Journal of Organometallic Chemistry 694 (2009) 3500–3505

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Asymmetric synthesis of 1,2-bis(diphenylphosphino)-1-phenylethane *via* a chiral palladium template promoted hydrophosphination reaction

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ARTICLE INFO

Article history:
Received 5 May 2009
Received in revised form 6 June 2009
Accepted 18 June 2009
Available online 26 June 2009

Keywords:
Asymmetric hydrophosphination reaction
Chiral phosphine ligand
Chiral metal template

ABSTRACT

An organopalladium(II) complex derived from (*S*)-N,N-dimethyl-1-(1-naphthyl)-ethylamine was employed as the chiral auxiliary to promote the asymmetric hydrophosphination reactions between diphenylphosphine and (*E*) or (*Z*)-diphenylphosphinostyrene in high regio- and stereoselectivities at low temperature with triethyl amine as external base. Optically active free ligand (*R*)-1,2-bis(diphenylphosphino)-1-phenylethane was obtained in high yield subsequently. Mechanistic pathways explaining the stereoselectivity of the chiral organopalladium template promoted hydrophosphination reactions are also proposed.

1. Introduction

Diphosphines with one chiral carbon center have been shown to be effective ligands in asymmetric hydrogenation of prochiral olefins and cross-coupling reactions [1–3]. It has been demonstrated that a single chiral center may control the stereochemistry of these catalytical reactions when the phosphine coordinates with metal to form a rigid five-membered chelate ring [4]. The fixed phenyl moiety in such scenarios provide a mechanism for enantiofacial discrimination between substituents on the coordinated substrates and the catalysts. 1,2-Bis(diphenylphosphino)-1-phenylethane (Phenphos) is such a chiral ditertiary phosphine. It was first synthesised from chiral Mandelic Acid *via* a 3-steps transformation by King and Brown independently in 1978 and 1979, respectively [5,6]. However, no improved synthetic approach was reported to date. An attractive objective is the development of universal methods for the synthesis of such useful chiral phosphines from non-chiral starting materials as opposed to the limited pool of natural chirons. Our group have previously reported a series of chiral palladium template assisted asymmetric 1,2-addition reactions with alkynes or alkenes in the absence of a base promoter [7–10]. It has been reported that external bases play an important role in some reactions, such as changing the addition pathways [11]. Herein we present the preparation of PhenPhos by chiral metal template promoted asymmetric hydrophosphination reaction between diphenylphosphine and (*E*) or (*Z*)-diphenylphosphinostyrene [12] with triethylamine as external base.

2. Results and discussion

In the absence of a metal ion, diphenylphosphine shows no reactivity with (*E*)- or (*Z*)-diphenylphosphinostyrene under ambient conditions. Therefore, as illustrated in Scheme 1, the (*E*)- and (*Z*)-diphenylphosphinostyrene were coordinated to the chiral template (*S*)-1 regioselectively to form complexes **2a** and **2b**, respectively as solid powders in 99% isolated yields. The ^{31}P NMR spectrum in $CDCl_3$ exhibited one single peak at δ 33.3 and 23.7, respectively for each coordination product. Complex **2a** could not be crystallized from the reaction solution while **2b** was crystallized from dichloromethane-hexane as yellow prisms (81% yield), $[\alpha]_D$ +36.7 (*c* 0.3, CH_2Cl_2). The molecular structure and the coordination chemistry of **2b** were determined by X-ray crystallography (Fig. 1). Selected bond lengths and angles are given in Table 1.

Addition of stoichiometric quantities of aqueous silver perchlorate to the dichloromethane solution containing the chloro complexes **2a,b** yielded the intermediate perchlorato complexes **3a,b**, respectively. Complexes **3a** and **3b** were used for hydrophosphination reactions separately. They were not isolated from their corresponding previous reaction mixtures but were subsequently treated with diphenylphosphine separately at −78 °C in the presence of 50% equivalent of triethylamine to give the hydrophosphination products, **4a–d** in 12 h with different ratios, respectively (Scheme 1). It is noteworthy that the hydrophosphination reactions did not occur without triethylamine as external base, even in the presence of the chiral amine template. It needs to be highlighted that the reactions were highly regioselective, as the diphenylphosphino groups were added to the β-carbon of the diphenylphosphinostyrene to form five-membered chelate rings exclusively [7–11].

