Metal Template Promoted Hydroamination of Ethynylphosphines and Aniline. Asymmetric Synthesis, Coordination Chemistry, and the Imine−Enamine Tautomerism of *P*-Chiral Iminophosphines

Xueming Liu, K. F. Mok, and Pak-Hing Leung*

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260

Received April 23, 2001

In the presence of the organopalladium template containing the orthometalated (*S*)-(1-(dimethylamino)ethyl)naphthylene auxiliary, both diphenyl(phenylethynyl)phosphine and di(phenylethynyl)phenylphosphine were reactive toward the novel hydroamination reaction with aniline to give the corresponding bidentate iminophosphines in high yields. These novel P−N ligands exhibited an interesting imine−enamine tautomerism in solution. Spectroscopic studies confirmed that the uncoordinated ligands adopted the stable imino form but could be transformed to the enamino form upon complexation with palladium. The relative stability of the imino and enamino chelates is sensitive to the substituents on the phosphorus donor atoms. When di(phenylethynyl)phenylphosphine was used as the starting material, the hydroamination reaction gave a 4:1 mixture of the chelating diastereomeric *P*-chiral iminophosphine on the chiral template. These diastereomeric complexes could be separated efficiently via silica gel column chromatography. A pair of novel and enantiomerically pure *P*-chiral iminophosphines was obtained in high yields from the separated diastereomeric template complexes by treatment with KCN.

Introduction

Organometallic complexes containing η^1-M−C≡CR alkynyl ligands are important starting materials for the synthesis of carbocyclic and heterocyclic compounds.[1] In many organoalkynyl complexes, the carbon−carbon triple bonds are chemically reactive and are able to undergo electrophilic additions, Diels−Alder reaction, and cycloalkenation processes. Similar reactivities are observed with the carbon−phosphorus triple bonds in phospha-alkyne η^1-M−P≡CR derivatives.[2] On the other hand, the carbon−carbon triple bond in coordinated phosphinoalkynes has been reported to undergo P−C bond cleavages, insertion, and coupling reactions.[3] Furthermore, phosphinoalkynes can be activated by metal complexation toward nucleophilic attack by water, ethanol, hydrogen halides, and diphenylphosphine.[4] Phosphinoalkynes function typically as monodentate or bidentate ligands in coordination chemistry. In M−P−C≡CR complexes, the carbon−carbon triple bonds are polarized, with the carbons attached to the phosphorus being partially negatively charged.[5] We therefore believe that this electronic induction effect on the M−P−C≡CR triple bond would render coordinated phosphinoalkynes susceptible to electrophilic and nucleophilic reactions. In this paper, we present the first examples of the palladium template activated intermolecular hydroamination between aniline and ethynylphosphines. Chelating iminophosphine ligands were generated efficiently from these hydroamination reactions. It is noteworthy that iminophosphines are important ligands, as they are potential catalyst supporters.[6]

Results and Discussion

Hydroamination of the Achiral Diphenyl(phenylethynyl)phosphine. The achiral diphenyl(phenylethynyl)phosphine was selected as the model compound for the subsequent asymmetric hydroamination reaction. No reaction between the free $Ph_2PC{\equiv}CPh$ and

(1) Li, C. L.; Liu, R. S. *Chem. Rev.* **2000**, *100*, 3127.

(2) Mahh, M. J.; Nixon, J. F. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; John Wiley: West Sussex, 1990; Vol. 1, Chapter 9.

(3) For examples, see: Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 10. Carty, A. J.; Nucciarone, D.; MacLaughlin, S. A.; Taylor, N. J. *Organometallics* **1988**, *7*, 106. Jeffery, J. C.; Pereira, R. M. S.; Vargas, M. D.; Went, M. J. *J. Chem. Soc., Dalton Trans.* **1995**, 1805. Ara, I.; Falvello, L. R.; Fernandez, S.; Fornies, J.; Lalinde, E.; Martin, A.; Moreno, M. T. *Organometallics* **1997**, *16*, 5923. Cadiero, V.; Zablocka, M.; Donnadieu, B.; Igau, A.; Majoral, J. P.; Skowronska, A. *J. Am. Chem. Soc.* **1999**, *121*, 11086. Belluco, U.; Bertani, R.; Michelin, R. A.; Mozzon, M. *J. Organomet. Chem.* **2000**, *600*, 37. Ara, I.; Berenguer, J. R.; Eguizabal, E.; Fornies, J.; Gomez, J.; Lalinde, E.; Saez-Rocher, J. M. *Organometallics* **2000**, *19*, 4385.

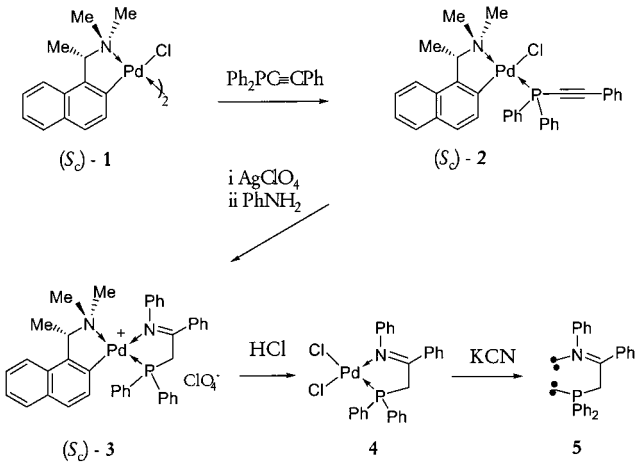
(4) For examples, see: Tayor, N. J.; Carty, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 799. Carty, A. J.; Jacobson, S. E.; R. T. Taylor, N. J. *J. Am. Chem. Soc.* **1975**, *97*, 7254. Carty, A. J.; Johnson, D. K.; Jacobson, S. E. *J. Am. Chem. Soc.* **1979**, *101*, 5612.

(5) Louattani, E.; Lledos, A.; Suades, J.; Alvarez-Larena, A.; Piniella, J. F. *Organometallics* **1995**, *14*, 1053. Ara, I.; Falvello, L. R.; Fernández, S.; Forniés, J.; Lalinde, E.; Martin, A.; Moreno, M. T. *Organometallics* **1997**, *16*, 5926. Dickson, R. J.; de Simon, T.; Parker, R. J.; Fallon, G. D. *Organometallics* **1997**, *16*, 1531. Louattani, E.; Suades, J.; Alvarezlarena, A.; Piniella, J. F.; Germain, G. *J. Organomet. Chem.* **1996**, *506*, 121. Orama, O. *J. Organomet. Chem.* **1986**, *314*, 273. Sappa, E. *J. Organomet. Chem.* **1988**, *352*, 327. Louattani, E.; Suades, J. *J. Organomet. Chem.* **2000**, *604*, 234.

(6) Shirakawa, E.; Yoshida, H.; Kurahashi, T.; Nakao, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1998**, *120*, 2975. Van den Beuken, E. K.; Smeets, W. J. J.; Spek, A. L.; Feringa, B. L. *J. Chem. Soc., Chem. Commun.* **1998**, 223. Reddy, K. R.; Chen, C. L.; Liu, Y. H.; Peng, S. M.; Chen, J. T.; Liu, S. T. *Organometallics* **1999**, *18*, 2574.

10.1021/om010333k CCC: $20.00
Publication on Web 08/08/2001

Scheme 1



aniline was observed in the absence of a transition metal ion. However, the hydroamination reaction proceeded smoothly when both $Ph_2PC{\equiv}CPh$ and aniline were coordinated onto the same metal template. We found the dimeric complex (S_c)-**1** to be an efficient template for this intramolecular coupling reaction. As illustrated in Scheme 1, the reaction initially involved the regiospecific coordination of the phosphinoalkyne ligand onto the orthometalated naphthylamine complex to form the monomeric chloro complex (S_c)-**2**. The regiospecificity is due to the distinct electronic directing effects originating from the σ-donating nitrogen and the π-accepting aromatic carbon of the orthopalladated naphthylamine ring. Furthermore, it has been well established that the chloro ligands in this class of organopalladium complexes are thermodynamically and kinetically stable and cannot be displaced efficiently by most other monodentate ligands, including phosphines and aniline.[7] Indeed, there was no reaction observed between aniline and the chloro complex (S_c)-**2**. Evidently, the coordinated phosphino alkyne ligand in (S_c)-**2** is not chemically reactive toward free aniline. Thus it was necessary to remove the chloro ligand in (S_c)-**2** by the treatment with silver perchlorate in order to allow the coordination of aniline onto the metal.[8] The intramolecular hydroamination reaction was subsequently carried out at 100 °C in toluene for 10 h to give the desired iminophosphine complex (S_c)-**3** as pale yellow prisms (56%), mp > 200 °C (dec), $[\alpha]_D$ −193° (*c* 0.5 CH_2Cl_2). The ^{31}P NMR spectrum of (S_c)-**3** in $CDCl_3$ exhibited a singlet signal at δ 48.8. A single crystal X-ray structural analysis of the highly crystalline cationic complex (S_c)-**3** was achieved (Figure 1). Selected bond distances and angles are given in Table 1. The X-ray structural analysis of (S_c)-**3** establishes unambiguously that the desired iminophosphine P−N chelate was formed regiospecifically on the palladium template. The N(2)−C(15) [1.293(4) Å] and C(15)−C(16) [1.492(5) Å] distances are typical for C=N and C−C bonds, respectively. A noticeable feature of the square-planar complex is the

