Journal of Organometallic Chemistry 693 (2008) 3289–3294

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Asymmetric synthesis of a chiral hetero-bidentate As–P ligand containing both As and P-stereogenic centres

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ARTICLE INFO

Article history:
Received 13 June 2008
Received in revised form 21 July 2008
Accepted 23 July 2008
Available online 31 July 2008

Keywords:
Asymmetric Diels–Alder reaction
Chiral As–P Ligand
Palladium complex

ABSTRACT

The organopalladium complex containing ortho-metalated (*S*)-[1-(dimethylamino)ethyl]naphthalene as the chiral auxiliary has been used as the chiral template to promote the asymmetric cycloaddition reaction between phenyldivinylphosphine and 3,4-dimethyl-1-phenylarsole. The reaction was completed in 1 h at room temperature, with the formation of two isomeric cycloadducts in the ratio 1:3. The major phenylvinylphosphino-substituted asymmetrical hetero-bidentate arsanorbornene ligand with chirality residing on both As and P centers was obtained stereoselectively on the chiral palladium template in moderate yield. The chiral heterobidentate ligand was isolated in its enantiomerically pure form by removal of the chiral auxiliary using concentrated hydrochloric acid and subsequent cleavage from the neutral complex [(As–P)$PdCl_2$] by using potassium cyanide. Similar to the earlier reported analogous diphenylphosphino-substituted asymmetrical heterobidentate arsanorbornene (As–P) ligand, an arsenic elimination process was also found in the dichloro and dibromo palladium complex whereas the diiodo species did not show similar reactivity, but the corresponding η^2 diiodo complex could be obtained from the η^2 dibromo complex by treatment with sodium iodide.

1. Introduction

Optically active heterobidentate ligands bearing two or more stereogenic centers offer enormous potential as chiral auxiliaries in asymmetric synthesis. Their utility in such scenarios is attributed mainly to their ability to exercise stereoelectronic control over the reactions of coordinated substrates. Although many reports on such compounds containing two dissimilar asymmetric donor atoms have been reported for chiral and non-chiral phosphine based ligands (mainly involving P and N/O/S) [1], a review of literature reveals that very few studies involving development of a heterobidentate As*–P* ligand system have been reported so far. It is also noteworthy that the sole report on such a ligand system utilized a method that involved multi-step separation and resolution of the antipodes by the method of metal complexation. For example, the well known optical resolution of 1-(methylphenylarsino)-2-(methylphenylphosphino)benzene required the somewhat difficult separation of the (R*, R*) and (R*, S*) diastereoisomers prior to the individual resolution of the two racemic diasteoreoisomers [2].

As part of our efforts to develop a more efficient procedure for achieving asymmetric ligand transformation reactions such as cycloaddition, hydroamination, hydrophosphination and hydroarsination, we have successfully employed an easily accessible orthometallated chiral amine auxiliary as a chiral template to achieve all the above goals with a wide variety of substrates [3]. We have also utilized this chiral template for the generation of the As–P* [4] as well as As*–P [5] systems wherein the chirality resides on either the phosphorus or arsenic centre as well as the carbon backbone. Interesting results including new insights into the influence of *trans* ligand in a novel arsine elimination process observed during the course of that study prompted us to attempt the challenging task of simultaneous generation of P and As chiral centers in an asymmetric manner thus providing a pathway for the development of a new class of compounds containing both As and P chiral centers associated with various functionalities. To our knowledge, no asymmetric synthesis involving the enantioselective generation of both As and P chiral centers has been reported in literature.

We herein report an efficient synthesis of a chiral heterobidentate As*–P* ligand *via* metal template promoted cycloaddition reaction between 3,4-dimethyl-1-phenylarsole (DMPA) and phenyldivinylphosphine. The norbornene based ligand system thus obtained is also useful for the study of the intricacies of the stability factors with respect to the As–C bond cleavage observed in our earlier studies.

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doi:10.1016/j.jorganchem.2008.07.029

2. Results and discussion

2.1. Metal template promoted asymmetric cycloaddition reaction between phenyldivinylphosphine and 3,4-dimethyl-1-phenylarsole

In contrast to those reported for their phosphorus analogues [6], cycloaddition reactions involving cyclic arsines are relatively rare in the literature [7]. The few reports involving attempted cycloaddition reactions of uncoordinated arsoles generally utilized high temperature and produced a mixture of products with resultant low yield [8]. We had earlier reported an alternative approach wherein the coordinated arsole can be activated to undergo asymmetric Diels–Alder reactions in the presence of a metal template. The metal template served the dual role of reaction promoter as well as chiral auxiliary during the course of the cycloaddition reaction. Considering the efficacy of that procedure, we decided to utilize the same methodology for the simultaneous generation of phosphorus and arsenic chiral centers in this novel [4 + 2] cycloaddition reaction between phenyldivinylphosphine and DMPA.

