DOI: 10.1002/ejic.200900460

Novel Enantioselective Synthesis of Functionalized Pyridylarsanes by a Chiral Palladium Template Promoted Asymmetric Hydroarsanation Reaction

Fengli Liu,[a] Sumod A. Pullarkat,[a] Yongxin Li,[a] Shuli Chen,[a] and Pak-Hing Leung*[a]

Keywords: Asymmetric synthesis / Palladium / As ligands / Template synthesis

The asymmetric hydroarsanation reactions between diphenylarsane and (*E*)-1-phenyl-3-(pyridin-2-yl)-2-propenone and (*E*)-1-methyl-3-(pyridin-2-yl)-2-propenoate have been achieved by use of the organopalladium complex containing *ortho*-metalated (*R*)-[1-(dimethylamino)ethyl]naphthalene as the chiral reaction template in high regio- and stereoselectivities under mild conditions. Hydroarsanation of (*E*)-1-phenyl-3-(pyridin-2-yl)-2-propenone with diphenylarsane generated two stereoisomeric products in the ratio of 3:1 as five-membered As–N bidentate chelates on the chiral naphthylamine palladium template. Using the same chiral metal template, the corresponding hydroarsanation reaction with (*E*)-1-methyl-3-(pyridin-2-yl)-2-propenoate gave only one product as a six-membered As–N bidentate chelate. The naphthylamine auxiliary could be removed chemoselectively by treatment with concentrated hydrochloric acid to form the corresponding optically pure neutral complexes. Subsequent ligands displacement from the palladium using aqueous potassium cyanide generated the optically pure keto- and ester-functionalized chiral pyridylarsane ligands. The absolute configuration and the coordination properties of the pyridylarsanes have been established by single-crystal X-ray analysis.

Introduction

Recently, organoarsenic compounds have been found to play important roles in many aspects of organic synthesis and catalytic reactions. Tertiary arsanes have been reported to be more appropriate ligands than phosphanes in a number of transition metal-catalyzed organic reactions, for example, Stille[1] and Heck reactions,[2] hydroformylation,[3] Suzuki–Miyaura coupling reaction,[4] carbonylation,[5] norbornene polymerization[6] and Wittig-type olefination of aldehydes.[7] Although several chiral arsane compounds have been used in asymmetric catalytic reactions,[8] these earlier studies have not involved optically active pyridylarsanes, which would provide a variety of applications in asymmetric catalysis as shown by their phosphorus analogues.[9] However, most available arsanation protocols are limited to compounds that are not base and reducible agent sensitive[10] and devoid of functionalities. The only straightforward method for synthesis of functionalized arsanes has been recently reported,[11] Pd-catalyzed arsanation of aryl triflates using triphenylarsane as the arsanating agent. However via that methodology, heteroatom-substituted pyridyl triflates did not react at all. Until now, no synthesis of enantiomerically pure keto- and ester-substituted C-chiral pyridylphosphanes have been reported. In this paper, we report an efficient approach for the enantioselective synthesis of keto- and ester-functionalized chiral pyridylarsanes via the asymmetric hydroarsanation reaction in which the chiral organopalladium complex (*R*)-**1** is used as both the reaction promoter and the stereochemical controller.

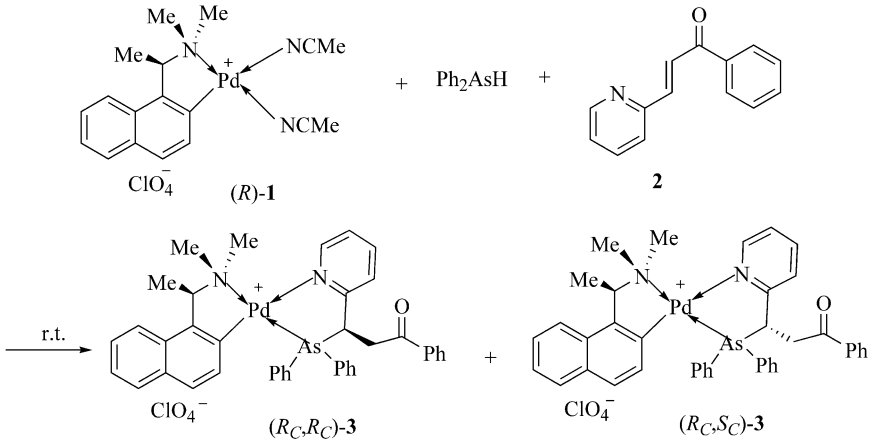
[a] Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University,
Singapore 637371, Singapore
E-mail: pakhing@ntu.edu.sg

Results and Discussion

Asymmetric Hydroarsanation of (*E*)-1-Phenyl-3-(pyridin-2-yl)-2-propenone

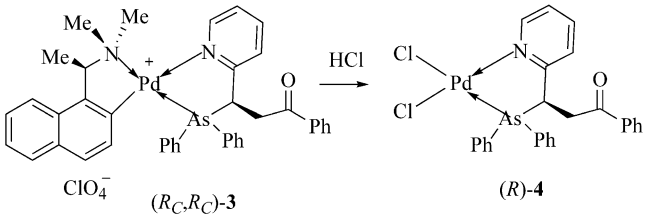
In the absence of a metal ion, diphenylarsane shows no reactivity with (*E*)-1-phenyl-3-(pyridin-2-yl)-2-propenone (**2**). However, as illustrated in Scheme 1, in the presence of chiral complex (*R*)-**1**, The reaction is completed in 12 d at room temperature to give a 3:1 diastereomeric mixture of (R_C,R_C)-**3** and (R_C,S_C)-**3**.

