2148 *Organometallics* **2010,** *29,* 2148–2156
DOI: 10.1021/om100234q

ORGANOMETALLICS
Article

Diphenylprolinol-Derived Symmetrical and Unsymmetrical Chiral Pincer Palladium(II) and Nickel(II) Complexes: Synthesis via One-Pot Phosphorylation/Metalation Reaction and C−H Activation

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Received March 26, 2010

The symmetrical P-stereogenic bis-phosphoramidite PCP pincer Pd(II) complexes **1** and **2** were easily prepared by a "four-component, one-pot phosphorylation/palladation" procedure via C−H bond activation of the related ligands. In this synthetic procedure, (*S*)-diphenyl(pyrrolidin-2-yl)methanol was first phosphonated with PCl_3 to afford the expected phosphorochloridate adduct, which then reacted in situ with resorcinol or disubstituted resorcinol, followed by treatment with $PdCl_2$. The first examples of the unsymmetrical P-stereogenic phosphoramidite- and imidazoline-containing PCN pincer Pd(II) complex **3** and Ni(II) complex **4** could be obtained in a similar manner by using a chiral imidazoline-containing *m*-phenol derivative instead of resorcinol as a backbone. ^{31}P NMR of the complexes confirmed the formation of a single diastereoisomer concerning the P-stereogenic center, and its absolute configuration was determined by an X-ray crystal structure determination. Preliminary investigations on the use of these complexes in the asymmetric allylation indicated that the unsymmetrical pincer Pd complex **3** exhibited higher catalytic activity than the related symmetrical ones. On the other hand, the more bulky Pd complex **2** gave better enantioselectivity, especially in the allylation of 4-nitrobenzenesulfonimine (69% ee).

Introduction

Pincer-type complexes have been extensively studied in recent years and widely applied in organic synthesis, organometallic catalysis, and materials science.[1] In these systems the facility to modify and tune the properties of pincer ligands provides a wealth of opportunities to influence the reactivities, stabilities, and other important properties of the ensuing pincer complexes. Much of the research has focused on symmetrical YCY-type pincer metal complexes, where the ligands coordinate to the metal center via two identical Y-donor groups and one aromatic carbon anion. The chiral versions of such tridentate ligands and their corresponding metal complexes have also been developed (Chart 1). The most common ones have an N-based ligand framework using amino alcohols or other natural products as chiral auxiliaries, such as those containing oxazoline (type **A**),[2,3] imidazoline (**B**),[4] imine (**C**),[5] and amine skeletons (**D**−**G**).[6−8]

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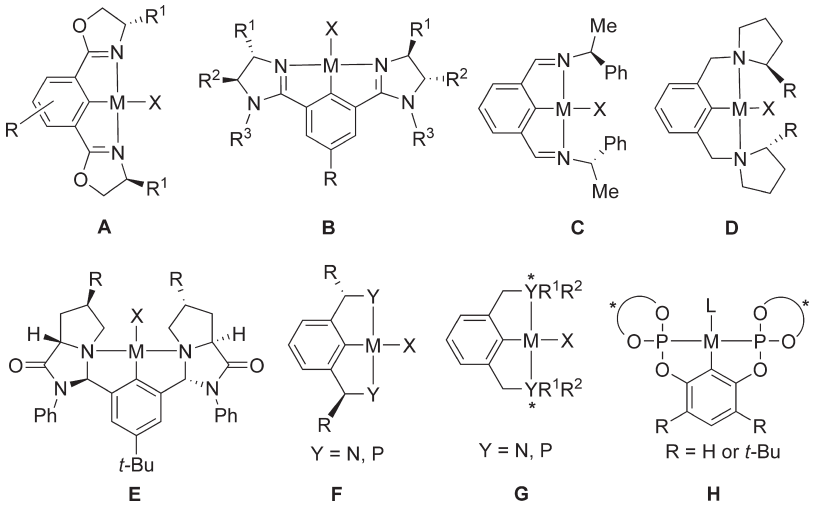
 Published on Web 04/16/2010

Chart 1. Examples of Chiral Pincer Metal Complexes



Among them, the NCN bis(oxazolinyl)phenyl−metal complexes including Rh, Pd, Pt, Ru, and Ni have been extensively investigated and widely used in asymmetric catalyses such as alkylation of aldimines (up to 82% ee), aldol reaction of isocyanides and aldehydes (up to 75% ee), conjugate reduction of α,β-unsaturated esters with hydrosilanes (up to 98% ee), hydrogenation (up to 98% ee), and transfer hydrogenation of ketones (up to 97% ee).[2,3] In contrast, the synthesis and applications of chiral pincer metal complexes with P-donor ligands for the chiral catalysts have been relatively unexplored.[9−12] The following two reasons may account for this: (a) finding an appropriate P-donor pincer ligand with stereochemical parameters has proven to be difficult and costly in comparison with the case for chiral N-donor ligands and (b) the air- and moisture-sensitive preligands usually need to be constructed and isolated under harsh conditions, thus resulting in laborious synthetic procedures required for the preparation of their corresponding metal complexes. Nonetheless, chiral pincer metal complexes with phosphines bearing either a stereogenic benzylic methylene center or a chiral phosphorus atom have been successfully synthesized (types **F** and **G**, Y = P).[9,10] Additionally, Szabó and Bedford independently reported chiral phosphite PCP palladium complexes by incorporating axially chiral 1,1′-bi-2-naphthol- and biphenanthrol-derived diols into the PCP-pincer backbone (type **H**).[11]

Generally, the formation of pincer metal complexes can be achieved by the method of direct metalation via C−H bond activation, transmetalation reaction, or oxidative addition. Among them, the direct C−H activation should be the most simple and convenient method for the construction of complexes because it does not require prefunctionalization of the pincer ligands to achieve regioselective metalation. In previous work, we reported a series of chiral pincer Pt(II) and Pd(II) complexes with 1,3-bis(2′-imidazolinyl)benzenes (Chart 1, type **B**),[4] achiral and chiral Pd(II) complexes with unsymmetrical oxazolinyl-containing ligands,[13a] and particularly a facile "three-component, one-pot phosphorylation/palladation" method for the preparation of Pd(II) complexes with mono- or diphosphinite ligands.[13b,c] These studies allowed us to obtain various PCP, NCN, and PCN pincer Pd(II) or Pt(II) complexes via direct C−H activation of the related ligands. As a part of our program to further extend one-pot phosphorylation/palladation, we synthesized P-chiral square-planar pincer metal complexes, including the symmetrical bis-phosphoramidite PCP pincer Pd(II) complexes **1** and **2** as well as the first unsymmetrical P-chiral PCN pincer Pd(II) complex (**3**) and Ni(II) complex (**4**) using easily available amino alcohols as chiral auxiliaries (Figure 1). In addition, preliminary investigations on the asymmetric allylation of aldehyde and sulfonimine catalyzed by these chiral PCP and PCN complexes are also described. It should be mentioned that during the study presented here, very recently Klein Gebbink and co-workers reported the related diphenylprolinol-derived chiral Pd(II) complex **5** via an oxidation addition (Figure 1).[14]

Results and Discussion

Synthesis of Symmetrical Chiral Bis-Phosphoramidite PCP-Pincer Palladium Complexes 1 and 2. The chiral pincer complex **1** was prepared from easily available starting materials in a four-component (including diphenylprolinol, PCl_3, resorcinol, and $PdCl_2$), one-pot manner, as shown in Scheme 1. First, the optically active amino alcohol (*S*)-diphenyl(pyrrolidin-2-yl)-methanol was phosphonated with PCl_3 in the presence of triethylamine in DCE (1,2-dichloroethane) to afford the expected

