DOI: 10.1002/ejic.201100208

Synthesis of Homo- and Hetero-Bimetallic Arsenic Complexes by Means of Regioselective Monoinsertion of Alkynylarsane into the Pd–C Bond of a Palladacycle

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

Keywords: Insertion / Arsenic / As ligands / Palladium / Platinum / Metallacycles / Bimetallic complexes

Cyclopalladated and cycloplatinated complexes, which incorporated the *N*,*N*-dimethylbenzylamine and *N*,*N*-dimethylnaphthylamine motifs, were successfully employed to promote a series of intermolecular monoinsertion reactions of diphenyl-1-propynylarsane, $Ph_2AsC{\equiv}CMe$, into the Pd–C bond of the chiral α-methyl *N*,*N*-dimethylbenzylamine palladacycles. The precursor complexes were prepared by means of the coordination of the $Ph_2AsC{\equiv}CMe$ moiety onto the metal center *trans* to the benzylamine– or naphthylamine–N donor atom of the cyclometallated complexes. Subsequently a series of monoinsertion reactions were carried out between these precursor complexes and the enantiomerically pure *N*,*N*-dimethyl benzylamine palladacycles. These insertion reactions showed high regioselectivity under mild conditions and a variety of homo- and heterobimetallic arsenic functionalized complexes were formed. The coordination chemistry and the absolute stereochemistry of the monoinsertion products were determined by X-ray crystallography.

Introduction

It is well known that arsenic forms weaker bonds with the metal centers than phosphorus does due to its inherently poorer σ-donor and π-acceptor properties. Although the reactivity of the arsenic ligands has been explored less than that of their phosphane counterparts, the arsane ligands offer some advantages over the phosphane analogues. For instance, tertiary arsanes have reduced air-sensitivity, increased pyramidal stability, and are easier to recover from the arsonium salts and metal complexes than their phosphane analogues.[1] Furthermore, the arsane-based ligands have more synthetic applications in the generation of nucleophilic arsonium ylides than the corresponding phosphonium ylides[2] and they are easily recycled for reuse after immobilization onto a polymer support.[3] Compared with the structurally analogous phosphanes, the use of the arsane ligands has proved more advantageous in a variety of palladium-catalyzed cross-coupling reactions, which include the Stille coupling reactions,[4] the Suzuki couplings,[3c,5] and the Heck couplings.[5b,6]

Our group has previously applied chiral cyclometallated amine complexes as efficient chiral auxiliaries that promote a series of asymmetric transformations, like Diels–Alder reactions,[7] hydroamination reactions,[8] hydroarsination reactions,[9] and hydrophosphination reactions,[10] in order to synthesize chiral phosphanes. More recently, we have reported the insertion of dialkynylphosphane into the Pd–C bond of *ortho*-palladated benzylamine, which was activated by a ruthenium complex, or cyclopalladated/platinated naphthylamine templates to form bimetallic complexes.[11] The study of the insertion of alkynes into the Pd–C bond of the *ortho*-palladated complexes has attracted great interest in organic synthesis since the formation of C–C bonds by the insertion of an alkyne into a Pd–C bond can lead to substituted olefins with a high degree of regio- and stereocontrol.[12] Moreover, after depalladation these insertion products can provide novel heterocyclic compounds that would be otherwise hard to achieve by conventional organic synthetic methodology.[13] It should be noted that studies on alkynylphosphanes, which were focused towards C–H bond activation or insertion into the M–C bond, have also attracted interest.[14] In view of the aforementioned attributes of the arsane ligands and their relatively unexplored chemistry in the insertion scenario in comparison to their P analogues, we aim to extend our exploration into the application of the cyclometallated–amine complexes for transformations that involve the insertion of the arsane-functionalized alkynes into Pd–C bonds. We herein report on the efficiency of the cyclopalladated and cycloplatinated benzylamine/naphthylamine metallacycles in promoting a series of intermolecular monoinsertion reactions of diphenylalkynylarsane, $Ph_2AsC{\equiv}CMe$, into the Pd–C bond of an enantiomerically pure *ortho*-palladated benzylamine with high regioselectivity under mild conditions to provide a variety of novel chiral homo- and heterobimetallic arsenic-functionalized complexes. To the best of our knowledge, this is

[a] Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University,
Singapore 637616, Singapore
E-mail: pakhing@ntu.edu.sg

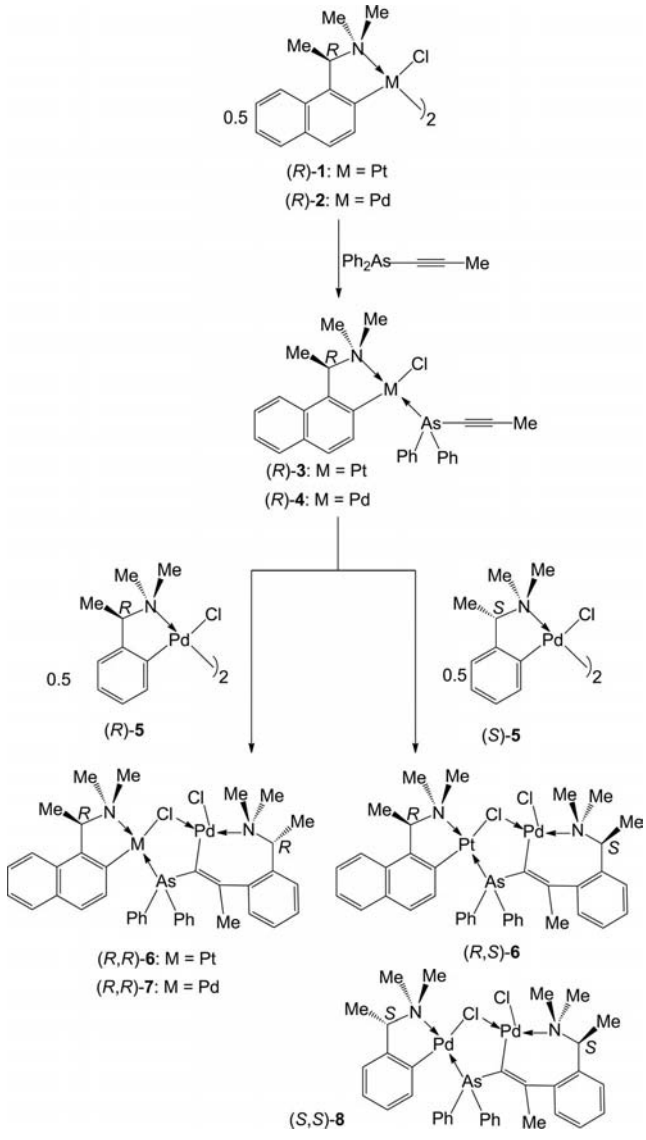
the first report of an insertion reaction that involves an arsenic-functionalized alkyne moiety into an M–C bond that led to the selective formation of the enlarged bimetallic heterocyclic rings.

Results and Discussion

Monoinsertion Reactions of the Alkynylarsane-Bearing Cycloplatinated Naphthylamine Complex

As illustrated in Scheme 1, the preliminary reaction involved the preparation of the precursor complex (R_c)-**3** by treatment of diphenyl-1-propynylarsane, $Ph_2AsC{\equiv}CMe$, with the dimeric naphthylamine platinum(II) complex, (R_c)-**1**. Due to the unique electronic directing effects that originate from the π-accepting aromatic carbon and the σ-donating nitrogen donor of the *ortho*-palladated naphthylamine ring, the monodentate arsane ligand split the chlorine bridge in the dimeric (R_c)-**1** and regioselectively coordinated to the *ortho*-palladated naphthylamine complex in the *trans* position to the naphthylamine–*N* donor atom to form the monomeric chloro complex (*R*)-**3**.[15] The monoinsertion reaction between the naphthylamine platinum(II) complex, (*R*)-**3**, and half an equivalent of the benzylamine palladium(II) dimer, (*R*)-**5**, was subsequently carried out at room temperature by using CH_2Cl_2 as the solvent (Scheme 1). This reaction was monitored by thin layer chromatography (TLC) as well as ^1H NMR spectroscopy, which showed that only one product formed, and the reaction was found to be complete in 5 d at room temp. The crude reaction mixture was purified by column chromatography and was subsequently crystallized from an acetone/hexane solution to give complex (*R*,*R*)-**6** as yellowish-orange crystals in 86% yield.

The single-crystal X-ray diffraction structural analysis of complex (*R*,*R*)-**6** unambiguously established that the desired monoinsertion product had been formed. As shown in Figure 1, the carbon–carbon triple bond of the alkynylarsane bond, C(15)–C(16), was inserted into the palladium–carbon bond, Pd(1)–C(27), of the cyclopalladated benzylamine dimer, (*R*)-**5**, to form a new carbon–carbon bond, C(16)–C(27), together with a new metal–carbon bond between Pd(1) and C(15). The C(15)–C(16) bond was consequently changed from C≡C to C=C. The ring expansion by the insertion of one carbon–carbon triple bond from the alkynylarsane into the palladium–carbon bond of cyclopalladated complex (R_c)-**5** led to the formation of a new stable seven-membered ring. Furthermore, the platinum and palladium centers are bridged by the Cl atom to give a new five-membered bimetallic heterocycle, in which the arsenic donor atom is coordinated regiospecifically in the *trans* position to the naphthylamine–*N* donor atom with a Pt–As bond length of 2.339(1) Å. Moreover, as expected, the absolute configuration of the stereocenters at C(11) and C(21) remained unchanged over the course of the insertion reaction. It should be noted that this monoinsertion reaction is highly regioselective as the methyl group of the alkynylarsane is located exclusively at the position next to the



Scheme 1.

phenyl ring of the benzylamine. The geometry at the platinum and palladium centers are slightly distorted square planar for complex (*R*,*R*)-**6**. The C(15)–C(16) bond length in (*R*,*R*)-**6** [1.339(9) Å] clearly indicated that it is a C=C bond. Table 1 shows the selected bond lengths and angles for complex (*R*,*R*)-**6**.