The cyclic arsine, DMPA, was coordinated regiospecifically to (+)-**1** to give monomeric neutral complex (+)-**2** as stable yellow prisms in 64% isolated yield, $[\alpha]_D$ +259.1° (*c* 0.6, CH_2Cl_2) (Scheme 1). The regioselectivity and molecular structure of (+)-**2** was confirmed by X-ray crystallography (Fig. 1). Selected bond lengths and angles are listed in Table 1. As observed in other analogous arsine complexes, the arsenic atom in DMPA is *trans* to the NMe_2 group by virtue of the hard soft donor preference exhibited by the chiral amine based auxiliary [4]. Treatment of the chloro complex (+)-**2** with silver perchlorate yielded the intermediate cationic perchlorate species in essentially quantitative yield [9]. This highly reactive species was not isolated and was treated directly with a stoichiometric amount of phenyldivinylphosphine. The Diels–Alder reaction was found to complete in an hour at room temperature. Prior to purification, the $^{31}P\{^1H\}$ NMR spectrum of the crude Diels–Alder reaction product in $CDCl_3$ exhibited two singlets at δ 49.0 and 48.6 in the ratio 1:3, respectively. The major diasteoreomer (−)-**3** could be separated by column chromatography as yellow solid in 56% yield, $[\alpha]_D$ −40.0° (*c* 0.6, CH_2Cl_2). Attempts to crystallize the complex as single crystals suitable for X-ray crystallographic studies were unsuccessful. The chiral amine auxiliary on (−)-**3** could however be removed from metal complex chemoselectively and efficiently using concentrated hydrochloric acid. The resultant neutral dichloro complex (−)-**4** was thus obtained as pale yellow needles in 72% yield, $[\alpha]_D$ −146.7° (*c* 0.6, CH_2Cl_2). The X-ray structural analysis of (−)-**4** confirmed that the desired cycloadduct

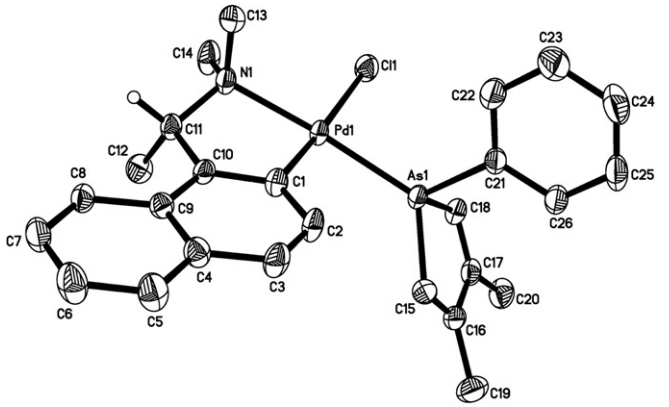
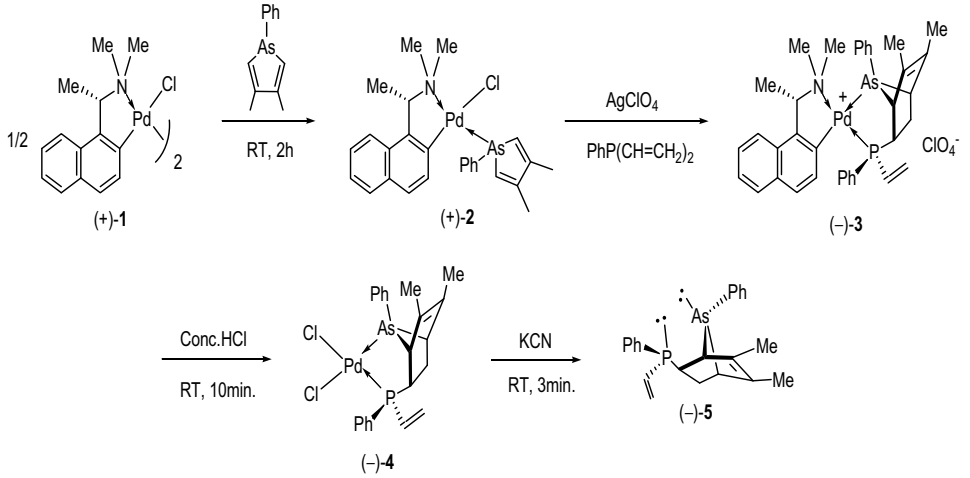


Fig. 1. Molecular structure of complex (+)-**2**.