While the addition of the secondary phosphane to vinylic phosphanes resulted in *cis*/*trans* regioisomeric products,[12] the addition of diphenylarsane to vinylic pyridines is 100% regioselective, wherein the As atom occupies the coordination site *trans* to the N atom. The high regioselectivity observed in the present case is in agreement with what has been observed for similar N–P heterobidentate ligands.[13] The diastereomeric products were subsequently separated by column chromatography. The major diastereomer (R_C,R_C)-**3** was obtained as a pale yellow solid in 30% isolated yield. Although it is stable in the solid state and in



Scheme 1.

solution, it is highly soluble in most organic solvents and could not be induced to crystallize. Upon subsequent treatment of the perchlorate salt with concentrated hydrochlorc acid, the resultant neutral dichloro complex (*R*)-**4** was obtained as yellow prisms in 87% isolated yield, $[a]_D$ = –122 (c = 0.6, CH_2Cl_2) (Scheme 2). The chelating properties and the absolute configuration of the coordinated pyridine-substituted arsane ligand in complex (*R*)-**4** were studied by X-ray crystallography (Figure 1). Selected bond lengths and angles of the complex are given in Table 1. The structure analysis established that the newly formed stereogenic center at C(6) adopted the *R* absolute configuration. The geometry at the Pd center is distorted square planner with angles of 84.3(1)–92.8(1) and 171.0(1)–179.3(1)°. Both the Pd–As and Pd–N bond lengths, 2.278(1) and 2.071(2) Å, are typical, but the two Pd–Cl distances 2.305(1) and 2.376(1) Å differ significantly, with the bond trans to the As being noticeably larger than the bond trans to the N. This reflects the stronger electronic trans effect of the As relative to the aromatic nitrogen donor. The C(6)–C(7) bond length [1.536(4) Å] showed marked lengthening, which is clearly attributed to the intrachelate repulsive interactions between the COPh moiety at C(7) and the phenyl groups on the As donor atom. The CH_2COPh substituent of the five-membered Pd–N chelate is in the preferred equatorial disposition.[14] The bond length of Pd–As in (*R*)-**4** [2.278(1) Å] is longer than that of the corresponding Pd–P [2.184(4) Å],[13] which is in agreement with the 0.10–0.11 Å difference in the covalent bond radii of As (1.21 Å) and P (1.10 Å).[15]



Scheme 2.

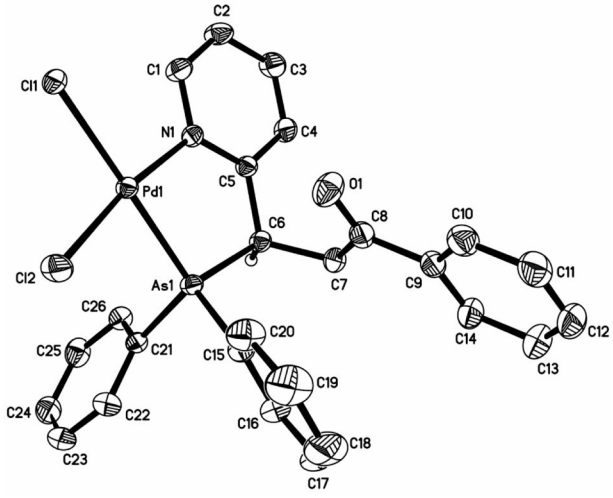


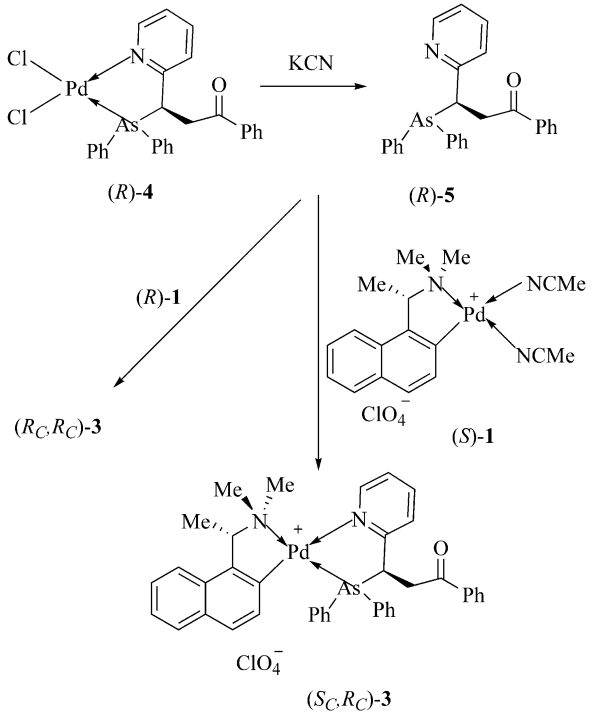
Figure 1. Molecular structure of the dichloro complex (*R*)-**4**.

Table 1. Selected bond lengths [Å] and angles [°] for (*R*)-4.