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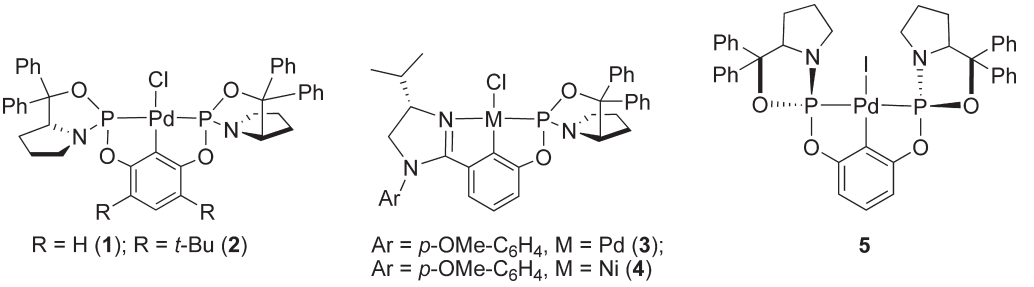
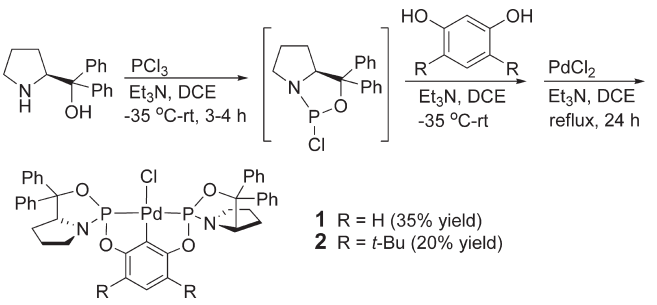


Figure 1

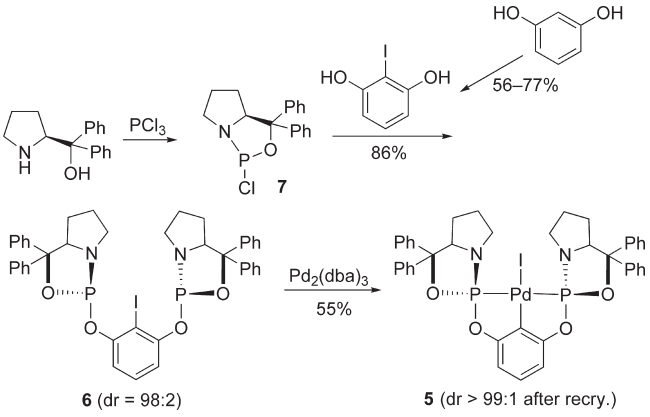
Scheme 1. Synthesis of Symmetrical Chiral Bis-Phosphoramidite PCP Pincer Palladium Complexes 1 and 2 via C−H Bond Activation



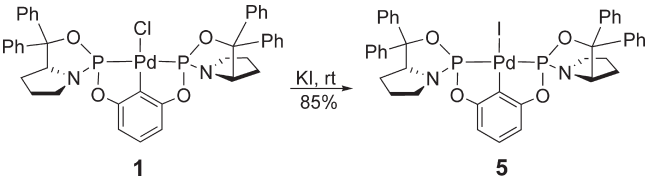
phosphorochloridate adduct. Then the adduct reacted in situ with resorcinol, followed by treatment with $PdCl_2$. The pure air- and moisture-stable complex **1** was successfully obtained in 35% isolated yield (based on resorcinol) as a white solid after chromatography on silica gel. Bedford and co-workers[11b] reported that incorporation of *tert*-butyl groups into the 4- and 6-positions of resorcinol could increase the rate of metalation in the preparation of bis-phosphite pincer Pd complexes and also led to enhanced activity in the asymmetric allylation of aldehydes in comparison with the less bulky pincer complexes. Therefore, we tried to synthesize complex **2** with the more hindered *tert*-butyl group on the central aromatic ring. The process was carried out in a fashion similar to that described for complex **1** using 4,6-di-*tert*-butylbenzene-1,3-diol instead of resorcinol as a backbone. Surprisingly, the optically pure complex **2** was obtained in a lower yield (20%, based on di-*t*-Bu-substituted resorcinol). The formation of a single diastereoisomer for complexes **1** and **2** concerning the P-stereogenic center was confirmed by the singlet resonances at 155.8 and 159.1 ppm, respectively, in the ^{31}P NMR spectra.

Klein Gebbink and co-workers recently described an oxidative addition route for the synthesis of the symmetrical chiral bis-phosphoramidite **5** (Scheme 2).[14] In their synthetic route, 2-iodoresorcinol, which could be prepared from resorcinol,[15] was needed for metalation via oxidative addition. In addition, both the ligand **6** and the pincer Pd complex **5** were obtained as two diastereoisomers with regard to the P-stereogenic center (dr = 98:2 and >99:1 after recrystallization, respectively, estimated by ^{31}P NMR). In fact, they also tried the C−H activation method, but without success. In their experiments, when 4,6-di-*tert*-butylbenzene-1,3-diol was used to couple with phosphorochloridate adduct **7** to

Scheme 2. Klein Gebbink's Oxidative Addition Route for the Synthesis of the Symmetrical Chiral Bis-Phosphoramidite PCP Pincer Pd(II) Complex 5



Scheme 3. Conversion of Pd−Cl Complex 1 to Pd−I Complex 5 by the Halogen Exchange Reaction



form the corresponding bis-phosphoramidite ligand, a complete loss of stereospecificity on the phosphorus atom occurred, which was confirmed by two sharp singlets of equal intensity at 145.3 and 147.6 ppm in the ^{31}P NMR spectra. In contrast, 4,6-di-*tert*-butylbenzene-1,3-diol could react with the phosphorochloridate obtained from treatment of (*S*)-(+)-indolinemethanol with PCl_3 to afford the bis-phosphoramidite ligand in excellent diastereoselectivity (dr = 96:4). However, subsequent metalation with $PdCl_2(MeCN)_2$ via C−H activation was found to proceed very sluggishly and a pure sample of the pincer Pd complex could not be isolated.

We think the racemization of P-chirality may be caused by the high reaction temperature (refluxing toluene) in the coupling of 4,6-di-*tert*-butylbenzene-1,3-diol with phosphorochloridate adduct **7** in Klein Gebbink's experiments. In our case, the coupling was carried out at low temperature (−35 °C to room temperature). Although the yields of the pincer metal complexes by this "four-component, one-pot" strategy were not very high, the synthetic procedure was simplified and had some advantages: (a) it avoided the troublesome step of isolating the air- and moisture-sensitive P-containing species, (b) the synthesis was highly stereoselective, yielding a single diastereoisomer with