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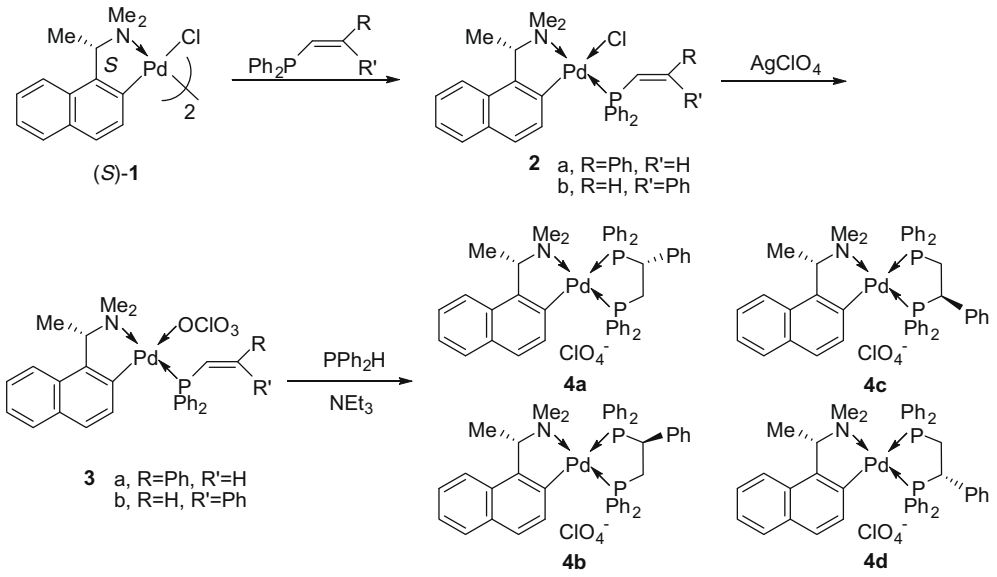
doi:10.1016/j.jorganchem.2009.06.024



Scheme 1.

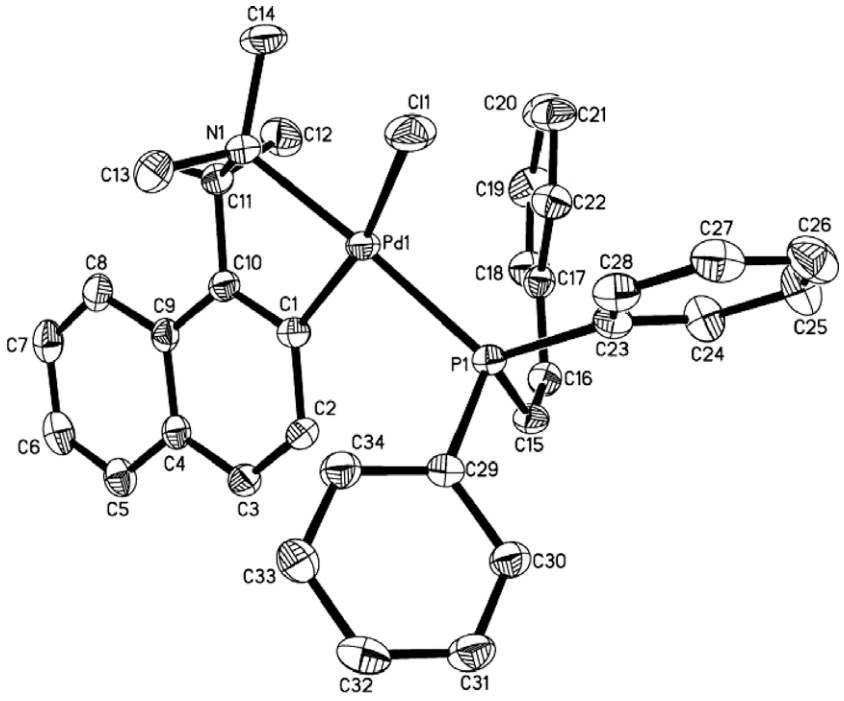


Fig. 1. Molecular structure and absolute configuration of **2b**.

Upon treatment of complex **3a** with diphenylphosphine, three products were formed exhibiting three pairs of doublets in the crude ^{31}P NMR spectrum in the ratio 12:2:1: δ 48.2, 50.5 (J_{PP} = 36.3 Hz) for **4a**, 46.5, 50.1 (J_{PP} = 36.6 Hz) for **4b** and 25.1, 67.9 (J_{PP} = 37.4 Hz) for **4c**. Similarly, upon treatment of complex **3b** with diphenylphosphine, the reaction gave a 6:1 mixture of diastereomers **4a** and **4b,** along with trace amounts of **4c** and **4d** (δ 25.9 and 66.6 (J_{PP} = 37.6 Hz)). Unfortunately, the major product **4a** could not be isolated efficiently by chromatography or fractional crystallization. The two diastereomers **4a** and **4b** always co-crystallized together as a mixture. The mixture of **4a** and **4b** could be obtained from dichloromethane-hexane with the ratio of 6:1 as yellow crystals. The minor diastereomers, **4c** or **4d**, were not present in this crystallized material. The diastereomeric mixture **4a** and **4b** was subsequently redissolved in dichloromethane and fractional crystallization was attempted. A 1:1 mixture of **4a** and **4b** co-crystallized as yellow prisms from dichloromethane-diethyl ether and its X-ray structure was determined. Selected bond lengths and angles are given in Table 2 and Table 3. The optically pure complex **4a** was left in the mother liquid. The X-ray crystallography affirms that two independent molecules are present in one asymmetric unit. The two molecules not only differ in relative bond lengths and angles but also in the absolute configuration of the chiral carbon centers (C_{16} and C_{62}). The molecular structure

Table 1
Selected bond lengths (Å) and bond angles (°) of **2b**.