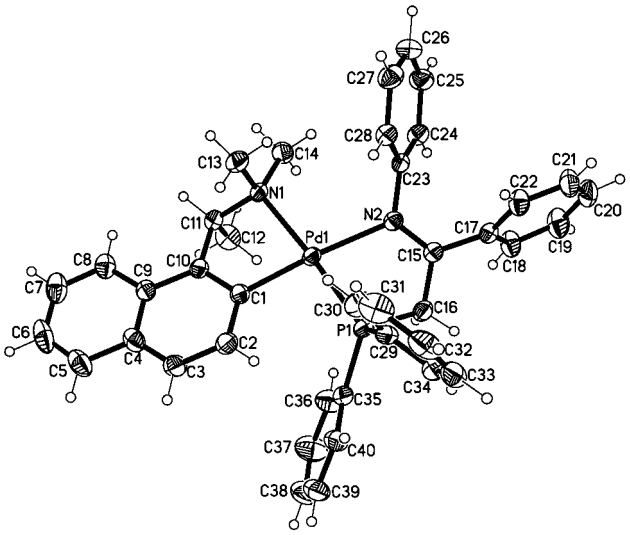


Figure 1. Molecular structure and absolute stereochemistry of the cationic complex (S_c)-**3**. Thermal ellipsoids enclose 50% probability levels.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Template Complex (S_c)-3

Pd(1)−C(1)	2.001(3)	Pd(1)−N(1)	2.164(2)
Pd(1)−N(2)	2.206(3)	Pd(1)−P(1)	2.217(1)
N(2)−C(15)	1.293(4)	N(2)−C(23)	1.439(4)
C(15)−C(16)	1.492(5)	C(15)−C(17)	1.490(4)
P(1)−C(16)	1.841(4)	P(1)−C(29)	1.817(3)
C(1)−Pd(1)−N(1)	80.4(1)	C(1)−Pd(1)−N(2)	175.4(1)
C(1)−Pd(1)−P(1)	96.4(1)	N(1)−Pd(1)−N(2)	104.2(1)
N(1)−Pd(1)−P(1)	174.7(1)	N(2)−Pd(1)−P(1)	79.1(1)
P(1)−C(16)−C(15)	108.7(2)	C(16)−C(15)−N(2)	117.7(3)
C(15)−N(2)−C(23)	120.7(3)	C(15)−N(2)−Pd(1)	119.6(2)
Pd(1)−P(1)−C(16)	100.7(1)	Pd(1)−P(1)−C(29)	113.8(1)
Pd(1)−P(1)−C(35)	122.2(1)	Pd(1)−N(2)−C(23)	119.7(2)

marked expansion in the N(1)−Pd(1)−N(2) angle to 104.2(1)°. This is clearly a consequence of the steric repulsion between the substituents on the two neighboring nitrogen donor atoms.[9]

The ^1H NMR spectrum of (S_c)-**3** in $CDCl_3$ exhibited two characteristic doublet of doublet (dd) signals for the two nonequivalent prochiral PCH_2 protons at δ 3.87 ($^2J_{PH}$ = 14.3 Hz, $^2J_{HH}$ = 16.7 Hz) and δ 5.42 ($^2J_{PH}$ = 9.8 Hz, $^2J_{HH}$ = 16.7 Hz). These dd signals are useful handles in the spectroscopic investigation of the imine−enamine tautomerism process, which takes place within the chelating iminophosphine ligand in complex (S_c)-**3**. Interestingly, the dd signal at δ 5.42 disappeared almost immediately upon adding D_2O into an NMR sample of (S_c)-**3**. At the same time, the other dd signal at δ 3.87 became a simple doublet ($^2J_{PH}$ = 14.3 Hz). Eventually the simplified doublet at δ 3.87 diminished in intensity after the NMR mixture was allowed to stand for 1 h. This simple spectroscopic experiment thus revealed that in $CDCl_3$ the bidentate ligand indeed undergoes rapid imine−enamine tautomerism, as C−H protons in the imino form are generally inert to D_2O exchange, whereas

(7) Kerr, P. G.; Leung, P. H.; Wild, S. B. *J. Am. Chem. Soc.* **1987**, *109*, 4321. Dunina, V. V.; Golovan, E. B.; Gulyukina, N. S.; Buyevich, A. V. *Tetrahedron: Asymmetry* **1995**, *6*, 2731. Hockless, D. C, R.; Gugger, P. A.; Leung, P. H.; Mayadunne, R. C.; Pabel, M.; Wild, S. B. *Tetrahedron* **1997**, *53*, 4083. He, G.; Loh, S. K.; Vittal, J. J.; Mok, K. F.; Leung, P. H. *Organometallics* **1998**, *17*, 3931.

(8) Loh, S. K.; Mok, K. F.; Leung, P. H.; White, A. J. P.; Williams, D. J. *Tetrahedron: Asymmetry* **1996**, *7*, 45.

(9) Leung, P. H.; McLaughlin, G. M.; Martin, J. W. L.; Wild, S. B. *Inorg. Chem*. **1986**, *25*, 3392. Chooi, S. Y. M.; Hor, T. S. A.; Leung, P. H.; Mok, K. F. *Inorg. Chem*. **1992**, *31*, 1494. Leung, P. H.; Quek, G. H.; Lang, H.; Liu, A. M.; Mok, K. F.; White, A. J. P.; Williams, D. J.; Rees, N. H.; McFarlane, W. *J. Chem. Soc., Dalton Trans*. **1998**, 1639. Song, Y.; Vittal, J. J.; Chan, S. H.; Leung, P. H. *Organometallics* **1999**, *18*, 650. Liu, X.; Mok, K. F.; Vittal, J. J.; Leung, P. H. *Organometallics* **2000**, *19*, 3722.

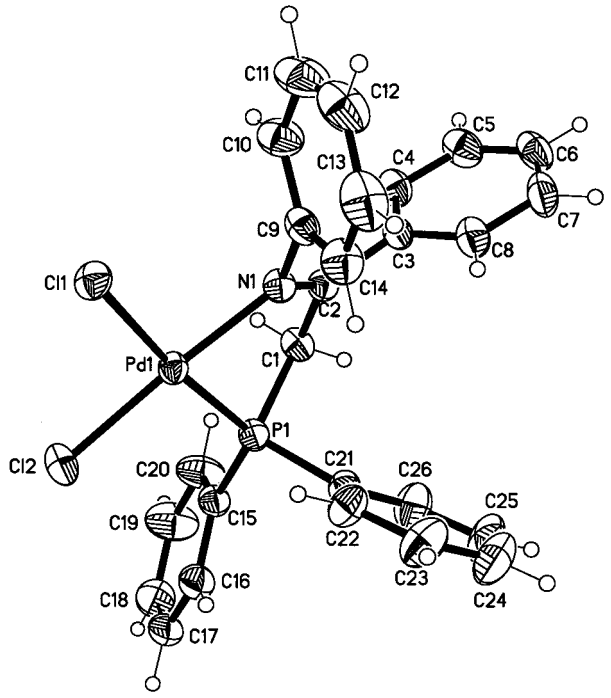


Figure 2. Molecular structure of the dichloro complex **4**. Thermal ellipsoids enclose 50% probability levels.

N−H protons in the enamino form are prone to the exchange. It is important to note that the ^{31}P NMR spectrum of the same sample recorded the original singlet signal at δ 48.8 throughout the course of D_2O exchange. Thus the P−N chelate in (S_c)-**3** exists predominately in its imino form in solution. To date, there are several examples of monodentate *N*-imino donor atoms that undergo such a dynamic imine−enamine tautomerism in organopalladium complexes.[10] However, the imine−enamine tautomerism observed in complex (S_c)-**3** is the first example that such a dynamic process could occur within a bidentate metal chelate. Such tautomeric processes may affect the electronic properties of these unsaturated ligands.[11]

The naphthylamine ligand on the template complex (S_c)-**3** could be removed chemoselectively by treatment with concentrated HCl. Thus the achiral dichloro complex **4** was obtained as yellow prisms in 88% yield, mp > 200 °C (dec). The ^{31}P NMR spectrum of **4** in $CDCl_3$ exhibited a singlet at δ 46.1. A single-crystal X-ray structural analysis of **4** confirmed that while the ortho-metalated naphthylamine ligand could be efficiently removed by concentrated HCl, the iminophosphine P−N chelate remained unchanged in this acid treatment (Figure 2). Selected bond distances and angles are given in Table 2. In contrast to (S_c)-**3**, no major interchelate repulsion exists within the dichloro complex and the geometry at palladium is regular planar with *cis* angles ranging between 80.8(1)° and 94.1(1)°, with the most acute being associated with the five-membered chelate ring. The two Pd−Cl bond distances [2.288(1) and 2.363(1) Å] differ significantly, with the bond *trans* to the phosphorus being noticeably enlarged from normal, reflecting the stronger electronic *trans* influence of the phosphorus versus nitrogen.[12] Similar to (S_c)-**3**, ^{1}H NMR studies revealed that the imino-substituted phosphine ligand in the dichloro complex exists predominately in its imino form, although the imine−enamine tautomerism process was found to take place rapidly in solution.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of the Dichloro Complex 4