Table 1
Selected bond lengths (Å) and angles (deg) for (+)-**2**

Pd(1)–C(1)	1.987(2)	Pd(1)–N(1)	2.128(2)
Pd(1)–As(1)	2.359(1)	Pd(1)–Cl(1)	2.410(1)
As(1)–C(15)	1.921(2)	As(1)–C(18)	1.906(2)
As(1)–C(21)	1.946(2)	C(15)–C(16)	1.337(3)
C(16)–C(17)	1.497(4)	C(16)–C(19)	1.501(4)
C(17)–C(18)	1.338(3)	C(17)–C(20)	1.503(3)
C(1)–Pd(1)–N(1)	81.1(1)	C(1)–Pd(1)–As(1)	95.4(1)
N(1)–Pd(1)–As(1)	175.8(1)	C(1)–Pd(1)–Cl(1)	173.6(1)
N(1)–Pd(1)–Cl(1)	96.5(1)	As(1)–Pd(1)–Cl(1)	87.2(1)
C(18)–As(1)–C(15)	87.4(1)	C(15)–C(16)–C(17)	115.6(2)
C(18)–C(17)–C(16)	115.1(2)	C(17)–C(18)–As(1)	111.3(2)

was formed with the norbornene skeletal framework coordinated to the Pd center through both As and P donors. The study also confirmed that the absolute configurations of the five new chiral centers formed at As(1), P(1), C(7), C(12) and C(14) are *R*, *S*, *R*, *R* and *S*, respectively (Fig. 2). Selected bond lengths and angles are listed in Table 2. In complex (−)-**4** the geometry at Pd is slightly distorted square-planar with angles at Pd in the ranges 82.7(1)–95.8(1) and 171.6(1)–174.8(1)°, the smallest of these former bond angles being associated with the bite of the novel As–P ligand. The Pd–As [2.320(1) Å] and Pd–P [2.246(1) Å] distances are unexceptional. The two Pd–Cl distances are similar [2.366(1) and 2.360(1) Å].



Scheme 1.

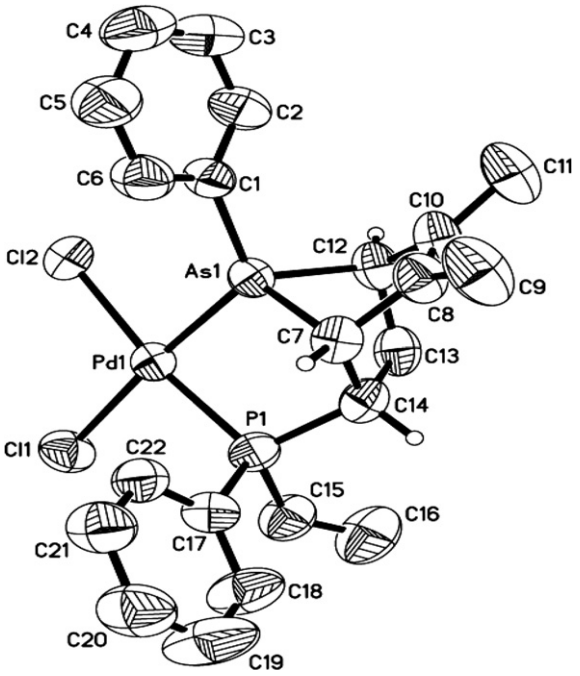


Fig. 2. Molecular structure of dichloro complex (−)-**4**.

Table 2
Selected bond lengths (Å) and angles (deg) for (−)-**4**

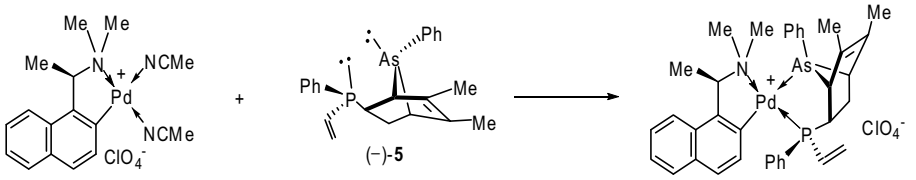
Pd(1)–Cl(1)	2.366(1)	Pd(1)–Cl(2)	2.360(1)
Pd(1)–As(1)	2.320(1)	Pd(1)–P(1)	2.246(1)
As(1)–C(12)	1.971(4)	As(1)–C(7)	1.974(4)
P(1)–C(15)	1.801(5)	P(1)–C(14)	1.853(5)
C(7)–C(8)	1.521(6)	C(7)–C(14)	1.556(6)
C(8)–C(10)	1.336(6)	C(10)–C(12)	1.514(6)
C(12)–C(13)	1.548(7)	C(13)–C(14)	1.554(6)
C(15)–C(16)	1.289(8)		
P(1)–Pd(1)–As(1)	82.7(1)	P(1)–Pd(1)–Cl(2)	171.6(1)
As(1)–Pd(1)–Cl(2)	89.4(3)	P(1)–Pd(1)–Cl(1)	92.1(1)
As(1)–Pd(1)–Cl(1)	174.8(1)	Cl(2)–Pd(1)–Cl(1)	95.8(1)
C(12)–As(1)–C(7)	77.4(2)	C(14)–C(7)–As(1)	94.9(2)
C(8)–C(7)–C(14)	111.9(3)	C(8)–C(7)–As(1)	100.9(3)
C(10)–C(8)–C(7)	111.7(4)	C(8)–C(10)–C(12)	112.0(4)
C(13)–C(12)–As(1)	98.9(3)	C(10)–C(12)–C(13)	107.4(4)
C(10)–C(12)–As(1)	100.6(3)	C(12)–C(13)–C(14)	107.6(3)
C(7)–C(14)–P(1)	107.3(3)	C(13)–C(14)–C(7)	106.2(3)
C(13)–C(14)–P(1)	109.2(3)		