Pd(1)–P(1)	2.2617(6)
Pd(1)–Cl(1)	2.4047(6)
Pd(1)–N(1)	2.1283(19)
Pd(1)–C(1)	2.014(2)
P(1)–C(15)	1.810(2)
C(15)–C(16)	1.338(3)
N(1)–C(11)	1.510(3)
C(11)–C(10)	1.506(3)
C(10)–C(1)	1.384(3)
P(1)–Pd(1)–Cl(1)	93.90(2)
P(1)–Pd(1)–N(1)	174.74(5)
P(1)–Pd(1)–C(1)	93.78(6)
C(1)–Pd(1)–Cl(1)	164.92(6)
Cl(1)–Pd(1)–N(1)	91.36(5)
C(1)–Pd(1)–N(1)	81.05(8)
P(1)–C(15)–C(16)	128.96(17)
C(15)–C(16)–C(17)	130.83(19)

Table 2
Selected bond lengths (Å) and bond angles (°) of **4a**.

Pd(1)–C(1)	2.073(3)
Pd(1)–P(1)	2.3587(7)
Pd(1)–N(1)	2.146(3)
Pd(1)–P(2)	2.2442(8)
P(1)–C(16)	1.863(3)
P(2)–C(15)	1.842(3)
C(1)–Pd(1)–N(1)	80.19(12)
N(1)–Pd(1)–P(2)	175.28(8)
N(1)–Pd(1)–P(1)	100.17(8)
C(1)–Pd(1)–P(2)	95.12(9)
C(1)–Pd(1)–P(1)	177.98(10)
P(1)–Pd(1)–P(2)	84.50(3)
P(1)–C(16)–C(15)	104.47(19)
P(2)–C(15)–C(16)	110.3(2)

Table 3
Selected bond lengths (Å) and bond angles (°) of **4b**.

Pd(2)–C(47)	2.065(3)
Pd(2)–P(4)	2.2358(8)
Pd(2)–N(2)	2.136(3)
Pd(2)–P(3)	2.3684(8)
P(3)–C(62)	1.871(4)
P(4)–C(61)	1.839(4)
C(47)–Pd(2)–N(2)	80.05(12)
N(2)–Pd(2)–P(4)	170.19(9)
N(2)–Pd(2)–P(3)	101.24(8)
C(47)–Pd(2)–P(4)	95.39(9)
C(47)–Pd(2)–P(3)	170.87(10)
P(4)–Pd(2)–P(3)	84.65(3)
P(3)–C(62)–C(61)	105.5(2)
P(4)–C(61)–C(62)	110.6(3)

of complex **4a** is given in Fig. 2, which has an *R* absolute configuration at the newly formed chiral carbon center C_{16} and the molecular structure of complex **4b** is given in Fig. 3, which has an *S* absolute configuration at the newly formed chiral carbon center C_{62}. The geometry at Pd_1 in complex **4a** is slightly distorted square plane with a distortion angle of 2.0° and a mean deviation from planarity of 0.013 Å; the newly formed five-membered ring is found to adopt the λ ring conformation. On the other hand, the geometry at Pd_2 in complex **4b** exhibits a significantly distorted square plane with a distortion angle of 13.2° and a mean deviation from planarity of 0.165 Å; the newly formed five-membered ring is found to adopt δ ring conformation. Based on the X-ray crystallography studies, complex **4b** is adopting a sterically unfavorable δ ring conformation as it shows a significant distortion angle at the palladium(II) center and significant deviation from the planarity.