Pd(1)–N(1)	2.071(2)	Pd(1)–As(1)	2.278 (1)
Pd(1)–Cl(2)	2.305 (1)	Pd(1)–Cl(1)	2.376 (1)
C(1)–N(1)	1.341(4)	C(5)–N(1)	1.368(3)
C(6)–As(1)	1.971(3)	C(8)–O(1)	1.216(4)
C(6)–C(7)	1.536(4)	C(5)–C(6)	1.510(4)
N(1)–Pd(1)–As(1)	84.3(1)	N(1)–Pd(1)–Cl(2)	171.0(1)
As(1)–Pd(1)–Cl(2)	86.7(1)	N(1)–Pd(1)–Cl(1)	96.1(1)
As(1)–Pd(1)–Cl(1)	179.3(1)	N(1)–C(5)–C(6)	120.8(2)
Cl(2)–Pd(1)–Cl(1)	92.8(1)	C(4)–C(5)–C(6)	118.7(2)
C(5)–C(6)–C(7)	114.4(2)	C(5)–C(6)–As(1)	108.7(2)
C(7)–C(6)–As(1)	112.8(2)	C(8)–C(7)–C(6)	113.8(2)
C(1)–N(1)–C(5)	118.1(2)	C(5)–N(1)–Pd(1)	118.6(2)
C(6)–As(1)–Pd(1)	102.3(1)		

The liberation of the free As–N ligand (*R*)-**5** was achieved by the treatment of the dichloro complex with aqueous potassium cyanide (Scheme 3). Thus the pyridylarsane was obtained as a white solid in 75% yield, $[a]_D$ = +78 (c = 0.4, CH_2Cl_2). Because of the air-sensitivity of the noncoordinated As atoms, liberated (*R*)-**5** was not stored in its pure form but was recoordinated again to (*R*)-**1**. The recoordination process is also a means of verifying the op-

tical purity of the released ligand to establish the identity of the minor isomers that were generated in the original hydroarsanation reaction.[16,12] The recoordination procedure was monitored by ^{1}H NMR spectroscopy. In $CDCl_3$, the ^{1}H NMR spectrum of the recoordination product showed only one product, thus confirming that the liberated (*R*)-**5** is optically pure.

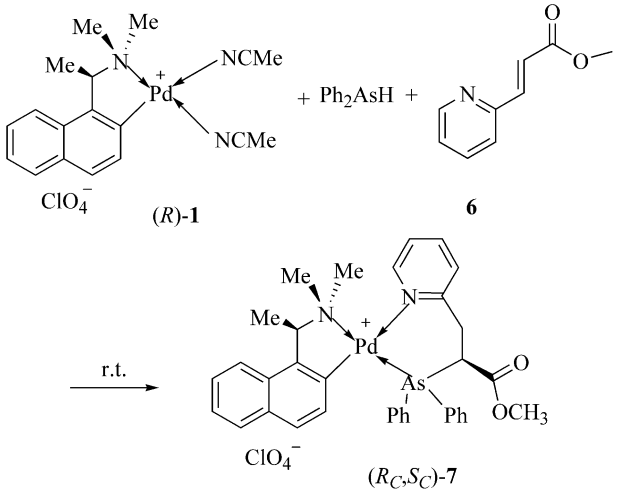


Scheme 3.

In order to establish the identity of the minor product that was formed from hydroarsanation reaction, (*R*)-**5** was recoordinated regiospecifically to (S_C)-**1** to generate the diastereomeric complex (S_C,R_C)-**3** (Scheme 3). The ^{1}H NMR spectrum of the complex (S_C,R_C)-**3** was identical with those observed from the minor product generated from the hydroarsanation reaction. Hence it could be confirmed that complex (R_C,S_C)-**3** is the minor product in the original hydroarsanation reaction. No ^{1}H NMR signals could be detected for the major diastereomer thus reaffirming that liberated (*R*)-**5** is enantiomerically pure.

Asymmetric Hydroarsanation of (*E*)-1-Methyl-3-(pyridin-2-yl)-2-propenoate

In principle, the hydroarsanation reaction between (*E*)-1-methyl-3-(pyridin-2-yl)-2-propenoate and Ph_2AsH should generate similar five-membered As–N chelate products as that obtained from the reaction involving (*E*)-1-phenyl-3-(pyridinyl-2-yl)-2-propenone (**6**). Interestingly, after 14 d at room temperature the chelating As–N complex (R_C,S_C)-**7** was generated as the sole product in the hydroarsanation reaction (Scheme 4). After purification by column chromatography, the product (R_C,S_C)-**7** was subsequently crystallized from dichloromethane/diethyl ether as pale yellow prisms in 51% yield, $[a]_D$ = –77 (*c* = 0.6, CH_2Cl_2).



Scheme 4.

The X-ray crystallographic analysis of the complex confirmed that an enantiomerically pure product has been formed in which the six-membered As–N chelate coordinated to palladium as a bidentate chelate (Figure 2) with a twist-boat conformation. Furthermore, the structure analysis unambiguously established that the newly formed stereogenic center at C(21) adopts the *S* configuration. The As and N donor atoms of the new heterobidentate ligand are bonded regiospecifically to the Pd atom, with the softer As donor expectedly taking up the position *trans* to the NMe_2 group. Selected bond lengths and angles are listed in Table 2. The angles formed by the As–N chelate and the naphthylamine template at the Pd metal center were in the range of 81.0(2)–97.8(2) and 169.6(1)–171.6(2)°. The C(21)–As(1) and C(20)–C(21) distances [2.002(5) and 1.533(7) Å] are elongated noticeably by the intrachelate interactions. The bond length of Pd–As in (R_C,S_C)-**7** [2.345(1) Å] is also longer than that of the corresponding Pd–P [2.239(1) Å].[13]