In order to obtain further evidence in support of the monoinsertion of the alkynylarsane into the Pd–C bond of cyclopalladated benzylamine, a similar insertion reaction was performed between the naphthylamine platinum(II) complex (*R*)-**3** and half an equivalent of the benzylamine palladium(II) dimer (*S*)-**5** at room temperature in CH_2Cl_2 (Scheme 1) and the reaction was found to be complete in 6 d. Similar to the insertion reaction between complexes (*R*)-**3** and (*R*)-**5**, only one single product was formed in the crude reaction mixture, which was then purified by column chromatography and was subsequently crystallized from an acetone/hexane solution to give complex (*R*,*S*)-**6** as yellowish-orange crystals in 80% yield.

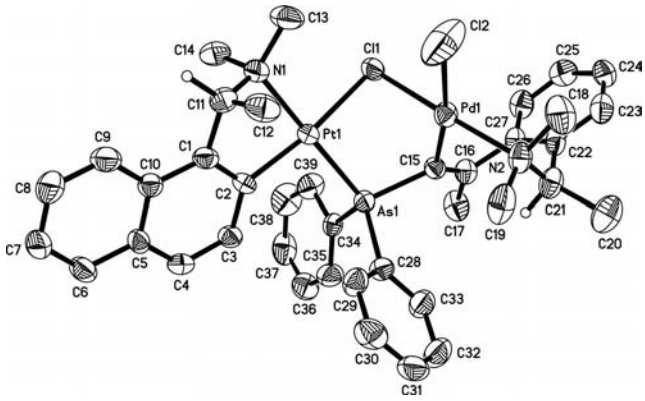


Figure 1. The molecular structure of complex (*R*,*R*)-**6**.

Table 1. The selected bond lengths [Å] and angles [°] for complexes (*R*,*R*)-**6** and (*R*,*S*)-**6**.

	(*R*,*R*)-**6**	(*R*,*S*)-**6**
Pd(1)–C(2)	1.987(6)	2.006(4)
Pt(1)–N(1)	2.105(6)	2.113(4)
Pt(1)–As(1)	2.339(1)	2.345(1)
Pt(1)–Cl(1)	2.405(2)	2.390(1)
Pd(1)–C(15)	1.977(6)	1.996(4)
Pd(1)–N(2)	2.123(6)	2.138(4)
Pd(1)–Cl(1)	2.355(2)	2.339(1)
Pd(1)–Cl(2)	2.405(2)	2.447(1)
C(15)–C(16)	1.339(9)	1.334(6)
C(2)–Pt(1)–N(1)	81.4(2)	80.7(2)
C(2)–Pt(1)–As(1)	98.8(2)	98.6(1)
N(1)–Pt(1)–As(1)	178.0(2)	175.6(1)
C(2)–Pt(1)–Cl(1)	171.8(2)	174.7(1)
N(1)–Pt(1)–Cl(1)	93.6(2)	94.0(1)
As(1)–Pt(1)–Cl(1)	86.4(1)	86.7(1)
C(15)–Pd(1)–N(2)	92.5(2)	95.0(2)
C(15)–Pd(1)–Cl(1)	83.5(2)	86.3(1)
N(2)–Pd(2)–Cl(1)	173.2(2)	170.8(1)
C(15)–Pd(1)–Cl(2)	170.7(2)	167.0(1)
N(2)–Pd(1)–Cl(2)	94.8(2)	92.7(1)
Cl(1)–Pd(1)–Cl(2)	89.8(1)	87.8(1)
Pd(1)–Cl(1)–Pt(1)	88.3(1)	105.6(1)

The single-crystal X-ray diffraction structural analysis of complex (*R*,*S*)-**6** confirmed the formation of the expected monoinsertion product by means of the insertion of the carbon–carbon triple bond of the alkynylarsane bond, C(15)–C(16), into the palladium–carbon bond, Pd(1)–C(27), of the cyclopalladated benzylamine dimer, (*S*)-**5** (Figure 2). This was accompanied by the formation of two new bonds, C(16)–C(27) and Pd(1)–C(15), and an enlarged seven-membered ring was generated with high regioselectivity, which is similar to what was observed in the formation of the monoinsertion product, complex (*R*,*R*)-**6**. The absolute configuration of the stereocenters at C(11) and C(21) remained unchanged as *R* and *S*, respectively. The Pt–As bond is 2.345(1) Å, which is comparable to that of complex (*R*,*R*)-**6**. The geometry at the platinum and palladium centers are slightly distorted square planar for complex (*R*,*S*)-**6**. The C(15)–C(16) bond length in (*R*,*S*)-**6** [1.334(6)] clearly indicated that it is a C=C bond. Table 1 shows the selected bond lengths and angles for complex (*R*,*S*)-**6**.

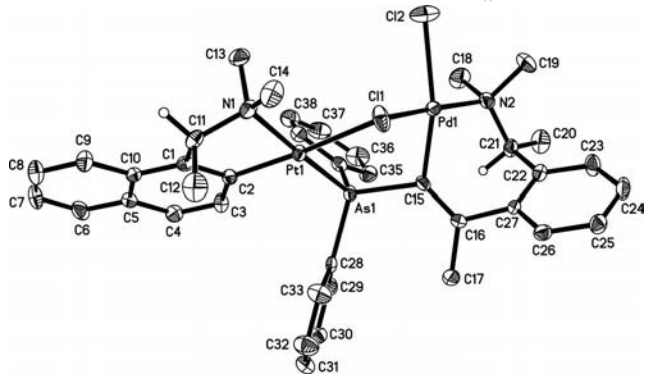


Figure 2. The molecular structure of complex (*R*,*S*)-**6**.

Monoinsertion Reactions of the Alkynylarsane-Bearing Cyclopalladated Naphthylamine Complex

In order to investigate the metal effect that arises from palladium and platinum, the platinum naphthylamine template, (*R*)-**1**, was replaced by the analogous chiral palladium naphthylamine template, (*R*)-**2**, to perform two more insertion reactions. As illustrated in Scheme 1, complex (*R*)-**4** was separately treated with half an equivalent of the benzylamine palladium(II) dimers, (*R*)-**5** and (S_c)-**5**, at room temperature in CH_2Cl_2 and the reactions were found to be complete in 3 and 2 d, respectively, which is much faster than the reaction that involved the platinum analogue. After purification by column chromatography and crystallization from acetone/hexane, complex (*R*,*R*)-**7** was obtained as yellowish-orange crystals. The X-ray structural analysis of complex (*R*,*R*)-**7** confirmed the formation of the monoinsertion dipalladium product by means of the insertion of the carbon–carbon triple bond of alkynylarsane into the Pd–C bond of benzylamine compex (*R*)-**5** (Figure 3). Dipalladium complex (*R*,*R*)-**7** and its platinum analogue, (*R*,*R*)-**6**, are isostructural. The Pd–As bond length is 2.353(1) Å, which is consistent with the literature report.[16] Table 2 shows the selected bond lengths and angles of complex (*R*,*R*)-**7**.

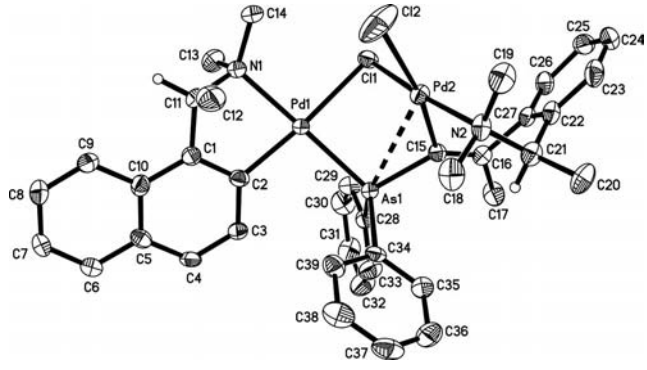


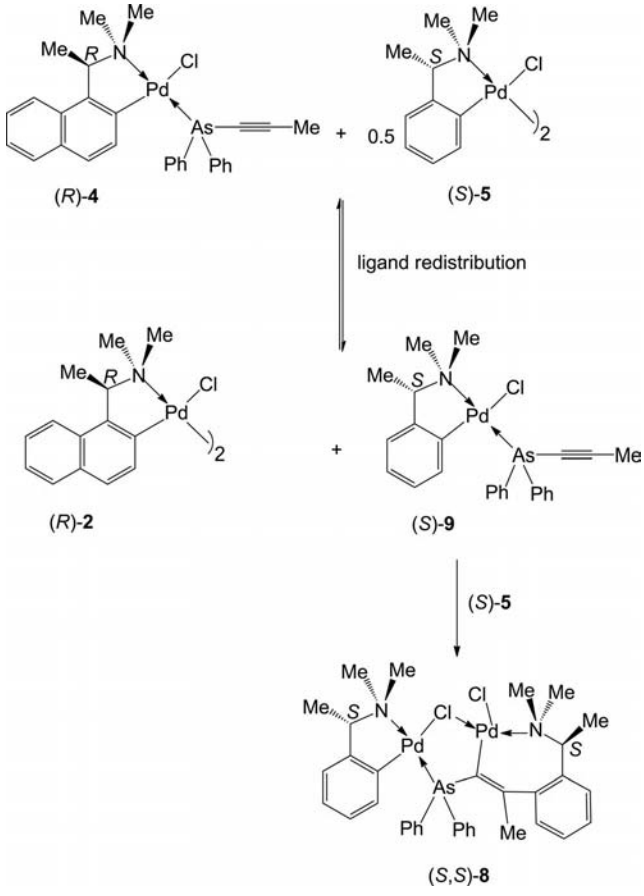
Figure 3. The molecular structure of complex (*R*,*R*)-**7**.

