Formation of Imino−Phosphine Bidentate Chelates by an Unprecedented Organopalladium Complex Promoted Oxidative Coupling Reaction between Diphenylvinylphosphine and Imines

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Received May 16, 2000

Oxidative coupling reaction between $Ph_2P-CH=CH_2$ and a series of imines $PhC(R)=N(R')$ [where R = H, D; R′ = H, Ph, *p*-$Me(C_6H_4)$, *p*-$Cl(C_6H_4)$, *p*-$MeO(C_6H_4)$] in the presence of (*S*)-ortho-palladated[1-(dimethylamino)ethyl]naphthylene as the reaction template produced the unexpected imino−phosphine ligands $(R')N=C-C(=CPhR)PPh_2$ where the P,N-bidentate chelates to the chiral palladium template. The coupling reactions initially adopted a [2+2] cycloaddition mechanism followed by the ring-opening pathway to generate the acyclic ligands. The rate of these coupling reactions was affected by the electronic properties of the R′ group on the imines. No coupling reaction was observed between $Ph_2P-CH=CH_2$ and *p*-$CF_3(C_6H_4)N=CPh(H)$, which contains a strong electronic withdrawing group at the *p*-position. In all the product complexes the nitrogen donors from the imine and from the naphthylamine chelates are coordinated regiospecifically in the cis positions. Similarly the R substituent and the PPh_2 moiety are invariably located in the cis positions on the newly generated C=C bonds. The imino−phosphine chelates are stable in strong sulfuric acid, while the naphthylamine moiety in the template complexes is removed chemoselectively in the presence of this acid. Upon the removal of the naphthylamine chelate, the imino−phosphines could be liberated from palladium by the treatment with aqueous cyanide. Except for $HN=C-C(=CPhH)PPh_2$, which decomposed readily in aqueous solution, all the other liberated imino−phosphines were obtained as air-stable low-melting solids.

Introduction

The importance of metals and metal ions in synthetic organic chemistry has been well established.[1] In numerous synthetic processes, the utilization of these classic inorganic materials provides dramatic activation and product selectivity. Recently we have applied a chiral organopalladium−amine template complex as well as its platinum analogue for the activation of $Ph_2As-CH=CH_2$,[2] a variety of vinylphosphines,[3] and cyclic phospholes as dienophiles[4] or dienes[5] in asymmetric Diels−Alder reactions. Thus an interesting range of P-chiral diphosphines, P-As, and functionalized monodentate phosphines with the rigid phosphanorbornene skeleton have been produced efficiently. In continuing our interest in this class of ligand transformation reactions, we herein report the coupling reaction between a series of benzylic imines and the coordinated vinylphosphine $Ph_2PCH=CH_2$. It has been reported that in the presence of indium trichloride benzylic imines react as heterodienes toward dienophiles via their C=N and neighboring aromatic C=C bonds.[6] As imines are known to coordinate to palladium(II) ions,[7] it is thus anticipated that in the presence of the organopalladium−amine template, benzylic imines and vinyl phosphines could undergo the analogous [4+2] cycloaddition reaction.

Results and Discussion

It has been well established that the Pd−Cl bond in the chiral complex (*S*)-**1** is thermodynamically and

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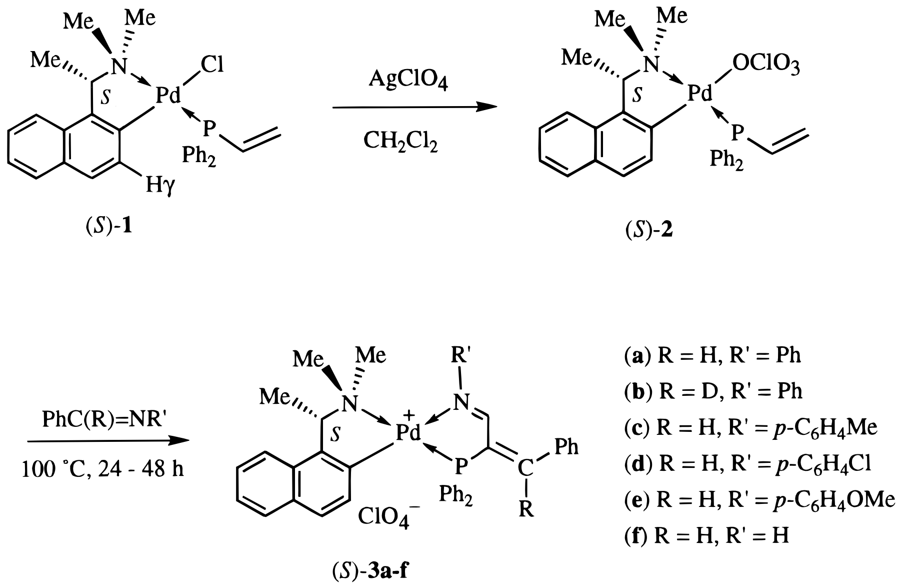
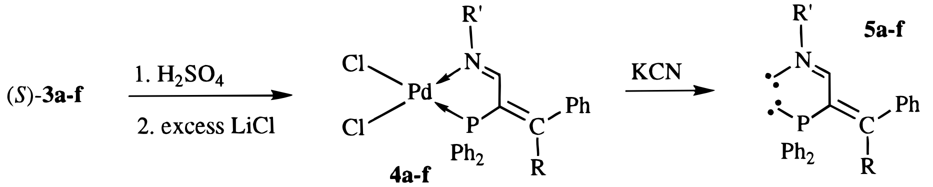
10.1021/om000416l CCC: $19.00

Scheme 1



(**a**) R = H, R' = Ph
(**b**) R = D, R' = Ph
(**c**) R = H, R' = *p*-C_6H_4Me
(**d**) R = H, R' = *p*-C_6H_4Cl
(**e**) R = H, R' = *p*-C_6H_4OMe
(**f**) R = H, R' = H

Scheme 2



kinetically stable (Scheme 1).[8] In general, the anionic ligand is inert to ligand exchange reactions, even in the presence of strong ligands such as monodentate phosphines and arsines. In contrast, the perchlorato ligand in (*S*)-**2** is labile and readily replaced by most donor atoms.[9] By utilizing this readily available coordination site, we have previously used (*S*)-**2** as the chiral template for the asymmetric cycloaddition reaction between the diphenylvinylphosphine ligand in (*S*)-**2** and dimethylphenylphosphole. This reaction adopts an intramolecular mechanism in which both the phosphole and vinylphosphine ligand are coordinated simultaneously on the chiral palladium template during the course of cycloaddition reaction.[3−5] This crucial intermediate could not be achieved with the stable chloro complex. By using a similar methodology, a series of stereochemically demanding P-chiral diphosphines were produced from dimethylphenylphosphole and selected substituted vinylphosphines. It is important to note that, without metal complexation, vinylphosphines are not reactive dienophiles. Thus no intermolecular cycloaddition reaction has been observed between free vinylphosphines and cyclic phospholes.