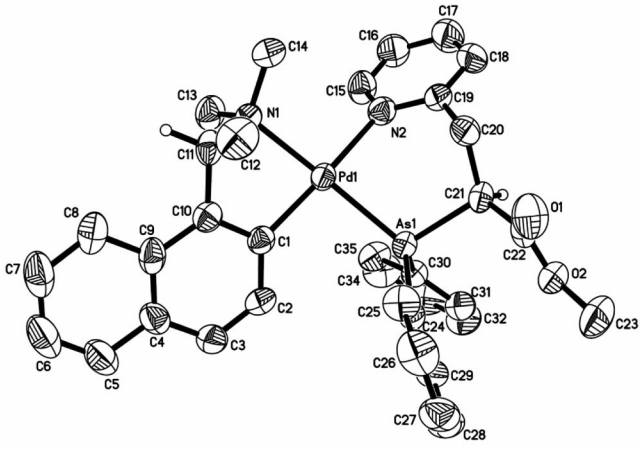
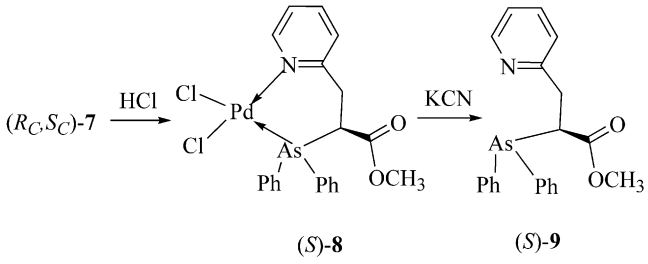


Figure 2. Molecular structure of the cationic complex (R_C,S_C)-**7**.

Table 2. Selected bond lengths [Å] and angles [°] for (R_C,S_C)-7.

Pd(1)–C(1)	1.994(5)	Pd(1)–N(1)	2.123(4)
Pd(1)–N(2)	2.168(4)	Pd(1)–As(1)	2.345(1)
C(15)–N(2)	1.348(6)	C(19)–N(2)	1.346(6)
C(19)–C(20)	1.505(7)	C(20)–C(21)	1.533(7)
C(21)–As(1)	2.002(5)	C(22)–O(1)	1.195(6)
C(22)–O(2)	1.334(7)	C(30)–As(1)	1.938(4)
C(1)–Pd(1)–N(1)	81.0(2)	C(1)–Pd(1)–N(2)	171.6(2)
N(1)–Pd(1)–N(2)	97.8(2)	C(1)–Pd(1)–As(1)	94.9(1)
N(1)–Pd(1)–As(1)	169.6(1)	N(2)–Pd(1)–As(1)	87.6(1)
N(2)–C(19)–C(20)	117.1(4)	C(19)–C(20)–C(21)	111.0(4)
C(22)–C(21)–C(20)	110.9(4)	C(22)–C(21)–As(1)	110.6(3)
C(20)–C(21)–As(1)	110.0(3)	C(15)–N(2)–C(19)	118.5(4)
C(19)–N(2)–Pd(1)	124.7(3)	C(21)–As(1)–Pd(1)	106.4(1)

The treatment of complex (R_C,S_C)-**7** with concentrated hydrochloric acid generated (*S*)-**8** (Scheme 5). The dichloro complex was subsequently crystallized from dichloromethane/diethyl ether as yellow prisms in 91% yield, $[\alpha]_D$ = –113 (c = 0.6, CH_2Cl_2). Further treatment of (*S*)-**8** with aqueous cyanide liberated the optically pure (*S*)-**9** as pale yellow solid in 80% yields, $[\alpha]_D$ = –102 (c = 1.0, CH_2Cl_2). The recoordination of the free ligand to (*R*)- and (*S*)-**1** employing the same protocol used for (*R*)-**5** confirmed that (*S*)-**9** is optically pure.



Scheme 5.

Conclusions

From a mechanistic standpoint, we believe that the mechanism involved in the asymmetric hydroarsanation is similar to that of hydrophosphanation.[17] The simultaneous coordination of diphenylarsane and pyridine complex on the chiral palladium template polarized the As–H and vinylic C=C bonds concurrently. An intermediate involving the deprotonated form of the highly reactive coordinated arsenido ligand could thus be generated in the presence of excess pyridine complex. This nucleophilic arsenido moiety subsequently undergoes addition to the activated alkene. A correlation between the X-ray crystallography data of the hydroarsanation product and a Dreiding model study confirmed that the formation of the As–Pd–N six-membered ring would markedly relieve the interchelate repulsive interactions than a five-membered ring. Therefore the formation of the six-membered ring between (*E*)-1-methyl-3-(pyridin-2-yl)-2-propenoate and Ph_2AsH must be due to the predominant steric factors. The X-ray crystallographic analysis of (R_C,S_C)-**7** revealed that the CO_2Me group at C(21) occupies the sterically favorable equatorial position in the twist boat conformation (Figure 3).[14] The 6-H of the pyridine ring is far away from the two NMe group and there should not be any significant steric repulsion. In addition, less steric repulsion exists between the naphthylene proton H_γ and the quasi-axial phenyl group on As.[18] However model studies shows that in (R_C,R_C)-**7**, the CO_2Me group occupies the sterically unfavorable axial position. Although the 6-H of the pyridine ring is far away from to the two NMe groups, there is still significant steric repulsion between the naphthylene proton H_γ and the quasi-equatorial phenyl group on As. We believe that these interchelate repulsive forces are the discriminating factors that hinder the formation of the unfavored diastereomer.