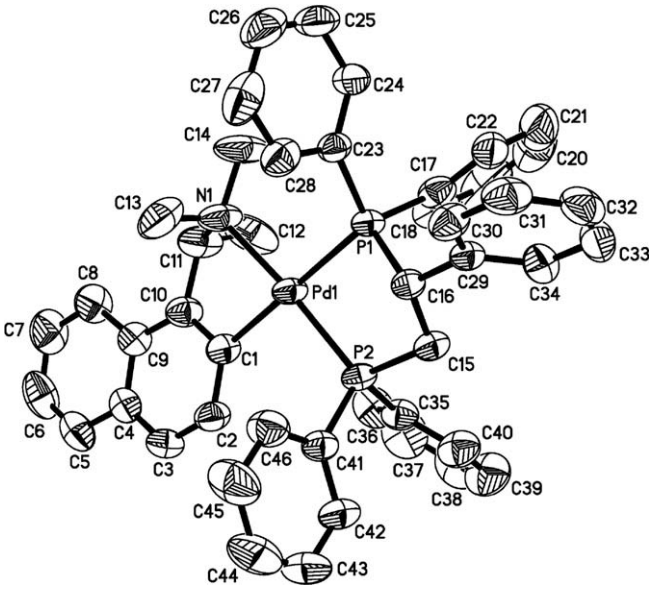


Fig. 2. Molecular structure and absolute configuration of **4a**.

The optically pure complex **4a** was obtained form the mother liquid after removal of co-crystallized **4a** and **4b** completely. As illustrated in Scheme 2, conc. HCl was added subsequently to remove the chiral naphthylamine auxiliary resulting in the optically active dichloro complex (*R*)-**5** as yellow prisms (90% yield) from dichloromethane-diethyl ether: $[\alpha]_D$ +113 (*c* 0.3, CH_2Cl_2). The ^{31}P NMR spectrum of (*R*)-**5** in $CDCl_3$ exhibited two doublets at δ 43.0, 74.0 (J_{PP} = 2.6 Hz). The molecular structure and the absolute stereochemistry of (*R*)-**5** were determined by X-ray crystallography (Fig. 4). The five-membered chelate ring has the asymmetric skew conformation of λ helicity with the phenyl substituent on the new formed carbon center of *R* absolute configuration occupying an equatorial position. Aqueous potassium cyanide was added to a dichloromethane solution of (*R*)-**5**. After stirring vigorously for 1 h, the colorless organic layer was separated, washed with water and dried ($MgSO_4$). Upon the removal of solvent, a white solid

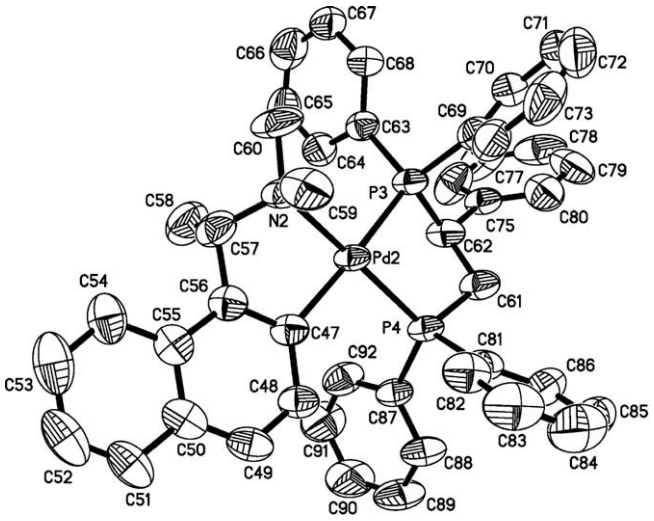
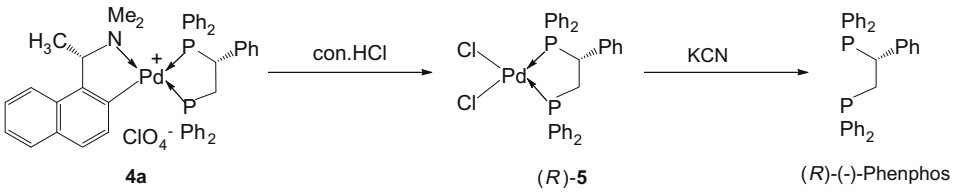


Fig. 3. Molecular structure and absolute configuration of **4b**.



Scheme 2.