As intimated above, benzylic imines are potential dienes and may show reactivities toward dienophiles.[6] We were therefore interested in the coupling reaction between these potential heterodienes and vinylphosphines. As expected, no reaction occurred between the uncoordinated *N*-benzylideneaniline and free diphenylvinylphosphine, or (*S*)-**1**, despite the strong reaction conditions used. Apparently, it is necessary to activate imines and vinylphosphines simultaneously via the metal complexation. Hence the stable chloro ligand in (*S*)-**1** was removed quantitatively by our standard treatment with silver perchlorate to generate the reactive template (*S*)-**2**. As illustrated in Scheme 1, this perchlorato complex reacted smoothly with excess *N*-benzylideneaniline at 100 °C in toluene. The reaction was monitored by ^{31}P NMR spectroscopy and found to be complete in 48 h. The ^{31}P NMR spectrum exhibited a sharp singlet at δ 52.2. This relatively lower field shift indicated that the phosphorus donor is involved in a five-membered bidentate metal chelate.[10] The resulting template complex (*S*)-**3a** was crystallized from dichloromethane−diethyl ether as stable yellow needles in 33% yield with $[\alpha]_D$ +212.5 (CH_2Cl_2). Unfortunately, single crystals of the complex suitable for structural investigation could not be produced, despite numerous attempts with many solvent systems. Thus (*S*)-**3a** was converted quantitatively to the highly crystalline dichloro complex **4a** (Scheme 2). The conversion process involved first the chemoselective removal of the naphthylamine moiety from (*S*)-**3a** using concentrated sulfuric acid, followed by the addition of excess lithium chloride to the acidic solution to generate the dichloro complex **4a**. Similar to (*S*)-**3a**, the ^{31}P NMR spectrum of **4a** exhibits a sharp singlet at δ 51.7. The X-ray structure of **4a**, however, revealed that the ligand transformation process produced an unexpected imino−phosphine chelate, rather than the expected [4+2]

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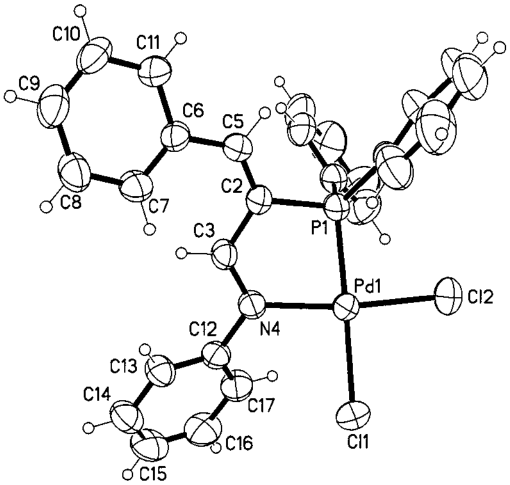

Figure 1. Molecular structure of complex **4a**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Dichloro Complexes 4a, 4c, and 4f

		4c		
	4a	molecule **A**	molecule **B**	**4f**
Pd(1)−Cl(1)	2.371(1)	2.372(1)	2.355(1)	2.356(1)
Pd(1)−Cl(2)	2.286(1)	2.286(1)	2.293(1)	2.285(1)
Pd(1)−P(1)	2.206(1)	2.199(1)	2.203(1)	2.211(1)
Pd(1)−N(4)	2.071(2)	2.060(2)	2.074(1)	1.998(2)
C(3)−N(4)	1.301(4)	1.299(3)	1.289(3)	1.277(3)
C(2)−C(5)	1.352(4)	1.354(3)	1.345(4)	1.347(3)
P(1)−Pd(1)−Cl(1)	171.1(1)	169.5(1)	177.5(1)	173.3(1)
P(1)−Pd(1)−Cl(2)	89.6(1)	90.0(1)	89.2(1)	93.0(1)
P(1)−Pd(1)−N(4)	83.1(1)	82.6(1)	82.7(1)	82.7(1)
Cl(1)−Pd(1)−N(4)	95.3(1)	94.6(1)	95.6(1)	90.9(1)
Cl(2)−Pd(1)−N(4)	170.5(1)	170.9(1)	170.8(1)	175.1(1)
P(1)−C(2)−C(3)	110.3(2)	109.8(2)	109.7(2)	110.3(2)
P(1)−C(2)−C(5)	123.5(2)	123.6(2)	124.2(2)	124.3(2)
C(2)−C(3)−N(4)	120.3(3)	119.8(2)	121.4(2)	119.5(3)
C(3)−C(2)−C(5)	126.2(3)	126.2(2)	126.1(2)	125.3(2)

cycloadduct (Figure 1). Clearly, the aromatic C=C bonds in the =N−Ph function were not involved in the ligand transformation reaction. Selected bond distances and angles of the imino−phosphine complex are given in Table 1. In this new P−N chelate, the short C(2)−C(5) [1.352(4) Å] and the C(3)−N(4) [1.301(4) Å] bond distances clearly indicated that they are C=C and C=N double bonds, as illustrated diagrammetrically in Scheme 2. Hence, despite the fact that the phosphorus and the nitrogen donor atoms have been connected by a carbon−carbon linkage, a new imino C=N bond and a new P-vinylic function have been regenerated within the product ligand. Another interesting feature of this molecule is the new location of the PhC(H)= moiety. The C-phenyl group originally in the imine precursor is now located on the new C=C function, which is trans to the PPh_2 moiety. We believe that the C−Ph bond is intact throughout the reaction, as it is perhaps one of the most stable C−C bondings in classic organic chemistry. Thus, the migration of this PhC(H)= group must have involved the cleavage of the C=N bond in the original PhC(H)=NPh precursor. From the product structure, a new C=N bond must also be formed between nitrogen and the β-carbon of the originally vinylic P−C=C function. Yet another interesting and important feature of this coupling reaction is the elimination of two hydrogen atoms from the precursors. Hence, the formation of this new P−N chelate can be regarded as an oxidative coupling reaction between the vinylphosphine ligand and *N*-benzylideneaniline.

To investigate the origins of the eliminated hydrogen atoms, the coupling reaction was repeated with labeled imine ligand PhC(D)=NPh and (*S*)-**2**. Unfortunately, single crystals of the deuterium-labeled complex (*S*)-**3b** also could not be obtained, although it is readily crystallized from dichloromethane−diethyl ether as pale yellow opaique prisms. These opaique crystals were treated with sulfuric acid and lithium chloride to give the dichloro complex **4b**. The ^{31}P NMR spectrum of **4b** exhibited a singlet signal identical with that recorded for **4a**. A detailed spectroscopic study of the ^{1}H and ^{1}H-ROESY NMR spectra of both complexes confirmed that the deuterium atom is retained within the PhC(D) group in complex **4b**. This spectroscopic study thus indirectly suggested that the α- and the β-vinylic carbons of the reacting phosphine ligand had each eliminated a hydrogen during the course of ligand transformation reaction.