Pd(1)−Cl(1)	2.363(1)	Pd(1)−Cl(2)	2.288(1)
Pd(1)−N(1)	2.074(3)	Pd(1)−P(1)	2.197(1)
N(1)−C(2)	1.294(4)	C(1)−C(2)	1.501(4)
P(1)−C(1)	1.826(3)	P(1)−C(15)	1.797(3)
P(1)−C(21)	1.817(3)	N(1)−C(9)	1.458(4)
Cl(1)−Pd(1)−N(1)	94.1(1)	Cl(1)−Pd(1)−P(1)	174.0(1)
Cl(1)−Pd(1)−Cl(2)	92.6(1)	N(1)−Pd(1)−P(1)	80.0(1)
N(1)−Pd(1)−Cl(2)	172.6(1)	P(1)−Pd(1)−Cl(2)	93.3(1)
P(1)−C(1)−C(2)	105.1(2)	C(1)−C(2)−N(1)	117.7(3)
C(2)−N(1)−C(9)	121.3(3)	C(2)−N(1)−Pd(1)	118.9(2)
Pd(1)−P(1)−C(1)	97.5(1)	Pd(1)−P(1)−C(15)	124.5(1)
Pd(1)−P(1)−C(21)	111.1(1)	Pd(1)−N(1)−C(9)	120.1(2)

The liberation of the iminophosphine ligand from the dichloro complex **4** was achieved by treatment of the complex with potassium cyanide. Thus the free ligand **5** was obtained as an air-stable solid in 65.2% yield. The ^{31}P NMR spectrum of **5** in $CDCl_3$ exhibits a singlet resonance at δ −13.1. The ^{1}H NMR spectrum of the ligand in the same solvent exhibited the characteristic doublet at δ 3.55 ($^2J_{PH}$ = 2.0 Hz) for the two equivalent PCH_2 protons. This doublet signal was not affected by the D_2O exchange experiment. The spectroscopic analysis thus revealed that, in $CDCl_3$ the iminophosphine ligand **5** exists exclusively in its imino form and does not transform into the corresponding enamino counterpart in solution. Apparently the rapid imine−enamine tautomeric equilibriums observed in the chelating iminophosphine ligands in both complexes (S_c)- **3** and **4** were triggered by the metal complexation.

Asymmetric Hydroamination of the Prochiral Di(phenylethynyl)phenylphosphine: Synthesis of a Pair of Diastereomeric Complexes Containing the *P*-Chiral Iminophosphines (S_c,R_p)-7 and (S_c,S_p)-7. The above hydroamination reaction has been modified successfully for the asymmetric synthesis of a pair of *P*-chiral iminophosphines by using the prochiral phosphinoalkyne $PhP(C{\equiv}CPh)_2$ as the starting material (Scheme 2). Thus, upon the removal of chloro ligand in (S_c)-**6** by silver perchlorate, the coupling reaction proceeded smoothly at room temperature. The reaction was monitored by ^{31}P NMR spectroscopy and was found to be complete in 16 h. The ^{31}P NMR spectrum of the reaction mixture in $CDCl_3$ exhibited two sharp singlets at δ 15.1 and 17.3 with relative intensities of 4:1. Accordingly, two stereochemically nonequivalent products were generated in this reaction. The mixture could

(10) O'Connor, J. M.; Uhrhammer, R.; Rheingold, A. L.; Roddick, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 4530. Alías, F. M.; Belderraín, T. R.; Paneque, M.; Poveda, M. L.; Carmona, E. *Organometallics* **1997**, *16*, 301. Alías, F. M.; Belderraín, T. R.; Paneque, M.; Poveda, M. L.; Carmona, E. *Organometallics* **1998**, *17*, 5620. Veya, P.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, L. *Organometallics* **1993**, *12*, 4899.

(11) Casey, C. P.; Czerwinski, C. J.; Fusie, K. A.; Hayashi, R. K. *J. Am. Chem. Soc.* **1997**, *119*, 3971. De los Rios, I.; Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529. Wakatsuki, Y.; Koga, N.; Werner, H.; Morkuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 360.

(12) For examples, see: Leung, P.-H.; Siah, S.-Y.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1998**, 893. Leung, P.-H.; He, G. S.; Lang, H. F.; Liu, A. M.; Loh, S.-K.; Selvaratnam, S.; Mok, K. F.; White, A. J. P.; Williams, D. J. *Tetrahedron* **2000**, *56*, 7. Leung, P.-H.; Loh, S. K.; Mok, K. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1996**, 591. Leung, P.-H.; Lang, H. F.; White, A. J. P.; Williams, D. J. *Tetrahedron: Asymmetry* **1998**, *9*, 2961.

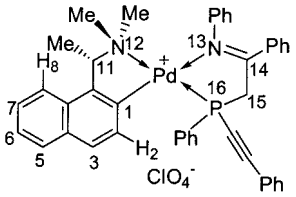
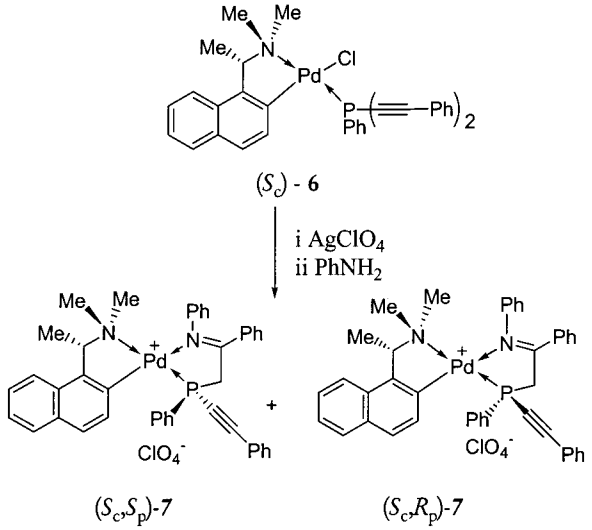


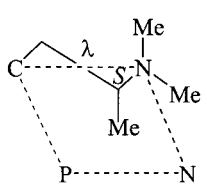
Figure 3. Numbering scheme of the diastereomeric complex **7** for the ROESY NMR studies.

Scheme 2



be separated efficiently by silica gel column chromatography. The major isomer was obtained as yellow solids in 56% yield, $[\alpha]_D$ −266.1° (CH_2Cl_2), and the minor isomer was isolated in similar form in 15% yield, $[\alpha]_D$ +62.5° (CH_2Cl_2). Both isomeric complexes showed similar elemental analysis results. Furthermore, their ES-MS spectral patterns were identical with their molecular weights recorded at the same 708.9 (M^+) position. Hence it can be deduced that they are diastereomeric products (S_c,R_p)-**7** and (S_c,S_p)-**7**. The two complexes have similar molecular connectivities but, as desired, differ in the absolute chiralities at their stereogenic phosphorus donors. Both isomers are chemically stable and readily soluble in organic solvents. However, they could not be induced to form single crystals suitable for X-ray structure analysis. Accordingly, it was necessary to determine the absolute stereochemistry of these isomeric hydroamination products by the 2D rotating frame nuclear Overhauser enhancement (ROESY) ^{1}H NMR technique.[13] We have previously applied this reliable 2D NMR technique for the assignments of the absolute stereochemistry in a series of coordinated *P*-chiral phosphines containing the same orthometalated naphthylamine auxiliary.

Assignments of Absolute Stereochemistry in the Diastereomeric Complexes. The Chiral Auxiliary and Internal Stereochemical References. Figure 3 shows the numbering scheme of the diastereomeric complexes **7** used in the 2D ROESY NMR analysis. In these NMR analyses, the well-established stereochemical features of the orthometalated (*S*)-naphthylamine unit within the diastereomeric complexes **7** are used as the internal stereochemical references. Due to the repulsive interaction between Me(11) and the proximal H(8) naphthylene proton, Me(11) invariably takes up the axial position in the stable five-membered organopalladium ring which adopts the static λ absolute conformation (Figure 4). This axial Me(11) group projects perpendicularly below the square-plane. On the other hand, the prochiral N-Me groups attached to the organopalladium ring are locked by the rigid λ ring conformation into the nonequivalent axial and equatorial positions. The axial NMe group projects perpendicularly above the square-plane, while the equatorial NMe group protrudes somewhat below the plane and toward the adjacent nitrogen donor in the P−N ring. Similarly, the rigid organometallic ring also locks the H(2) naphthylene proton in the position slightly above the plane and close to the phosphorus donor atom. With reference to the unique structural feature of the auxiliary, appropriate interchelate NOE interactions between the naphthylamine auxiliary and the iminophosphine chelates would allow the assignment of the absolute stereochemistry of the P−N chelates.