The insertion reaction that involved (*R*)-**4** and (*S*)-**5**, however, did not yield the desired insertion product. After purification of the crude reaction mixture by column chromatography, dimeric naphthylamine palladium(II)

Table 2. The selected bond lengths [Å] and angles [°] for complex (*R*,*R*)-**7**.

Pd(1)–C(2)	1.990(4)	N(1)–Pd(1)–As(1)	177.1(1)
Pd(1)–N(1)	2.127(3)	C(2)–Pd(1)–Cl(1)	171.9(1)
Pd(1)–As(1)	2.353(1)	N(1)–Pd(1)–Cl(1)	94.6(1)
Pd(1)–Cl(1)	2.408(1)	As(1)–Pd(1)–Cl(1)	86.8(1)
Pd(2)–C(15)	1.993(4)	C(15)–Pd(2)–N(2)	92.5(1)
Pd(2)–N(2)	2.123(4)	C(15)–Pd(2)–Cl(1)	83.8(1)
Pd(2)–Cl(1)	2.355(1)	N(2)–Pd(2)–Cl(1)	172.0(1)
Pd(2)–Cl(2)	2.412(1)	C(15)–Pd(2)–Cl(2)	169.4(1)
C(15)–C(16)	1.327(5)	N(2)–Pd(2)–Cl(2)	94.3(1)
C(2)–Pd(1)–N(1)	81.3(2)	Cl(1)–Pd(2)–Cl(2)	90.4(1)
C(2)–Pd(1)–As(1)	97.6(1)	Pd(2)–Cl(1)–Pd(1)	86.6(1)

complex (*R*)-**2** and an unexpected insertion product, (*S*,*S*)-**8**, were obtained instead (Scheme 1). The yield of complex (*S*,*S*)-**8**, which was based on the mass of As, was only 14%, which indicated that complex (*S*,*S*)-**8** should be the minor product of the current insertion reaction. We assumed that there was an alkynylyarsane ligand redistribution process that occurred prior to the insertion reaction. As illustrated in Scheme 2, during the ligand redistribution process, the labile alkynylarsane ligand was redistributed from the naphthylamine template, (*R*)-**4**, to the benzylamine template, (*S*)-**5**, to form dimeric naphthylamine palladium(II) complex (*R*)-**2** and monomeric chloro benzyamine complex (*S*)-**9**, which subsequently underwent an insertion reaction with (*S*)-**5** to afford the insertion product, (*S*,*S*)-**8**. As shown in Figure 4, the absolute stereochemistry of complex (*S*,*S*)-**8** was confirmed by X-ray crystallography. Table 3 shows the selected bond lengths and angles of complex (*S*,*S*)-**8**. We believe that in the insertion reaction between complex (*R*)-**4** and benzylamine palladium(II) dimer (*R*)-**5** the same ligand redistribution process should occur, however, the minor product could not be obtained.



Scheme 2.

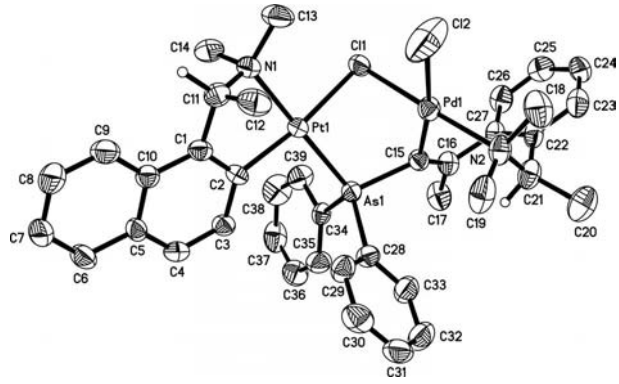


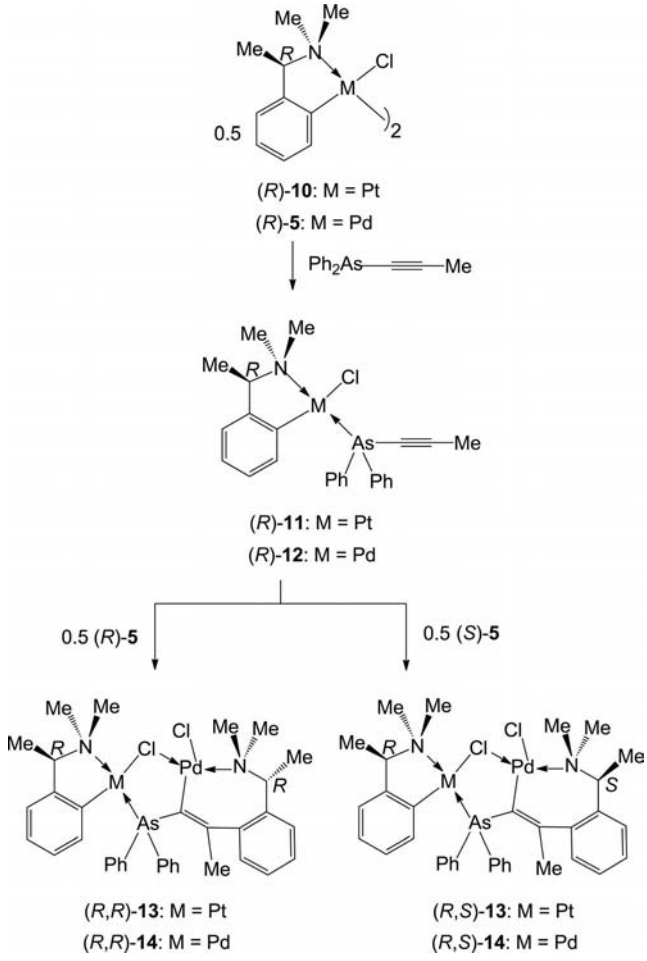
Figure 4. The molecular structure of complex (*S*,*S*)-**8**.

Table 3. The selected bond lengths [Å] and angles [°] for complex (*S*,*S*)-**8**.

Pd(1)–C(2)	1.993(4)	N(1)–Pd(1)–As(1)	179.6(1)
Pd(1)–N(1)	2.121(3)	C(2)–Pd(1)–Cl(1)	172.3(1)
Pd(1)–As(1)	2.349(1)	N(1)–Pd(1)–Cl(1)	93.5(1)
Pd(1)–Cl(1)	2.413(1)	As(1)–Pd(1)–Cl(1)	86.9(1)
Pd(2)–C(11)	1.991(3)	C(11)–Pd(2)–N(2)	92.6(1)
Pd(2)–N(2)	2.125(3)	C(11)–Pd(2)–Cl(1)	83.3(1)
Pd(2)–Cl(1)	2.351(1)	N(2)–Pd(2)–Cl(1)	172.5(1)
Pd(2)–Cl(2)	2.434(1)	C(11)–Pd(2)–Cl(2)	169.6(1)
C(11)–C(12)	1.326(4)	N(2)–Pd(2)–Cl(2)	95.9(1)
C(2)–Pd(1)–N(1)	82.7(2)	Cl(1)–Pd(2)–Cl(2)	88.8(1)
C(2)–Pd(1)–As(1)	96.9(1)	Pd(2)–Cl(1)–Pd(1)	91.1(1)

Monoinsertion Reactions of the Alkynylarsane-Bearing Cyclometallated Benzylamine Complex

It has been well established that *ortho*-metallated naphthylamine complexes (*R*)-**1** and (*R*)-**2** have similar electronic properties to the *ortho*-metallated benzylamine complexes, (*R*)-**5** and (*R*)-**10** (Scheme 3). They both contain two readily available coordination sites: one that is *trans* to the strong π-accepting aromatic carbon donor and the other that is *trans* to the σ-donating nitrogen.[17] However, the *ortho*-metallated naphthylamine template proved superior to the benzylamine analogue in many applications due to the unique stereochemistry associated with the *ortho*-metallated five-membered ring, which is conformationally rigid in both the solid and the solution form.[18] The organometallic ring conformation of benzylamine, on the other hand, undergoes rapid interconversion between the λ and *δ* conformations in both the solution and the solid state.[19] In order to explore the subtle metal template effect that arises from the benzylamine and napthylamine auxiliaries, a series of insertion reactions that involved the cycloplatinated/palladated benzylamine templates were conducted.