Treatment of the dichloro complex (−)-**4** with aqueous potassium cyanide liberated the optically pure heterobidentate arsanorbornene ligand (−)-**5** as a white solid in 91% yield, $[\alpha]_D$ −40.8° (*c* 1.3, CH_2Cl_2). The $^{31}P\{^1H\}$ NMR spectrum of this liberated chiral free ligand in $CDCl_3$ exhibited a sharp singlet at δ −13.3. Owing to the configurational instability of the uncoordinated bridgehead arsenic stereogenic center, the liberated ligand was re-coordinated immediately to other selected metal ions. When (−)-**5** was coordinated to the enantiomeric bis(acetonitrile)[(*R*)-1-[1-(dimethylamino)-ethyl]-2-naphthalenyl-*C*,*N*] palladium(II) perchlorate, the $^{31}P\{^1H\}$ NMR spectrum of the crude product exhibited only one singlet at δ 46.5, which is attributed to the diastereomer that was not formed in the original cycloaddition reaction (Scheme 2). The signal due to the original major isomer was not detected thus confirming the optical purity of the isolated ligand.

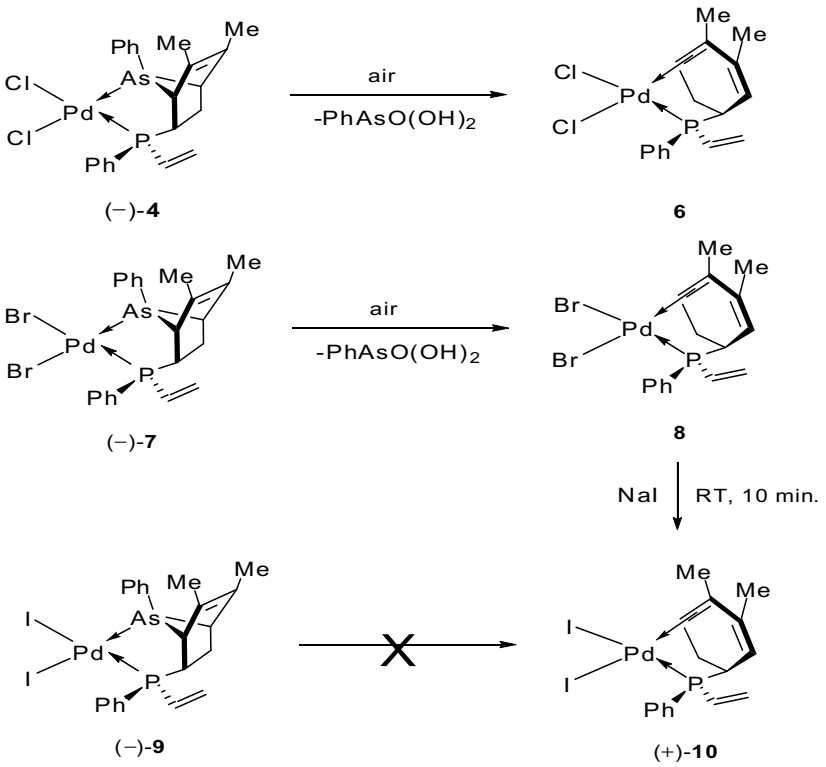
2.2. Arsenic elimination reaction

Recently, we have observed an interesting arsenic elimination process with the similar heterobidentate arsanorbornene (As–P) palladium complexes obtained from the cycloaddition reaction between DMPA and diphenylvinylphosphine. The *trans* ligand in these complexes appeared to affect the rate of the elimination process. These eliminations had led to the generation of an interesting 1-(diphenylphosphino)-3,4-dimethyl-2,4-cyclohexadiene ligand which coordinated to Pd *via* its phosphorous donor and the η^2-C–C bond. The present reaction allowed an opportunity to study the various factors affecting this process in further detail as well as the opportunity to develop such ligand systems further with introduction of additional chirality on the phosphine donor atoms. Previous work from our research group has given some indication that a concerted mechanism exists wherein two As–C bonds in the norbornene bridgehead system breaks along with the formation of the η^2-Pd coordination during the course of such elimination reactions.