From a mechanistic standpoint, it is important to note that some imino complexes are sensitive to mineral acids and may undergo ligand rearrangement reactions in acidic solutions.[10] Since complexes **4a** and **4b** were obtained from complexes (*S*)-**3a** and (*S*)-**3b**, respectively, via strong acid treatment, it is therefore necessary to confirm that these precursor complexes indeed contain the same P-N chelates. Thus the analogous complexes (*S*)-**3c** and (*S*)-**3d** were prepared by treating (*S*)-**2** with imine ligand *p*-$Me(C_6H_4)N{=}CPh(H)$ and *p*-$Cl(C_6H_4)$-$N{=}CPh(H)$, respectively. Interestingly, *p*-$Me(C_6H_4)$-$N{=}CPh(H)$ seems to be more reactive than *p*-$Cl(C_6H_4)$-$N{=}CPh(H)$, as (*S*)-**3c** was obtained within 24 h, but the formation (*S*)-**3d** required 48 h under similar reaction conditions. In $CDCl_3$ the ^{31}P NMR spectra of (*S*)-**3c** and (*S*)-**3d** each exhibits one sharp singlet, at δ 52.6 and 51.5, respectively. In contrast to their unsubstituted analogues, both the *p*-substituted complexes were obtained as highly crystalline yellow prisms. The molecular structure of these complexes was determined by X-ray structural analyses. Both complexes crystallized as two independent molecules in their unit cells (labeled **A** and **B**). In each complex, the pair of independent molecules have the same molecular connectivity and differ slightly only in the bond distances and the rotational angles of the phenyl rings with respect to the coordination plane. For clarity, only molecules **A** of (*S*)-**3c** and (*S*)-**3d** are depicted in Figures 2 and 3, respectively. Selected bond distances and angles of the complexes are given in Table 2. The X-ray analyses of both complexes confirm that the analogous *p*-substituted imino−phosphine chelates have indeed been generated on the palladium template. In both complexes, the phosphorus donor atoms are coordinated regiospecifically in the position trans to the naphthylamine-N donor atom. Such regiopecificity has been invariably observed with heterobidentate complexes containing this cyclopalladated naphthylamine unit and has been attributed to the trans electronic influences originating from the σ-donating nitrogen and the π-accepting aromatic carbon atoms of the organometallic ring. The N(2)−C(15) bond distances in (*S*)-**3c** [1.294(6) and 1.265(6) Å for molecules **A** and **B**, respectively] and (*S*)-**3d** [1.289 (10) Å for both molecules] are consistent with the imino

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Cationic Complexes (*S*)-3c, (*S*)-3d, and (*S*)-3f

	(*S*)-**3c**		(*S*)-**3d**		(*S*)-**3f**	
	molecule **A**	molecule **B**	molecule **A**	molecule **B**	molecule **A**	molecule **B**
Pd(1)−C(1)	2.017(5)	2.012(6)	1.984(9)	2.034(8)	2.031(6)	2.017(6)
Pd(1)−N(1)	2.169(4)	2.144(4)	2.152(6)	2.134(6)	2.123(5)	2.120(5)
Pd(1)−P(1)	2.223(1)	2.232(1)	2.225(2)	2.233(2)	2.246(2)	2.231(2)
Pd(1)−N(2)	2.167(4)	2.201(5)	2.193(7)	2.173(8)	2.117(6)	2.119(6)
C(16)−C(17)	1.344(7)	1.339(7)	1.345(12)	1.351(11)	1.331(8)	1.352(8)
C(15)−N(2)	1.294(6)	1.265(6)	1.281(11)	1.289(10)	1.280(9)	1.275(8)
C(1)−Pd(1)−N(1)	81.0(2)	80.3(2)	81.6(3)	79.7(3)	80.3(2)	80.9(2)
C(1)−Pd(1)−N(2)	176.3(2)	170.4(2)	175.7(3)	170.3(2)	176.3(3)	176.9(3)
C(1)−Pd(1)−P(1)	98.4(1)	100.0(2)	97.9(2)	100.4(2)	101.5(2)	99.6(2)
N(1)−Pd(1)−N(2)	101.0(2)	102.9(2)	101.0(2)	103.2(3)	97.0(2)	99.1(2)
N(1)−Pd(1)−P(1)	177.6(1)	166.9(1)	177.1(2)	166.0(2)	178.1(2)	173.2(2)
N(2)−Pd(1)−P(1)	79.7(1)	79.0(1)	79.7(2)	79.1(2)	81.2(2)	80.8(2)
P(1)−C(16)−C(15)	108.8(3)	109.2(4)	109.5(6)	109.2(5)	110.5(4)	110.4(4)
P(1)−C(16)−C(17)	124.7(4)	125.1(4)	126.0(7)	124.0(7)	124.2(5)	123.8(5)
C(15)−C(16)−C(17)	125.8(5)	124.9(5)	123.8(9)	126.0(8)	125.2(6)	125.8(6)
N(2)−C(15)−C(16)	120.8(5)	121.0(5)	120.7(8)	120.3(8)	119.8(6)	120.1(6)

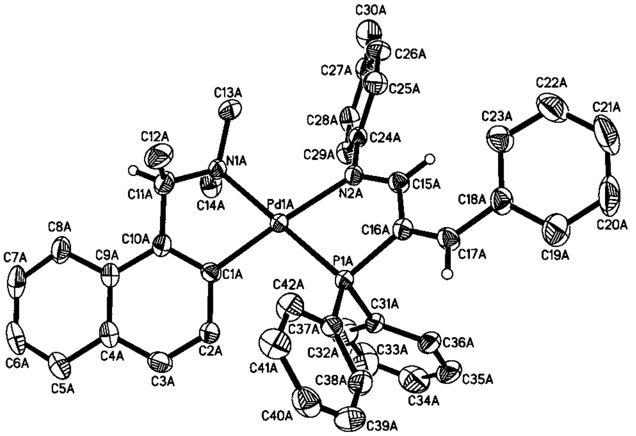

Figure 2. Molecular structure and absolute stereochemistry of complex (*S*)-**3c**.

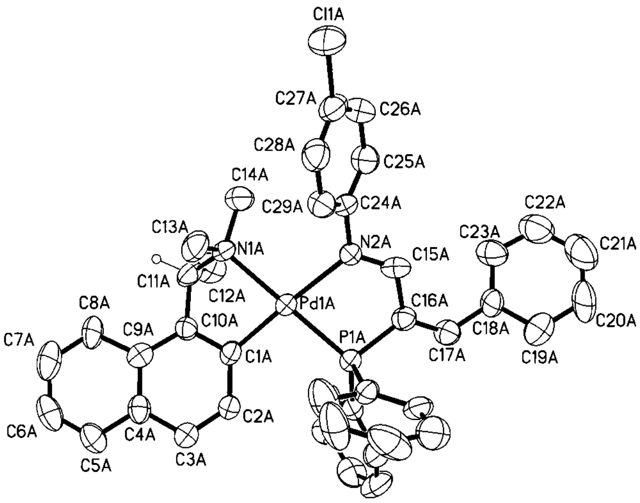

Figure 3. Molecular structure and absolute stereochemistry of complex (*S*)-**3d**.

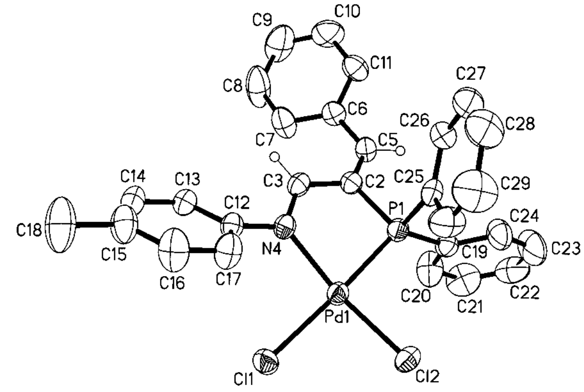

Figure 4. Molecular structure of complex **4c**.