Scheme 3.

As illustrated in Scheme 3, the precursor complex (*R*)-**11** was separately treated with half an equivalent of the enantiomeric benylamine palladium(II) dimmers, (*R*)-**5** and (*S*)-**5**, at room temperature in CH_2Cl_2 and the reaction was found to be complete in 4 and 5 d, respectively. In each of the reactions, only one single product was formed. The crude reaction mixtures were then purified by column chromatography and were subsequently crystallized from dichloromethane/hexane to give complexes (*R*,*R*)-**13** and (*R*,*S*)-**13** as yellowish-orange crystals in 67% and 88% yields, respectively.

The X-ray structural analysis of complexes (*R*,*R*)-**13** and (*R*,*S*)-**13** confirmed that the desired diastereomeric insertion products had been formed (Figures 5 and 6). No interconversion of the organometallic ring conformations were observed. The conformation of the 5-membered Pt(1)–C(2)–N(1) ring in complex (*R*,*R*)-**13** is λ, while the 5-membered platinacycle in complex (*R*,*S*)-**13** adopts the δ conformation. In both of the complexes, the arsenic donor atoms were coordinated regiospecifically in the *trans* position to the benzylamine–*N* donor atom and had Pt–As bond lengths of 2.334(1) and 2.332(1) Å, respectively, and the methyl group of the alkynylarsane was located exclusively adjacent to the phenyl ring of the palladated benzylamine. Moreover, as expected, the absolute configuration of the stereocenters at C(7) and C(17) remained unchanged in the two complexes. The molecular structure of complex (*R*,*R*)-**13** showed that the carbon–carbon triple bond of the alkynylarsane bond, C(11)–C(12), had inserted into the Pd(1)–C(23) bond of benzylamine dimer (*R*)-**5**. As a result of this insertion, two new bonds, C(22)–C(20) and Pd(1)–C(21), were generated and the C(11)–C(12) bond changed from C≡C to C=C. The platinum and palladium metal centers are connected by Cl to give a 5-membered bimetallic heterocycle. Complex (*R*,*S*)-**13** has the same molecular connectivity as complex (*R*,*R*)-**13** and only differs in the bond lengths and angles. The geometry at the platinum and palladium centers is slightly distorted square planar for complexes (*R*,*R*)-**13** and (*R*,*S*)-**13**. The C(11)–C(12) bond length in complex (*R*,*R*)-**13** [1.321(6)] and in complex (*R*,*S*)-**13** [1.343(5)] were clearly indicative of C=C bonds. Table 4 shows the selected bond lengths and angles for complexes (*R*,*R*)-**13** and (*R*,*S*)-**13**.

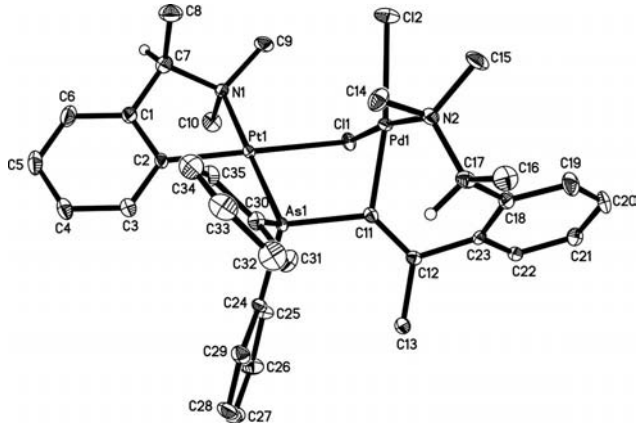


Figure 5. The molecular structure of complex (*R*,*R*)-**13**.

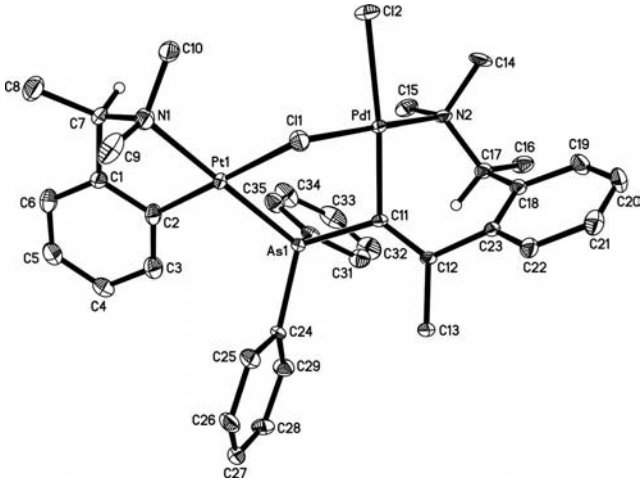


Figure 6. The molecular structure of complex (*R*,*S*)-**13**.

Two more insertion reactions were carried out separately between complex (*R*)-**12** and half an equivalent of the enantiomeric benzylamine palladium(II) dimers, (*R*)-**5** and (*S*)-

Table 4. The selected bond lengths [Å] and angles [°] for complexes (*R*,*R*)-**13** and (*R*,*S*)-**13**.

	(*R*,*R*)-**13**	(*R*,*S*)-**13**
Pt(1)–C(2)	1.996(5)	2.002(4)
Pt(1)–N(1)	2.110(4)	2.114(4)
Pt(1)–As(1)	2.334(1)	2.332(1)
Pt(1)–Cl(1)	2.406(1)	2.411(1)
Pd(1)–C(11)	1.997(4)	2.004(3)
Pd(1)–N(2)	2.113(4)	2.118(4)
Pd(1)–Cl(1)	2.343(1)	2.329(1)
Pd(1)–Cl(2)	2.433(1)	2.415(1)
C(11)–C(12)	1.321(6)	1.343(5)
C(2)–Pt(1)–N(1)	82.1(2)	82.1(2)
C(2)–Pt(1)–As(1)	98.3(2)	97.2(1)
N(1)–Pt(1)–As(1)	179.6(1)	178.7(1)
C(2)–Pt(1)–Cl(1)	172.5(1)	173.5(1)
N(1)–Pt(1)–Cl(1)	92.8(1)	94.5(1)
As(1)–Pt(1)–Cl(1)	86.8(1)	86.3(1)
C(11)–Pd(1)–N(2)	92.0(2)	93.8(1)
C(11)–Pd(1)–Cl(1)	83.7(1)	85.2(1)
N(2)–Pd(1)–Cl(1)	173.0(1)	178.2(1)
C(11)–Pd(1)–Cl(2)	170.2(1)	171.0(1)
N(2)–Pd(1)–Cl(2)	96.4(1)	95.1(1)
Cl(1)–Pd(1)–Cl(2)	88.4(1)	85.9(1)
Pd(1)–Cl(1)–Pt(1)	92.1(1)	96.3(1)

5, at room temperature in CH_2Cl_2 (Scheme 4). Both of the reactions were found to be complete in 6 and 4 d, respectively. The crude reaction mixtures were purified by column chromatography and were subsequently crystallized from acetone/hexane to give complexes (*R*,*R*)-**14** and (*R*,*S*)-**14** as yellowish-orange crystals in 68% and 90% yields, respectively.

Figures 7 and 8 show the molecular structures of complex (*R*,*R*)-**14** and (*R*,*S*)-**14**, which indicated that the desired insertion products had been formed. Similar to the formation of the complexes (*R*,*R*)-**13** and (*R*,*S*)-**13**, no interconversion of the organometallic ring conformation was observed. The conformation of the 5-membered Pt(1)–C(2)–N(1) ring in complex (*R*,*R*)-**14** is λ, while the 5-membered platinacycle in complex (*R*,*S*)-**14** adopts the *δ* conformation. For both of the complexes the arsenic donor atoms are coordinated regiospecifically in the *trans* position to the benzylamine–*N* donor atom and both of the Pd–As bond lengths are 2.355(1) Å. The methyl group of the alkynylarsane was located exclusively adjacent to the phenyl ring