Unlike in the case of our previous work, the complex (−)-**4** was found to convert with difficulty into the possible analogous retrodiene complex **6** (Scheme 3). From the analysis of the $^{31}P\{^1H\}$ NMR spectrum of (−)-**4** in $CDCl_3$, we found that its $^{31}P\{^1H\}$ NMR value shifted from δ 34.0 to 135.9 over a period of 17 days at room temperature indicating the formation of complex **6**. Further evidence for the formation of the complex was obtained from the ^1H NMR spectrum in which we observed the two new hydrogen signals of the retrodiene complex at δ 5.6 (doublet) and 6.0 (singlet), respectively. Another proof was obtained by the isolation of phenylarsonic acid from the reaction system which confirmed that the arsenic elimination process has indeed occurred. The dichloro complex (−)-**4** was treated with potassium bromide for 10 min at room temperature and the analogous dibromo complex (−)-**7** was obtained as yellow solid in 90% yield, $[\alpha]_D$ −146.7° (*c* 0.6, CH_2Cl_2). The $^{31}P\{^1H\}$ NMR spectrum exhibited only one signal at δ 35.0 indicating the absence of any side reaction. This complex was subsequently recrystallized with $CHCl_3$–Et_2O to give the product as yellow needle crystals. The molecular structure of (−)-**7** was confirmed by X-ray crystallography (Fig. 3). Selected bond lengths and angles are listed in Table 3. Unfortunately, the arsenic elimination product arising from complex (−)-**7**, viz., complex **8**, could not be isolated by fractional crystallization or by column chromatography using a wide range of solvent systems. Finally, the dichloro complex (−)-**4** was converted into the analogous diiodo derivative (−)-**9** by treatment of the dichloro complex with sodium iodide. The diiodo complex was isolated as yellow solid in 95% yield, $[\alpha]_D$ −97.8° (*c* 0.5, CH_2Cl_2). Similar to the reported analogous diphenylphosphino-substituted asymmetrical heterobidentate arsanorbornene complex [(As–P)PdI_2], the arsenic elimination reaction in this case did not occur when the diiodo complex (−)-**9** was dissolved in solution. On the contrary the complex



Scheme 2.



Scheme 3.

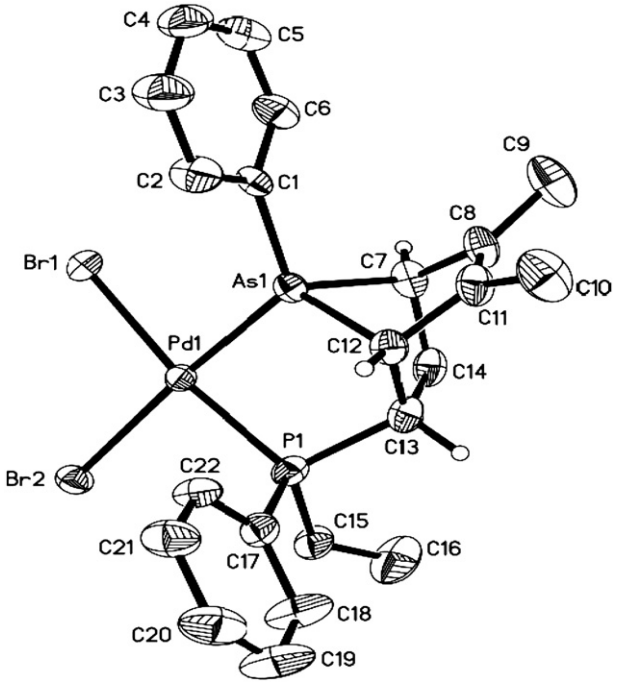


Fig. 3. Molecular structure of dibromo complex (−)-**7.**

Table 3
Selected bond lengths (Å) and angles (deg) for (−)-**7**

Pd(1)–Br(1)	2.481(1)	Pd(1)–Br(2)	2.492(1)
Pd(1)–As(1)	2.328(1)	Pd(1)–P(1)	2.256(1)
As(1)–C(12)	1.973(4)	As(1)–C(7)	1.982(5)
P(1)–C(15)	1.797(5)	P(1)–C(13)	1.853(5)
C(7)–C(8)	1.528(6)	C(7)–C(14)	1.540(7)
C(8)–C(11)	1.338(8)	C(11)–C(12)	1.513(7)
C(12)–C(13)	1.556(7)	C(13)–C(14)	1.577(8)
C(15)–C(16)	1.307(8)		
P(1)–Pd(1)–As(1)	82.8(1)	P(1)–Pd(1)–Br(1)	171.2(1)
As(1)–Pd(1)–Br(1)	89.1(1)	P(1)–Pd(1)–Br(2)	92.8(1)
As(1)–Pd(1)–Br(2)	175.4(1)	Br(1)–Pd(1)–Br(2)	95.4(1)
C(12)–As(1)–C(7)	77.5(2)	C(14)–C(7)–As(1)	99.4(3)
C(8)–C(7)–C(14)	107.4(4)	C(8)–C(7)–As(1)	99.7(3)
C(11)–C(8)–C(7)	112.1(5)	C(8)–C(11)–C(12)	111.7(4)
C(13)–C(12)–As(1)	94.8(3)	C(11)–C(12)–C(13)	111.7(4)
C(11)–C(12)–As(1)	101.8(3)	C(14)–C(13)–P(1)	110.0(3)
C(12)–C(13)–C(14)	106.0(4)	C(12)–C(13)–P(1)	107.9(3)
C(7)–C(14)–C(13)	107.1(4)		