C═N linkage. Similarly their C(16)−C(17) bond distances [1.344(7), 1.339(7), 1.345(12), and 1.351(11) Å for (*S*)-**3cA**, (*S*)-**3cB**, (*S*)-**3dA**, and (*S*)-**3dB**, respectively] clearly indicated that they are C═C bonds. Thus the structural analyses of complexes (*S*)-**3c** and (*S*)-**3d** confirmed that the imino−phosphine chelates were indeed produced directly from the treatment of the coordinated vinylphosphine with imines. It is noteworthy that, as previously described, the formation of complex (*S*)-**3c** is faster (24 h) than that observed for complexes (*S*)-**3a**,**b**,**d** (48 h). The difference in the reaction rates seems to indicate that the reaction can be accelerated by introducing an electronic donating group into the *p*-position of the ═N−Ph phenyl ring. To confirm this possible electronic effect, the *p*-substituted imines *p*-MeO(C_6H_4)N═CPh(H) and *p*-CF_3(C_6H_4)-N═CPh(H) were treated individually with (*S*)-**2**. No coupling was observed in the reaction involving *p*-CF_3-(C_6H_4)N═CPh(H). However, with *p*-MeO(C_6H_4)N═C-Ph(H), the corresponding imino−phosphine complex (*S*)-**3e** was obtained within 24 h. These observations thus confirmed that the electronic properties of the *p*-substituents on the N−Ph ring affected the rate of the ligand transformation reaction. The acid treatment of the cationic complexes (*S*)-**3c**−**e** gave the corresonding dichloro complexes **4c**−**e**. The dichloro complex **4c** was selected for the single-crystal X-ray crystallographic characterization. The structural analysis of the two crystallographically independent molecules in **4c** revealed that they have the same molecular architecture but differ in the absolute orientation of the P−Ph rings (Figure 4). The bond distances and angles of the imino−phosphine ring are similar to those observed in complexes (*S*)-**3c**,**d** and **4a** (Table 1).

Evidently, the imino−phosphine chelates in this series of compounds are stable in strong acidic condition, as heating complexes (*S*)-**3a**−**e** in concentrated sulfuric acid only removed the ortho-metalated naphthylamine ligand chemoselectively (Scheme 2). This is in contrast to many reports that coordinated imines are reactive in acidic conditions. It was not clear if the C═N bond

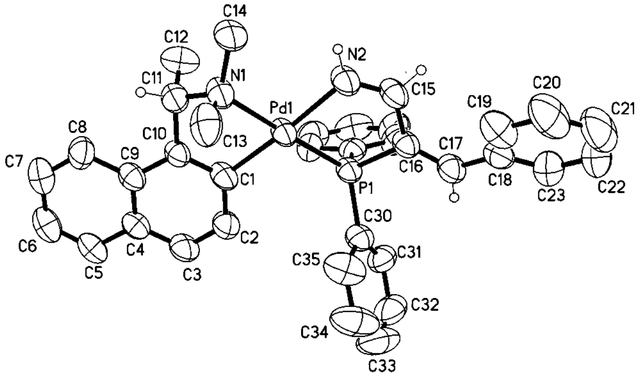

Figure 5. Molecular structure and absolute stereochemistry of complex (*S*)-**3f**.

in the new P-N chelates was stabilized by the =N−Ph aromatic ring or by metal complexation. Thus the reaction involving the imine HN=CPh(H) was carried out. The primary imine showed reactivities similar to *p*-Me(C_6H_4)N=CPh(H) and *p*-MeO(C_6H_4)N=CPh(H) toward (*S*)-**2**. The imino−phosphine complex (*S*)-**3f** was obtained in 24 h as highly crystalline pale yellow prisms. The complex was analyzed by X-ray crystallography. Interestingly, like (*S*)-**3c** and (*S*)-**3d**, complex (*S*)-**3f** also crystallized as two crystallographically independent molecules in the asymmetric unit cell due to the slightly different rotations of the phenyl rings with respect to the coordination plane. The cationic molecule (*S*)-**3fA** is depicted in Figure 5. The N(2)−C(15) distances of the imino C=N bonds in the two molecules are 1.280(9) and 1.275(8) Å, repectively, for molecules **A** and **B**. The corresponding C(16)−C(17) distances for these two molecules are 1.331(1) and 352(8) Å (Table 2). It is noteworthy that the N(1)−Pd−N(2) angles observed in both molecules of (*S*)-**3f** are slightly smaller than those observed in the complexes (*S*)-**3c** and (*S*)-**3d**. Clearly there is no significant interchelate repulsion interaction between the N-substituents in complex (*S*)-**3f**.

The stability of the imino−phosphine chelate in (*S*)-**3f** was examined by heating the complex with concentrated sulfuric acid. It was found that the C=N bond remained intact, and the corresponding dichloro complex **4f** was obtained quantitatively after LiCl was added to the acidic solution. The complex was obtained as pale yellow needles in 86% isolated yield. In $CDCl_3$ the ^{31}P NMR spectrum of **4f** exhibited a sharp singlet, at δ 55.6. The X-ray structural analysis of **4f** confirmed that the imino−phosphine remains coordinated to palladium as the P-N bidentate (Figure 6). The N(1)−C(2) and C(3)−C(4) distances are 1.277(3) and 1.347(3) Å, respectively (Table 1). Evidently, the imino−phosphine chelates in the present series of palladium complexes are stabilized by the strong metal complexation. The free imino−phosphine ligands **5a**−**f** could be liberated from the corresponding dichloro complexes **4a**−**f** by treatment with cyanide. Ligands **5a**−**e** are stable in inert atmosphere, but ligand **5f** decomposed rapidly in aqueous medium. It is noteworthy that similar cyanide treatments could not liberate the imino−phosphine ligands directly from complexes **3a**−**f**.

The formation of the imino−phosphine chelates in the present series of studies clearly does not involve the [4+2] cycloaddition reaction. In view of the regioselective migration of the C−Ph group from imines to the α-vinylic carbon atom of diphenylvinylphosphine, it is likely that a [2+2] cycloaddition reaction mechanism has taken place.[12] Analysis of all the product complexes also showed that the α- and one *β*-vinylic protons had been eleminated from the vinylphosphine. Thus the formation of these chelating imino−phosphine complexes suggest two possible reaction pathways in the ligand transformation process. The first possible pathway involves the elimination of two vinylic protons from vinylphosphine to form an alkyne function, which then undergoes the [2+2] cycloaddition process with the neighboring coordinated imine to generate an unstable four-membered cyclic intermediate. The subsequent ring-opening reaction gave the corresponding imino−phosphine chelate. However, the proposed alkyne species in this pathway could not be detected in the entire ligand transformation reaction. Similarly, in the absence of imine, we failed to oberve any alkyne formation when (*S*)-**2** alone was heated under similar or stronger reaction conditions. In a confirmation experiment, the diphenylvinylphosphine ligand in (*S*)-**2** was replaced with the analogous diphenylacetylenephosphine and used in the coupling reaction with all the six selected imines. However, complexes **3a**−**f** were not produced in these processes. The second possible reaction pathway initially involves a [2+2] cycloaddition between vinylphosphine and the neighboring C=N function, as illustrated in Figure 7. The subsequent oxidative ring-opening process generates the product complex as well as the elimination of a hydrogen molecule. It is noted that the formation of the four-membered cyclic intermediate on the palladium template is a sterically demanding step, and model studies suggest that the

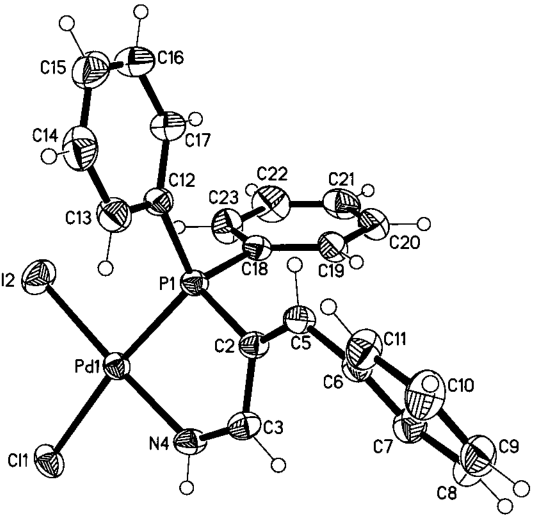

Figure 6. Molecular structure of complex **4f**.