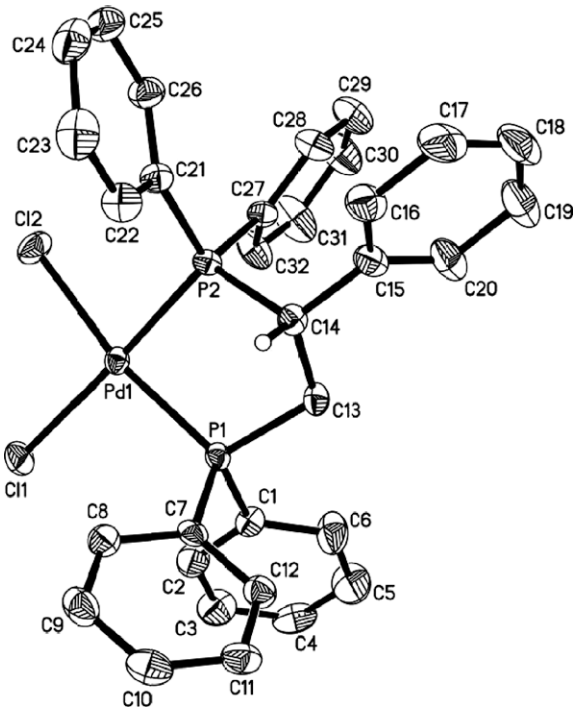


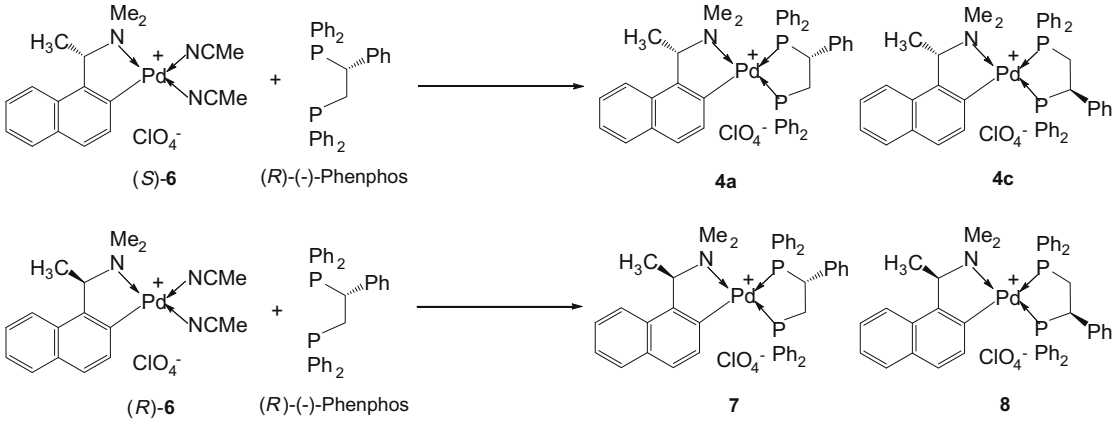
Fig. 4. Molecular structure and absolute configuration of (*R*)-**5**.

(*R*)-(-)-Phenphos [5] was obtained in 95% yield. The ^{31}P NMR spectrum of the free ligand (*R*)-(-)-Phenphos in $CDCl_3$ exhibited two doublets at δ −21.2, 3.6 (J_{PP} = 17.4 Hz).

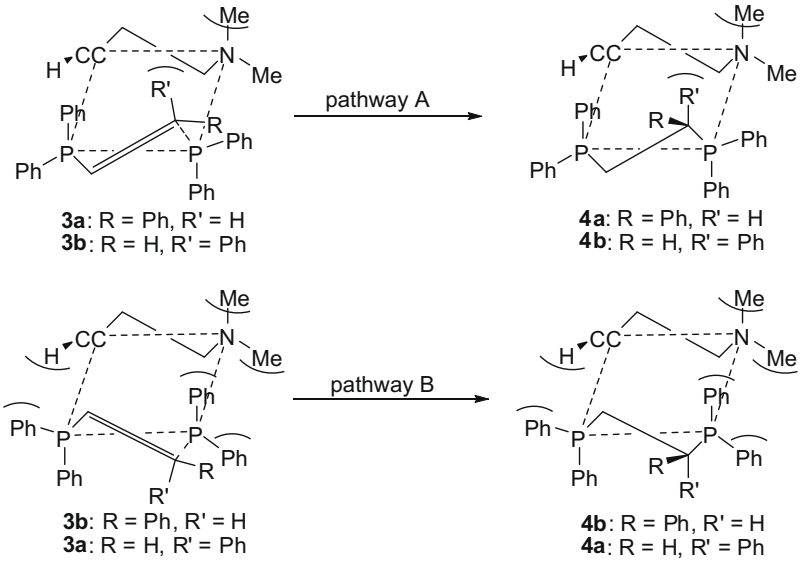
To establish the identities of the two minor products **4c** and **4d**, the liberated optically pure (*R*)-(-)-Phenphos was recoordinated to (*S*)-**6** as illustrated in Scheme 3. The ^{31}P NMR spectrum ($CDCl_3$) of the crude product exhibited only two pairs of doubles at δ 48.2, 50.5 (J_{PP} = 36.3 Hz) and 25.1, 67.9 (J_{PP} = 37.4 Hz). These signals are identical to those recorded for **4a** and **4c** generated in the original hydrophosphination reaction. The ^{31}P NMR spectrum ($CDCl_3$) of the crude recomplexation mixture form (*R*)-(-)-Phenphos and (*R*)-**6** exhibited two pairs of doubles at δ 46.5, 50.1 (J_{PP} = 36.6 Hz) and 25.9, 66.6 (J_{PP} = 37.6 Hz). These signals were identical with those observed for **4b** and **4d**. Complexes **4b** and **7**, **4d** and **8** are thus two pairs of enantiomers. As expected, the enantiomeric complexes exhibited the same NMR chemical signals. Thus, the NMR studies confirmed that diastereomer **4d** was indeed a minor product of the asymmetric synthesis.