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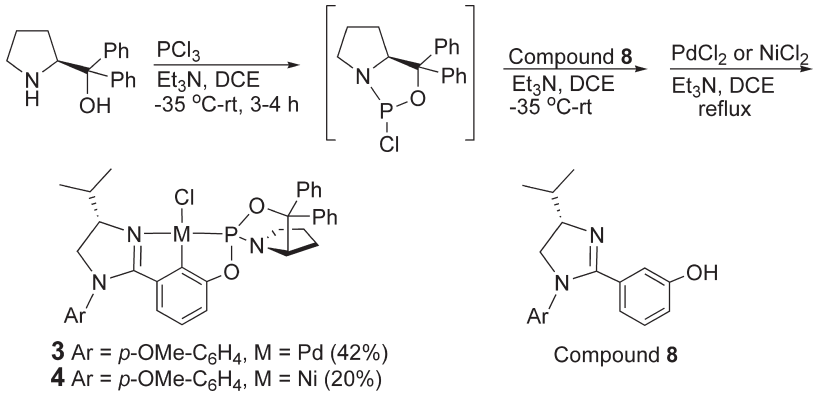
Scheme 4. Synthesis of the Unsymmetrical P-Chiral PCN Pincer Pd(II) Complex 3 and Ni(II) Complex 4



regard to the P-stereogenic center, and (c) the direct metalation via C−H activation of the related 1,3-disubstituted benzene was successfully achieved during the reaction by using a cheap and commercially available Pd(II) salt instead of more expensive and unstable Pd^0 sources and so the preparation of the appropriate 1,2,3-trisubstituted benzene was unnecessary. Actually, we found that the iodopalladium complex **5** could be prepared in good yield from the chloropalladium complex **1** by treatment with an excess of KI in acetone−MeOH at room temperature (Scheme 3). The ^{31}P NMR spectrum of complex **5** shows a singlet resonance at 159.7 ppm, shifted downfield in comparison with that of complex **1** (155.8 ppm).

Synthesis of the Unsymmetrical Chiral PCN-Pincer Pd(II) Complex 3 and Ni(II) Complex 4. To synthesize potentially hemilabile hybrid chiral PCN−pincer complexes, especially those containing a P-chiral moiety, we adopted displacement of one phospholidine cycle at the 2- or 6-position of the central aryl ring in the symmetrical complexes **1** and **2** by a chiral imidazoline unit. Thus, following a synthetic route similar to that for complexes **1** and **2**, the adduct obtained from treatment of (*S*)-diphenyl(pyrrolidin-2-yl)methanol with PCl_3 was reacted in situ with the imidazolinyl-containing *m*-phenol derivative **8**. The subsequent palladation also proceeded in situ by the addition of $PdCl_2$ (Scheme 4). The unsymmetrical Pd(II) complex **3** was successfully isolated as a yellow solid after chromatography on silica gel in 42% yield, which was higher than that for the symmetrical bis-phosphoramidite Pd(II) complex **1** (35%). Inspired by the successful preparation of the Pd(II) complex **3**, the nickelation of the related preligand was tried with $NiCl_2$ instead of $PdCl_2$. We were pleased to find that the corresponding PCN-pincer Ni(II) complex **4** could also be obtained via C−H activation as a pale yellow solid after chromatography on silica gel, albeit in a lower yield (20%). It should be noted that nickelation of the symmetrical bis-phosphoramidite ligand with $NiCl_2$ via C−H activation in a similar procedure did not yield the desired PCP pincer Ni(II) complex. The above results indicated that the nature of the pincer ligands had a major influence on the metalation step. The metalation of the imidazoline-containing unsymmetrical ligands was easier than that of the related symmetrical bis-phosphoramidite ligand, possibly due to the greater donor strength of imidazoline, which promoted metal coordination. To our knowledge, reports on the unsymmetrical and chiral pincer metal complexes are rather limited,[13a,16] and the PCN pincer metal complexes **3** and **4** are the first examples of unsymmetrical chiral pincer complexes containing a P-stereogenic center. Both complexes **3** and **4** were stable toward air and moisture and could be stored for several weeks at ambient temperature in an air atmosphere. Similar to the symmetrical PCP complexes **1** and **2**, ^{31}P NMR spectra of these unsymmetrical chiral PCN pincer complexes also confirmed the formation of a single diastereoisomer concerning the P-stereogenic center by the singlet resonance at 56.7 and 160.3 ppm, respectively.

It was reported in the literature that there was a correlation between the magnitude of the $^2J_{C(8)-P}$ value and the dihedral angle associated with the lone-pair orbital of the phosphorus atom and the β-carbon of the group attached to P (Figure 2).[17] With such a correlation, the ^{13}C NMR has been used to predict the configuration of the P-stereogenic phosphorus donor.[18] The large $^2J_{C(8)-P}$ values (Table 1) of triplet signals in the symmetrical PCP Pd(II) complexes **1**, **2**, and **5** indicate that the phospholidine cycle at the phosphorus atom is in a pseudoequatorial position and, therefore, that the P-stereogenic phosphorus atom has an *S* absolute configuration (without taking into account the formal priority of the metal atom), which is agreement with the X-ray analysis results. In the ^{13}C NMR spectra of unsymmetrical PCN complexes **3** and **4**, the large $^2J_{C(8)-P}$ values (Table 1) of doublet signals also suggest the *S* absolute configuration of the P-stereogenic phosphorus atom.

Molecular Structures of Pincer Complexes 1−4. The molecular structures of three symmetrical and two unsymmetrical pincer complexes **1**−**5** were determined by X-ray single-crystal analysis. In the unit cell of complexes **1** and **2**, there exist two crystallographically independent molecules which have essentially the same structure, and thus only one of them is shown in Figures 3 and 4, respectively. Molecular structures of **3** and **4** are shown in Figures 5 and 6 (that of **5** and the related data are given in Supporting Information). Selected bond lengths and bond angles for complexes **1**−**4** are collected in Tables 2 and 3. The general features of the five pincer complexes are the unique configurations of N- and P-stereogenic centers, which have *S* absolute configurations of N and P atoms for each complex (without taking into account the formal priority of the metal atom). This arrangement avoids the steric interactions between the exocyclic substituents at the phosphorus atom and the central

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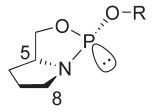
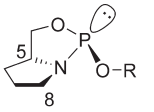


cis-location of C(8) and phosphorus lone pair: $^2J_{C(8)-P}$ ~ 40 Hz



trans-location of C(8) and phosphorus lone pair: $^2J_{C(8)-P}$ ~ 0 Hz

Figure 2. Correlation between the $^2J_{C(8)-P}$ value and the configuration of the P-stereocenter for the phospholidine cycle.

Table 1. Selected NMR Spectroscopic Data for Complexes 1−5 (in $CDCl_3$)

complex	^{31}P NMR (ppm)	$^2J_{C(8)-P}$ (Hz)	$^2J_{C(5)-P}$ (Hz)
1	155.8	9.5	0
2	159.1	10.0	0
3	56.7	18.0	2.8
4	160.3	15.4	2.0
5	159.7	9.6	0

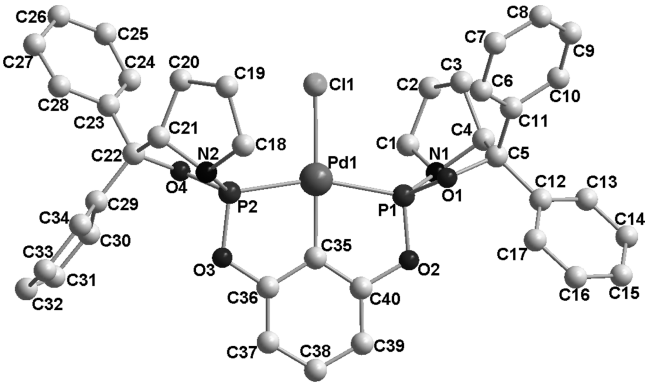


Figure 3. X-ray molecular structure of **1** (representation of one of the two independent crystal structures). Hydrogen atoms are omitted for clarity.