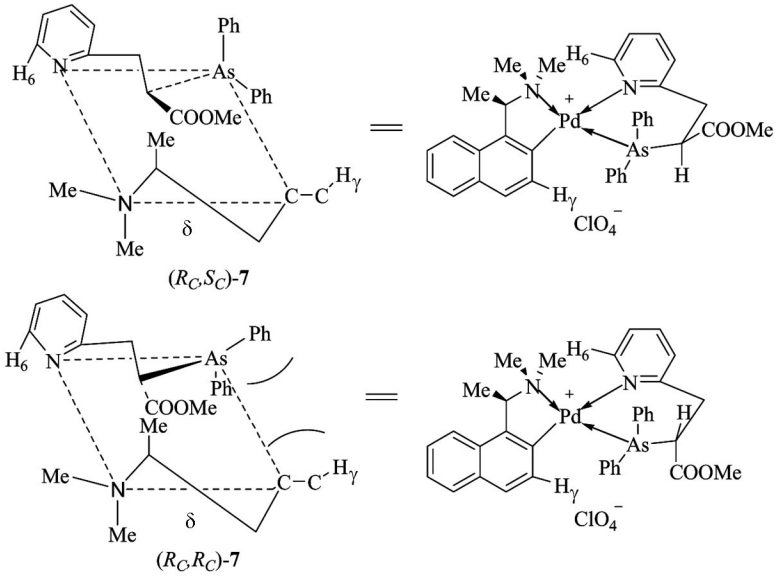


Figure 3. Interchelate interactions in (R_C,S_C)-**7** and (R_C,R_C)-**7**.

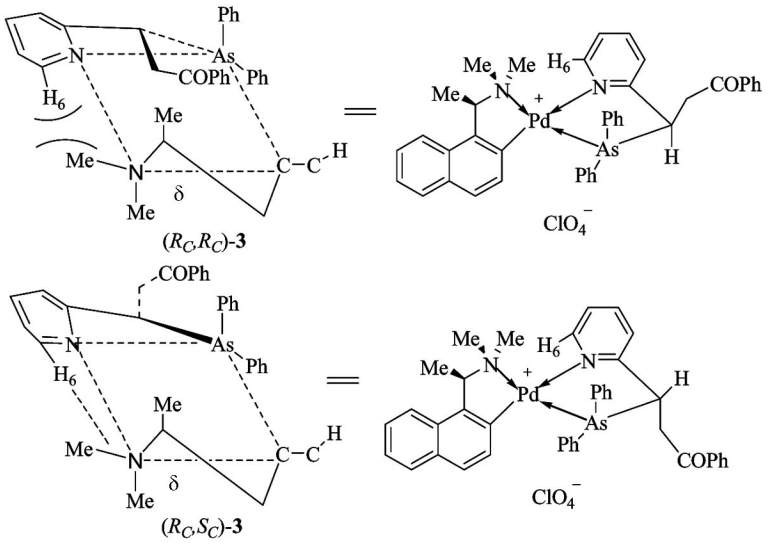


Figure 4. Interchelate interactions in (R_C,R_C)-**3** and (R_C,S_C)-**3**.

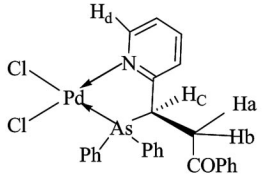
The formation of the five-membered ring between (*E*)-1-phenyl-3-(pyridin-2-yl)-2-propenone and Ph_2AsH is because there are more severe interchelate steric constrains within phenyl groups of Ph_2As and COPh in the six-mumbered ring. The model studies clearly indicate that in the major isomer (R_C,R_C)-**3**, the COPh group at C(6) of the five-membered As–Pd–N chelate occupies the sterically favorable equatorial position (Figure 4). In this molecule, however, the 6-H of the pyridine ring unfavorably oriented towards the NMe group which is in the equatorial position. In the minor isomer (R_C,S_C)-**3**, the COPh group occupies the sterically unfavorable axial position. In addition, the 6-H of the pyridine ring intrudes into the space between the two methyl groups on N to achieve the least steric repulsion state. Similar driving forces are present in the case of the analogue P–N ligands.

In conclusion, the efficient synthesis of keto- and ester-functionalized chiral pyridylarsanes via chiral organopalladium template promoted asymmetric hydroarsanation has been demonstrated. The hydroarsanation reactions proceed with high regio- and stereoselectivities under mild conditions. Further investigations on the catalytic properties of transition metal complexes containing these optically active ligands are currently in progress.

Experimental Section

General: Reactions involving air-sensitive compounds were performed under an inert atmosphere of argon using standard Schlenk techniques. NMR spectra were recorded at 25 °C on Bruker Avance 400 spectrometer. 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 enantiomerically pure forms of the complexes (R_c)-**1**, (S_c)-**1**,[19] (*E*)-1-phenyl-3-(pyridin-2-yl)-2-propenone,[20] and methyl (*E*)-1-methyl-3-(pyridin-2-yl)-2-propenoate[21] were prepared as previously reported.

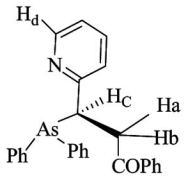
Dichloro-[(*R*)-1-phenyl-3-(diphenylarsanyl)-3-(pyridin-2-yl)propanone-(N^1,As^2)]palladium(II) [(*R*)-4]: The bis(acetonitrile)Pd complex (*R*)-**1** (1 g, 2.05 mmol) in dichloromethane (40 mL) was treated with (*E*)-1-phenyl-3-(pyridin-2-yl)-2-propenone (0.473 g, 2.26 mmol) and Ph_2AsH (0.473 g, 2.05 mmol) at room temperature for 12 d. Removal of solvent under reduced pressure gave the crude products as a yellow solid. The crude product mixture was then purified through a silica gel column with dichloromethane/acetone as the eluent and then crystallized from dichloromethane/diethyl ether to give the complex (R_C,R_C)-**3** as pale yellow glass (0.52 g, 30% yield) that could not be crystallized from any of the solvents tried. The cationic complex (0.50 g, 0.593 mmol) in dichloromethane (30 mL) was treated with concentrated hydrochloric acid (12 mL) for 1 h at room temperature. The reaction mixture was then washed with water (4 × 10 mL) and dried ($MgSO_4$). Subsequently fractional recrystallization from dichloromethane/diethyl ether gave complex (*R*)-**4** as yellow prisms; m.p. 207–208 °C (decomp.), $[a]_D$ = –122 (c = 0.6, CH_2Cl_2); 0.318 g (87% yield). $C_{26}H_{22}AsCl_2NOPd$ (616.7): calcd. C 50.6, H 3.6, N 2.3; found C 50.6, H 4.0, N 2.0. ^{1}H NMR (CD_2Cl_2): δ = 3.57 (dd, $^2J_{H,H}$ = 18.6, $^3J_{H,H}$ = 5.6 Hz, 1 H, CH_aH_b), 3.87 (dd, $^2J_{H,H}$ = 18.6, $^3J_{H,H}$ = 8.0 Hz, 1 H, CH_aH_b), 5.14 (dd, $^3J_{H,H}$ = 5.6, $^3J_{H,H}$ = 8.0 Hz, 1 H, H_c), 7.30–8.02 (m, 18 H, aromatics), 9.81 (d, $^3J_{H,H}$ = 5.9 Hz, 1 H, H_d) ppm.