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(11) Martin, J. W. L.; Organ, G. J.; Wainwright, K. P.; Weerasuria, K. D. V.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1987**, *26*, 2963. Duckworth, P. A.; Stephens, F. S.; Wainwright, K. P.; Weerasuria, K. D. V.; Wild, S. B. *Inorg. Chem.* **1989**, *28*, 4531. Martin, J. W. L.; Stephens, F. S.; Wainwright, K. P.; Weerasuria, K. D. V.; Wild, S. B. *J. Am. Chem. Soc.* **1988**, *110*, 4346. Gomez, M.; Granell, J.; Martinez, M. *Organometallics* **1997**, *16*, 2539. Crociani, B.; Antonaroli, S.; Bandoli, G.; Canovese, L.; Visentin, F.; Uguagliati, P. *Organometallics* **1999**, *18*, 1137.

(12) For examples of [2+2] cycloaddition reactions invoving imines, see: Palomo, C.; Ganboa, I.; Kot, A.; Dembkowski, L. *J. Org. Chem.* **1998**, *63*, 6398. Burwood, M.; Davies, B.; Diaz, I.; Grigg, R.; Molina, P.; Sridharan, V.; Hughes, M. *Tetrahedron Lett.* **1995**, *36*, 9053. Tanaka, H.; Abdul Hai, A. K. M.; Sadakane, M.; Okumoto, H.; Torii, S. *J. Org. Chem.* **1994**, *59*, 3040.

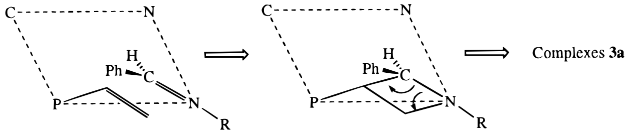

Figure 7. Proposed [2+2] cycloaddition reaction mechanism for the template synthesis of the P-N chelates in complexes (*S*)-**3a**−**f**.

C−Ph group must be located in a direction away from the palladium center. Perhaps this steric requirement accounts for the regioselectivity observed in the product complexes: the C−Ph group is always located in the position trans to the PPh_2 moiety. It should be noted that, however, such hetero four-membered rings are generally stable and can be isolated. Thus, if the second proposed pathway was indeed adopted, the palladium center must have played an important role in the oxidative ring-opening process. The mechanistic aspects of this ligand transformation process will be investigated further. In subsequent work, it will be shown that the coupling reaction can be modified for the asymmetric synthesis of optically active imino−phosphines.

Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. NMRs were recorded at 25 °C on Bruker ACF 300 and AMX 500 spectrometers. The phase-sensitive ROESY experiments were acquired into a 1024 × 512 matrix with a 250 ms spin locking time and a spin lock field strength such that $\gamma B1/2\pi = 5000$ Hz and then transformed into 1024 × 1024 points using a sine bell weighting function in both dimensions. Optical rotations were measured on the specified solution in a 1 dm cell at 25 °C with a Perkin-Elmer Model 341 polarimeter. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore.

Imines were prepared according to standard literature methods.[13] The enantiomerically pure form of [*SP*-4−4-(*S*)-chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][diphenylvinylphosphine-*P*]palladium(II), (*S*)-**1**, was prepared as previously described.[3−5]

Ligand Coupling Reactions. Synthesis of {(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{1,4-diphenyl-3-diphenylphosphino-1-aza-1,3-butadiene-*N*^{1},*P*$^{3'}$}palladium(II) Perchlorate, [(*S*)-3a]. A solution of the chloro complex (*S*)-**1** (1.0 g) in dichloromethane (40 mL) was subjected to chloride abstraction using silver perchlorate (0.8 g) in water (5 mL). The mixture was filtered, dried ($MgSO_4$), and evaporated to dryness, leaving a colorless glassy perchlorato species (*S*)-**2**. The complex was then redissolved in toluene (100 mL) and treated with *N*-benzylideneaniline (1.6 g) at 100 °C. The reaction was monitored by ^{31}P NMR spectroscopy and found to be complete in 48 h. The solvent was removed under reduced pressure to give a black residue. This material was chromatographed on a silica column giving (*S*)-**3a** as a yellow powder. The compound was subsequently crystallized from dichloromethane−diethyl ether as yellow needles, mp 197−199 °C (dec); $[\alpha]_D$ +212.5 (*c* 0.3, CH_2Cl_2); 0.47 g (33% yield). Anal. Calcd for $C_{41}H_{38}ClN_2O_4PPd$: C, 61.9; H, 4.8; N, 3.5. Found C, 62.1; H, 5.1; N, 3.6. ^{31}P NMR ($CDCl_3$): δ 52.2 (s). ^1H NMR ($CDCl_3$): δ 1.99 (d, 3H, $^3J_{HH} = 6.0$ Hz, CH*Me*), 2.18 (d, 3H, $^4J_{PH(trans)} = 3.6$ Hz, N*Me*), 2.60 (d, 3H, $^4J_{PH(trans)} = 1.6$ Hz, N*Me*), 4.27 (qn, 1H, $^3J_{HH} = {}^4J_{PH} = 6.0$ Hz, C*H*Me), 6.88 (dd, 1H, $^3J_{HH} = 8.4$ Hz, $^4J_{PH} = 6.0$ Hz, H_γ), 7.07 (d, 1H, $^3J_{HH} = 8.4$ Hz, H_δ), 7.26−7.73 (m, 23H, C═C*H* + *aromatics*), 8.25 (ddd, 2H, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.8$ Hz, $^3J_{PH} = 12.1$ Hz, *o*-P*Ph*), 8.55 (d, 1H, $^3J_{PH} = 22.5$ Hz, N═C*H*).

The following compounds were prepared similarly.

{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{1,4-diphenyl-3-diphenylphosphino-4-deuterium-1-aza-1,3-butadiene-*N*^{1},*P*$^{3'}$}palladium(II) perchlorate, [(*S*)-3b]: yellow needles, mp 196−198 °C (dec); $[\alpha]_D$ +212.5 (*c* 0.3, CH_2Cl_2); 33% yield. Anal. Calcd for $C_{41}H_{37}ClDN_2O_4PPd$: C, 61.8; H, 4.7; N, 3.5. Found: C, 62.1; H, 5.1; N, 3.6. ^{31}P NMR ($CDCl_3$): δ 52.2 (s). ^1H NMR ($CDCl_3$): δ 1.99 (d, 3H, $^3J_{HH} = 6.0$ Hz, CH*Me*), 2.18 (d, 3H, $^4J_{PH(trans)} = 3.6$ Hz, N*Me*), 2.60 (d, 3H, $^4J_{PH(trans)} = 1.6$ Hz, N*Me*), 4.27 (qn, 1H, $^3J_{HH} = {}^4J_{PH} = 6.0$ Hz, C*H*Me), 6.88 (dd, 1H, $^3J_{HH} = 8.4$ Hz, $^4J_{PH} = 6.0$ Hz, H_γ), 7.07 (d, 1H, $^3J_{HH} = 8.4$ Hz, H_δ), 7.32−7.73 (m, 22H, *aromatics*), 8.25 (dd, 2H, $^3J_{HH} = 7.6$ Hz, $^3J_{PH} = 12.1$ Hz, *o*-P*Ph*), 8.56 (d, 1H, $^3J_{PH} = 22.9$ Hz, N═C*H*).