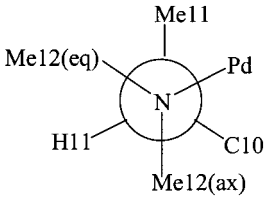


Figure 4. Absolute conformation of the PdCN ring and the staggered orientation of its C(11) and N(12) substituents.

Stereochemical Considerations of the Diastereomeric Complexes. On the basis of the absolute chirality of the phosphorus center and the absolute conformation of the iminophosphine P−N ring, the above asymmetric hydroamination reaction may generate up to four stereoisomeric products. Figure 5 shows the absolute stereochemistries of the four isomers. The absolute configuration at the stereogenic phosphorus centers of isomer **A** and **B** is *R*. They differ in their five-membered P−N ring conformation in that the P−N ring conformation in isomer **A** is δ, but in isomer **B** it is λ. Similarly, isomers **C** and **D** are conformers with the same *S* absolute configuration at the stereogenic phosphorus centers. A Dreiding model study indicated that in isomers **A** and **C**, the δ-iminophosphine rings dispose their N−Ph substituents in sterically unfavorable positions whereby they suffer from severe interchelate repulsions between their neighboring equatorial-NMe groups. On the other hand, these neighboring N-substituents in isomers **B** and **D** are located in sterically favorable staggered orientations. Similarly, the equatorially disposed *P*-substituents in both isomers **A** and **C** interact somewhat unfavorably with the protruding H(2) proton from the naphthylamine auxiliaries. Accordingly, isomers **A** and **C** are sterically unfavorable and the two diastereomeric products are likely to be isomers **B** and **D**. Nevertheless, the four isomers are stereochemically distinct molecules and should be readily identified by 2D-ROESY NMR spectroscopy.

(13) Bookham, J. L.; McFarlane, W. *J. Chem. Soc., Chem. Commun.* **1993**, 1352. Aw, B.-H.; Selvaratnam, S.; Leung, P. H.; Rees, N. H.; McFarlane, W. *Tetrahedron: Asymmetry* **1996**, *7*, 1753. Aw, B.-H.; Hor, A. T. S.; Selvaratnam, S.; Mok, K. F.; White, A. J. P.; Williams, D. J.; Rees, N. H.; McFarlane, W.; Leung, P.-H. *Inorg. Chem.* **1997**, *36*, 2138. Lang, H. F.; Leung, P. H.; Rees, N. H.; McFarlane, W. *Inorg. Chim. Acta* **1999**, *284*, 99.

Table 3. Selected ^{31}P and ^{1}H NMR Spectra Chemical Shift Values of (S_c)-3, (S_c,R_p)-7, and (S_c,S_p)-7 in $CDCl_3$ (coupling constants in Hz are given in parentheses)

	(S_c)-**3**	(S_c,R_p)-**7**	(S_c,S_p)-**7**
^{31}P	49.8 s	15.1 s	17.3 s
CH*Me*	2.06 d ($^3J_{HH}$ = 6.4)	2.08 d ($^3J_{HH}$ = 6.4)	2.02 d ($^3J_{HH}$ = 6.4)
N*Me(eq)*	2.09 d ($^4J_{PH}$ = 4.0)	2.08 d ($^4J_{PH}$ = 3.6)	2.00 d ($^4J_{PH}$ = 2.8)
N*Me(ax)*	2.41 d ($^4J_{PH}$ =1.6)	2.37 d ($^4J_{PH}$ = 2.0)	2.48 (d) ($^4J_{PH}$ = 2.0)
C*H*Me	4.21 qn ($^3J_{HH}$ =$^4J_{PH}$ = 6.4)	4.20 qn ($^3J_{HH}$ = $^4J_{PH}$ = 6.4)	4.23 qn ($^3J_{HH}$ = $^4J_{PH}$ = 6.4)
CH*H(eq)*	3.87 dd ($^2J_{HH}$ = 14.3, $^2J_{PH}$ = 16.7)	3.83 dd ($^2J_{HH}$ =$^2J_{PH}$ = 16.5)	3.83 dd ($^2J_{HH}$ = 16.9, $^2J_{PH}$ = 14.9)
CH*H(ax)*	5.42 dd ($^2J_{HH}$ = 16.7, $^2J_{PH}$ = 9.8)	5.13 dd ($^2J_{HH}$ = 16.5, $^2J_{PH}$ = 8.9)	5.27 dd ($^2J_{HH}$ = 16.9, $^2J_{PH}$ = 12.8)
Np-*H(2)*	6.88 dd ($^3J_{HH}$ =8.4, $^4J_{PH}$ = 6.9)	7.08 dd ($^3J_{HH}$ = $^4J_{PH}$ = 8.2)	signal not discernible
Np-*H(3)*	7.06 d ($^3J_{HH}$ = 8.4)	7.18 d ($^3J_{HH}$ = 8.2)	signal not discernible
o-P*Ph*	8.19 dd ($^3J_{HH}$ = 6.9, $^3J_{PH}$ = 11.8)	8.05 dd ($^3J_{HH}$ = 7.8, $^3J_{PH}$ = 14.6)	8.27 dd ($^3J_{HH}$ = 7.8, $^3J_{PH}$ = 13.8)

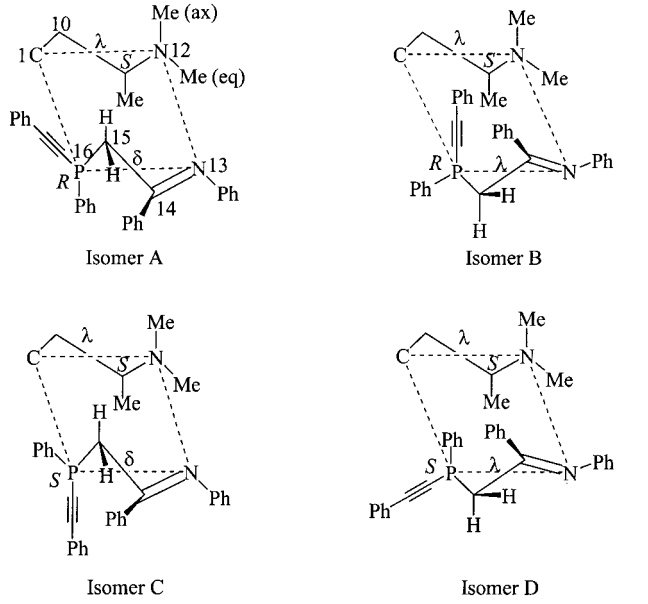


Figure 5. The four possible conformations of (S_c,R_p)-**7** and (S_c,S_p)-**7**.

Stereochemical Analysis of Diastereomers by 2D ROESY NMR Spectroscopy. Selected ^{31}P and ^{1}H NMR data of the two diastereomeric complexes **7** are given in Table 3. Selected data of the model complex (S_c)-**3** are included in the table for comparison purposes. These NMR assignments are based on a series of ^{1}H, ^{31}P,$^{1}H\{^{31}P\}$, and 2D ^{1}H-ROESY NMR studies of the complexes. Figures 6 and 7 show the 2D $^{1}H-^{1}H$ ROESY NMR spectra of the major and the minor hydroamination products, respectively. In both spectra, the characteristic NOE patterns within the orthometalated (*S*)-naphthylamine ring are clearly recorded. For example, strong NOE signals (A−C) are observed for the expected proximities between H(11) and the three methyl groups on N(12) and C(11). The driving forces for Me(11) to assume the axial position, i.e., the H(8)−H(11) (E) and H(8)−Me(11) (F) repulsive interactions, are clearly reflected in the spectrum. No interaction between Me11 and NMe(ax) is observed. Consistent with the exclusive adoption of the λ ring conformation by the (*S*)-naphthylamine auxiliary, Me(11) interacts only with one neighboring NMe group, i.e., NMe(eq). In the δ conformation, this CMe group would interact with both NMe groups.

