [C^5], 48.16 and 46.11 [N(CH_3)], 11.93 [CH_3], and 64.50 [>CH−]; phosphine fragment 137.36 [d, $C^{1'}$ (Ph)], 133.71 [d, $C^{2'}$ (Ph)], 128.5 [d, $C^{3'}$ (Ph)], 129.16 [d, $C^{4'}$ (Ph)], 128.58 [d, $C^{5'}$(Ph)], 132.07 [d, $C^{6'}$(Ph)], 42.23 [d, C^7], 26.74 [C^8], 25.34 [C^9], 24.24 [C^{10}], 35.72 [d, C^{11}], and 70.89 [d, C^{12}]. ^{31}P NMR (in ppm): 44.36.

(14) Labeling of the atoms refers to those shown in Scheme 1. For compounds **2b** and **3b**, the assignment of the signals is based on comparison of the spectrum of the enriched fractions and those of the pure complexes **2a** and **3a**, respectively.

Table 1. Summary of the Crystallographic Data

empirical formula	$C_{32}H_{39}ClFeNOPPd$
fw	682.31
cryst size, mm	0.1 × 0.1 × 0.2
cryst syst	orthorhombic
space group	$P2_12_12_1$
a, Å	11.963(2)
b, Å	13.981(2)
c, Å	17.637(2)
$\alpha = \beta = \gamma$, deg	90.0
V, Å^3	2949.7(7)
D_{expti}, g cm^{-3}	1.536
μ (Mo Kα), cm^{-1}	1.272
λ(Mo Kα), Å	0.710 69
F(000)	1400
θ range for data collection, deg	2.06−29.96
index ranges	$0 \le h \le 16$; $0 \le k \le 19$, $\le l \le 24$
no. of rflns collected	4817
no. of indep rflns	4748 (*R*(int) = 0.1011)
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	4698/0/372
goodness of fit on F^2	0.956
final *R* indices ($I > \sigma(I)$)	R1 = 0.0408; wR2 = 0.0815
R indices for all data	R1 = 0.0911; wR2 = 0.1012
abs structure param	−0.02(4)
extinction coefficient	0.0000(2)
largest diff peak and hole, e Å^{-3}	0.753 and −0.532