(*R*)-**4**

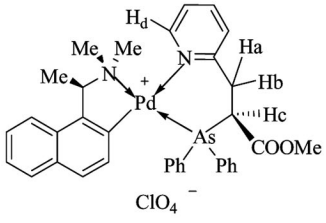
(*R*)-1-Phenyl-3-(diphenylarsanyl)-3-(pyridin-2-yl)propanone [(*R*)-5]: A solution of (*R*)-**4** (0.0617 g, 0.1 mmol) in dichloromethane (15 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (0.2 g) for 5 min. The resulting colorless organic layer was separated, washed with water, and dried ($MgSO_4$).

Upon the removal of solvent, a white solid (*R*)-**5** was obtained, $[\alpha]_D$ = +78 (*c* = 0.4, CH_2Cl_2); 0.033 g (75% yield). ^1H NMR (CD_2Cl_2): δ = 3.23 (d, $^3J_{H,H}$ = 16 Hz, 1 H, CH_aH$_b$), 4.30–4.41 (m, 2 H, H_c + CH$_a$$H_b$), 6.84–7.88 (m, 18 H, aromatics), 8.48 (d, $^3J_{H,H}$ = 4.6 Hz, 1 H, H_d) ppm.



(*R*)-**5**

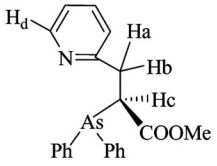
{(*R*)-1-[1-(Dimethylamino)ethyl]naphthyl-(C^2,*N*)}[(*S*)-methyl-2-(diphenylarsanyl)-3-(pyridin-2-yl)propanoate-(N^1,As^2)]palladium(II) Perchlorate [(R_C,S_C)-7]:. The bis(acetonitrile)Pd complex (*R*)-**1** (1.1 g, 2.3 mmol) in dichloromethane (40 mL) was treated with (*E*)-1-methyl-3-(pyridin-2-yl)-2-propenoate (0.411 g, 2.53 mmol) and Ph_2AsH (0.529 g, 2.3 mmol) at room temperature for 14 d. Removal of solvent under reduced pressure gave the crude products as a yellow solid. The crude product mixture was then purified through a silica gel column with dichloromethane/acetone as the eluent and then crystallized from dichloromethane/diethyl ether to give the complex (R_C,S_C)-**7** as pale yellow crystals; m.p. 204–205 °C (decomp.), $[\alpha]_D$ = –77 (*c* = 0.6, CH_2Cl_2); 0.92 g (51% yield). $C_{35}H_{36}AsClN_2O_6Pd$ (797.5): calcd. C 52.7, H 4.6, N 3.5; found C 52.3, H 4.5, N 3.1. ^1H NMR (CD_2Cl_2): δ = 2.23 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, CH*Me*), 2.60 (s, 3 H, N*Me*), 3.00 (s, 3 H, N*Me*), 3.09 (s, 3 H, COO*Me*), 3.49 (dd, $^3J_{H,H}$ = 13.0, $^2J_{H,H}$ = 2.3 Hz, 1 H, H_a), 3.82 (dd, $^2J_{H,H}$ = 14.3, $^3J_{H,H}$ = 2.3 Hz, 1 H, H_b), 4.13 (m, 1 H, H_c), 4.56 (qn, $^3J_{H,H}$ = 6.3 Hz, 1 H, C*H*Me), 6.63–8.08 (m, 19 H, aromatics), 8.80 (d, $^3J_{H,H}$ = 5.3 Hz, 1 H, H_d) ppm.



(R_C,S_C)-**7**

Dichloro [(*S*)-Methyl-2-(diphenylarsanyl)-3-(pyridin-2-yl)propanoate-(N^1,As^2)]palladium(II) [(*S*)-8]: The naphthylamine auxiliary in (R_C,S_C)-**7** was removed chemoselectively by adding concentrated hydrochloric acid (15 mL) to a solution of the complex (R_C,S_C)-**7** (0.3705 g, 0.46 mmol) in dichloromethane (20 mL). The reaction mixture was stirred vigorously for 1 h at room temperature. The reaction mixture was then washed with water (4 × 10 mL) and dried ($MgSO_4$). Subsequently fractional crystallization from dichloromethane/diethyl ether gave complex (*S*)-**8** as yellow prisms; m.p. 233–234 °C (decomp.), $[\alpha]_D$ = –113 (*c* = 0.6, CH_2Cl_2); 0.2 g (91% yield). $C_{21}H_{20}AsCl_2NO_2Pd$ (570.6): calcd. C 44.2, H 3.5, N 2.5; found C 44.3, H 3.9, N 2.1. ^1H NMR (CD_2Cl_2): δ = 3.18 (s, 3 H, COOCH_3), 3.35 (dd, $^2J_{H,H}$ = 12.3, $^3J_{H,H}$ = 2 Hz, 1 H, H_a), 3.78 (dd, $^2J_{H,H}$ = 14.5, $^3J_{H,H}$ = 2 Hz, 1 H, H_b), 4.04 (dd, $^3J_{H,H}$ = 14.5, $^3J_{H,H}$ = 12.3 Hz, 1 H, H_c), 7.34–8.14 (m, 14 H, aromatics), 9.34 (d, $^3J_{H,H}$ = 5.3 Hz, 1 H, H_d) ppm.