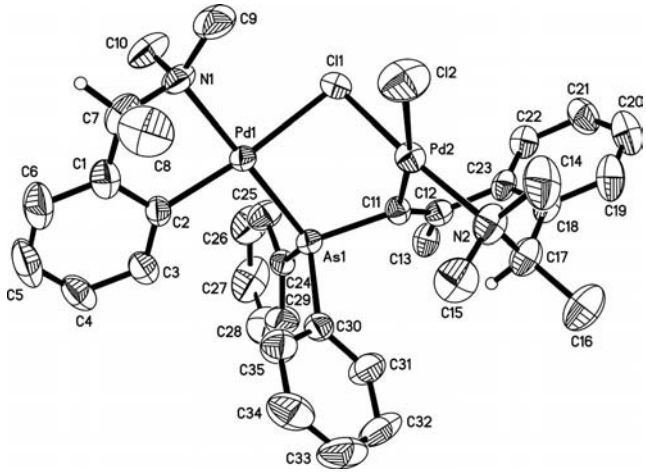
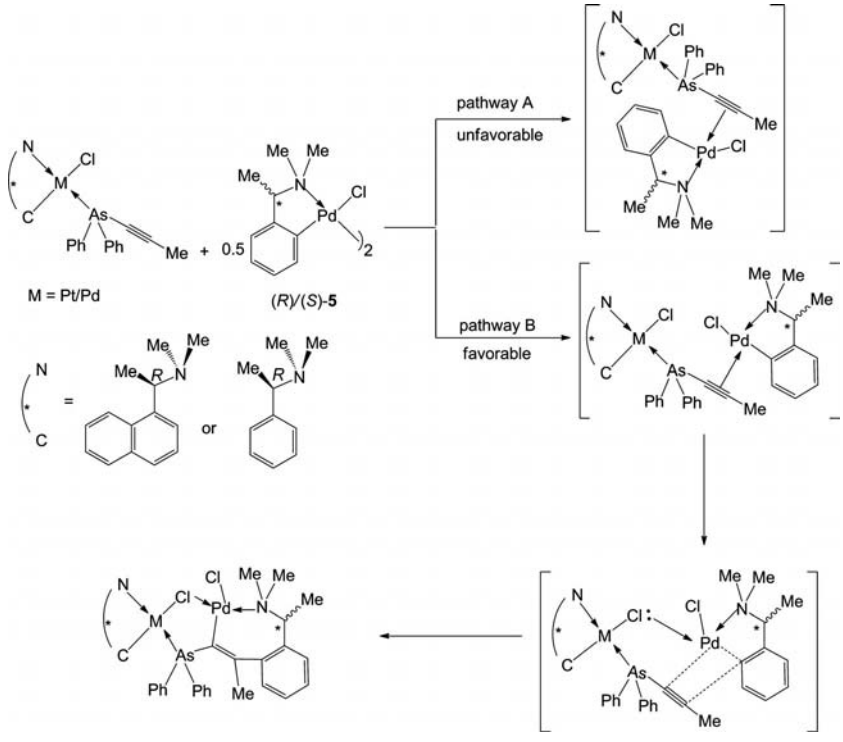


Figure 7. The molecular structure of complex (*R*,*R*)-**14**.



Scheme 4.

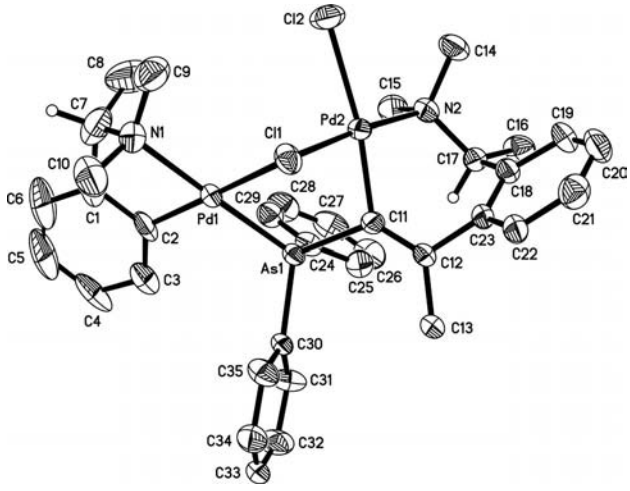


Figure 8. The molecular structure of complex (*R*,*S*)-**14**.

of the palladated benzylamine. Moreover, as expected, the absolute configurations of the stereocenters at C(7) and C(17) remained unchanged for the two complexes. Dipalladium complex (*R*,*R*)-**14** and its platinum analogue, (*R*,*R*)-**13**, are isostructural, while complex(*R*,*S*)-**14** and its platinum analogue, (*R*,*S*)-**13**, are also isostructural. Complex (*R*,*R*)-**14** is an enantiomer of complex (*S*,*S*)-**8**.

The molecular structure of complex (*R*,*R*)-**14** showed that the carbon–carbon triple bond of the alkynylarsane, C(11)–C(12), had inserted into the Pd(2)–C(23) bond of the benzylamine dimer (R_c)-**5**. As a result of this insertion, two new bonds, C(22)–C(20) and Pd(2)–C(21), were generated, while the C(11)–C(12) bond was changed from C≡C to C=C. The two palladium metal centers are connected by Cl to give a 5-membered bimetallic heterocycle. Complex (*R*,*S*)-**14** has the same molecular connectivity as complex (*R*,*R*)-**14**, and only differs in the bond lengths and angles. The geometry at both of the palladium centers is slightly distorted square planar for complexes (*R*,*R*)-**14** and (*R*,*S*)-**14**. The C(11)–C(12) bond lengths in (*R*,*R*)-**14** [1.319(5) Å] and in complex (*R*,*S*)-**14** [1.325(7) Å] clearly indicated that they are C=C bonds. The selected bond lengths and angles for complexes (*R*,*R*)-**14** and (*R*,*S*)-**14** are shown in Table 5.

Table 5. The selected bond lengths [Å] and angles [°] for complexes (*R*,*R*)-**14** and (*R*,*S*)-**14**.

	(*R*,*R*)-**14**	(*R*,*S*)-**14**
Pd(1)–C(2)	1.992(4)	2.004(6)
Pd(1)–N(1)	2.122(3)	2.134(5)
Pd(1)–As(1)	2.355(1)	2.355(1)
Pd(1)–Cl(1)	2.411(2)	2.404(2)
Pd(2)–C(11)	1.994(4)	1.993(5)
Pd(2)–N(2)	2.123(4)	2.131(5)
Pd(2)–Cl(1)	2.347(2)	2.344(2)
Pd(2)–Cl(2)	2.432(2)	2.428(2)
C(11)–C(12)	1.319(5)	1.325(7)
C(2)–Pd(1)–N(1)	82.5(2)	82.4(2)
C(2)–Pd(1)–As(1)	97.0(2)	97.0(2)
N(1)–Pd(1)–As(1)	179.5(2)	177.8(2)
C(2)–Pd(1)–Cl(1)	172.4(2)	173.3(2)
N(1)–Pd(1)–Cl(1)	93.5(2)	93.6(2)
As(1)–Pd(1)–Cl(1)	86.9 (1)	87.3(1)
C(11)–Pd(2)–N(2)	92.8(2)	92.8(2)
C(11)–Pd(2)–Cl(1)	83.4(2)	83.4(2)
N(2)–Pd(2)–Cl(1)	172.4(2)	173.8(2)
C(11)–Pd(2)–Cl(2)	169.8(2)	171.0(2)
N(2)–Pd(2)–Cl(2)	95.7(2)	95.5(2)
Cl(1)–Pd(2)–Cl(2)	88.8(1)	95.6(2)
Pd(2)–Cl(1)–Pd(1)	91.1(1)	88.5(1)

Mechanistic Considerations

It is worth noting that the current insertion reactions should proceed by means of an intermolecular pathway since the carbon–carbon triple bond of the alkynylarsane was exclusively inserted into the Pd–C bond of the chiral α-methyl benzylamine palladacycle instead of into the M–C bond of the original benzylamine or naphthylamine complex, which originally bore the alkynylarsane moeity. This was especially evident for the insertion reactions that involved the benzylamine palladium(II) complex, (*R*)-**12**, and the benzylamine palladium(II) dimers (*R*)/(*S*)-**5**, (Scheme 3), where even though both of the reactants involved contained a Pd–C bond attached to the phenyl ring, the C≡C bond of the alkynylarsane still exclusively inserted into the Pd–C bond of the benzylamine palladium(II) dimers (*R*)/(*S*)-**5**, which thus confirmed the intermolecular manner of the reaction.

It has been generally accepted that the insertion reactions of alkynes involves the η^2-coordination of the alkyne to the metal center followed by the migratory insertion of C≡C into the metal–carbon bond of the palladacycles.[19] We believe that a similar mechanism is involved in the current insertions of the alkynylarsane into the Pd–C bond of the *ortho*-palladated benzylamine. As illustrated in Scheme 4, upon coordination to the chiral cyclometallated template, the C≡C of the alkynylarsane coordinates in the η^2 mode to the Pd center of the *ortho*-palladated benzylamine to form a four-coordinate complex by means of a chloro bridge-splitting reaction on the *ortho*-palladated benzylamine template.[19–20] Since the alkynylarsane is not symmetrical, the η^2-coordination step may proceed by two different pathways, paths A and B (Scheme 4). The steric repulsion that arises from the phenyl group of the *ortho*-palladated benzylamine complex and the naphthyl/phenyl ring of the coordinated cyclometallated complex in pathway A is higher than that of the phenyl group of the *ortho*-palladated benzylamine and the Me group of the coordinated alkynylarsane in pathway B. Furthermore, in pathway B it is easier for the Cl atom on the M center to donate a lone pair of electrons to the Pd center of the *ortho*-palladated benzylamine. It is clear that pathway B, where the methyl group is located close to the phenyl group of the *ortho*-palladated benzylamine, is sterically and electronically much more favorable than pathway A, in which the methyl group is adjacent to the Cl atom. Therefore, the subsequent insertion of the C≡C of the alkynylarsane-bearing chiral cyclometallated template into the Pd–C bond of the *ortho*-palladated benzylamine proceeded with excellent regioselec-

tivity to form a seven-membered ring, where the methyl group was invariably located adjacent to the phenyl group of the *ortho*-palladated benzylamine. The lone pair of electrons on the Cl in the chiral cyclometallated template were donated to the Pd center of the *ortho*-palladated benzylamine and generated a five-membered bimetallic homo- or heterocycle.