***(R_P,S_C,1*S*,2*S*,4*R*)*-(+)-[Pd{[(η^5-C_5H_3)CH(CH_3)N(CH_3)$_2$]-Fe(η^5-C_5H_5)}Cl{L_2}] (3a; L_2 = *trans*-2-(Diphenylphosphino)-1-methyl-4-isopropenylcyclohexanol).** A 21 mg (2.6×10^{-2} mmol) amount of **1** was suspended in 2 mL of $CDCl_3$, and then 5.2×10^{-2} mmol of the racemic mixture of the phosphine *trans*-2-(diphenylphosphino)-1-methyl-4-isopropenylcyclohexanol was added. The reaction mixture was stirred for 2 days. After this period the solution was evaporated to dryness at room temperature. The yellow solid formed (yield 80%), which consisted of a mixture (50%) of the isomers **3a** and **3b**, was then dissolved in the minumum amount of CH_2Cl_2 and layered with CH_3OH. Slow evaporation of the solution at room temperature produced complex **3a** as the most insoluble product (yield 35%). The resulting filtrate was enriched in the other isomer in the molar ratio **3a**:**3b** = 23:77. Anal. Calcd (found) for $C_{40}H_{45}NPPdClFeO$: C, 58.1 (57.95); H, 6.0 (6.15); N, 1.93 (1.8). *Characterization data*[14] for **3a** are as follows. ^{1}H NMR data (in ppm): ferrocenyl moiety protons 4.06 [5H, s, C_5H_5], 3.02 [1H, s, H^3], 3.95 [1H, s, H^4], 3.74 [1H, s, H^5], 2.67 [3H, s, N(CH_3)], 3.13 [3H, s, N(CH_3)], 1.55 [3H, d, CH_3], and 4.22 [1H, m, >CH−]; phosphine protons 7.79−8.09 [10H, m, $H^{2'}$, $H^{3'}$, $H^{4'}$, $H^{5'}$, and $H^{6'}$ (Ph)], 2.88 [1H, m, H^7], 1.98 [1H, m, H^{8a}], 1.42 [1H, br m, H^{8b}], 2.15 [2H, m, H^{9a} and H^{11a}], 1.57 [2H, br., H^{10}], 1.40 [3H, d, H^{14}], 5.03 [1H, s, H^{15a}], 4.83 [1H, s, H^{15b}], and 1.09 [3H, s, CH_3]. ^{13}C NMR (in ppm): ferrocenyl moiety 70.18 [C_5H_5], [d, C^1], 71.3 [C^3], 67.38 [C^4], 65.71 [C^5], 49.28 and 48.56 [s, N(CH_3)$_2$], 12.06 [CH_3] and 62.91 [>CH−]; phosphine group 132.50 and 133.46 [d, $C^{2'}$ and $C^{6'}$ (Ph)], 129.36 [m, $C^{3'}$ and $C^{5'}$ (Ph)], 129.3 [$C^{4'}$ (Ph)], 49.27 [d, C^7], 28.76 [d, C^8], 38.04 [d, C^9], 24.42 [C^{10}], 38.43 [d, C^{11}], 71.91 [d, C^{12}], 144.38 [C^{13}], 23.47 [C^{14}], 113.31 [C^{15}], and 23.07 [CH_3]. ^{31}P NMR (in ppm): 49.25]. $[\alpha]_{20\ °C}$ (0.01 g/100 mL) = +88.7°. Data for **3b** are as follows. ^{1}H NMR data (in ppm): ferrocenyl moiety protons 3.51 [5H, s, C_5H_5], 3.20 [1H, s, H^3], 3.90 [2H, br m, H^4 and >CH−], 3.69 [1H, s, H^5], 2.89 [3H, s, N(CH_3)], 3.43 [3H, s, N(CH_3)], and 1.26 [3H, d, CH_3]; phosphine protons 7.79−8.09 [10H, m, $H^{2'}$, $H^{3'}$, $H^{4'}$, $H^{5'}$, and $H^{6'}$ (Ph)], 2.88 [1H, m , H^7], 1.98 [1H, m, H^{8a}], 1.41 [1H, br m, H^{8b}], 2.17 [2H, m, H^{9a} and H^{11a}], 1.61 [2H, br m, H^{10}], 1.40 [3H, d, H^{14}], 4.89 [1H, s, H^{15a}], and 4.58 [1H, s, H^{15b}]. ^{13}C NMR (in ppm): ferrocenyl moiety 70.18 [C_5H_5], [d, C^1], 71.3 [C^3], 67.38 [C^4], 65.71 [C^5], 49.28 and 48.56 [s, N(CH_3)$_2$], 13.8 [CH_3] and 61.59 [>CH−]; phosphine group 132.52 and 133.46 [d, $C^{2'}$ and $C^{6'}$ (Ph)], 129.36 [m, $C^{3'}$ and $C^{5'}$ (Ph)], 129.3 [$C^{4'}$ (Ph)], 48.62 [d, C^7], 29.27 d, C^8], 38.04 [d, C^9], 26.26 [C^{10}], 38.32

[d, C^{11}], 71.13 [d, C^{12}], 144.70 [C^{13}], 22.81 [C^{14}], 112.90 [C^{15}], and 22.81 [CH_3]. ^{31}P NMR (in ppm): 50.32.