Methyl (*S*)-2-(Diphenylarsanyl)-3-(pyridin-2-yl)propanoate [(*S*)-9]: A solution of (*S*)-**8** (0.057 g, 0.1 mmol) in dichloromethane (15 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (0.2 g) for 5 min. The resulting colorless organic layer was separated, washed with water, and dried ($MgSO_4$). Upon the removal of solvent, a white solid (*S*)-**9** was obtained, $[\alpha]_D$ = –102 (*c* = 1.0, CH_2Cl_2); 0.031 g (80% yield). ^1H NMR (CD_2Cl_2): δ = 3.13 (dd, $^3J_{H,H}$ = 14.8, $^2J_{H,H}$ = 4.7 Hz, 1 H, H_a), 3.22 (s, 3 H, COOCH_3), 3.47 (dd, $^3J_{H,H}$ = 14.8, $^3J_{H,H}$ = 10.9 Hz, 1 H, H_c), 3.93 (dd, $^3J_{H,H}$ = 10.9, $^2J_{H,H}$ = 4.7 Hz, 1 H, H_b), 7.07–7.63 (m, 14 H, aromatics), 8.49 (d, $^3J_{H,H}$ = 4.5 Hz, 1 H, H_d) ppm.



(*S*)-**9**

Crystal Structure Determination of (*R*)-4 and (R_C,S_C)-7: X-ray crystallographic data for the two complexes (*R*)-**4** and (R_C,S_C)-**7** are given in Table 3. Diffraction data were collected on a Bruker X8Apex diffractometer with Mo-K_α radiation (graphite monochromator). SADABS absorption corrections were applied. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at fixed distances from carbon atoms and were assigned to fixed thermal parameters. The absolute configurations of all chiral complexes were determined unambiguously using the Flack parameter.[22]

Table 3. Crystallographic data for complexes (*R*)-**4** and (R_C,S_C)-**7**.

	(*R*)-**4**	(R_C,S_C)-**7**
Formula	$C_{26}H_{22}AsCl_2NOPd$	$C_{36}H_{38}AsCl_3N_2O_6Pd$
fw	616.67	882.35
Space group	$P2_12_12_1$	$P2_1$
Crystal system	orthorhombic	monoclinic
a [Å]	8.9848(4)	10.0428(6)
b [Å]	10.5337(5)	17.9964(11)
c [Å]	25.0414(12)	10.3669(6)
α [°]	90	90
β [°]	90	94.719(3)
γ [°]	90	90
V [Å^3]	2370.00(19)	1867.30(19)
Z	4	2
T [K]	173(2)	296(2)
$\rho_{calcd.}$ [g cm^{-3}]	1.728	1.569
λ [Å]	0.71073 (Mo)	0.71073 (Mo)
μ [mm^{-1}]	2.414	1.637
F(000)	1224	892
Flack parameter	0.020(7)	0.009(10)
R_1 (obsd. data)[a]	0.0245	0.0414
wR_2 (obsd. data)[b]	0.0556	0.0966

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $wR2 = \sqrt{\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}}$, $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

CCDC-732832 [for (*R*)-**4**] and -732833 [for (R_C,S_C)-**7**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.cdcc.cam.ac.uk/data_request/cif.

Acknowledgments

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

[1] a) V. K. Farina, B. Krishnan, *J. Am. Chem. Soc.* **1991**, *113*, 9585–9595; b) K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem. Int. Ed.* **2005**, *44*, 4442–4489; c) K. C. Y. Lau, P. Chiu, *Tetrahedron Lett.* **2007**, *48*, 1813–1816.

[2] R. A. Baber, S. Collard, M. Hooper, A. G. Orpen, P. G. Pringle, M. J. Wilkinson, R. L. Wingad, *Dalton Trans.* **2005**, 1491–1498.

[3] L. A. van der Veen, P. K. Keeven, P. C. Kamer, P. W. N. M. van Leeuwen, *Chem. Commun.* **2000**, 333–334.

[4] a) C. R. Johnson, M. P. Braun, *J. Am. Chem. Soc.* **1993**, *115*, 11014–11015; b) R. B. Bedford, C. S. J. Cazin, S. J. Coles, T. Gelbrich, M. B. Hursthouse, V. J. M. Scordia, *Dalton Trans.* **2003**, 3350–3356.

[5] S. Ceccarelli, U. Piarulli, C. Gennari, *J. Org. Chem.* **2000**, *65*, 6254–6256.

[6] J. A. Casares, P. Espinet, G. Salas, *Organometallics* **2008**, *27*, 3761–3769.

[7] P. Cao, C.-Y. Li, Y.-B. Kang, Z. Xie, X.-L. Sun, Y. Tang, *J. Org. Chem.* **2007**, *72*, 6628–6630.