decomposed rapidly in solution. But interestingly, the retrodiene diiodo complex (+)-**10** was subsequently obtained *via* an alternate pathway. This involved treatment of complex **8** with sodium iodide for 10 min at room temperature. The complex (+)-**10** thus obtained was isolated by column chromatography in 55% yield, $[\alpha]_D$ +756.7° (*c* 0.3, CH_2Cl_2). It is noteworthy that the rate of arsenic elimination reaction in (−)-**4** apparently decelerated relative to the analogous complex obtained *via* cycloaddition between diphenylvinylphosphine and DMPA in our earlier studies. The reason can be attributed to the fact that the two As–C bonds [1.971(4) and 1.974(4) Å] within the arsanorbornene skeleton of (−)-**4** are significantly symmetrical than that of the analogue [1.961(3) and 1.980(3) Å]. The deviance between the two As–C bond distances in the latter (0.019 Å) is much bigger than that of the former (0.003 Å), thus resulting in an enhanced configurational instability in the analogue compared to that of (−)-**4**.

In conclusion, we have synthesized a new chiral heterobidentate As–P ligand containing both As and P-stereogenic centers *via* a facile metal template promoted cycloaddition reaction. This has provided us with an avenue for the synthesis of a new class of heterobidentate ligand system which can incorporate various functionalities. We have also obtained a better understanding of the arsenic elimination process occurring in such systems leading to the formation of the novel chiral phosphine-olefin ligand. It needs to be noted that such

chiral phosphine-olefin systems themselves are assuming importance as "spectator" ligands in catalysis [10].

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 ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 25 °C on Bruker Avance 300 and 400 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 are uncorrected.

Phenyldivinylphosphine [11], DMPA [12] and (+)-**1** [13] were prepared according to the literature procedures.

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

3.1. Preparation of complex (+)-*2*

A mixture of DMPA (1.15 g, 4.95 mmol) and (+)-**1** (1.68 g, 2.47 mmol) in dichloromethane (80 mL) was stirred at room temperature for 2 h. The solvent was removed from the reaction mixture, and the complex (+)-**2** was isolated by column chromatography on a silica column with dichloromethane–*n*-hexane to give a yellow solid, which was recrystallized from chloroform–*n*-hexane in the form of bright yellow prisms (1.81 g, 64%). $[\alpha]_D$ = +259.1° (*c* 0.6, CH_2Cl_2). M.p.: 168–169 °C. Anal. Calc. for $C_{26}H_{29}AsClNPd$: C, 54.6; H, 5.1; N, 2.5. Found: C, 54.5; H, 4.9; N, 2.6%. ^1H NMR ($CDCl_3$, δ): 1.92 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CHCH_3), 2.08 (s, 3H, =CCH_3), 2.11 (s, 3H, =CCH_3), 2.88 (s, 3H, NCH_3), 2.95 (s, 3H, NCH_3), 4.35 (q, $^3J_{HH}$ = 6.4 Hz, 1H, *CH*CH_3), 6.69 (s, 1H, As*CH*), 6.97 (s, 1H, As*CH*), 7.18–7.82 (m, 11H, aromatics).

3.2. Cycloaddition reaction: preparation of complex (−)-*3*

A solution of (+)-**2** (0.67 g, 1.17 mmol) in dichloromethane (60 mL) was stirred for 2 h in the presence of a solution of silver perchlorate (0.39 g) in water (1 mL). The organic layer, after the removal of AgCl then washed with water (3 × 60 mL), dried ($MgSO_4$) and subsequently treated with phenyldivinylphosphine (0.19 g, 1.17 mmol) at room temperature for 1 h. The solvent was removed from the reaction mixture and the complex (−)-**3** was isolated by column chromatography on a silica column with dichloromethane–diethyl ether, to give a yellow solid (0.52 g, 56%). $[\alpha]_D$ = −40.0° (*c* 0.6, CH_2Cl_2). M.p.: 166–167 °C. Anal. Calc. for $C_{36}H_{40}AsClNO_4PPd$: C, 54.2; H, 5.0; N, 1.8. Found: C, 53.8; H, 5.2; N, 1.8%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 48.6. ^1H NMR ($CDCl_3$, δ): 1.33 (s, 3H, =CCH_3), 1.64 (s, 3H, =CCH_3), 1.95 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CHCH_3), 2.14 (ddd, $^3J_{HH}$ = 20.3, $^2J_{HH}$ = 9.8 Hz, $^3J_{HH}$ = 3.7 Hz, 1H, CHCH_2), 2.61 (s, 1H, As*CH*), 2.68 (m, 1H, CHCH_2), 2.75 (s, 3H, NCH_3), 2.85 (m, 1H, P*CH*), 2.89 (d, $^4J_{PH}$ = 2.6 Hz, 3H, NCH_3), 3.77 (s, 1H, As*CH*), 4.42 (qn, $^3J_{HH}$ = $^4J_{PH}$ = 5.9 Hz, 1H, *CH*CH_3), 6.15 (dd, $^3J_{PH}$ = 21.9, $^3J_{HH}$ = 4.2 Hz, 1H, =CH_2), 6.24 (dd, $^3J_{PH}$ = 34.7, $^3J_{HH}$ = 11.9 Hz,1H, =CH_2), 6.72 (ddd, $^2J_{PH}$ = 16.4, $^3J_{HH}$ = 12.0, $^3J_{HH}$ = 4.4 Hz, 1H, =C*H*), 6.80–8.15 (m, 16H, aromatics).