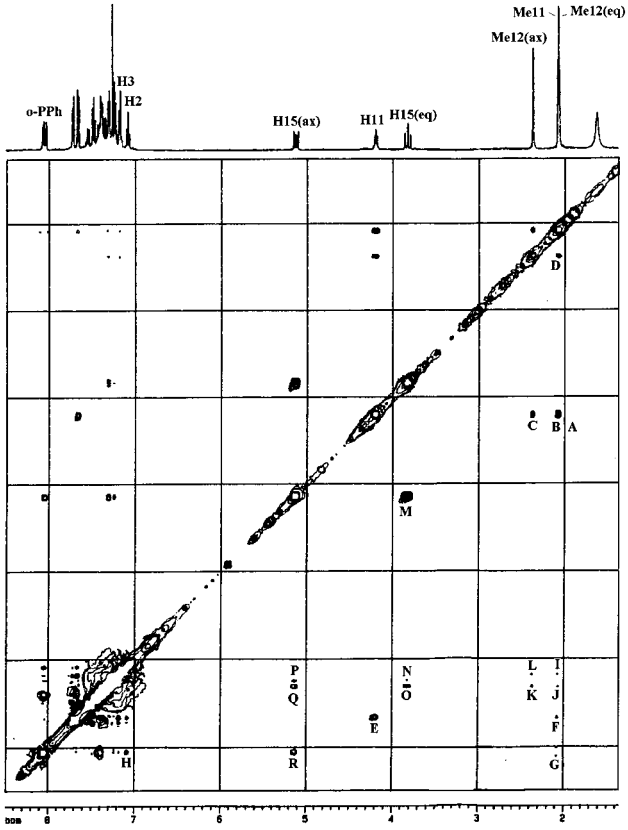


Figure 6. Two-dimensional ^{1}H ROESY NMR spectrum of complex (S_c,R_p)-**7** in $CDCl_3$. All off-diagonal peaks are of negative intensity. Selected NOE contacts: A, H11−Me12-(eq); B, Me11−H11; C, H11−Me12(ax); D, Me12(ax)−Me12-(eq); E, H11−H8; F, Me11−H8; G, Me11−*o*-PPh; H, H2−*o*-PPh; I, Me12(eq)−Ph13; J, Me12(eq)−Ph14; K, Me12(ax)−Ph14; L, Me12(ax)−Ph13; M, H15(ax)−H15(eq); N, H15(eq)−*o*-Ph14; O, H15(eq)−Ph14; P, H15(ax)−*o*-Ph14; Q, H15(ax)−Ph14; R, H15(ax)−*o*-PPh.

In Figure 6, the 2D ROESY NMR spectrum of the major product shows a long-range interchelate NOE interaction between the *o*-PPh protons and the Me(11) (signal G). This NOE signal thus indicates that these two groups are located on the same side below the

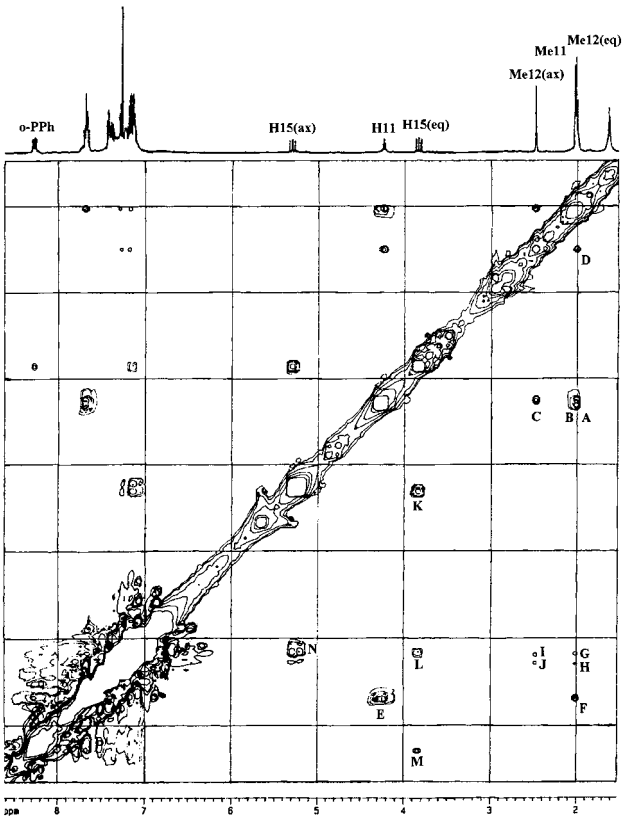
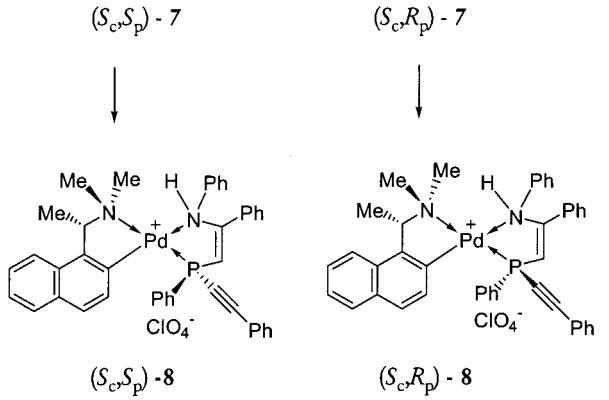


Figure 7. Two-dimensional ^{1}H ROESY NMR spectrum of complex (S_c,S_p)-**7** in $CDCl_3$. All off-diagonal peaks are of negative intensity. Selected NOE contacts: A, H11−Me12-(eq); B, Me11−H11; C, H11−Me12(ax); D, Me12(ax)−Me12-(eq); E, H11−H8; F, Me11−H8; G, Me12(eq)−Ph14; H, Me12(eq)−Ph13; I, Me12(ax)−Ph14; J, Me12(ax)−Ph13; K, H15(ax)−H15(eq); L, H15(eq)−Ph14; M, H15(eq)−*o*-PPh; N, H15(ax)−Ph14.

square plane. Accordingly, the absolute configuration at the phosphorus center is *R*. Furthermore, the regiochemistry of the two asymmetric bidentate chelates can be confirmed by the NOE interaction (signal H) between the *o*-PPh protons and the adjacent naphthylene proton H(2). Consistent with their regioarrangements, the NMe groups in the chiral auxiliary show NOE interaction signals with the imino N−Ph group and the phenyl group attached to C(14) (signals I−L). Within the iminophosphine chelate, the two nonequivalent PCH_2 protons show the expected strong NOE interaction with each other (signal M). Both PCH_2 protons interact with the neighboring phenyl group attached to C(14) (signals N−Q). Most importantly, the axially oriented PC*H* proton shows a strong NOE interaction with the *o*-PPh protons (signal R). This NOE signal thus confirms that the iminophosphine ring adopts the λ absolute conformation, i.e., isomer B (Figure 5). The λ rather than δ conformation adopted by the P−N ring is indeed in agreement with our earlier findings from the model studies. The intense interchelate repulsions between the equatorially disposed NMe group of the naphthylamine auxiliary and the N−Ph group of the imino donor indeed deter the adoption of the δ conformation by the P−N ring, as depicted in isomer A of Figure 5. In isomer B, these N-substituents are oriented in the favorable staggered orientation. The above spectroscopic studies confirm unambiguously that the major product obtained from the asymmetric hydroamination reaction is complex (S_c,R_p)-**7**.

Scheme 3



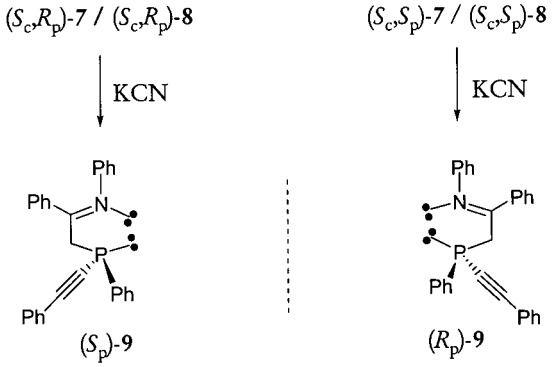
Similarly, the 2D ROESY NMR studies of the minor hydroamination product confirm that the complex is (S_c,S_p)-**7**. As seen in Figure 7, there is no NOE interaction between Me(11) and *o*-PPh. The absence of this NOE signal suggests that the two groups are located at different sides of the square plane. This information allows the assignment of the *S* absolute configuration at the phosphorus stereogenic center in the minor isomer. Another major difference between the two ROESY spectra is that, in Figure 7, the *o*-PPh protons do not interact with the axially orientated PCH proton, but a strong interaction is observed with the equatorially disposed PCH proton (signal M). This clearly indicates that the *o*-PPh and the axial PCH are on opposite sides of the plane. This NOE interaction, taken in conjunction with the fact that both NMe groups of the chiral auxiliary interact with the imino N-Ph group (signals H and J), confirms that the P−N ring of the minor isomer also adopts the λ absolute conformation. It is noteworthy that, with this λ ring conformation, the P-Ph group in complex (S_c,S_p)-**7** is orientated in the axial position. Model studies indicated that, however, the P-Ph group at this axial position suffers from considerable steric constraints due to the phenyl ring which is attached to C(14). In contrast, the λ ring conformation allows the P-Ph group in the major (S_c,R_p)-**7** isomer to occupy a sterically more favorable equatorial position. We believe that this is indeed the major discriminating effect on the relative populations of the two diastereomeric hydroamination products.

Imine−Enamine Tautomeric Equilibrium of (S_c,R_p)-7 and (S_c,S_p)-7. Similar to the model complexes containing the PPh_2 moiety, both *P*-chiral template complexes undergo the tautomerism process in solution. Indeed, they are significantly more potent to adopt their enamine forms than the model complexes. In dichloromenthane, (S_c,R_p)- and (S_c,S_p)-**7** transformed quantitatively into their enamino counterparts (S_c,R_p)- and (S_c,S_p)-**8**, respectively within one week (Scheme 3). Both pure enamino complexes (S_c,R_p)- and (S_c,S_p)-**8** were isolated as light yellow solids in quantitative yields. Similar to their imino counterparts, however, the enamino complexes could not be induced to crystallize for structural analysis. The ES-MS spectra of both the enamino complexes and their imino parent compounds show similar molecular ion isotopic distribution patterns, which agree with the theoretical calculation.