(R*$_P$*,S*$_C$*,R*$_P$*)-(−)-[Pd{[(η*^{5}*-C*$_5$*H*$_3$*)CH(CH*$_3$*)N(CH*$_3$*)*$_2$*]Fe(η*^{5}*-C*$_5$*H*$_5$*)}{(+)-binap}] (4a). A 23 mg (2.9×10^{-2} mmol) amount of **1**, was suspended in 2 mL of $CDCl_3$, and then 12.6×10^{-2} mmol of (±)-binap was added. The reaction mixture was stirred for 8 days at room temperature. After this period the dark violet solution was concentrated to dryness on a rotary evaporator. The gummy residue was then dissolved in the minimum amount of chloroform and the solution passed through an SiO_2 chromatography column. Elution with chloroform produced a violet solution, and concentration to dryness gave **4a** (yield 41%). Then a mixture of $CHCl_3$ and MeOH (100/5) was used as eluant, and a pale yellow solution was collected. Complex **5b** was isolated from this solution by concentration to dryness on a rotary evaporator (yield 36%). *Characterization data*[14] for **4a** are as follows. Anal. Calcd (found) for $C_{46}H_{70}NFePdP_2Cl$: C, 61.61 (61.7); H, 7.87 (7.95); N, 1.56 (1.6). ^{1}H NMR data (in ppm): ferrocenyl moiety protons 3.51 [5H, s, C_5H_5], 3.20 [1H, s, H^3], 3.90 [2H, br m, H^4 and >CH−], 3.69 [1H, s, H^5], 2.89 and 3.43 [6H, s, $N(CH_3)_2$], and 1.26 [3H, d, CH_3]; phosphine protons 6.80 [2H, d, H^8] and 7.8−7.8 [8H, br m, H^9, H^{10}, H^{11}, and H^{12}]. ^{13}C NMR (in ppm): ferrocenyl moiety 69.82 [C_5H_5], 69.28 [C^3], 70.31 [C^4], 72.39 [C^5], 42.10 and 48.56 [s, $N(CH_3)$], 12.12 [CH_3], 61.62 [>CH−] (the signals due to C^1 and C^2 carbons were not observed due to NOE effects and low solubility of the complex); phosphine group (a) phenyl carbons 132.5 and 133.46 [d, $C^{2'}$ and $C^{6'}$ (Ph)], 129.36 [m, $C^{3'}$ and $C^{5'}$ (Ph)], and 129.3 [$C^{4'}$(Ph)], (b) naphthyl carbons 138.70, 137.52, 135.13, 135.21, 134.18, 134.03, 133.65, 133.80, 133.25, 132.85, 128.88, 128.12, 127.88, 127.8, 127.63, 127.56, 127.40, 127.30, 126.80 and 122.66. ^{31}P NMR (in ppm): 39.77 [d, ^2J(PP) = 48.39 Hz] and 15.32 [d, ^2J(PP) = 48.39 Hz]. $[\alpha]_{20\ °C}$ (0.01 g/100 mL) = −277°. Data for **4b** are as follows.[15] ^{1}H NMR data (in ppm): ferrocenyl moiety protons 3.51 [5H, s, C_5H_5], 3.20 [1H, s, H^3], 3.90 [2H, br m, H^4 and >CH−], 3.69 [1H, s, H^5], 2.89 [3H, s, $N(CH_3)$], 3.43 [6H, s, $N(CH_3)$] and 1.26 [3H, d, CH_3]; phosphine protons 6.75 [2H, d, H^9] and 7.8−7.8 [8H, br m, H^9, H^{10}, H^{11}, and H^{12}]. ^{31}P NMR (in ppm): 39.77 [d, ^2J(PP) = 48.39 Hz] and 15.32 [d, ^2J(PP) = 48.39 Hz].

X-ray Structure Analysis. Data Collection. A prismatic crystal of compound **2a** (sizes in Table 1) was selected and mounted on an Enraf-Nonius CAD-4 four-circle diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections in the range $12° \le \Theta \le 21°$ and refined by least-squares methods. Intensities were collected with graphite-monochromated Mo Kα radiation, using the $\omega-2\Theta$ scan technique. Three reflections were measured every 2 h as orientation and intensity control, and no significant intensity decay was observed. A total of 4817 reflections were collected in the range $2.06° < \Theta < 29.96°$, of which 4748 were nonequivalent by symmetry (R_{int}(on I) = 0.010); 3413 reflections were assumed as observed, applying the condition $I > 2\sigma(I)$. Lorentz−polarization, but not absoption, corrections were made.

Structure Solution and Refinement. The structure was solved by Patterson synthesis using the SHELXS computer program[16] and refined by the full-matrix least-squares method with the SHELX96 computer program,[17] using 8479 reflections (very negative intensities were not assumed). The function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = \{\sigma^2(I) + (0.0503P)^2\}^{-1}$, and $P = \{|F_o|^2 + 2|F_c|^2\}/3$. f, f' and f'' were taken from ref 18. The absolute configuration of the structure was determined from the Flack coefficient[19] (0.02(4) for the results given). The final R (on F) factor was 0.040, R_w (on $|F|^2$) was 0.081, and the goodness of fit was 0.953. The number of refined parameters was 372. Further details concerning the crystal structure are also given in Table 1.

Acknowledgment. We are indebted to the DGICYT, the Comision Interministerial de Ciencia y Tecnologia, and the Generalitat de Catalunya (projects PB93-0804, QFN-95-4708, and 1995-SGR-0044) for financial support.

Supporting Information Available: Tables containing final atomic coordinates for all atoms, complete lists of bond lengths and angles, and anisotropic thermal parameters (11 pages). Ordering information is given on any current masthead page.

OM970098Z

(15) Data given have for complex **4b** were obtained at 240 K inmediately after the mixing of compound **1** and the stoichiometric amount of (−)-binap. The number of signals and their multiplicities were identical with those obtained from the comparison of the spectra recorded at 240 K for the solution obtained immediately after the mixing of compound **1** and the stoichiometric amount of (±)-binap and that of pure **4a** at 240 K.

(16) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *A46*, 467.
(17) Sheldrick, G. M. Manuscript in preparation.
(18) *International Tables of X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, pp 99−100, 149.
(19) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 876.