Conclusions

In conclusion, a series of regioselective, intermolecular, monoinsertion reactions of the diphenyl-1-propynylarsane moiety into the Pd–C bonds of the chiral α-methyl benzylamine palladacycles were demonstrated under mild reaction conditions in appreciable yields. A variety of new chiral homo- or hetero-bimetallic arsenic functionalized complexes were thus isolated and characterized. In this study, cyclopalladated and cycloplatinated complexes that contained the benzylamine and naphthylamine systems were found to be efficient promoters for the reaction that gave a variety of bimetallic compounds.

Experimental Section

General: The reactions that involved air-sensitive compounds were performed under a positive pressure of purified nitrogen. The NMR spectra were recorded at 25 °C with the Bruker ACF300 and AMX500 spectrometers. The optical rotations were measured for the specified solution in a 1 dm cell at 25 °C with a Perkin–Elmer 341 polarimeter. The melting points were determined with a Büchi melting point B-540. The elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore.

The dimeric naphthylamine platinum(II) (*R*)-**1**,[21] dimeric naphthylamine palladium(II) complex (*R*)-**2**,[22–23] dimeric benzylamine palladium(II) complexes (*R*/*S*)-**5**,[24] and dimeric benzylamine platinum(II) complex (R_c)-**10**[25] were prepared according to the standard methods. The diphenyl-1-propynylarsane was prepared by a revised literature method.[26]

Complex (*R*)-3: Complex (*R*)-**1** (1.30 g, 1.51 mmol) was added to a solution of diphenyl-1-propynylarsane (0.81 g, 3.02 mmol) in CH_2Cl_2 and the reaction mixture was stirred for 4 h at room temperature. Upon completion of the reaction, the solvent was removed and dried in vacuo to yield the product as yellow solid, which was not isolated. M.p. 177–179 °C. $[\alpha]_D$ = –30 (*c* = 0.5, CH_2Cl_2). $C_{29}H_{29}AsClNPt$ (697.01): calcd. C 50.0, H 4.2, N 2.0; found C 50.1, H 4.1, N 2.2. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.68 (d, $J_{H,H}$ = 6.7 Hz, 3 H, CH*Me*), 2.06 (s, 3 H, ≡C*Me*), 2.89 (s, 3 H, N*Me*), 3.02 (s, 3 H, N*Me*), 4.00 (q, $J_{H,H}$ = 4.4 Hz, 1 H, C*H*Me), 6.90–7.88 (m, 16 H, aromatics) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 5.5 (s, 1 C, ≡C*Me*), 22.7 (s, 1 C, CH*Me*), 48.8 (s, 1 C, N*Me*), 53.3 (s, 1 C, N*Me*), 68.8 (s, 1 C, As*C*≡C), 75.6 (s, 1 C, *C*HMe), 105.5 (s, 1 C, AsC≡*C*), 123.3–148.1 (m, 22 C, Ar) ppm.

Complex (*R*,*R*)-6: Complex (*R*)-**3** (0.50 g, 0.72 mmol) was dissolved in CH_2Cl_2 (50 mL) and then treated with complex (*R*)-**5** (0.21 g, 0.36 mmol). The mixture was stirred at room temperature for 5 d. Upon completion of the reaction, the solvent was removed to give a brown residue, which was purified by column chromatography (with an eluting gradient of hexane/acetone, 5:1 to 3:1) to give a yellowish-orange solid. Crystallization from acetone/hexane gave complex (*R*,*R*)-**6** as yellowish-orange crystals: 0.61 g (86% yield); m.p. 229–231 °C (dec.). $[\alpha]_D$ = +385 (*c* = 0.5, CH_2Cl_2). $C_{39}H_{43}AsCl_2N_2PdPt$ (987.10): calcd. C 47.5, H 4.4, N 2.8; found C 47.2, H 4.4, N 3.1. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.06 (d, $J_{H,H}$ = 6.8 Hz, 3 H, CH*Me′*), 1.87 (s, 3 H, =C*Me*), 2.03 (s, 3 H, N*Me′*), 2.21 (d, $J_{H,H}$ = 6.4 Hz, 3 H, CH*Me*), 2.55 (s, 3 H, N*Me′*), 2.76 (s, 3 H, N*Me*), 3.36 (s, 3 H, N*Me*), 3.80 (q, $J_{H,H}$ = 6.8 Hz, 1 H, C*H′*Me), 4.58 (q, $J_{H,H}$ = 6.8 Hz, 1 H, C*H*Me), 6.79–7.95 (m, 20 H, aromatics) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 8.6 (s, 1 C, C′H*Me′*), 22.9 (s, 1 C, CH*Me*), 23.7 (s, 1 C, =C*Me*), 42.2 (s, 1 C, N*Me′*), 49.1 (s, 1 C, N*Me′*), 50.4 (s, 1 C, N*Me*), 53.7 (s, 1 C, N*Me*), 62.2 (s, 1 C, *C′*HMe′), 74.6 (s, 1 C, *C*HMe), 123.2–148.8 (m, 30 C, Ar and *C*=*C*) ppm.

Complex (*R*,*S*)-6: Complex (*R*)-**3** (0.50 g, 0.72 mmol) was dissolved in CH_2Cl_2 (50 mL) and then treated with complex (*S*)-**5** (0.21 g, 0.36 mmol). The mixture was stirred at room temperature for 6 d. Upon completion of the reaction, the solvent was removed to give a brown residue, which was purified by column chromatography (with an eluting gradient of hexane/acetone, 5:1 to 3:1) to give a yellowish-orange solid. Crystallization from acetone/hexane gave complex (*R*,*S*)-**6** as yellowish-orange crystals: 0.57 g (80% yield); m.p. 190–191 °C (dec.). $[\alpha]_D$ = –242 (*c* = 0.5, CH_2Cl_2). $C_{39}H_{43}AsCl_2N_2PdPt$ (987.10): calcd. C 47.5, H 4.4, N 2.8; found C 47.3, H 4.3, N 3.1. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.18 (d, $J_{H,H}$ = 7.0 Hz, 3 H, CH*Me′*), 1.72 (d, $J_{H,H}$ = 6.3 Hz, 3 H, CH*Me*), 1.81 (s, 3 H, =C*Me*), 1.91 (s, 3 H, N*Me′*), 2.55 (s, 3 H, N*Me′*), 3.20 (s, 3 H, N*Me*), 3.24 (s, 3 H, N*Me*), 4.01 (q, $J_{H,H}$ = 7.0 Hz, 1 H, C*H′*Me), 4.58 (q, $J_{H,H}$ = 6.4 Hz, 1 H, C*H*Me), 6.91–8.47 (m, 20 H, aromatics) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 8.9 (s, 1 C, C′H*Me′*), 22.7 (s, 1 C, CH*Me*), 23.9 (s, 1 C, =C*Me*), 42.3 (s, 1 C, N*Me′*), 48.5 (s, 1 C, N*Me′*), 48.8 (s, 1 C, N*Me*), 54.1 (s, 1 C, N*Me*), 62.1 (s, 1 C, *C′*HMe′), 73.6 (s, 1 C, *C*HMe), 123.1–148.4 (m, 30 C, Ar and *C*=*C*) ppm.

Complex (*R*)-4: Complex (*R*)-**2** (1.29 g, 1.90 mmol) was added to a solution of diphenyl-1-propynylarsane (1.02 g, 3.80 mmol) in CH_2Cl_2 and the reaction mixture was stirred for 1 d at room temperature. Upon completion of the reaction, the solvent was removed and dried in vacuo to yield the product as a yellow solid, which was not isolated. M.p. 125–126 °C. $[\alpha]_D$ = –88 (*c* = 0.5, CH_2Cl_2). $C_{29}H_{29}AsClNPd$ (608.35): calcd. C 57.3, H 4.8, N 2.3; found C 57.2, H 4.8, N 2.3. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.95 (d, $J_{H,H}$ = 6.2 Hz, 3 H, CH*Me*), 2.07 (s, 3 H, ≡C*Me*), 2.89 (s, 3 H, N*Me*), 3.15 (s, 3 H, N*Me*), 4.55 (q, $J_{H,H}$ = 6.4 Hz, 1 H, C*H*Me), 7.17–7.97 (m, 16 H, aromatics) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 5.5 (s, 1 C, ≡C*Me*), 23.9 (s, 1 C, CH*Me*), 48.9 (s, 1 C, N*Me*), 52.3 (s, 1 C, N*Me*), 74.0 (s, 1 C, *C*HMe), 106.1 (s, 2 C, As*C*≡*C*), 123.4–149.3 (m, 22 C, Ar) ppm.