In general, (*E*)- and (*Z*)-diphenylphosphinostyrene generated the hydrophosphination products **4a** and **4b** with the same ratio of 6:1, which is not in agreement with what we observed in our previous experiments of hydrophosphination reactions [9]. In the previous studies, *trans* and *cis* coordinated alkenes did not yield major products with same chirality. However, this can be explained by consideration of the possible reaction pathways as illustrated in Scheme 4. In principle, the transition state A and B are electronically more favorable than other possible pathways. The π-accepting styrenylphosphine is coordinated in the *trans* position to the σ-donating NMe group, while the electron-rich phosphido moiety is located *trans* to the strong π-accepting ortho-metalated carbon atom [13]. With pathway A, the (*E*)-isomer **3a** would generate complex **4a** as the major product, in which the new stereogenic carbon center adopts the *R* absolute configuration. In this transition state, severe interchelate repulsions between the chiral auxiliary and the reacting phosphorus substrates are absent. With pathway B, the (*E*)-isomer **3a** would generate complex **4b** as minor product due to the influence of the interchelate repulsions by which the new stereogenic carbon center adopts the *S* absolute configuration. However, with pathway A, the (*Z*)-isomer **3b** would only generate complex **4b** as minor product because of the severe interchelate repulsions between the chiral auxiliary and phenyl substrate present in **3b**.

For this reason, the (*Z*)-isomer **3b** would prefer generation of complex **4a** as major product through pathway B. It is noteworthy that complex **4a** which was generated from **3b** through pathway B



Scheme 3.



Scheme 4.

adopted a δ ring conformation initially. It would however transfer to a more stable λ ring conformation easily in solution. From the discussions above, we believe that (*E*)- and (*Z*)-diphenylphosphinostyrene both generate complex **4a** as major product but through different pathways.

In conclusion, the synthesis of chiral diphosphine *via* chiral amine template assisted asymmetric hydrophosphination has been demonstrated. Triethylamine is essential to this reaction as it play the role as external base. The reactions proceeded with high regio- and stereoselectivities. Further investigations on the synthesis of similar class chiral diphosphines with various substituents and functionalities are currently in progress as well as their applications in various catalytic scenarios.

3. Experimental

Reactions involving air-sensitive compounds were performed under an inert atmosphere of argon using standard Schlenk techniques. Solvents were dried and freshly distilled according to standard procedures and degassed prior to use when necessary. The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at 25 °C on Bruker Avance 300 and 500 spectrometers. Optical rotations were measured on the specified solution in a 0.1 dm cell at 20 °C with a Perkin–Elmer 341 polarimeter. Elemental analysis was performed by the Elemental Analysis Laboratory of the Division of Chemistry and Biological Chemistry at Nanyang Technological University. Melting points were measured using the SRS Optimelt Automated Melting Point System, SRS MPA100.

The chiral palladium complex (*S*)-**1** [14], tertiary phosphine (*E*) or (*Z*)-diphenylphosphinostyrene [12] were prepared according to literature methods.

Caution: Perchlorate salts of metal complexes are potentially explosive compounds and should be handled with care.

3.1. Preparation of complex [(S)-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-C,N][(E)-Diphenyl-phosphinostyrene-P]palladium(II), ***2a***

A mixture of (*S*)-1 (0.590 g, 0.867 mmol) and (*Z*)-diphenylphosphinostyrene (0.501 g, 1.738 mmol) was stirred in dichloromethane (50 mL) at room temperature for 2 h. The solvent was removed and complex **2a** was obtained as yellow powder, 1.090 g (99% yield). $[\alpha]_D$ +75.6 (*c* 0.2, CH_2Cl_2); Mp 120–121 °C (dec).Anal. Calc. for $C_{34}H_{33}ClNPPd$: C, 65.0; H, 5.3; N, 2.2. Found: C, 64.7; H, 5.4; N, 2.2% ^{31}P NMR ($CDCl_3$) δ 33.3; ^{1}H NMR ($CDCl_3$) δ 2.09 (d, 3H, CH*Me,* $^3J_{HH}$ = 6.2 Hz*)*, 2.82 (s, 3H, N*Meeq*), 3.03 (d, 3H, $^4J_{PH}$ = 3.3 Hz, N*Meax*), 4.41 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, C*H*Me), 6.61 (dd, 1H, $^2J_{PH}$ = 17.6 Hz, $^3J_{HH}$ = 8.8 Hz, PC*H*), 6.76 (dd, 1H, $^3J_{PH}$ = 6.1 Hz, $^3J_{HH}$ = 8.8 Hz, PCC*H*), 6.79–8.07 (m, 21H, aromatics).