[8] a) A. D. Calhoun, W. J. Kobos, T. A. Nile, C. A. Smith, *J. Organomet. Chem.* **1979**, *170*, 175–179; b) B. A. Murrer, J. M. Brown, P. A. Chaloner, P. N. Nicholson, D. Parker, *Synthesis* **1979**, 350–352; c) A. Kojima, C. D. J. Boden, M. Shibasaki, *Tetrahedron Lett.* **1997**, *38*, 3459–3460; d) Y. Cho, M. Shibasaki, *Tetrahedron Lett.* **1998**, *39*, 1773–1776; e) D.-M. Tan, K. S. Chan, *Tetrahedron Lett.* **2005**, *46*, 503–505; f) C. Y. Wang, D.-M. Tan, K. S. Chan, Y.-H. Liu, S.-M. Peng, S.-T. Liu, *J. Organomet. Chem.* **2005**, *690*, 4920–4925; g) N. C. Payne, D. W. Stephan, *Inorg. Chem.* **1982**, *21*, 182–188.

[9] a) G. R. Newkome, *Chem. Rev.* **1993**, *93*, 2067–2089; b) Z. Z. Zhang, H. Cheng, *Coord. Chem. Rev.* **1996**, *147*, 1–37; c) P. Espinet, K. Soulantica, *Coord. Chem. Rev.* **1999**, *499*, 499–556; d) G. Chelucci, G. Orru, G. A. Pinna, *Tetrahedron* **2003**, *59*, 9471–9515; e) P. J. Guiry, C. P. Saunders, *Adv. Synth. Catal.* **2004**, *346*, 497–537; f) X. Cui, K. Burgess, *Chem. Rev.* **2005**, *105*, 3272–3296.

[10] F. Y. Kwong, C. W. Lai, K. S. Chan, *J. Am. Chem. Soc.* **2001**, *123*, 8864–8865.

[11] F. Y. Kwong, C. W. Lai, D.-M. Tan, F. L. Lam, A. S. C. Chan, K. S. Chan, *Organometallics* **2005**, *24*, 4170–4178.

[12] W. C. Yeo, S. T. Tee, G. K. Tan, L. L. Koh, P. H. Leung, *Inorg. Chem.* **2004**, *43*, 8102–8109.

[13] F. Liu, S. A. Pullarkat, Y. Li, S. Chen, M. Yuan, Z. Lee, P. H. Leung, *Organometallics*, in press.

[14] a) E. J. Corey, J. C. Bailar, *J. Am. Chem. Soc.* **1959**, *81*, 2620–2629; b) M. D. Fryzuk, B. J. Bosnich, *J. Am. Chem. Soc.* **1977**, *99*, 6262–6267; c) P. A. MacNeil, N. K. Roberts, B. Bosnich, *J. Am. Chem. Soc.* **1981**, *103*, 2273–2280.

[15] L. Pauling, *The Nature of the Chemical Bond*; Cornell University Press, Ithaca, NY, **1967**.

[16] W. C. Yeo, L. Tang, B. Yan, S. Y. Tee, L. L. Koh, K. Geok, P. H. Leung, *Organometallics* **2005**, *24*, 5581–5585.

[17] a) E. Costa, P. G. Pringle, M. B. Smith, K. Worboys, *J. Chem. Soc., Dalton Trans.* **1997**, 4277–4282 and references cited therein; b) D. K. Wicht, I. V. Kourkine, I. Kovacik, D. S. Glueck, T. E. Concolino, G. P. A. Yap, C. D. Incarvito, A. L. Rheingold, *Organometallics* **1999**, *18*, 5381–5394; c) M. O. Shulyupin, M. A. Kazankova, I. P. Beletskaya, *Org. Lett.* **2002**, *4*, 761–763 and references cited therein; d) M. R. Douglass, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **2001**, *123*, 10221–10238; e) W. Malisch, B. Klüpfel, D. Schumacher, M. Nieger, *J. Organomet. Chem.* **2002**, *661*, 95–110; f) A. D. Sadow, A. Togni, *J. Am. Chem. Soc.* **2005**, *127*, 17012–17024; g) A. Kondoh, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2007**, *129*, 4099–4104; h) M. L. Bungabong, K. W. Tan, Y. Li, S. V. Selvaratnam, K. G. Dongol, P. H. Leung, *Inorg. Chem.* **2007**, *46*, 4733–4736.

[18] a) S. Y. M. Chooi, M. K. Tan, P. H. Leung, K. F. Mok, *Inorg. Chem.* **1994**, *33*, 3096–3103; b) M. Gomez, J. Granell, M. Martinez, *Organometallics* **1997**, *16*, 2539–2546; c) C. López, R. Bosque, D. Sainz, M. Font-Bardía, *Organometallics* **1997**, *16*, 3261–3266; d) M. Gomez, J. Granell, M. Martinez, *J. Chem. Soc., Dalton Trans.* **1998**, 37–44.

[19] S. Y. M. Chooi, P. H. Leung, C. C. Lim, K. F. Mok, G. H. Quek, K. Y. Sim, M. K. Tan, *Tetrahedron: Asymmetry* **1992**, *3*, 529–532.

[20] T. Bakó, P. Bakó, G. Keglevich, N. Báthori, M. Czugler, J. Tatai, T. Novák, G. Parlagh, L. Töke, *Tetrahedron: Asymmetry* **2003**, *14*, 1917–1923.

[21] S. D. Bull, S. G. Davies, D. J. Fox, M. Gianotti, P. M. Kelly, C. Pierres, E. D. Savory, A. D. Smith, *J. Chem. Soc. Perkin Trans. 1* **2002**, 1858–1868.

[22] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876–881.

Received: May 21, 2009
Published Online: August 10, 2009