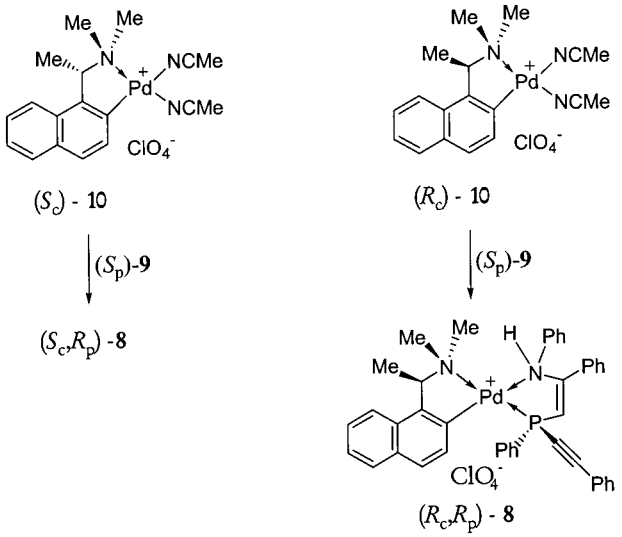
Table 4. Selected ^{31}P and ^{1}H NMR Spectra Chemical Shift Values of (S_c,R_p)-8 and (S_c,S_p)-8 in $CDCl_3$ (coupling constants in Hz are given in parentheses)

	(S_c, R_p)-**8**	(S_c,S_p)-**8**
^{31}P	−7.6 s	−6.2 s
CH*Me*	2.00 d ($^3J_{HH}$ = 6.0)	2.02 d ($^3J_{HH}$ = 6.0)
N*Me(eq)*	2.98 d $^4J_{PH}$ = 3.6)	2.96 d ($^4J_{PH}$ = 4.0)
N*Me(ax)*	2.72 d ($^4J_{PH}$ = 1.6)	2.82 d ($^4J_{PH}$ = 1.6)
C*H*Me	4.32 qn ($^3J_{HH}$ = $^4J_{PH}$ = 6.0)	4.30 qn ($^3J_{HH}$ = $^4J_{PH}$ = 6.0)
C=C*H*	5.45 dd ($^2J_{PH}$ = 18.1, $^4J_{HH}$ = 3.2)	5.20 dd ($^2J_{PH}$ = 18.5, $^4J_{HH}$ = 3.0)
N*H*	5.92 dd ($^3J_{PH}$ = 16.9,$^4J_{HH}$ = 3.2)	561 dd ($^3J_{PH}$ = 18.3,$^4J_{HH}$ = 3.0)
o-P*Ph*	8.29 ddd ($^3J_{HH}$ = 7.6,$^3J_{PH}$ = 12.5, $^4J_{HH}$ = 1.6)	8.17 ddd ($^3J_{HH}$ = 7.6, $^3J_{PH}$ = 12.8, $^4J_{HH}$ = 2.0)

Scheme 4



Scheme 5



Interestingly, both the enamino complexes are thermodynamically more stable than their parent imino counterparts. The reverse isomerization was not observed when the enamino complexes were dissolved in solution. Selected NMR data of the diastereomeric enamino complexes are given in Table 4.

Liberation of the *P*-Chiral Iminophosphines (R_p)- and (S_p)-9. The liberation of the enantiomerically pure *P*-chiral iminophosphines from (S_c,R_p)- and (S_c,S_p)-**7** was achieved by separate treatments of the diastereomers with aqueous KCN (Scheme 4). Thus (S_p)-**9** was liberated from (S_c,R_p)-**7** as an air-stable pale yellow solid in 68% yield, $[\alpha]_D$ + 105.3° (CH_2Cl_2). It should be noted that the apparent inversion of configuration that takes place at the phosphorus stereogenic center when the *P*-chiral iminophosphine is liberated from the complex is merely a consequence of the Cahn−Ingold−Prelog (CIP) sequence rule.[14] The ^{31}P NMR spectrum of the liberated ligand in $CDCl_3$ exhibited a sole singlet at δ −21.7. The 300 MHz ^1H NMR spectrum of (S_p)-**9** in the same solvent showed two simple doublets at δ 5.80 and 5.83 ($^2J_{HH}$ = 9.6 Hz) for the two nonequivalent PCH_2 protons. Interestingly, these PCH_2 resonance signals did not diminish when the NMR sample was treated with D_2O for one week. The D_2O exchange experiment does reveal that, without metal complexation, (S_p)-**9** adopts the thermodynamically stable imino form. This finding clearly reveals that, once again, the imine−enamine tautomerisms oberved in the chelating iminophosphine complexes were indeed triggered by the metal complexation. It is noteworthy that the same iminophosphine (S_p)-**9** was obtained when the enamino complex (S_c,R_p)-**8** was treated with aqueous KCN. The enantiomeric iminophosphine, (R_p)-**9**, with $[\alpha]_D$ − 105.3° (CH_2Cl_2), could be liberated from either (S_c,S_p)-**7** or (S_c,S_p)-**8** in similar yields. The enantiomerically pure ligands are stable in the solid state. In solution however, they are sensitive to air and racemize slowly under ambient conditions.

The optical purity of the liberated **9** was established by the recomplexation of the liberated ligand to the enantiomeric complexes (R_c)- and (S_c)-**10** (Scheme 5). Interestingly, only the enamino forms of complexes were regenerated in these complexation reactions. Thus, when (S_P)-**9** was treated with (S_c)-**10**, the ^{31}P NMR spectrum of the crude product in $CDCl_3$ exhibited a sole singlet at δ −7.6. When the same ligand was treated with (R_c)-**10**, however, the ^{31}P NMR spectrum did not show any signal at δ −7.6. Instead, a new singlet was recorded at δ −6.2. This is consistent with the formation of (R_c,R_p)-**8**, as the same signal was observed for (S_c,S_p)-**8**. In the absence of external chiral environment, enantiomers show the same NMR signals.

In conclusion, the present study provides a novel and effective way to synthesize enantiomerically pure *P*-chiral iminophosphine ligands, which show interesting dynamic properties and coordination chemistry. We are currently investigating further synthetic applications of this novel asymmetric hydroamination reaction.

(14) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. NMR spectra were recorded at 25 °C on Bruker ACF300 and AMX500 spectrometers. The phase-sensitive ROESY NMR experiments were acquired into a 1024 × 512 matrix with a 250 ms spin locking time and a spin lock field strength such that $\gamma B_1/2\pi =$ 5000 Hz and then transformed into 1024 × 1024 points using a sine bell weighting function in both dimensions. Electrospray mass spectroscopic experiments were recorded on a Finnigan TSQ 7000 triple stage quadropole mass spectrometer by positive electrospray ionization. Optical rotations were measured on the specified solution in a 1 dm cell at 25 °C with a Perkin-Elmer 341 polarimeter. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore.

The phosphinoalkynes were prepared by the literature methods.[15] The enantiomerically pure form of the dimeric palladium complex (S_c)-**1** and the cationic bis(acetonitrile) complexes (R_c)- and (S_c)-**10** were prepared as previously described.[16]

Caution! *All the cationic complexes described were isolated as perchlorate salts and should be handled as potentially explosive compounds.*

[*SP*-4-4-(*S*)-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][diphenylphenylethynylphosphine-*P*]palladium(II), (S_c)-2. A mixture of the dimeric complex (S_c)-**1** (3.75 g) and diphenyl(phenylethynyl)phosphine (3.16 g) in dichloromethane (50 mL) was stirred at room temperature for 0.5 h. The solution was concentrated to give a yellow residue. Crystallization of the crude product from dichloromethane−diethyl ether gave the complex (S_c)-**2** as pale yellow crystals: 6.3 g (91% yield); mp > 200 °C (dec); $[\alpha]_D$ +81.8° (*c* 0.3, CH_2Cl_2). Anal. Calcd for $C_{34}H_{31}ClNPPd$: C, 65.2; H, 5.0; N, 2.2. Found: C, 65.4; H, 5.0; N, 2.2. ^{31}P NMR ($CDCl_3$): δ 11.6 (s). ^{1}H NMR ($CDCl_3$): δ 2.05 (d, 3H, $^3J_{HH} = 6.4$ Hz, CH*Me*), 2.73 (d, 3H, $^4J_{PH(trans)} = 1.6$ Hz, N*Me*), 2.95 (d, 3H, $^4J_{PH(trans)} = 3.6$ Hz, N*Me*), 4.35 (qn, 1H, $^3J_{HH} = {}^4J_{PH} = 6.4$ Hz, C*H*Me), 7.22−7.73 (m, 20H, aromatics), 7.80 (dd, 2H, $^3J_{HH} = 6.8$ Hz, $^3J_{PH} =$ 12.8 Hz, *o*-P*Ph*), 8.19 (dd, 2H, $^3J_{HH} = 7.7$ Hz, $^3J_{PH} = 13.3$ Hz, *o*-P*Ph′*).