{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{1-(*p*-methylphenyl)-3-diphenylphosphino-4-phenyl-1-aza-1,3-butadiene-*N*^{1},*P*$^{3'}$}palladium(II) perchlorate, [(*S*)-3c]: yellow needles, mp 181−183 °C (dec); $[\alpha]_D$ +182.9 (*c* 0.3, CH_2Cl_2); 36% yield. Anal. Calcd for $C_{42}H_{40}ClN_2O_4PPd$: C, 62.3; H, 5.0; N, 3.5. Found: C, 62.0; H, 5.0; N, 3.5. ^{31}P NMR ($CDCl_3$): δ 52.6 (s). ^1H NMR ($CDCl_3$): δ 1.97 (d, 3H, $^3J_{HH} = 6.4$ Hz, CH*Me*), 2.19 (d, 3H, $^4J_{PH(trans)} = 3.6$ Hz, N*Me*), 2.37 (s, 3H, C_6H_4-*Me*), 2.62 (d, 3H, $^4J_{PH(trans)} = 1.6$ Hz, N*Me*), 4.30 (qn, 1H, $^3J_{HH} = {}^4J_{PH} = 6.0$ Hz, C*H*Me), 6.90 (dd, 1H, $^3J_{HH} = 8.4$ Hz, $^4J_{PH} = 6.0$ Hz, H_γ), 7.07 (d, 1H, $^3J_{HH} = 8.4$ Hz, H_δ), 7.27−7.75 (m, 22H, C═C*H* + *aromatics*), 8.25 (ddd, 2H, $^3J_{HH} = 7.2$ Hz, $^4J_{HH} = 2.6$ Hz, $^3J_{PH} = 12.1$ Hz, *o*-P*Ph*), 8.52 (d, 1H, $^3J_{PH} = 22.5$ Hz, N═C*H*).

{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{1-(*p*-chlorophenyl)-3-diphenylphosphino-4-phenyl-1-aza-1,3-butadiene-*N*^{1},*P*$^{3'}$}palladium(II) perchlorate, [(*S*)-3d]: yellow needles, mp >210 °C (dec); $[\alpha]_D$ +214.3 (*c* 0.3, CH_2Cl_2); 21% yield. Anal. Calcd for $C_{41}H_{37}Cl_2N_2O_4PPd$: C, 59.3; H, 4.5; N, 3.4. Found: C, 58.9; H, 4.4; N, 3.5.^{31}P NMR ($CDCl_3$): δ 51.9 (s). ^1H NMR ($CDCl_3$): δ 1.97 (d, 3H, $^3J_{HH} = 6.4$ Hz, CH*Me*), 2.24 (d, 3H, $^4J_{PH(trans)} = 3.6$ Hz, N*Me*), 2.60 (d, 3H, $^4J_{PH(trans)} = 1.2$ Hz, N*Me*), 4.27 (qn, 1H, $^3J_{HH} = {}^4J_{PH} = 6.0$ Hz, C*H*Me), 6.87 (dd, 1H, $^3J_{HH} = 8.4$ Hz, $^4J_{PH} = 6.0$ Hz, H_γ), 7.07 (d, 1H, $^3J_{HH} = 8.4$ Hz, H_δ), 7.29−7.78 (m, 22H, C═C*H* + *aromatics*), 8.24 (ddd, 2H, $^3J_{HH} = 7.2$ Hz, $^4J_{HH} = 1.6$ Hz, $^3J_{PH} = 12.1$ Hz, *o*-P*Ph*), 8.52 (d, 1H, $^3J_{PH} = 22.5$ Hz, N═C*H*).

{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{1-(*p*-methoxyphenyl)-3-diphenylphosphino-4-phenyl-1-aza-1,3-butadiene-*N*^{1},*P*$^{3'}$}palladium (II) perchlorate, [(*S*)-3e]: yellow needles, mp 200−202 °C (dec); $[\alpha]_D$ +118.4 (*c* 0.3, CH_2Cl_2); 36% yield. Anal. Calcd for $C_{42}H_{40}ClN_2O_5PPd$: C, 61.1; H, 4.9; N, 3.4. Found: C, 59.7; H, 5.1; N, 3.5. ^{31}P NMR ($CDCl_3$): δ 52.9 (s). ^1H NMR ($CDCl_3$): δ 1.99 (d, 3H, $^3J_{HH} = 6.4$ Hz, CH*Me*), 2.22 (d, 3H, $^4J_{PH(trans)} = 3.6$ Hz, N*Me*), 2.62 (d, 3H, $^4J_{PH(trans)} = 1.6$ Hz, N*Me*), 3.83 (s, 3H, C_6H_4−O*Me*), 4.29 (qn, 1H, $^3J_{HH} = {}^4J_{PH} = 6.0$ Hz, C*H*Me), 6.88 (dd, 1H, $^3J_{HH} = 8.4$ Hz, $^4J_{PH} = 6.0$ Hz, H_γ), 7.00−7.73 (m, 20H, C═C*H* + *aromatics*), 7.02 (d, 2H, $^3J_{HH} = 8.9$ Hz, 2x*H*CC−OMe), 7.07 (d, 1H, $^3J_{HH} = 8.4$ Hz, H_δ), 8.24 (ddd, 2H, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 1.2$ Hz, $^3J_{PH} = 12.0$ Hz, *o*-P*Ph*), 8.53 (d, 1H, $^3J_{PH} = 22.5$ Hz, N═C*H*).

{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{3-diphenylphosphino-4-phenyl-1-aza-1,3-butadiene-*N*^{1},*P*$^{3'}$}-palladium(II) perchlorate, [(*S*)-3f]. The imine HN═CPh(H) was generated in situ by heating PhCH{N═CPh(H)}$_2$ in toluene at 100 °C. The complex (*S*)-**3f** was isolated as yellow needles, mp 140−141 °C (dec); $[\alpha]_D$ +65.8 (*c* 0.3, CH_2Cl_2); 39% yield. Anal. Calcd for $C_{35}H_{34}ClN_2O_4PPd$: C, 58.4; H, 4.8; N, 3.9. Found: C, 58.0; H, 5.0; N, 4.0. ^{31}P NMR ($CDCl_3$): δ 48.6 (s). ^1H NMR ($CDCl_3$): δ 1.87 (d, 3H, $^3J_{HH} = 6.0$ Hz, CH*Me*), 2.94 (s, 3H, N*Me*), 3.17 (d, 3H, $^4J_{PH(trans)} = 3.2$ Hz, N*Me*), 4.49 (qn, 1H, $^3J_{HH} = {}^4J_{PH} = 7.0$ Hz, C*H*Me), 6.72 (dd, 1H, $^3J_{HH} =$

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[13] Roe, A.; Montgomery, J. A. *J. Am. Chem. Soc.* **1953**, *75*, 910. Katogiri, N.; Miura, Y.; Niwa, R.; Kato, T. *Bull. Chem. Pharm.* **1983**, *31*, 538.