3.2. Preparation of complex [(S)-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-C,N][(Z)-Diphenyl-phosphinostyrene -P]palladium(II), ***2b***

A mixture of (*S*)-1 (0.594 g, 0.873 mmol) and (*Z*)-diphenylphosphinostyrene (0.504 g, 1.748 mmol) was stirred in dichloromethane (50 mL) at room temperature for 2 h. The solvent was removed and complex **2b** was obtained from dichloromethane and diethyl ether as yellow crystals, 0.889 g (81% yield). $[\alpha]_D$ +36.7 (*c* 0.3, CH_2Cl_2); Mp183-184 °C (dec). Anal. Calc. for $C_{34}H_{33}ClNPPd$: C, 65.0; H, 5.3; N, 2.2. Found: C, 64.8; H, 5.4; N, 2.2%. ^{31}P NMR ($CDCl_3$) δ 23.7; ^{1}H NMR ($CDCl_3$) δ 1.80 (d, 3H, CH*Me,* $^3J_{HH}$ = 6.2 Hz*)*, 2.58 (d, 3H, $^4J_{PH}$ = 1.2 Hz, N*Meeq*), 2.94 (d, 3H, $^4J_{PH}$ = 3.3 Hz, N*Meax*), 4.29 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, C*H*Me), 6.72 (dd, 1H, $^2J_{PH}$ = 13.1 Hz, $^3J_{HH}$ = 6.6 Hz, PC*H*), 6.84 (dd, 1H, $^3J_{PH}$ = 8.6 Hz, $^3J_{HH}$ = 6.6 Hz, PCC*H*), 7.03–7.87 (m, 21H, aromatics).

3.3. Hydrophosphination of [(S)-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-C,N][(E/Z)-Diphenyl-phosphinostyrene-P]palladium (II), ***2a/b****. Preparation of diastereomeric complexes* ***4a,b***

Complex **2a** or **2b** (0.582 g, 0.926 mmol) in dichloromethane (100 mL) and aqueous silver perchlorate (0.400 g, 1.775 mmol) were stirred vigorously at room temperature for 2 h. The mixture was filtered through Celite, washed with water (3 × 30 mL) and dried with $MgSO_4$. The mixture was then degassed and treated with diphenylphosphine (0.172 g) and triethylamine (0.047 g) at −78 °C for 12 h. The crude product was recrystallized from dichloromethane and diethyl ether to give the 1:1 mixture of **4a,b** as yellow crystals, 0.171 g (21% yield). $[\alpha]_D$ +48.4 (*c* 0.6, CH_2Cl_2); Mp 235 °C (dec). Anal. Calc. for $C_{46}H_{44}ClNO_4P_2Pd$: C, 62.9; H, 5.1; N, 1.6. Found: C, 62.4; H, 5.2; N, 1.6%.

Spectroscopic assignments follow. [(*S*)-chloro[1-[1-(dimethylamino) ethyl]-2-naphthalenyl-*C,N*][(*R*)-1,2-bis(diphenylphos-

Table 4
Selected bond lengths (Å) and bond angles (°) of (*R*)-**5**.

Pd(1)–P(2)	2.2346(9)
Pd(1)–P(1)	2.2474(9)
Pd(1)–Cl(1)	2.3693(10)
Pd(1)–Cl(2)	2.3540(9)
P(1)–C(13)	1.836(3)
P(2)–C(14)	1.874(3)
C(13)–C(14)	1.536(4)
C(14)–C(15)	1.522(4)
P(2)–Pd(1)–P(1)	85.81(3)
P(2)–Pd(1)–Cl(1)	175.31(4)
P(1)–Pd(1)–Cl(1)	95.34(3)
P(2)–Pd(1)–Cl(2)	86.56(4)
P(1)–Pd(1)–Cl(2)	170.09(3)
Cl(1)–Pd(1)–Cl(2)	92.77(4)
P(2)–C(14)–C(13)	105.16(19)
P(1)–C(13)–C(14)	109.1(2)

phino)-1-phenylethane-P^1,P^2] palladium (II) Perchlorate **4a**: ^{31}P NMR ($CDCl_3$) δ 48.2, 50.5 (J_{PP} = 36 Hz); ^{1}H NMR ($CDCl_3$) δ 1.98 (d, 3H, CH*Me*, $^3J_{HH}$ = 6.2 Hz), 2.40 (s, 3H, N*Meeq*), 2.58 (s, 3H, N*Meax*), 2.62–3.25 (m, 2H, PCH_2), 3.51–3.65 (m, 1H, PC*H*), 4.55 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, C*H*Me), 6.36–8.35 (m, 31H, aromatics).