Hydroamination Reaction of the Achiral Diphenyl(phenylethynyl)phosphine. Synthesis of {(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C,N*}{1,2-diphenyl-3-diphenylphosphino-1-aza-1-propene-N^1,$P^{3'}$}palladium(II) Perchlorate, (S_c)-3. A solution of the chloro complex (S_c)-**2** (0.5 g) in dichloromethane (20 mL) was treated with silver perchlorate (0.3 g) in water (1 mL) for 30 min. The mixture was then filtered through Celite, washed with water, and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The resulting perchlorato complex was dissolved in toluene (50 mL) and treated with aniline (0.37 g). The mixture was then heated at 100 °C for 10 h. Removal of the solvent gave the crude hydroamination product as a black residue. Subsequent purification of the crude product by silica gel column chromatography (ethyl acetate−hexane, 1:1) gave pure (*S*)-**3** as a pale yellow solid. The product was recrystallized from dichloromethane−diethyl ether as pale yellow crystals: 0.35 g (56% yield); mp > 200 °C (dec); $[\alpha]_D$ −193.2° (*c* 0.3, CH_2Cl_2). Anal. Calcd for $C_{40}H_{38}ClN_2O_4PPd$: C, 61.3; H, 4.9; N, 3.6. Found: C, 61.2; H, 5.3; N, 3.5. ^{31}P NMR ($CDCl_3$): δ 49.8 (s). ^{1}H NMR ($CDCl_3$): δ 2.06 (d, 3H, $^3J_{HH} = 6.4$ Hz, CH*Me*), 2.09 (d, 3H, $^4J_{PH(trans)} = 4.0$ Hz, N*Me*), 2.41 (d, 3H, $^4J_{PH(trans)} = 1.6$ Hz, N*Me*), 3.87 (dd, 1H, $^2J_{PH} = 14.3$ Hz, $^2J_{HH} = 16.7$ Hz, suppressed by D_2O, C*H*H), 4.21 (qn, 1H, $^3J_{HH} = {}^4J_{PH} = 6.4$ Hz, C*H*Me), 5.42 (dd, 1H, $^2J_{PH} = 9.8$ Hz, $^2J_{HH} = 16.7$ Hz, suppressed by D_2O, CH*H*), 6.88 (dd, 1H, $^3J_{HH} = 8.4$ Hz, $^4J_{PH} = 6.9$ Hz, H_2), 7.06 (d, 1H, $^3J_{HH} = 8.4$ Hz, H_3), 6.98−7.76 (m, 22H, aromatics) 8.19 (dd, 2H, $^3J_{HH} = 6.9$ Hz, $^3J_{PH} = 11.8$ Hz, *o*-P*Ph*).

Removal of the Naphthylamine Auxiliary. Isolation of Dichoro{1,2-diphenyl-3-diphenylphosphino-1-aza-1-propene-N^1,$P^{3'}$}palladium (II), 4. A dichloromethane solution (5 mL) of the hyroamination product (S_c)-**3** (0.2 g) was treated with concentrated HCl (5 mL) at room temperature for 1 h. The mixture was then diluted with dichloromethane (50 mL), washed with water, and dried ($MgSO_4$). Removal of the solvent gave a yellow solid, which readily recrystallized from dichloromethane−diethyl ether to give **4** as yellow crystals: 0.13 g (88% yield); mp > 220 °C (dec). Anal. Calcd for $C_{26}H_{22}Cl_2NPPd$: C, 56.1; H, 4.0; N, 2.5. Found: C, 55.8; H, 4.0; N, 2.8. ^{31}P NMR ($CDCl_3$): δ 46.1 (s). ^{1}H NMR ($CDCl_3$): δ 4.52 (d, 2H, $^2J_{PH} = 13.3$ Hz, suppressed by D_2O, CH_2), 6.91−7.59 (m, 18H, aromatics), 7.96 (dd, 2H, $^3J_{HH} = 7.2$ Hz, $^3J_{PH} =$ 13.3 Hz, *o*-P*Ph*).

Liberation of the Iminophosphine Ligand. Isolation of 1,2-Diphenyl-3-diphenylphosphino-1-aza-1-propene, 5. A dichloromethane solution of the dichloro complex (0.1 g) was treated with potassium cyanide (0.2 g) in water (2 mL). The reaction mixture was stirred vigorously at room temperature for 0.5 h. The organic layer was separated, washed with water, and dried ($MgSO_4$). Removal of the solvent under high vacuum gave the iminophosphine ligand **5** as an air-stable solid, 44 mg (65% yield). Anal. Calcd for $C_{26}H_{22}NP$: C, 82.3; H, 5.8; N, 3.7. Found: C, 82.3; H, 5.5; N, 4.0. ^{31}P NMR ($CDCl_3$): δ −13.1 (s). ^{1}H NMR ($CDCl_3$): δ 3.55 (d, 2H, $^2J_{PH} = 2.0$ Hz, CH_2), 6.37 (d, 2H, $^3J_{HH} = 8.2$ Hz, *m*-N*Ph*), 6.10−7.50 (m, 16H, aromatics), 7.83 (d, 2H, $^3J_{HH} = 8.2$ Hz, *o*-N*Ph*).

[*SP*-4-4-(*S*)-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][di(phenylethynyl)phenylphosphine-*P*]palladium (II), (S_c)-6. A mixture of the dimeric complex (S_c)-**1** (2.0 g) and di(phenylethynyl)phenylphosphine (1.9 g) in dichloromethane (50 mL) was stirred at room temperature for 0.5 h. Removal of the solvent gave (S_c)-**6** as a yellow residue, 3.9 g (100%); mp > 200 °C (dec); $[\alpha]_D$ +78.6° (*c* 0.3, CH_2Cl_2). ^{31}P NMR ($CDCl_3$): δ −19.5 (s). ^{1}H NMR ($CDCl_3$): δ 2.05 (d, 3H, $^3J_{HH} = 6.4$ Hz, CH*Me*), 2.78 (d, 3H, $^4J_{PH(trans)} = 2.0$ Hz, N*Me*), 3.01 (d, 3H, $^4J_{PH(trans)} = 4.0$ Hz, N*Me*), 4.35 (qn, 1H, $^3J_{HH} = {}^4J_{PH} = 6.4$ Hz, C*H*Me), 7.25−7.73 (m, 22H, aromatics), 8.29 (dd, 2H, $^3J_{HH} = 9.6$ Hz, $^3J_{PH} = 14.4$ Hz, *o*-P*Ph*). The complex decomposed slowly in solution and was used directly without further purification for the subsequent hydroamination reaction.

Asymmetric Hydroamination of the Prochiral Di(phenylethynyl)phenylphosphine. Synthesis of {(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C,N*}{(3*R*)-1,2-diphenyl-3-phenyl(phenylethynyl)phosphino-1-aza-1-propene-N^1,$P^{3'}$}palladium(II) Perchlorate, (S_c,R_p)-7, and {(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C,N*}{(3*S*)-1,2-diphenyl-3-phenyl(phenylethynyl)phosphino-1-aza-1-propene-N^1,$P^{3'}$}palladium(II) Perchlorate, (S_c,S_p)-7. A solution of the chloro complex (S_c)-**6** (1 g) in dichloromethane (50 mL) was treated with silver perchlorate (0.6 g) in water (5 mL) for 30 min. The reaction mixture was filtered through Celite, washed with water, and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude perchlorato complex was dissolved in chloroform (100 mL) and treated with excess aniline (1.4 g) at room temperature for 16 h. Upon completion, the solvent was removed under reduced pressure. Subsequent purification by silica gel column chromatography (ethyl acetate/hexane, 1:1) gave the diastereomeric products (S_c,R_p)-**7** and (S_c,S_p)-**7** as yellow solids. (S_c,R_p)-**7**: 0.7 g (56% yield); mp > 180 °C (dec); $[\alpha]_D$ −266.1° (*c* 0.3, CH_2Cl_2). Anal. Calcd for $C_{42}H_{38}N_2ClO_4PPd$: C, 62.5; H, 4.7; N, 3.5. Found: C, 62.4; H, 4.6; N, 3.5. ^{31}P NMR ($CDCl_3$): δ 15.1 (s). ^{1}H NMR ($CDCl_3$): δ

(15) Carty, A. J.; Hota, N. K.; Ng, T. W.; Patel, H. A.; O'Connor, T. J. *Can. J. Chem.* **1971**, *49*, 2707.

(16) Liu, X. M.; Mok, K. F.; Vittal, J. J.; Leung, P. H. *Organometallics* **2000**, *19*, 3722. Leung, P. H.; Quek, G. H.; Lang, H.; Liu, A.; Mok, K. F.; White, A. J. P.; Williams, D. J.; Rees, N. H.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1639.