Table 3. Crystallographic Data for Complexes (*S*)-3c, (*S*)-3d, (*S*)-3f, 4a, 4c, and 4f

	(*S*)-**3c**	(*S*)-**3d**	(*S*)-**3f**	**4a**	**4c**	**4f**
formula	$C_{42}H_{40}ClN_2O_4PPd$	$C_{41}H_{37}Cl_2N_2O_4PPd$	$C_{35}H_{35}ClN_2O_4PPd\cdot 0.5H_2O$	$C_{27}H_{22}Cl_2NPPd\cdot 0.5H_2O\cdot 0.5CHCl_3$	$C_{28}H_{24}Cl_2NPPd$	$C_{21}H_{18}Cl_2NPPd$
fw	809.58	830.00	728.47	637.42	582.75	492.63
space group	$P2_1$	$P2_1$	$P2_1$	$P(-1)$	$P(-1)$	$P2(1)/c$
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
a/Å	12.584(1)	12.473(1)	8.379(1)	10.015(1)	12.607(1)	9.403(1)
b/Å	12.041(1)	12.014(1)	19.288(1)	10.226(1)	14.535(1)	20.901(1)
c/Å	25.878(1)	25.954(1)	22.074(1)	15.213(1)	15.131(1)	10.430(1)
α/deg	90(1)	90	90	94.33(1)	79.26(1)	90
β/deg	96.18(1)	96.79(1)	98.48(1)	95.22(1)	79.32(1)	96.96(1)
γ/deg	90(1)	90	90	113.51(1)	76.34(1)	90
V/Å^3	3889.5(1)	3861.9(1)	3528.4(2)	1412.1(1)	2617.7(1)	2034.7(1)
Z	4	4	4	2	4	4
T/K	293(2)	293(2)	293(2)	293(2)	223(2)	293(2)
$d_{(calcd)}$/g cm^{-3}	1.379	1.428	1.371	1.499	1.479	1.608
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ/cm^{-1}	6.28	7.03	6.87	10.64	9.91	12.58
F(000)	1664	1696	1492	640	1176	984
R_1 (obs data)[a]	0.0423	0.0472	0.0389	0.0335	0.0264	0.0292
wR_2 (obs data)[b]	0.1139	0.1191	0.1120	0.1005	0.0595	0.0603

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

8.4 Hz, $^4J_{PH}$ = 5.2 Hz, H$_\gamma$), 7.00−7.73 (m, 20H, C═C*H* + *aromatics*), 7.14 (d, 1H, $^3J_{HH}$ = 8.4 Hz, H$_\delta$), 8.24 (ddd, 2H, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.9 Hz, $^3J_{PH}$ = 12.0 Hz, *o*-P*Ph*), 9.26 (dd, 1H, $^3J_{HH}$ = 11.6 Hz, $^3J_{PH}$ = 25.9 Hz, N═C*H*), 11.0 (d, 1H, $^3J_{HH}$ = 11.6 Hz, N*H*). The $^3J_{HH}$ coupling between the two protons in the N*H*═C*H* function could be suppressed upon treatment of the NMR sample with D_2O.

Dichloro{1,4-diphenyl-3-diphenylphosphino-1-aza-1,3-butadiene-*N*^{1},*P*$^{3'}$}palladium(II), 4a. The naphthylamine auxiliary in (*S*)-**3a** was removed chemoselectively by treating the cationic complex (0.2 g) with concentrated sulfuric acid (70%, 3 mL) for 0.5 h. The acidic solution was then poured onto ice (ca. 15 g), and lithium chloride (0.5 g) was added. The mixture was stirred for 1 h. Addition of dichloromethane (50 mL) gave a clear yellow organic layer, which was subsequently separated, and the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with water and then dried over anhydrous $MgSO_4$. Removal of solvent and recrystallization from dichloromethane−diethyl ether gave the dichloro complex (*S*)-**4a** as pale yellow prisms: mp >210 °C (dec); 0.13 g (91% yield). Anal. Calcd for $C_{27}H_{22}Cl_2NPPd$: C, 57.0; H, 3.9; N, 2.5. Found: C, 57.0; H, 4.1; N, 2.7. ^{31}P NMR ($CDCl_3$): δ 51.7 (s). ^{1}H NMR ($CDCl_3$): 7.30−7.67 (m, 17H, C═C*H* + *aromatics*), 7.94 (dd, 4H, $^3J_{HH}$ = 7.6 Hz, $^3J_{PH}$ = 12.8 Hz, *o*-P*Ph*), 8.43 (d, 1H, $^3J_{PH}$ = 33.7 Hz, N═C*H*).

The following compounds were prepared similarly.

Dichloro{1,4-diphenyl-3-diphenylphosphino-4-deuterium-1-aza-1,3-butadiene-*N*^{1},*P*$^{3'}$}palladium(II), 4b: pale yellow prisms, mp >210 °C (dec); 91% yield. Anal. Calcd for $C_{27}H_{21}Cl_2DNPPd$: C, 56.9; H, 3.7; N, 2.5. Found: C, 56.9; H, 4.1; N, 2.7. ^{31}P NMR ($CDCl_3$): δ 51.6 (s). ^{1}H NMR ($CDCl_3$): 7.30−7.67 (m, 16H, *aromatics*), 7.94 (dd, 4H, $^3J_{HH}$ = 7.6 Hz, $^3J_{PH}$ = 12.8 Hz, *o*-P*Ph*), 8.45 (d, 1H, $^3J_{PH}$ = 33.7 Hz, N═C*H*).

Dichloro{1-(*p*-methylphenyl)-3-diphenylphosphino-4-phenyl-1-aza-1,3-butadiene-*N*^{1},*P*$^{3'}$}palladium(II), 4c: pale yellow prisms, mp >220 °C (dec); 91% yield. Anal. Calcd for $C_{28}H_{24}Cl_2NPPd$: C, 57.7; H, 4.2; N, 2.4. Found: C, 57.5; H, 4.0; N, 2.5. ^{31}P NMR ($CDCl_3$): δ 51.9 (s). ^{1}H NMR ($CDCl_3$): 2.34 (s, 3H, C_6H_4-*Me*), 7.14−7.63 (m, 16H, C═C*H* + *aromatics*), 7.95 (dd, 4H, $^3J_{HH}$ = 7.6 Hz, $^3J_{PH}$ = 13.3 Hz, *o*-P*Ph*), 8.40 (d, 1H, $^3J_{PH}$ = 34.1 Hz, N═C*H*).

Dichloro{1-(*p*-chlorophenyl)-3-diphenylphosphino-4-phenyl-1-aza-1,3-butadiene-*N*^{1},*P*$^{3'}$}palladium(II), 4d: pale yellow prisms, mp >250 °C (dec); 89% yield. Anal. Calcd for $C_{27}H_{21}Cl_3NPPd\cdot 0.5CH_2Cl_2$: C, 51.2; H, 3.4; N, 2.2. Found: C, 51.4; H, 3.5; N, 2.3. ^{31}P NMR ($CDCl_3$) δ 51.2 (s). ^{1}H NMR ($CDCl_3$): 7.30−7.73 (m, 16H, C═C*H* + *aromatics*), 7.93 (dd, 4H, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 13.2 Hz, *o*-P*Ph*), 8.42 (d, 1H, $^3J_{PH}$ = 33.7 Hz, N═C*H*).