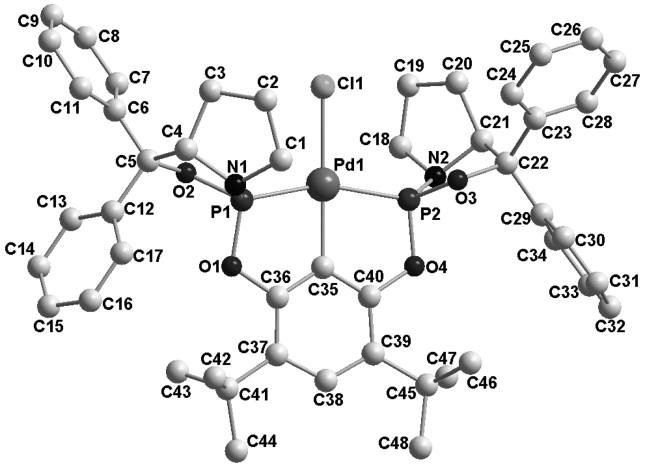


Figure 4. X-ray molecular structure of **2**·CH_3COCH_3 (representation of one of the two independent crystal structures). Hydrogen atoms and the noncoordinated CH_3COCH_3 molecule are omitted for clarity.

aryl ring. The ligand in each complex is coordinated to the metal in a tridentate manner, and the two five-membered-ring metallacycles that formed are approximately coplanar with the central aryl ring. The metal atom adopts a typical distorted-square-planar configuration with bond angles of

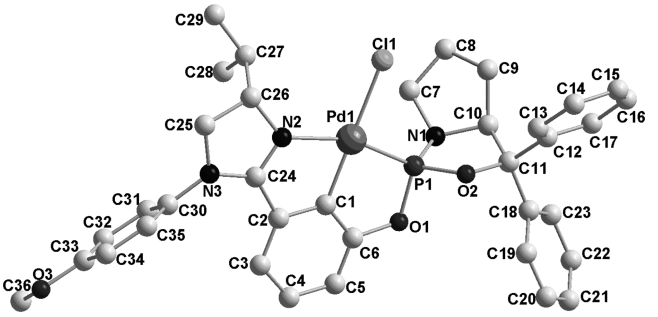


Figure 5. X-ray molecular structure of **3**. Hydrogen atoms are omitted for clarity.

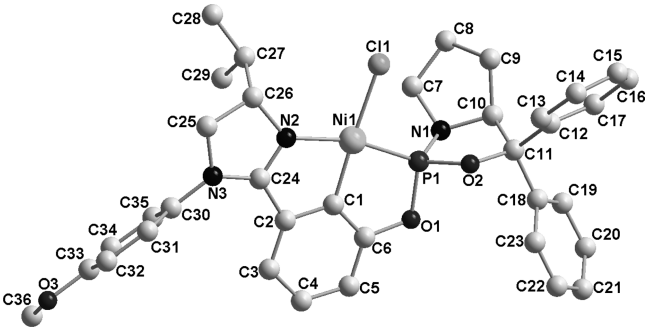


Figure 6. X-ray molecular structure of **4**. Hydrogen atoms are omitted for clarity.

P−Pd−P (or N−M−P) being around 160° and C−M−X being 176−179°. The phospholidine cycle occupies a pseudo-equatorial position at the phosphorus atom.

Including the Pd−I complex **5**, all three symmetrical PCP-pincer Pd(II) complexes have similar bond lengths and angles around Pd(II), except for shorter Pd−P (2.2454(11)−2.2632(11) Å) and longer Pd−C (around 2.005 Å) bond lengths in complex **2**, which is attributable to the steric hindrance of the 2-*tert*-butyl moiety. The phospholidine cycles in complex **1** and **2** adopt slightly twisted conformations (in the unshown structure of complex **1**, the phospholidine cycles take an envelope conformation), while the pyrrolidine cycles have envelope conformations.

In comparison with the corresponding symmetrical bis-phosphoramidite PCP pincer Pd complex **1** or NCN bis-(imidazoline) Pd complex,[4b] the unsymmetrical PCN Pd complex **3** has a slightly shorter Pd−C bond distance (1.949(5) Å). The Pd−N bond distance (2.079(5) Å) is longer than the related distances in the symmetrical NCN complex (Pd(1)−N(1) = 2.031(13) Å and Pd(1)−N(3) = 2.078(12) Å), while the Pd−P distance (2.1786(16) Å) is shorter than those in the PCP complex **1**, implying an increased trans influence of the phosphoramidite moiety compared with the imidazoline ligand. A comparison between the unsymmetrical PCN pincer Pd(II) complex **3** and Ni(II) complex **4** reveals that the two complexes possess the same structural architectures and chiralities except for the different metal atoms. However, they exhibit significantly different bond lengths and angles for the metal coordination sphere (Table 3). Similarly to the previously reported results,[19] the metal−tridentate ligand bond lengths in the two complexes follow the expected pattern Ni < Pd. For example,

(19) Fossey, J. S.; Richards, C. J. *J. Organomet. Chem.* **2004**, *689*, 3056.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Chiral PCP-Pincer Pd(II) Complexes 1 and 2·CH_3COCH_3

	1	2		1′	2′
Pd(1)−C(35)	1.958(5)	2.009(4)	Pd(1′)−C(35′)	1.976(4)	2.000(4)
Pd(1)−Cl(1)	2.3561(16)	2.3795(13)	Pd(1′)−Cl(1′)	2.3756(14)	2.3735(14)
Pd(1)−P(1)	2.2717(13)	2.2454(11)	Pd(1′)−P(1′)	2.2989(14)	2.2632(11)
Pd(1)−P(2)	2.2759(13)	2.2574(11)	Pd(1′)−P(2′)	2.2748(14)	2.2575(11)
P(1)−O(1)	1.613(3)	1.635(3)	P(1′)−O(1′)	1.611(3)	1.588(3)
P(1)−O(2)	1.612(4)	1.596(3)	P(1′)−O(2′)	1.636(3)	1.630(3)
P(2)−O(3)	1.631(4)	1.590(3)	P(2′)−O(3′)	1.641(3)	1.582(3)
P(2)−O(4)	1.599(3)	1.625(3)	P(2′)−O(4′)	1.590(3)	1.638(3)
P(1)−N(1)	1.649(4)	1.660(4)	P(1′)−N(1′)	1.625(4)	1.655(4)
P(2)−N(2)	1.650(3)	1.667(4)	P(2′)−N(2′)	1.621(3)	1.657(4)
P(1)−Pd(1)−P(2)	160.98(5)	160.12(4)	P(2′)−Pd(1′)−P(1′)	160.30(4)	161.50(4)
C(35)−Pd(1)−P(1)	80.37(13)	80.40(11)	C(35′)−Pd(1′)−P(1′)	79.10(10)	80.81(12)
C(35)−Pd(1)−P(2)	80.98(14)	80.99(11)	C(35′)−Pd(1′)−P(2′)	81.24(10)	80.80(12)
C(35)−Pd(1)−Cl(1)	178.08(14)	177.18(12)	C(35′)−Pd(1′)−Cl(1′)	178.37(10)	176.66(13)
P(1)−Pd(1)−Cl(1)	100.94(6)	98.06(4)	P(1′)−Pd(1′)−Cl(1′)	102.26(4)	99.46(5)
P(2)−Pd(1)−Cl(1)	97.61(6)	100.24(4)	P(2′)−Pd(1′)−Cl(1′)	97.42(5)	98.79(5)
O(2)−P(1)−O(1)	104.17(16)	104.05(16)	O(1′)−P(1′)−O(2′)	98.69(17)	104.68(16)
O(2)−P(1)−N(1)	105.8(2)	97.40(17)	N(1′)−P(1′)−O(2′)	104.93(19)	105.23(18)
O(1)−P(1)−N(1)	96.65(16)	107.05(17)	O(1′)−P(1′)−N(1′)	96.58(16)	97.18(15)
O(4)−P(2)−O(3)	103.77(17)	105.05(16)	O(4′)−P(2′)−N(2′)	96.69(17)	104.12(17)
O(4)−P(2)−N(2)	96.28(16)	104.66(18)	O(4′)−P(2′)−O(3′)	102.51(19)	105.19(18)
O(3)−P(2)−N(2)	106.21(19)	96.87(16)	N(2′)−P(2′)−O(3′)	105.8(2)	97.16(16)

Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for Chiral PCN-Pincer Pd(II) Complex 3 and Ni(II) Complex 4

	3 (M = Pd)	4 (M = Ni)
M(1)−C(1)	1.949(5)	1.851(6)
M(1)−N(2)	2.079(5)	1.900(5)
M(1)−P(1)	2.1786(16)	2.0930(18)
M(1)−Cl(1)	2.3687(15)	2.2171(15)
P(1)−O(2)	1.588(4)	1.594(4)
P(1)−O(1)	1.647(4)	1.639(4)
P(1)−N(1)	1.655(5)	1.650(5)
C(1)−M(1)−N(2)	78.6(2)	82.0(2)
C(1)−M(1)−P(1)	81.71(16)	82.50(17)
N(2)−M(1)−P(1)	160.31(13)	164.38(14)
C(1)−M(1)−Cl(1)	179.23(17)	177.17(17)
N(2)−M(1)−Cl(1)	101.15(13)	99.96(15)
P(1)−M(1)−Cl(1)	98.51(6)	95.58(6)
O(2)−P(1)−O(1)	103.3(2)	103.1(2)
O(2)−P(1)−N(1)	96.7(2)	96.6(2)
O(1)−P(1)−N(1)	105.9(3)	105.5(2)
N(2)−C(24)−N(3)	113.8(5)	114.8(5)
M(1)−P(1)−O(1)−C(6)	−2.2(4)	−0.6(4)
C(2)−C(24)−N(2)−M(1)	2.1(6)	0.1(7)
N(2)−M(1)−C(1)−C(2)	0.0(4)	−0.2(4)

the Ni complex **4** has a Ni−C bond length of 1.851(6) Å, a Ni−N bond length of 1.900(5) Å, a Ni−P bond length of 2.0930(18) Å, and a Ni−Cl bond length of 2.2171(15) Å. The corresponding values in the Pd complex **3** are 1.949(5), 2.079(5), 2.1786(16), and 2.3687(15) Å, respectively. The shorter Ni−Cl bond length in **4** is likely due to a reduced trans influence of the metalated carbanion. The bond lengths and angles around the phosphorus atom in **3** and **4** are almost identical (see Table 3). Additionally, the imidazoline and pyrrolidine cycles in the two complexes adopt envelope conformations, and the phospholidine cycles have twisted conformations.

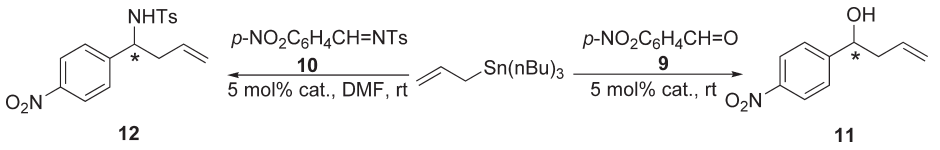
Catalytic Studies. The discovery of Szabó's and Bedford's complexes,[11] 1,1′-bi-2-naphthol- and biphenanthrol-based PCP chiral pincer palladium complexes, acting as effective catalysts for the asymmetric allylation of aldehydes or sulfonimines opened the door for developing this reaction catalyzed by chiral pincer complexes with P-donor ligands. Additionally, Nishiyama and co-workers applied the chiral bis(oxazolinyl)phenylrhodium(III) NCN-pincer complexes as Lewis acid catalysts in the enantioselective allylation of aldehydes (up to 80% ee).[20] As a preliminary investigation, the activity and the stereocontrolling potential of the obtained pincer complexes **1**−**4** in the asymmetric allylation were evaluated. Klein Gebbink recently reported that the electron-withdrawing nitro group on the aryl substituent of sulfonimine led to both higher product yield and improved enantioselectivity when chiral amino alcohol derived bis-phosphoramidite pincer Pd complexes were used as the catalysts.[14] Accordingly, allylation of 4-nitrobenzaldehyde (**9**) and 4-nitrobenzenesulfonimine (**10**) with allyltributyltin were chosen as the model reactions. The results are summarized in Table 4.

The enantioselectivities of the symmetrical PCP pincer Pd complexes **1** and **2** in the allylation of 4-nitrobenzaldehyde (**9**) were overall rather moderate (entries 1−4). Nonetheless, it was notable that the more bulky complex **2** displayed higher product yield and particularly enhanced enantioselectivity (about 2-fold) in comparison with complex **1** (30% yield, 11% ee vs 42% yield, 23% ee). This was in accordance with the findings of Bedford and co-workers. They demonstrated that both the yield and enantioselectity improved significantly by the incorporation of *tert*-butyl groups into the 3- and 5-positions of chiral 1,1′-bi-2-naphthol-bis-phosphite pincer Pd complexes in the asymmetric allylation of benzaldehyde (82% yield, 62% ee vs 18% yield, 6% ee).[11b]

Further studies indicated that complex **2** exhibited more promising enantioselectivity in the asymmetric allylation of 4-nitrobenzenesulfonimine (**10**) (69% ee, entries 5 and 6). The enantioselectivity was much higher than that of the related bis-phosphoramidite PCP pincer Pd complex derived from chiral indolinemethanol reported by Klein Gebbink and co-workers (12% ee).[14] In comparison with the symmetrical PCP Pd complex **2**, the unsymmetrical chiral imidazoline-containing PCN pincer Pd complex **3** provided higher product yield (90%) and moderate enantioselectity (33% ee, entry 7) under the same reaction conditions. Interestingly, the enantiomer of **12** possessed the *opposite* absolute

(20) (a) Motoyama, Y.; Narusawa, H.; Nishiyama, H. *Chem. Commun.* **1999**, 131. (b) Motoyama, Y.; Okano, M.; Narusawa, H.; Makihara, N.; Aoki, K.; Nishiyama, H. *Organometallics* **2001**, *20*, 1580.

Table 4. Asymmetric Allylation of Aldehyde 9 and Sulfonimine 10 Catalyzed by Symmetrical and Unsymmetrical P-Chiral Pincer Metal Complexes 1−4 and the Related Symmetrical Bis(imidazoline) NCN Pd Complex 13[a]

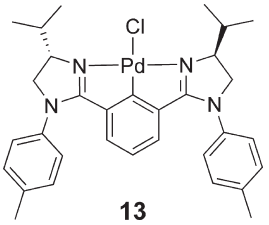


12 11

entry	cat.	substrate	product	solvent	time (h)	yield (%)[b]	ee (%)[c,d]
1	**1**	**9**	**11**	DMF	24	34	7
2	**1**	**9**	**11**	DMF	96	78	0
3	**1**	**9**	**11**	CH_2Cl_2	24	30	11
4	**2**	**9**	**11**	CH_2Cl_2	24	42	23
5	**1**	**10**	**12**	DMF	96	75	30
6	**2**	**10**	**12**	DMF	96	77	69
7	**3**	**10**	**12**	DMF	96	90	33[e]
8	**13**	**10**	**12**	DMF	96	19	0
9	**4**	**10**	**12**	DMF	96	11	0