3.3. Removal of chiral auxiliary: synthesis of complex (−)-*4*

The complex (−)-**3** (0.21 g, 0.26 mmol) was dissolved in dichloromethane (60 mL) and treated with excess concentrated hydrochloric acid (2 mL) at room temperature for 10 min. The mixture was then washed with water (3 × 60 mL), dried ($MgSO_4$), and subsequently recrystallized from chloroform–diethyl ether as pale yellow needle crystals (−)-**4** (0.13 g, 72%). $[\alpha]_D$ = −146.7° (*c* 0.6, CH_2Cl_2). M.p.: 191–192 °C. Anal. Calc. for $C_{22}H_{24}AsCl_2PPd \cdot CHCl_3$: C, 40.0; H, 3.7. Found: C, 39.9; H, 3.6%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 34.0. ^1H NMR ($CDCl_3$, δ): 1.56 (s, 3H, =CCH_3), 1.67 (d, $^5J_{PH}$ = 0.9 Hz, 3H, =CCH_3), 2.12 (ddd, $^3J_{HH}$ = 21.6, $^2J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 3.1 Hz, 1H, CHCH_2), 2.68 (m, 1H, CHCH_2), 2.78 (m, 1H, P*CH*), 2.86 (s, 1H, As*CH*), 3.54 (d, $^3J_{HH}$ = 3.0 Hz, 1H, As*CH*), 6.22 (dd, $^3J_{PH}$ = 20.9, $^3J_{HH}$ = 18.4 Hz, 1H, =CH_2), 6.33 (dd, $^3J_{PH}$ = 31.4, $^3J_{HH}$ = 12.4 Hz,1H, =CH_2), 6.83 (ddd, $^2J_{PH}$ = 23.0, $^3J_{HH}$ = 18.3, $^3J_{HH}$ = 12.4 Hz, 1H, =C*H*), 7.39–8.11 (m, 10H, aromatics).

3.4. Liberation of the (As–P) ligand (−)-*5*

A solution of (−)-**4** (0.10 g, 0.14 mmol) in dichloromethane (20 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1.0 g) for 3 min. The organic layer was separated, then washed with water (3 × 20 mL) and dried ($MgSO_4$). Upon removal of the solvent, the free ligand (−)-**5** was obtained as an air-sensitive white solid (0.05 g, 91%). $[\alpha]_D$ = −40.8° (*c* 1.3, CH_2Cl_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −13.3.

3.5. Preparation of the dibromo complex (−)-*7*

The solution of (−)-**4** (0.07 g, 0.10 mmol) in dichloromethane (50 mL) was added to potassium bromide (0.05 g) in acetone (50 mL) and water (10 mL) and stirred vigorously for 10 min. The organic solvents were removed and the residue was extracted with dichloromethane and water, dried with $MgSO_4$, Removal of solvent gave (−)-**7** as a solid, which was then recrystallized from chloroform–diethyl ether to give the product as yellow needle crystals (0.07 g, 90%). $[\alpha]_D$ = −146.7° (*c* 0.6, CH_2Cl_2). M.p.: 188–189 °C. Anal. Calc. for $C_{22}H_{24}AsBr_2PPd{\cdot}CHCl_3$: C, 35.4; H, 3.2. Found: C, 35.9; H, 3.4%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 35.0. ^1H NMR (CD_2Cl_2, δ): 1.47 (s, 3H, =CCH_3), 1.65 (d, $^5J_{PH}$ = 1.0 Hz, 3H, =CCH_3), 2.15 (ddd, $^3J_{HH}$ = 22.3, $^2J_{HH}$ = 10.6 Hz, $^3J_{HH}$ = 3.3 Hz, 1H, CHCH_2), 2.68 (m, 1H, CHCH_2), 2.76 (m, 1H, P*CH*), 2.87 (s, 1H, As*CH*), 3.59 (d, $^3J_{HH}$ = 3.2 Hz, 1H, As*CH*), 6.17 (dd, $^3J_{PH}$ = 20.4, $^3J_{HH}$ = 18.5 Hz, 1H, =CH_2), 6.33 (dd, $^3J_{PH}$ = 42.3, $^3J_{HH}$ = 12.4 Hz,1H, =CH_2), 6.92 (ddd, $^2J_{PH}$ = 23.8, $^3J_{HH}$ = 18.5, $^3J_{HH}$ = 12.4 Hz, 1H, =C*H*), 7.45–8.06 (m, 10H, aromatics).