Dichloro{1-(*p*-methoxyphenyl)-3-diphenylphosphino-4-phenyl-1-aza-1,3-butadiene-*N*^{1},*P*$^{3'}$}palladium(II), 4e: pale yellow prisms, mp >260 °C (dec); 90% yield. Anal. Calcd for $C_{28}H_{24}Cl_2NOPPd$: C, 56.2; H, 4.0; N, 2.3. Found: C, 55.5; H, 3.7; N, 2.6. ^{31}P NMR ($CDCl_3$): δ 52.1 (s). ^{1}H NMR ($CDCl_3$): 3.79 (s, 3H, C_6H_4−O*Me*), 7.28−7.67 (m, 16H, C═C*H* + *aromatics*), 6.87 (d, 2H, $^3J_{HH}$ = 9.2 Hz, 2×*H*CC−OMe), 7.93 (dd, 4H, $^3J_{HH}$ = 8.4 Hz, $^3J_{PH}$ = 12.8 Hz, *o*-P*Ph*), 8.40 (d, 1H, $^3J_{PH}$ = 33.7 Hz, N═C*H*).

Dichloro{3-diphenylphosphino-4-phenyl-1-aza-1,3-butadiene-*N*^{1},*P*$^{3'}$}palladium(II), 4f: pale yellow prisms, mp >250 °C (dec); 86% yield. Anal. Calcd for $C_{21}H_{18}Cl_2NPPd$: C, 51.2; H, 3.7; N, 2.8. Found: C, 50.9; H, 3.2; N, 3.1. ^{31}P NMR ($CDCl_3$): δ 55.6 (s). ^{1}H NMR ($CDCl_3$): 7.40−7.65 (m, 12H, C═C*H* + *aromatics*), 7.88 (dd, 4H, $^3J_{HH}$ = 9.6 Hz, $^3J_{PH}$ = 13.2 Hz, *o*-P*Ph*), 8.87 (dd, 1H, $^3J_{HH}$ = 10.0 Hz, $^3J_{PH}$ = 38.5 Hz, N═C*H*), 11.2 (d, 1H, $^3J_{HH}$ = 10.0 Hz, N*H*).

Liberation of Imino−Phosphine Ligand. Isolation of 1,4-Diphenyl-3-diphenylphosphino-1-aza-1,3-butadiene, 5a. A solution of **4a** (0.5 g) in dichloromethane (100 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (0.5 g) for 30 min. The resulting colorless organic layer was separated, washed with water, and then dried ($MgSO_4$). Upon the removal of solvent, an air-stable low-melting solid was obtained, 0.22 g (80% yield). ^{31}P NMR ($CDCl_3$): δ −5.4 (s). ^{1}H NMR ($CDCl_3$): 6.77 (d, 1H, $^3J_{PH}$ = 4.8 Hz, C═C*H*), 6.87 (d, 2H, $^3J_{HH}$ = 8.4 Hz, *m*-NPh), 7.08−7.50 (m, 18H, *aromatics*), 8.56 (dd, 1H, $^4J_{HH}$ = 0.8 Hz, $^3J_{PH}$ = 8.4 Hz, N═C*H*).

The following compounds were prepared similarly.

1,4-Diphenyl-3-diphenylphosphino-4-deuterium-1-aza-1,3-butadiene, 5b: pale yellow solid, 80% yield. ^{31}P NMR ($CDCl_3$): δ -5.4 (s). ^{1}H NMR ($CDCl_3$): 6.80 (d, 2H, $^3J_{HH}$ = 8.2 Hz, *m*-NPh), 7.08−7.56 (m, 18H, *aromatics*), 8.56 (dd, 1H, $^4J_{HH}$ = 0.8 Hz, $^3J_{PH}$ = 8.4 Hz, N═C*H*).

1-(*p*-Methylphenyl)-3-diphenylphosphino-4-phenyl-1-aza-1,3-butadiene, 5c: pale yellow solid, 80% yield. δ -5.4 (s). ^{1}H NMR ($CDCl_3$): 2.28 (s, 3H, C_6H_4-*Me*), 6.74 (d, 1H, $^3J_{PH}$ = 4.4 Hz, C═C*H*), 6.81 (d, 2H, $^3J_{HH}$ = 8.2 Hz, *m*-NAr), 7.05 (d, 2H, $^3J_{HH}$ = 8.2 Hz, *o*-NAr), 7.24−7.50 (m, 15H, *aromatics*), 8.58 (dd, 1H, $^4J_{HH}$ = 0.8 Hz, $^3J_{PH}$ = 8.0 Hz, N═C*H*).

(*p*-Chlorophenyl)-3-diphenylphosphino-4-phenyl-1-aza-1,3-butadiene 5d: pale yellow solid; 81% yield. ^{31}P NMR ($CDCl_3$): δ -5.5 (s). ^{1}H NMR ($CDCl_3$): 6.79 (d, 1H, $^3J_{PH}$ = 4.4 Hz, C═C*H*), 6.79 (d, 2H, $^3J_{HH}$ = 8.4 Hz, *m*-NAr), 7.19 (d, 2H,

$^3J_{HH}$ = 8.4 Hz, *o*-NAr), 7.23−7.49 (m, 15H, *aromatics*), 8.53 (d, 1H, $^3J_{PH}$ = 8.0 Hz, N═C*H*).

1-(*p*-Methoxyphenyl)-3-diphenylphosphino-4-phenyl-1-aza-1,3-butadiene 5e: pale yellow solid, 79% yield. ^{31}P NMR (CDCl$_3$): δ -5.6 (s). ^{1}H NMR (CDCl$_3$): 3.75 (s, 3H, C_6H_4−O*Me*), 6.71 (d, 1H, $^3J_{PH}$ = 4.4 Hz, C═C*H*), 6.78 (d, 2H, $^3J_{HH}$ = 9.2 Hz, *m*-NAr), 6.91 (d, 2H, $^3J_{HH}$ = 9.2 Hz, *o*-NAr), 7.30−7.49 (m, 15H, *aromatics*), 8.60 (dd, 1H, $^4J_{HH}$ = 0.8 Hz, $^3J_{PH}$ = 8.4 Hz, N═C*H*).

Crystal Structure Determination of (*S*)-3c, (*S*)-3d, (*S*)-3f, 4a, 4c, and 4f. Crystal data for all six complexes and a summary of the crystallographic analyses are given in Table 3. 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.[14] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at fixed distance from carbon and nitrogen atoms and were assigned fixed thermal parameters. The absolute configurations of all chiral complexes were determined unambiguously using the Flack parameter and by internal reference to the known naphthylamine center.

Acknowledgment. We are grateful to the National University of Singapore for support of this research (Grant No. RP 979905) and a research scholarship to L.X.

Supporting Information Available: For (*S*)-**3c**, (*S*)-**3d**, (*S*)-**3f**, **4a**, **4c**, and **4f** 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.

OM000416L

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[14] Sheldrick, G. M. *SHELXL 93, Program for Crystal Structure Refinement*; University of Gottingen: Germany 1993.