[a] All reactions were performed with 1 equiv of **9** or **10** and 1.2 equiv of allyltributyltin. A 5 mol % amount of catalyst was used. [b] Isolated yield. [c] Detected by chiral HPLC. [d] The absolute configurations of the allylic products have not been assigned. [e] *Opposite* absolute configuration.

configuration in comparison to that of the product catalyzed by complex **2**. The performance of the related symmetrical bis(imidazoline) NCN Pd complex **13** in the same reaction was also investigated. A racemic product in low yield was obtained (entry 8). The above results indicated that the more electron-deficient phosphoramidite ligand could improve the catalytic activity of the corresponding pincer complexes, and a hemilabile hybrid PCN ligand with phosphoramidite led to further enhancement of the catalytic activity. On the other hand, bulky ligand substituents were in favor of good stereocontrol, and the absolute configuration of the enantiomer of **12** may depend much on the configuration of the chiral center in the imidazoline moiety. Finally, the unsymmetrical PCN-pincer Ni(II) complex **4** afforded a racemic product in a rather low yield (11%, entry 9).



13

Conclusions

In summary, we have developed an operationally simple procedure for the highly diastereoselective preparation of P-chiral symmetrical PCP and particularly unsymmetrical PCN pincer metal complexes using easily available amino alcohols as chiral auxiliaries. This "four-component, one-pot phosphorylation/metalation" procedure avoided the troublesome isolating step of unstable P-containing species and achieved the metalation of the related ligands via C−H bond activation. It was found that the nature of the pincer ligands has a major influence not only on the metalation step but also on the properties of the ensuing pincer complexes in the asymmetric allylation of aldehydes or sulfonimines. The metalation of the imidazoline-containing unsymmetrical ligand was easier than that of the corresponding symmetrical bis-phosphoramidite ligand. Also, its unsymmetrical pincer Pd complex exhibited catalytic activity higher than that for the related symmetrical complexes. On the other hand, the more bulky Pd complex **2** gave better enantioselectivity, especially in the allylation of 4-nitrobenzenesulfonimine (69% ee). Further studies will focus on the synthesis of bulky P-chiral unsymmetrical pincer metal complexes as well as their applications in asymmetric catalysis.

Experimental Section

General Procedures. Unless otherwise noted, all reactions were carried out under nitrogen using standard Schlenk and vacuum line techniques. Solvents were dried with standard methods and freshly distilled prior to use if needed. (*S*)-Diphenyl(pyrrolidin-2-yl)methanol,[21] the imidazolinyl-containing *m*-phenol derivative **8**,[22] and 4,6-di-*tert*-butylbenzene-1,3-diol[23] were prepared according to the literature methods. Other reagents were obtained from commercial sources and used as received without further purification. Melting points were determined using an XT4A melting point apparatus and are uncorrected. Elemental analyses were determined with a Thermo Flash EA 1112 elemental analyzer. Optical rotations were measured with a Perkin-Elmer Model 341 polarimeter at 20 °C in CH_2Cl_2. The enantiomeric purity was determined by HPLC using a chiral column with hexane−propan-2-ol (ratio as indicated) as the eluent. The column used was a Chiracel AD-H from Daicel Chemical Ind., Ltd. (Japan). The column was operated at ambient temperature. ^1H, ^{13}C NMR, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX-400 or Bruker DPX-300 spectrometer in $CDCl_3$ with TMS as an internal standard for ^1H and ^{13}C NMR and 85% H_3PO_4 as external standard for $^{31}P\{^1H\}$ NMR. *J* values are given in Hz. IR spectra were determined on a Thermo Nicolet IR 200 spectrophotometer.

General Procedure for the Synthesis of Chiral PCP- and PCN-Pincer Metal Complexes. To a stirred mixture of Et_3N (2 mmol) and PCl_3 (0.525 mmol) in 1,2-dichloroethane (1 mL) was added dropwise a solution of (*S*)-diphenyl(pyrrolidin-2-yl)methanol (0.5 mmol) in 1,2-dichloroethane (3 mL) at −35 °C. After the mixture was stirred for 3.5 h at room temperature, Et_3N (1 mmol) and the resorcinol−based ligand (0.25 mmol) or compound **8** (0.5 mmol) were added at −35 °C followed by stirring at room temperature for 15−20 h. MX_2 (0.5 mmol of $PdCl_2$ or $NiCl_2$) was then added, and the reaction mixture was refluxed for 24 h (6 h in the case of $NiCl_2$).

(21) (a) Kanth, J. V. B.; Periasamy, M. *Tetrahedron* **1993**, *49*, 5127. (b) Xavier, L. C.; Mohan, J. J.; Mathre, D. J.; Thompson, A. S.; Carroll, J. D.; Corley, E. G.; Desmond, R. *Org. Synth.* **1997**, *74*, 50.

(22) Zhang, B. S.; Wang, W.; Shao, D. D.; Hao, X. Q.; Gong, J. F.; Song, M. P. Submitted for publication in *Organometallics*.

(23) Halfpenny, P. J.; Johnson, P. J.; Robinson, M. J. T.; Ward, M. G. *Tetrahedron* **1976**, *32*, 1873.

Table 5. Selected Crystallographic Data for Complexes 1, 2·CH_3COCH_3, 3, and 4

	1	2·CH_3COCH_3	3	4
formula	$C_{40}H_{37}ClN_2O_4P_2Pd$	$C_{96}H_{106}Cl_2N_4O_8P_4Pd_2 \cdot C_3H_6O$	$C_{36}H_{37}ClN_3O_3PPd$	$C_{36}H_{37}ClN_3NiO_3P$
fw	813.51	1909.51	732.51	684.82
temp (K)	291(2)	291(2)	293(2)	293(2)
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	*P*1	$P2_1$	$P2_1$	$P2_1$
cryst size (mm)	0.20 × 0.17 × 0.17	0.20 × 0.17 × 0.16	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.20
a (Å)	10.274(2)	14.581(3)	10.277(2)	10.232(2)
b (Å)	13.535(3)	15.906(3)	9.5577(19)	9.4811(19)
c (Å)	14.458(3)	20.557(4)	17.088(3)	17.026(3)
α (deg)	97.62(3)	90	90	90
β (deg)	97.78(3)	91.33(3)	96.50(3)	96.66(3)
γ (deg)	108.03(3)	90	90	90
V (Å^3)	1861.3(6)	2676.5(8)	1667.7(6)	1640.5(6)
Z	2	2	2	2
D_{calcd} (g cm^{-3})	1.452	1.331	1.459	1.386
abs coeff (mm^{-1})	0.700	0.558	0.725	0.762
F(000)	832	1984	752	716
θ range (deg)	1.45−25.00	0.99−26.00	3.07−26.07	2.00−25.99
index range	$-12 \le h \le 11$	$0 \le h \le 17$	$-12 \le h \le 12$	$-12 \le h \le 12$
	$0 \le k \le 16$	$-19 \le k \le 19$	$-11 \le k \le 11$	$-11 \le k \le 11$
	$-17 \le l \le 16$	$-25 \le l \le 25$	$-21 \le l \le 18$	$-20 \le l \le 20$
no. of rflns coll	6097	17 187	13 383	10 882
no. of indep rflns	6097	16 883	6334	6083
no. of data/restraints/params	6097/7/874	16 883/1/1082	6334/1/396	6083/1/407
goodness of fit on F^2	1.077	1.018	1.012	1.006
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0395	R1 = 0.0406	R1 = 0.0470	R1 = 0.0598
	wR2 = 0.1002	wR2 = 0.0809	wR2 = 0.0933	wR2 = 0.1295
R indices (all rflns)	R1 = 0.0447	R1 = 0.0519	R1 = 0.0591	R1 = 0.0799
	wR2 = 0.1035	wR2 = 0.0852	wR2 = 0.1009	wR2 = 0.1490
largest diff peak/hole (e Å^{-3})	0.442/−0.480	0.336/−0.427	0.338/−0.395	0.671/−0.362

After cooling, filtration, and evaporation, the residue was purified by preparative TLC on silica gel plates to afford the corresponding PCP- or PCN-pincer Pd(II) or Ni(II) complexes.