[(*S*)-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][(*S*)-1,2-bis(diphenylphosphino)-1-phenylethane-P^1,P^2]palladium(II) Perchlorate **4b**: ^{31}P NMR ($CDCl_3$) δ 46.5, 50.1 (J_{PP} = 37 Hz), ^{1}H NMR ($CDCl_3$) δ 1.64 (d, 3H, CH*Me*, $^3J_{HH}$ = 6.2 Hz), 2.24 (s, 3H, N*Meeq*), 2.62–3.25 (m, 2H, PCH_2), 2.96 (s, 3H, N*Meax*), 3.51–3.65 (m, 1H, PC*H*), 4.44 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, C*H*Me), 6.36–8.35 (m, 31H, aromatics).

3.4. Removal of chiral auxiliary: synthesis of (R)-Dichloro[1,2-bis(diphenylphosphino)-1-phenylethane-P^1,P^2]palladium(II), (R)-5

Concentrated HCl (10 mL) was added to a solution of **4a** (0.200 g, 0.228 mmol) in dichloromethane (30 mL). The reaction mixture was stirred vigorously at room temperature for 12 h, washed with water (3 × 20 mL), and dried ($MgSO_4$). Crystallization of the crude product form dichloromethane and diethyl ether gave the dichloro complex as yellow crystals, 0.150 g (90% yield). $[\alpha]_D$ +113 (*c* 0.3, CH_2Cl_2); Mp: 210 °C (dec). Anal. Calc. for $C_{33}H_{30}Cl_4P_2Pd$: C, 53.8; H, 4.1. Found: C, 53.5; H, 4.3%. ^{31}P NMR ($CDCl_3$): δ 43.0, 74.0 (J_{PP} = 2.6 Hz); ^{1}H NMR ($CDCl_3$) δ 2.70–2.97 (m, 2H, PCH_2CHPh), 3.93–4.00 (m, 1H, PC*H*Ph), 6.55–8.29 (m, 25H, aromatics).

3.5. Liberation of (R)-1,2-bis(diphenylphosphino)-1-phenylethane,(R)-(-)-Phenphos

A solution of (*R*)-**5** (0.066 g, 0.0896 mmol) in dichloromethane was stirred vigorously with a saturated aqueous solution of potassium cyanide (1.00 g) for 2 h. The organic layer was separated, washed with water (3 × 20 mL), and dried ($MgSO_4$). Upon removal of solvent, a white solid was obtained: 0.050 g (95% yield). ^{31}P NMR ($CDCl_3$) δ −21.2, 3.6 (J_{PP} = 17.4 Hz). Other physical properties are consistent with those reported previously [3] (Table 4).

3.6. X-ray crystal structure determination of complexes 2b,4a,b and (R)-5

Crystal data for all complexes and a summary of the crystallographic analysis are given in Table 5. Diffraction data were collected on a Bruker X8 CCD diffractometer with Mo *K*α radiation (graphite monochromator). SADABS absorption corrections were applied [15]. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. The absolute configuration of the chiral complex was determined unambiguously by using the Flack parameter [16].

Table 5
Crystallographic data for complexes **2b**, **4a,b**, (*R*)-**5**.

	2b	**4a**,**b**	(*R*)-**5**
Formula	$C_{34}H_{33}ClNPPd$	$C_{46}H_{44}ClNO_4P_2Pd$	$C_{33}H_{30}Cl_4NP_2Pd$
M	628.43	878.61	736.71
Space group	Cc	$P\bar{1}$	$P\bar{1}$
Crystal system	Orthorhombic	Triclinic	Triclinic
a (Å)	10.9100(2)	9.8084(4)	8.7544(4)
b (Å)	15.8210(3)	13.7477(4)	8.7570(4)
c (Å)	16.7419(3)	15.7166(5)	11.2458(5)
V (Å^3)	2889.77(9)	2081.31(12)	799.08(6)
Z	4	2	1
T (K)	273(2)	298(2)	173(2)
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	0.814	0.631	1.037
R_1(observed data)[a]	0.0291	0.0353	0.0311
wR_2 (observed data)[b]	0.0395	0.0457	0.0319
Flack parameter	−0.020(16)	−0.022(13)	0.023(18)

[a] $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$.
[b] $wR_2 = \{\Sigma[w(F_o2-F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$, $w^{-1} = \sigma^2(F_0)^2 + (aP)^2 + bP$.

Supplementary material

CCDC 728927, 728928 and 728929 contain the supplementary crystallographic data for complexes **4a,b**, (*R*)-**5**, and **2b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We are grateful to Nanyang Technological University for supporting this research and the research scholarships to Y.Z., L.L.T. and F.L.L.

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