Complex (*R*,*R*)-7: Complex (*R*)-**4** (0.50 g, 0.82 mmol) was dissolved in CH_2Cl_2 (50 mL) and then treated with complex (*R*)-**5** (0.24 g, 0.41 mmol). The mixture was stirred at room temperature for 3 d. Upon completion of the reaction, the solvent was removed to give a brown residue, which was purified by column chromatography (with an eluting gradient of hexane/acetone, 5:1 to 3:1) to give a yellowish-orange solid. Crystallization from acetone/hexane gave (*R*,*R*)-**7** as yellowish-orange crystals: 0.30 g (40% yield); m.p. 176–177 °C (dec.). $[\alpha]_D$ = +135 (*c* = 0.2, CH_2Cl_2). $C_{39}H_{43}AsCl_2N_2Pd_2$ (898.41): calcd. C 52.1, H 4.8, N 3.1; found C 51.9, H 4.8, N 3.2. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.06 (d, $J_{H,H}$ = 6.8 Hz, 3 H, CH*Me′*), 1.89 (s, 3 H, =C*Me*), 2.07 (s, 3 H, N*Me′*), 2.32 (d, $J_{H,H}$ = 6.4 Hz, 3 H, CH*Me*), 2.58 (s, 3 H, N*Me′*), 2.68 (s, 3 H, N*Me*), 3.14 (s, 3 H, N*Me*), 3.80 (q, $J_{H,H}$ = 6.8 Hz, 1 H, C*H′*Me), 4.34 (q,

$J_{H,H}$ = 6.0 Hz, 1 H, C*H*Me), 6.48–7.93 (m, 20 H, aromatics) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 8.6 (s, 1 C, C′H*Me′*), 23.8 (s, 1 C, =C*Me*), 24.3 (s, 1 C, CH*Me*), 42.1 (s, 1 C, N*Me′*), 49.1 (s, 1 C, N*Me′*), 50.1 (s, 1 C, N*Me*), 52.5 (s, 1 C, N*Me*), 62.1 (s, 1 C, *C*′HMe′), 73.1 (s, 1 C, *C*HMe), 122.4–150.3 (m, 30 C, Ar and *C*=*C*) ppm.

Complexes (*R*)-11 and (*R*)-12: Complexes (*R*)-**11** and (*R*)-**12** were prepared separately by a similar procedure to the preparation of complex (*R*)-**3**. Complex (*R*)-**11**: m.p. 113–115 °C. $[a]_D$ = –10 (*c* = 0.5, CH_2Cl_2). $C_{25}H_{27}AsClNPt$ (646.95): calcd. C 46.4, H 4.2, N 2.2; found C 46.2, H 4.8, N 2.3. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.03 (d, $J_{H,H}$ = 6.5 Hz, 3 H, CH*Me*), 2.05 (s, 3 H, ≡C*Me*), 2.82 (s, 3 H, N*Me*), 2.97 (s, 3 H, N*Me*), 4.33 (q, $J_{H,H}$ = 6.2 Hz, 1 H, C*H*Me), 7.35–8.01 (m, 14 H, aromatics) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 5.4 (s, 1 C, ≡C*Me*), 19.7 (s, 1 C, CH*Me*), 46.7 (s, 1 C, N*Me*), 51.7 (s, 1 C, N*Me*), 68.7 (s, 1 C, As*C*≡C), 77.0 (s, 1 C, *C*HMe), 105.2 (s, 1 C, AsC≡*C*), 121.9–153.2 (m, 18 C, Ar) ppm.

Complex (*R*)-12: M.p. 192–194 °C.$[a]_D$ = +106 (*c* = 0.5, CH_2Cl_2). $C_{25}H_{27}AsClNPd$ (558.29): calcd. C 53.8, H 4.9, N 2.5; found C 53.5, H 4.5, N 2.2. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.73 (d, $J_{H,H}$ = 5.1 Hz, 3 H, CH*Me*), 2.05 (s, 3 H, ≡C*Me*), 2.78 (s, 3 H, N*Me*), 2.94 (s, 3 H, N*Me*), 3.90 (q, $J_{H,H}$ = 6.1 Hz, 1 H, C*H*Me), 6.64–7.99 (m, 14 H, aromatics) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 5.5 (s, 1 C, ≡C*Me*), 23.9 (s, 1 C, CH*Me*), 46.6 (s, 1 C, N*Me*), 51.0 (s, 1 C, N*Me*), 105.6 (s, 2 C, As*C*≡*C*), 122.4–148.0 (m, 18 C, Ar) ppm.

Complex (*R*,*R*)-13: Complex (*R*)-**11** (0.50 g, 0.77 mmol) was dissolved in CH_2Cl_2 (50 mL) and then treated with complex (*R*)-**5** (0.22 g, 0.39 mmol). The mixture was stirred at room temperature for 4 d. Upon completion of the reaction, the solvent was removed to give a brown residue, which was purified by column chromatography (with an eluting gradient of hexane/acetone, 5:1 to 3:1) to give a yellowish-orange solid. Crystallization from dichloromethane/hexane gave (*R*,*R*)-**13** as yellowish-orange crystals: 0.48 g (67% yield); m.p. 223–224 °C (dec.). $[a]_D$ = +167 (*c* = 0.5, CH_2Cl_2). $C_{35}H_{41}AsCl_2N_2PdPt$ (937.04): calcd. C 44.5, H 4.4, N 3.0; found C 44.9, H 4.5, N 3.1. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.07 (d, $J_{H,H}$ = 6.8 Hz, 3 H, CH*Me′*), 1.84 (s, 3 H, =C*Me*), 2.00 (d, $J_{H,H}$ = 6.4 Hz, 3 H, CH*Me*), 2.04 (s, 3 H, N*Me′*), 2.54 (s, 3 H, N*Me′*), 2.78 (s, 3 H, N*Me*), 3.21 (s, 3 H, N*Me*), 3.75 (q, $J_{H,H}$ = 6.4 Hz, 1 H, C*H*′Me), 3.81 (q, $J_{H,H}$ = 7.2 Hz, 1 H, C*H*Me), 6.43–8.02 (m, 18 H, aromatics) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 8.7 (s, 1 C, C′H*Me′*), 23.5 (s, 1 C, CH*Me*), 23.7 (s, 1 C, =C*Me*), 42.2 (s, 1 C, N*Me′*), 49.1 (s, 1 C, N*Me′*), 49.6 (s, 1 C, N*Me*), 53.0 (s, 1 C, N*Me*), 62.2 (s, 1 C, *C*′HMe′), 77.1 (s, 1 C, *C*HMe), 121.6–154.9 (m, 26 C, Ar and *C*=*C*) ppm.

Complex (*R*,*S*)-13: Complex (*R*)-**11** (0.25 g, 0.39 mmol) was dissolved in CH_2Cl_2 (50 mL) and then treated with complex (*S*)-**5** (0.11 g, 0.19 mmol). The mixture was stirred at room temperature for 5 d. Upon completion of the reaction, the solvent was removed to give a brown residue, which was purified by column chromatography (with an eluting gradient of hexane/acetone, 5:1 to 3:1) to give a yellowish-orange solid. Crystallization from dichloromethane/hexane gave (*R*,*S*)-**13** as yellowish-orange crystals: 0.32 g (87% yield); m.p. 216 °C (dec.). $[a]_D$ = –206 (*c* = 0.5, CH_2Cl_2). $C_{35}H_{41}AsCl_2N_2PdPt$ (937.04): calcd. C 44.5, H 4.4, N 3.0; found C 44.8, H 4.5, N 3.2. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.07 (d, $J_{H,H}$ = 7.1 Hz, 3 H, CH*Me′*), 1.86 (s, 3 H, =C*Me*), 2.08 (s, 3 H, N*Me′*), 2.11 (d, $J_{H,H}$ = 6.5 Hz, 3 H, CH*Me*), 2.57 (s, 3 H, N*Me′*), 2.68 (s, 3 H, N*Me*), 3.01 (s, 3 H, N*Me*), 3.55 (q, $J_{H,H}$ = 6.4 Hz, 1 H, C*H*′Me), 3.81 (q, $^3J_{H,H}$ = 7.2 Hz, 1 H, C*H*Me), 6.15–7.95 (m, 18 H, aromatics) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 8.7 (s, 1 C, C′H*Me′*), 14.7 (s, 1 C, CH*Me*), 23.8 (s, 1 C, =C*Me*), 42.2 (s, 1 C, N*Me′*), 45.3 (s, 1 C, N*Me*), 48.9 (s, 1 C, N*Me′*), 51.5 (s, 1 C, N*Me*), 62.0 (s, 1 C, *C*′HMe′), 73.8 (s, 1 C, *C*HMe), 122.5–152.4 (m, 26 C, Ar and *C*=*C*) ppm.

Complex (*R*,*R*)-14: Complex (*R*)-**12** (0.50 g, 0.89 mmol) was dissolved in CH_2Cl_2 (50 mL) and then treated with complex (*R*)-**5** (0.26 g, 0.45 mmol). The mixture was stirred at room temperature for 6 d. Upon completion of the reaction, the solvent was removed to give a brown residue, which was purified by column chromatography (with an eluting gradient of hexane/acetone, 5:1 to 3:1) to give a yellowish-orange solid. Crystallization from acetone/hexane gave (*R*,*R*)-**14** as yellowish-orange crystals: 0.51 g (68% yield); m.p. 198–199 °C (dec.). $[a]_D$ = +73 (*c* = 0.5, CH_2Cl_2). $C_{35}H_{41}AsCl_2N_2Pd_2$ (848.35): calcd. C 49.6, H 4.9, N 3.3; found C 49.5, H 4.8, N 3.6. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.07 (d, $J_{H,H}$ = 6.8 Hz, 3 H, CH*Me′*), 1.85 (s, 3 H, =C*Me*), 2.09 (s, 3 H, N*Me′*), 2.11 (d, $J_{H,H}$ = 6.4 Hz, 3 H, CH*Me*), 2.57 (s, 3 H, N*Me′*), 2.68 (s, 3 H, N*Me*), 3.01 (s, 3 H, N*Me*), 3.55 (q, $J_{H,H}$ = 6.4 Hz, 1 H, C*H*′Me), 3.81 (q, $J_{H,H}$ = 7.2 Hz, 1 H, C*H*Me), 6.49–7.95 (m, 18 H, aromatics) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 8.7 (s, 1 C, C′H*Me′*), 23.8 (s, 1 C, CH*Me*), 24.9 (s, 1 C, =C*Me*), 42.1 (s, 1 C, N*Me′*), 49.1 (s, 1 C, N*Me′*), 49.3 (s, 1 C, N*Me*), 52.0 (s, 1 C, N*Me*), 62.1 (s, 1 C, *C*′HMe′), 75.8 (s, 1 C, *C*HMe), 122.5–156.0 (m, 26 C, Ar and *C*=*C*) ppm.