Chiral PCP-Pincer Pd(II) Complex 1. 1 was obtained as a white solid (69 mg, 34% yield): mp 275 °C dec. $[\alpha]^{20}_D = -150°$ (*c* = 0.044, CH_2Cl_2). ^{1}H NMR (400 Mz, $CDCl_3$): *δ* 7.23−7.60 (m, 20 H, Ph *H*), 6.92 (tt, *J* = 2.0, 8.0 Hz, 1H, central Ar *H*), 6.30 (d, *J* = 8.0 Hz, 2H, central Ar *H*), 4.67−4.74 (m, 2H, NC*H*), 4.25−4.35 (m, 2H, NCH_2), 3.33−3.39 (m, 2H, NCH_2), 1.93−2.02 (m, 2H, NCH_2CH_2), 1.75−1.86 (m, 2H, NCH_2CH_2), 1.57−1.66 (m, 4H, $NCHCH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 157.2 (t, J_{P-C} = 10.5 Hz), 143.4, 140.8 (t, J_{P-C} = 3.0 Hz), 129.3, 128.3, 128.2, 127.6, 127.0, 126.3, 106.9 (t, J_{P-C} = 9.5 Hz), 94.6 (t, J_{P-C} = 3.5 Hz), 70.7, 47.5 (t, J_{P-C} = 9.5 Hz), 30.2, 26.0. ^{31}P NMR (121 MHz, $CDCl_3$): *δ* 155.8 (s). IR *ν* (cm^{-1}): 3060, 2879, 1572, 1445, 1223, 1063, 965, 887, 747, 699. Anal. Calcd for $C_{40}H_{37}ClN_2O_4P_2Pd$: C, 59.05; H, 4.58; N, 3.44. Found: C, 59.10; H, 4.64; N, 3.38.

Chiral PCP-Pincer Pd(II) Complex 2. 2 was obtained as a white solid (46 mg, 20% yield): mp 272 °C dec. $[\alpha]^{20}_D = -150°$ (*c* = 0.046, CH_2Cl_2). ^{1}H NMR (400 Mz, $CDCl_3$): *δ* 7.27−7.58 (m, 20 H, Ph *H*), 6.89 (t, *J* = 1.8 Hz, 1H, central Ar *H*), 4.62−4.68 (m, 2H, NC*H*), 4.42−4.31 (m, 2H, NCH_2), 3.37−3.45 (m, 2H, NCH_2), 2.18−2.23 (m, 2H, NCH_2CH_2), 1.80−1.86 (m, 2H, NCH_2CH_2), 1.56−1.66 (m, 2H, $NCHCH_2$), 1.34−1.41 (m, 2H, $NCHCH_2$), 0.89 (s, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 152.9 (t, J_{P-C} = 10.0 Hz), 143.4, 141.7 (t, J_{P-C} = 3.5 Hz), 128.8 (t, J_{P-C} = 8.5 Hz), 128.4, 128.3, 128.1, 127.8, 127.4, 126.1, 124.3, 93.7 (t, J_{P-C} = 3.5 Hz), 70.6, 47.8 (t, J_{P-C} = 10.0 Hz), 34.3, 30.8, 29.5, 25.8. ^{31}P NMR (121 MHz, $CDCl_3$): *δ* 159.1 (s). IR *ν* (cm^{-1}): 3060, 2956, 1714, 1447, 1277, 1222, 1060, 939, 751, 698. Anal. Calcd for $C_{48}H_{53}ClN_2O_4P_2Pd$: C, 62.27; H, 5.77; N, 3.03. Found: C, 62.13; H, 6.01; N, 2.79.

Chiral PCN-Pincer Pd(II) Complex 3. 3 was obtained as a yellow solid (154 mg, 42% yield): mp 223 °C dec. $[\alpha]^{20}_D = -29°$ (*c* = 0.53, CH_2Cl_2). ^{1}H NMR (400 Mz, $CDCl_3$): *δ* 7.23−7.61 (m, 10H, Ph *H*), 7.20 (d, *J* = 8.4 Hz, 2H, NAr *H*), 6.95 (d, *J* = 8.4 Hz, 2H, NArH), 6.69 (td, *J* = 1.6, 8.0 Hz, 1H, central Ar H), 6.51 (d, *J* = 8.0 Hz, 1H, central Ar H), 6.05 (d, *J* = 7.6 Hz, 1H, central Ar *H*), 4.63−4.70 (m, 1H, Py *H*), 4.39−4.45 (m, 1H, Py *H*), 4.33−4.37 (m, 1H, Im *H*), 4.01 (app t, *J* = 10.6 Hz, 1H, Im *H*), 3.86 (s, 3H, OCH_3), 3.82 (dd, *J* = 6.0, 10.0 Hz, 1H, Im *H*), 3.27−3.37 (m, 1H, Py *H*), 2.76−2.84 (m, 1H, Im*H*), 2.04−2.13 (m, 1H, Py *H*), 1.74−1.85 (m, 1H, Py *H*), 1.61−1.71 (m, 1H, Py *H*), 1.45−1.52 (m, 1H, Py *H*), 0.97 (d, *J* = 6.8 Hz, 3H, CH_3CHCH_3), 0.95 (d, *J* = 6.8 Hz, 3H, CH_3CHCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 169.9 (d, J_{P-C} = 4.0 Hz), 159.2, 155.7 (d, J_{P-C} = 19.0 Hz), 151.8, 143.7, 141.0 (d, J_{P-C} = 7.0 Hz), 135.3, 132.7, 128.2 (t, J_{P-C} = 3.6 Hz), 128.1, 127.5, 126.9, 126.2, 126.0, 120.8, 114.9, 113.7 (d, J_{P-C} = 9.5 Hz), 93.7 (d, J_{P-C} = 10.0 Hz), 71.1 (d, J_{P-C} = 3.2 Hz), 66.3 (d, J_{P-C} = 3.9 Hz), 55.7 (d, J_{P-C} = 5.1 Hz), 55.6, 47.6 (d, J_{P-C} = 17.6 Hz), 30.6, 30.1, 25.8 (d, J_{P-C} = 3.2 Hz), 18.8, 14.6. ^{31}P NMR (121 MHz, $CDCl_3$): *δ* 56.7 (s). IR *ν* (cm^{-1}): 3455, 2921, 1602, 1534, 1441, 1291, 1249, 1028, 968, 876, 699. Anal. Calcd for $C_{36}H_{37}ClN_3O_3PPd$: C, 59.03; H, 5.09; N, 5.74. Found: C, 59.27; H, 5.56; N, 5.22.