2.08 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.08 (d, 3H, $^4J_{PH(trans)}$ = 3.6 Hz, N*Me*), 2.37 (d, 3H, $^4J_{PH(trans)}$ = 2.0 Hz, N*Me*), 3.83 (dd, 1H, $^2J_{PH}$ = $^2J_{HH}$ = 16.5 Hz, C*H*H), 4.20 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.4 Hz, C*H*Me), 5.13 (dd, 1H, $^2J_{HH}$ = 16.5 Hz, $^2J_{PH}$ = 8.9 Hz, CH*H*), 7.08 (dd, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 8.2 Hz), 7.18 (d, 1H, $^3J_{HH}$ = 8.2 Hz), 7.20−7.73 (m, 22H, aromatics), 8.05 (dd, 2H, $^3J_{HH}$ = 7.8 Hz, $^3J_{PH}$ = 14.6 Hz, *o*-P*Ph*). (S_c,S_p)-**7**: 0.2 g (15% yield); mp > 180 °C (dec); $[\alpha]_D$ +62.5° (*c* 0.3, CH_2Cl_2). Anal. Calcd for $C_{42}H_{38}N_2ClO_4PPd$: C, 62.5; H, 4.7; N, 3.5. Found: C, 62.3; H, 4.9; N, 4.0. ^{31}P NMR ($CDCl_3$): δ 17.3 (s). ^{1}H NMR ($CDCl_3$): δ 2.00 (d, 3H, $^4J_{PH(trans)}$ = 2.8 Hz, N*Me*), 2.02 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.48 (d, 3H, $^4J_{PH(trans)}$ = 2.0 Hz, N*Me*), 3.83 (dd, 1H, $^2J_{HH}$ = 16.9 Hz, $^2J_{PH}$ = 14.9 Hz, C*H*H), 4.23 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.4 Hz, C*H*Me), 5.27 (dd, 1H, $^2J_{HH}$ = 16.9 Hz, $^2J_{PH}$ = 12.8 Hz, CH*H*), 7.14−7.72 (m, 24H, aromatics); 8.27 (dd, 2H, $^3J_{HH}$ = 7.8 Hz,$^3J_{PH}$ = 13.8 Hz, *o*-P*Ph*).

Imine−Enamine Tautomerism. Isolation of {(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*,*N*}{(3*R*)-1,2-diphenyl-3-phenyl(phenylethynyl)phosphino-1-aza-2-propene-N^1,$P^{3'}$}palladium(II) Perchlorate (S_c,R_p)-8 and {(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*,*N*}{(3*S*)-1,2-diphenyl-3-phenyl(phenylethynyl)phosphino-1-aza-2-propene-N^1,$P^{3'}$}palladium(II) Perchlorate (S_c,S_p)-8. A dichloromethane solution of (S_c,R_p)-**7** (0.1 g) was kept at room temperature for 1 week. The ^{31}P NMR studied indicated that the imino complex was converted completely into its enamino form. Removal of the solvent gave the enamino complex (S_c,R_p)-**8** as a yellow solid: 0.1 g (100%), mp > 180 °C (dec); $[\alpha]_D$ −185.6° (*c* 0.3, CH_2Cl_2). Anal. Calcd for $C_{42}H_{38}N_2ClO_4PPd$: C, 62.5; H, 4.7; N, 3.5. Found: C, 62.3; H, 5.2; N, 3.1. ^{31}P NMR ($CDCl_3$): δ −7.6 (s). ^{1}H NMR ($CDCl_3$): δ 2.00 (d, 3H, $^3J_{HH}$ = 6.0 Hz, CH*Me*), 2.72 (d, 3H, $^4J_{PH(trans)}$ = 1.6 Hz, N*Me*), 2.98 (d, 3H, $^4J_{PH(trans)}$ = 3.6 Hz, N*Me*), 4.32 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.0 Hz, C*H*Me), 5.45 (dd, 1H, $^4J_{HH}$ = 3.2 Hz, $^2J_{PH}$ = 18.1 Hz, C═CH), 5.92 (dd, 1H, $^4J_{HH}$ = 3.2 Hz, $^3J_{PH}$ = 16.9 Hz, NH); 6.83−7.70 (m, 24H, aromatics); 8.29 (ddd, 2H, $^3J_{HH}$ = 7.6 Hz,$^3J_{PH}$ = 12.5 Hz, $^4J_{HH}$ = 1.6 Hz, *o*-P*Ph*). The diastereomeric enamino complex (S_c,S_p)-**8** was obtained similarly from (S_c,R_p)-**8**: mp > 180 °C (dec); $[\alpha]_D$ +139.2 (*c* 0.3, CH_2Cl_2). Anal. Calcd for $C_{42}H_{38}N_2ClO_4PPd$: C, 62.5; H, 4.7; N, 3.5. Found: C, 62.3; H, 5.2; N, 3.1. ^{31}P NMR ($CDCl_3$): δ −6.2 (s). ^{1}H NMR ($CDCl_3$): 2.02 (d, 3H, $^3J_{HH}$ = 6.0 Hz, CH*Me*), 2.82 (d, 3H, $^4J_{PH(trans)}$ = 1.6 Hz, N*Me*), 2.96 (d, 3H, $^4J_{PH(trans)}$ = 4.0 Hz, N*Me*), 4.30 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.0 Hz, C*H*Me), 5.20 (dd, 1H, $^4J_{HH}$ = 3.0 Hz, $^2J_{PH}$ = 18.5 Hz, C═CH), 5.67 (dd, 1H, $^4J_{HH}$ = 3.0 Hz, $^3J_{PH}$ = 18.3 Hz, NH); 6.83−7.70 (m, 24H, aromatics); 8.17 (ddd, 2H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 2.0 Hz, $^3J_{PH}$ = 12.8 Hz, *o*-P*Ph*).

Liberation of the *P*-Chiral Iminophosphines. Isolation of (3*S*)-1,2-Diphenyl-3-phenyl(phenylethynyl)phosphino-1-aza-1-propene, (S_p)-9. A solution of (S_c,R_p)-**7** (0.2 g) in dichloromethane (20 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (0.5 g) for 0.5 h. The resulting organic layer was separated and washed with water and dilute HCl followed by water again before being dried over $MgSO_4$. Removal of solvent under reduced pressure gave the liberated iminophosphine ligand (S_p)-**9** as an air-stable low melting yellow solid: 72 mg (72%); $[\alpha]_D$ −105.3° (*c* 0.3, CH_2Cl_2). Anal. Calcd for $C_{28}H_{22}NP$: C, 83.4; H, 5.5; N, 3.5. Found: C, 83.3; H, 5.2; N, 3.8. ^{31}P NMR ($CDCl_3$): δ −21.7. ^{1}H NMR ($CDCl_3$): δ 5.80 (d, 1H, $^2J_{HH}$ = 9.6, C*H*H′); δ 5.83 (d, 1H, $^2J_{HH}$ = 9.6, C*H*H′); 6.70−8.09 (20H, aromatics). The enantiomer (R_p)-**9**, with $[\alpha]_D$ +105.3° (*c* 0.3, CH_2Cl_2), was obtained similarly from (S_c,S_p)-**7**. The ^{31}P NMR and ^{1}H NMR spectra are identical to those recorded for (S_p)-**9**.

Table 5. Crystallographic Data for Complexes (S_c)-3 and 4

	(S_c)-**3**	**4**
formula	$C_{40}H_{38}N_2O_4ClPPd$	$C_{26}H_{22}NCl_2PPd\cdot0.5Et_2O$
fw	783.5	588.7
space group	$P2_12_12_1$	*Pbca*
cryst syst	orthorhombic	orthorhombic
a/Å	9.878(1)	16.374(1)
b/Å	18.360(1)	17.836(1)
c/Å	20.699(1)	18.212(1)
V/Å^3	3754.1(1)	5318.5(5)
Z	4	8
T/K	293(2)	293(2)
ρ_{cacld}/g cm^{-3}	1.386	1.471
λ/Å	0.71073	0.71073
μ/cm^{-1}	6.50	9.77
Flack params	−0.03(2)	
R_1 (obs data)[a]	0.037	0.038
wR_2 (obs data)[b]	0.082	0.106

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o||$. [b] $wR_2 = \sqrt{\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}}$, $w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP$.

Crystal Structure Determination of (S_c)-3 and 4. Crystal data for both complexes and a summary of the crystallographic analyses are given in Table 5. Diffraction data were collected on a Siemens SMART CCD diffractometer with Mo Kα radiation (graphite monochromator) using ω-scans. SADABS absorption corrections were applied, and refinements by full-matrix least-squares were based on SHELXL 93.[17] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at fixed distance from carbon atoms and were assigned fixed thermal parameters.

Acknowledgment. We are grateful to the National University of Singapore for the financial support and a Ph.D. research scholarship for X.M.L.

Supporting Information Available: For (S_c)-**3** and **4** tables of crystal data, data collection, solution and refinement, final positional parameters, bond distances and angles, thermal parameters of non-hydrogen atoms, and calculated hydrogen parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010333K

(17) Sheldrick, G. M. *SHELXL 93*, Program for Crystal Structure Refinement; University of Gottingen: Germany, 1993.