3.6. Synthesis of the diiodo complex (−)-*9*

The solution of (−)-**4** (0.05 g, 0.07 mmol) in dichloromethane (30 mL) was mixed with sodium iodide (0.1 g) in acetone (30 mL) and stirred vigorously for 10 min. The solvents were removed and the residue was extracted with dichloromethane. The solvent was removed from the reaction mixture and the complex (−)-**9** was isolated by column chromatography on a silica column with dichloromethane, to give a yellow solid (0.05 g, 95%). $[\alpha]_D$ = −97.8° (*c* 0.5, CH_2Cl_2). M.p.: 178–179 °C. Anal. Calc. for $C_{22}H_{24}AsI_2PPd$: C, 35.0; H, 3.2. Found: C, 34.6; H, 3.0%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 34.8. ^1H NMR ($CDCl_3$, δ): 1.45 (s, 3H, =CCH_3), 1.65 (d, $^5J_{PH}$ = 0.8 Hz, 3H, =CCH_3), 2.12 (ddd, $^3J_{HH}$ = 21.6, $^2J_{HH}$ = 9.6 Hz, $^3J_{HH}$ = 3.4 Hz, 1H, CHCH_2), 2.61 (m, 1H, P*CH*), 2.78 (m, 1H, CHCH_2), 2.75 (d, $^3J_{PH}$ = 1.9 Hz, 1H, As*CH*), 3.54 (d, $^3J_{HH}$ = 2.9 Hz, 1H, As*CH*), 6.06 (dd, $^3J_{PH}$ = 19.0, $^3J_{HH}$ = 18.8 Hz, 1H, =CH_2), 6.24 (dd, $^3J_{PH}$ = 40.7, $^3J_{HH}$ = 12.4 Hz,1H, =CH_2), 7.05 (ddd, $^2J_{PH}$ = 24.3, $^3J_{HH}$ = 18.4, $^3J_{HH}$ = 12.4 Hz, 1H, =C*H*), 7.40–8.01 (m, 10H, aromatics).

3.7. Arsenic-elimination reaction: isolation of complex (+)-*10*

The complex (−)-**7** (0.01 g, 0.013 mmol) was dissolved in dichloromethane (40 mL) and allowed to stir at room temperature for 8 days. Then sodium iodide (0.05 g) in acetone (40 mL) was added and stirred vigorously for 10 min. The solvents were

Table 4
Crystallographic data for complexes (+)-**2**, (−)-**4** and (−)-**7**

	(+)-**2**	(−)-**4**	(−)-**7**
Formula	$C_{26}H_{29}AsClNPd$	$C_{22}H_{24}AsCl_2PPd{\cdot}CHCl_3$	$C_{22}H_{24}AsBr_2PPd{\cdot}CHCl_3$
Formula weight	572.27	690.97	779.89
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
a (Å)	9.0856(2)	10.1493(3)	10.2852(3)
b (Å)	11.1569(3)	15.0866(4)	14.9894(5)
c (Å)	23.3671(6)	17.9988(5)	18.0683(5)
V (Å^3)	2368.66(10)	2755.95(13)	2785.57(15)
Z	4	4	4
T (K)	173(2)	296(2)	173(2)
D_{calcd} (g cm^{-3})	1.605	1.665	1.860
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	2.296	2.418	5.070
F(000)	1152	1368	1512
Flack param	0.006(6)	−0.002(10)	0.016(8)
R_1 (obs data)[a]	0.0195	0.0351	0.0374
wR_2 (obs data)[b]	0.0438	0.0846	0.0828

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

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

removed and the residue was extracted with dichloromethane. The complex (+)-**10** was isolated by column chromatography on a silica column with dichloromethane, to give a solid (4 mg, 52%). $[\alpha]_D$ = +756.7° (*c* 0.3, CH_2Cl_2). M.p.: 126–127 °C. Anal. Calc. for $C_{16}H_{19}I_2PPd$: C, 31.9; H, 3.2. Found: C, 32.0; H, 3.3%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 130.9. ^1H NMR ($CDCl_3$, δ): 1.84 (s, 3H, =CCH_3), 2.26 (m, 2H, CHCH_2), 2.51 (s, 3H, =CCH_3), 2.97 (s, 1H, PCH), 5.56 (d, $^3J_{HH}$ = 6.6 Hz, 1H, =CH), 6.18 (m, 1H, =CH), 6.30 (m, 2H, =CH_2), 6.69 (m, 1H, =CH), 7.40–7.69 (m, 5H, aromatics).

3.8. X-ray crystal structure determination of complexes (+)-2, (−)-4 and (−)-7

Crystal data for all complexes and a summary of the crystallographic analysis are given in Table 4. Diffraction data were collected on a Bruker X8 CCD diffractometer with Mo Kα radiation (graphite monochromator). SA-DABS absorption corrections were applied. 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.

Supplementary material

CCDC 691269, 691270 and 691271 contains the supplementary crystallographic data for (+)-**2**, (−)-**4** and (−)-**7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank Nanyang Technological University for support of this research and for a scholarship to Ma M.T.

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