Chiral PCN-Pincer Ni(II) Complex 4. 4 was obtained as a pale yellow solid (68 mg, 20% yield): mp 273 °C dec. $[\alpha]^{20}_D = +21°$ (*c* = 0.044, CH_2Cl_2). ^{1}H NMR (400 Mz, $CDCl_3$): *δ* 7.62 (d, *J* = 8.4 Hz, 2H, Ph *H*), 7.58 (d, *J* = 7.2 Hz, 2H, Ph *H*), 7.22−7.53 (m, 6H, Ph *H*), 7.20 (d, *J* = 8.8 Hz, 2H, NAr *H*), 6.95 (d, *J* = 8.4 Hz, 2H, NAr *H*), 6.62 (td, *J* = 1.2, 7.8 Hz, 1H, central Ar *H*), 6.28 (d, *J* = 8.0 Hz, 1H, central Ar *H*), 5.97 (d, *J* = 7.6 Hz, 1H, central Ar *H*), 4.53−4.60 (m, 2H, Py *H*), 4.13−4.19 (m, 1H, Im *H*), 4.05 (app t, *J* = 11.7 Hz, 1H, Im *H*), 3.86 (s, 3H, OCH_3), 3.82 (dd, *J* = 4.4, 10.0 Hz, 1H, Im *H*), 3.34−3.43 (m, 1H, Py *H*), 2.56−2.62 (m, 1H, Im *H*), 2.11−2.17 (m, 1H, Py *H*), 1.75−1.84 (m, 1H, Py *H*), 1.59−1.69 (m, 1H, Py *H*), 1.28−1.33 (m, 1H, Py *H*), 1.01 (dd, *J* = 2.8, 6.8 Hz, 3H, CH_3CHCH_3), 0.91 (d, *J* = 3.2, 6.8 Hz, 3H, CH_3CHCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 169.1 (d, J_{P-C} = 2.0 Hz), 159.1 (d, J_{P-C} = 3.0 Hz), 158.1 (d, J_{P-C} = 23.0 Hz), 143.8, 141.7 (d, J_{P-C} = 7.0 Hz), 136.4, 132.2, 128.1 (t, J_{P-C} = 3.5 Hz), 128.0, 127.3, 126.9, 126.0, 125.9, 119.5, 114.8, 112.5 (d, J_{P-C} = 15.0 Hz), 92.3 (d, J_{P-C} = 12.0 Hz), 71.4 (d, J_{P-C} = 2.1 Hz), 64.3 (d, J_{P-C} = 2.5 Hz), 56.3 (d, J_{P-C} = 3.1 Hz), 55.6, 47.4 (d, J_{P-C} = 15.5 Hz), 30.5, 30.4, 25.8 (d, J_{P-C} = 2.8 Hz), 18.8, 14.5. ^{31}P NMR (121 MHz, $CDCl_3$): *δ* 160.3 (s). IR (KBr pellet): 3431, 2925,

1537, 1443, 1287, 1248, 1029, 971, 873, 785, 702. Anal. Calcd for $C_{36}H_{37}ClNiN_3O_3P\cdot 0.5H_2O$: C, 62.32; H, 5.52; N, 6.06. Found: C, 62.30; H, 5.54; N, 5.94.

Procedure for the Synthesis of PCP-Pincer Iodopalladium Complex 5. A mixture of complex **1** (0.03 mmol, 24.7 mg) and potassium iodide (49.7 mg, 0.3 mmol) was stirred in methanol/acetone (1/1 v/v, 3 mL) at room temperature until a clear yellow solution was obtained (17 h), and the reaction mixture was filtered through Celite. Subsequently, the solvent was removed under reduced pressure, and the residue was purified by preparative TLC on silica gel plates (eluent 3/2 petroleum ether/dichloromethane) to give the product **5** as a yellow solid (23 mg, 85% yield). A single crystal suitable for X-ray crystal analysis was obtained by recrystallization from a solution of CH_2Cl_2/acetone: mp 270 °C dec. $[\alpha]^{20}_D = -90°$ (c = 0.070, CH_2Cl_2). ^{1}H NMR (400 Mz, $CDCl_3$): δ 7.23−7.62 (m, 20 H, Ph *H*), 6.92 (tt, J = 2.0, 8.0 Hz, 1H, central Ar *H*), 6.30 (d, J = 8.0 Hz, 2H, central Ar *H*), 4.74−4.79 (m, 2H, NC*H*), 4.20−4.32 (m, 2H, NCH_2), 3.30−3.37 (m, 2H, NCH_2), 2.15−2.22 (m, 2H, NCH$_2$CH_2), 1.71−1.87 (m, 4H, NCH$_2$CH_2 + NCHCH_2), 1.42−1.46 (m, 2H, NCHCH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9 (t, J_{P-C} = 10.0 Hz), 143.5, 141.1 (t, J_{P-C} = 4.0 Hz), 129.5, 128.3, 128.2, 128.1, 127.5, 127.1, 126.0, 106.5 (t, J_{P-C} = 10.0 Hz), 94.1 (t, J_{P-C} = 3.5 Hz), 70.8, 47.8 (t, J_{P-C} = 9.5 Hz), 30.5, 25.5. ^{31}P NMR (121 MHz, $CDCl_3$): δ 159.7 (s). IR (KBr pellet): 3059, 2874, 1571, 1445, 1223, 1065, 966, 844, 744, 698. Anal. Calcd for $C_{40}H_{37}IN_2O_4P_2Pd$: C, 53.09; H, 4.12; N, 3.10. Found: C, 53.13; H, 4.07; N, 3.11.

General Procedure for PCP- and PCN-Pincer Metal Complex Catalyzed Allylation of 9 or 10. To a mixture of **9** or **10** (0.15 mmol) and the pincer complex (0.0075 mmol, 5.0 mol %) in 1.0 mL of solvent was added allyltributyltin (0.18 mmol, 56 μL). The resulting solution mixture was stirred for the allotted times at room temperature (Table 4). Thereafter the reaction mixture was broken up by aqueous KF (10%, w/v) overnight. The organic layer was then separated, washed with brine, dried (Na_2SO_4), and concentrated. The crude product was purified by flash column chromatography to give the corresponding homoallylic alcohol **11** (CH_2Cl_2) or amine **12** (7/3 petroleum ether/EtOAc).[11,14] The enantiomeric excess was determined by chiral-phase HPLC (Daicel Chiracel AD-H column).

X-ray Crystallographic Studies. Crystals of **1**, **2**, and **5** were obtained by recrystallization from CH_2Cl_2/acetone at ambient temperature. **3** was recrystallized from CH_2Cl_2/hexane at ambient temperature. **4** was recrystallized from ethyl acetate/hexane at ambient temperature. Crystallographic data for **1** and **2** (the data for complex **5** are shown in the Supporting Information) were measured on a Rigaku-IV imaging plate area detector using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), respectively. Crystallographic data for **3** and **4** were collected on a Rigaku Saturn 724 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at ambient temperature, respectively. The structures were solved by direct methods and expanded using Fourier techniques and refined by full-matrix least-squares methods. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included but not refined. The absolute configuration was verified by the Flack parameter. Their raw data were corrected, and the structures were solved using the SHELXL-97 program.[24] Selected crystal data are given in Table 5. CCDC-769170 (**1**), -769172 (**2**), -769173 (**3**), -769174 (**4**), and -769171 (**5**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgment. We are grateful to the National Natural Science Foundation of China (Nos. 20872133 and 20972141) and the Innovation Fund for Outstanding Scholar of Henan Province (No. 074200510005) for financial support of this work.

Supporting Information Available: Figures giving ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra of complexes **1**−**5**, tables and a figure giving crystallographic data of complex **5**, and CIF files giving crystallographic data for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

(24) Sheldrick, G. M. *SHELXL-97, Program for Refinement of Crystal Structure*; University of Göttingen, Germany, 1997.