Complex (*R*,*S*)-14: Complex (R_c)-**12** (0.50 g, 0.89 mmol) was dissolved in CH_2Cl_2 (50 mL) and then treated with complex (*S*)-**5** (0.26 g, 0.45 mmol). The mixture was stirred at room temperature for 4 d. Upon completion of the reaction, the solvent was removed to give a brown residue, which was purified by column chromatography (with an eluting gradient of hexane/acetone, 5:1 to 3:1) to give a yellowish-orange solid. Crystallization from acetone/hexane gave (*R*,*S*)-**14** as yellowish-orange crystals: 0.68 g (90% yield); m.p. 183–185 °C (dec.). $[a]_D$ = +29 (*c* = 0.5, CH_2Cl_2). $C_{35}H_{41}AsCl_2N_2Pd_2$ (848.35): calcd. C 49.6, H 4.9, N 3.3; found C 49.3, H 4.8, N 3.4. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.07 (d, $J_{H,H}$ = 6.8 Hz, 3 H, CH*Me′*), 1.85 (s, 3 H, =C*Me*), 2.08 (s, 3 H, N*Me′*), 2.11 (d, $J_{H,H}$ = 6.8 Hz, 3 H, CH*Me*), 2.56 (s, 3 H, N*Me′*), 2.68 (s, 3 H, N*Me*), 3.01 (s, 3 H, N*Me*), 3.55 (q, $J_{H,H}$ = 6.4 Hz, 1 H, C*H*′Me), 3.81 (q, $J_{H,H}$ = 6.8 Hz, 1 H, C*H*Me), 6.49–8.05 (m, 18 H, aromatics) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 8.8 (s, 1 C, C′H*Me′*), 23.9 (s, 1 C, CH*Me*), 24.9 (s, 1 C, =C*Me*), 42.1 (s, 1 C, N*Me′*), 47.2 (s, 1 C, N*Me′*), 49.3 (s, 1 C, N*Me*), 52.5 (s, 1 C, N*Me*), 62.1 (s, 1 C, *C*′HMe′), 75.2 (s, 1 C, *C*HMe), 122.0–156.0 (m, 26 C, Ar and *C*=*C*) ppm.

X-ray Crystal Structure Determination: The single-crystal X-ray crystallographic data for (*R*,*R*)-**6**, (*R*,*S*)-**6**, (*R*,*R*)-**7**, (*S*,*S*)-**8**, (*R*,*R*)-**13**, (*R*,*S*)-**13**, (*R*,*R*)-**14**, and (*R*,*S*)-**14** are given in Tables 6 and 7. The diffraction data for complexes (*R*,*R*)-**6**, (*S*,*S*)-**8**, (*R*,*R*)-**13**, (*R*,*S*)-**13**, (*R*,*R*)-**14**, and (*R*,*S*)-**14** were collected with a SMART CCD diffractometer with graphite monochromated Mo-K_α radiation, while the diffraction data for complexes (*R*,*S*)-**6** and (*R*,*R*)-**7** were collected with a Bruker X8 CCD diffractometer with graphite-monochromated Mo-K_α radiation. For all of the complexes, SADABS absorption corrections were applied. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were introduced at a fixed distance from the carbon atoms and were assigned fixed thermal parameters. The absolute configurations of all of the chiral complexes were determined unambiguously by using the Flack parameter.[27]

CCDC-784885 [for (*R*,*R*)-**6**], -784886 [for (*R*,*S*)-**14**], -784887 [for (*S*,*S*)-**8**], -784888 [for (*R*,*S*)-**6**], -784889 [for (*R*,*R*)-**7**], -784890 [for (*R*,*R*)-**14**], -784891 [for (*R*,*R*)-**13**], and -784892 [for (*R*,*S*)-**13**] con-

Table 6. The crystallographic data for complexes (*R*,*R*)-**6**, (*R*,*S*)-**6**, (*R*,*R*)-**7**, and (*S*,*S*)-**8**.

	(*R*,*R*)-**6**	(*R*,*S*)-**6**	(*R*,*R*)-**7**	(*S*,*S*)-**8**
Formula	$C_{39.5}H_{44}AsCl_3N_2PdPt$	$C_{42}H_{49}AsCl_2N_2OPdPt$	$C_{40.5}H_{46}AsCl_2N_2O_{0.5}Pd_2$	$C_{35}H_{41}AsCl_2N_2Pd_2$
Fw	1029.53	1045.14	927.41	848.32
Space group	*P*4(3)2(1)2	*P*2(1)2(1)2(1)	*P*4(3)2(1)2	*P*2(1)2(1)2(1)
Crystal system	tetragonal	orthorhombic	tetragonal	orthorhombic
a [Å]	13.3254(5)	12.7470(18)	13.3104(5)	13.0336(3)
b [Å]	13.3254(5)	12.829(2)	13.3104(5)	13.1559(3)
c [Å]	43.827(3)	24.816(4)	43.640(3)	20.0112(6)
β [°]	90	90	90	90
V [Å^3]	7782.3(7)	4058.3(10)	7731.5(6)	3431.30(15)
Z	8	4	8	4
T [K]	223(2)	173(2)	173(2)	296(2)
ρ_{calcd} [g cm^{-3}]	1.757	1.711	1.593	1.642
λ [Å]	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	5.133	4.861	1.950	2.187
Flack parameters	0.001(6)	0.001(4)	0.031(10)	0.016(8)
R_1 (obsd. data)[a]	0.0392	0.0300	0.0308	0.0321
wR_2 (obsd. data)[b]	0.0855	0.0520	0.0691	0.0684

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \sqrt{\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}}$, $w - 1 = \sigma_2(F_o^2) + (aP)^2 + bP$.

Table 7. The crystallographic data for complexes (*R*,*R*)-**13**, (*R*,*S*)-**13**, (*R*,*R*)-**14**, and (*R*,*S*)-**14**.

	(*R*,*R*)-**13**	(*R*,*S*)-**13**	(*R*,*R*)-**14**	(*R*,*S*)-**14**
Formula	$C_{35}H_{41}AsCl_2N_2PdPt$	$C_{35}H_{41}AsCl_2N_2PdPt$	$C_{35}H_{41}AsCl_2N_2Pd_2$	$C_{35}H_{41}AsCl_2N_2Pd_2$
Fw	937.01	937.01	848.32	848.32
Space group	*P*2(1)2(1)2(1)	*C*2	*P*2(1)2(1)2(1)	*C*2
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic
a [Å]	12.9076(3)	22.4321(10)	13.0151(15)	22.3106(18)
b [Å]	13.0038(3)	12.4248(5)	13.1345(15)	12.9235(10)
c [Å]	19.8078(4)	13.2664(6)	19.995(2)	13.0378(10)
β [°]	90	116.1770(10)	90	115.438(2)
V [Å^3]	3324.70(13)	3318.3(2)	3418.1(7)	3394.7(5)
Z	4	4	4	4
T [K]	103(2)	103(2)	295(2)	223(2)
ρ_{calcd} [g cm^{-3}]	1.872	1.876	1.648	1.660
λ [Å]	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	5.920	5.931	2.196	2.211
Flack parameters	0.011(4)	0.014(4)	0.022(10)	0.019(11)
R_1 (obsd. data)[a]	0.0263	0.0265	0.0365	0.0415
wR_2 (obsd. data)[b]	0.0588	0.0603	0.0686	0.0917

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \sqrt{\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}}$, $w - 1 = \sigma_2(F_o^2) + (aP)^2 + bP$.

tain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[1] S. B. Wild, in: *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds* (Ed.: S. Patai), Wiley, Chichester, **1994**, p. 89–148.

[2] a) Y. Z. Huang, Y. C. Shen, *Adv. Organomet. Chem.* **1982**, *20*, 115–157; b) D. Lloyd, I. Gosney, R. A. Ormiston, *Chem. Soc. Rev.* **1987**, *16*, 45–74; c) W. M. Dai, J. Wu, X. Huang, *Tetrahedron: Asymmetry* **1997**, *8*, 1979–1982; d) H. S. He, C. W. Y. Chung, T. Y. S. But, P. H. Toy, *Tetrahedron* **2005**, *61*, 1385–1405; e) J. Goddard, P. Lixon, T. Le Gall, C. Mioskowski, *J. Am. Chem. Soc.* **2003**, *125*, 9242–9243.

[3] a) S. E. Jacobson, F. Mares, P. M. Zambri, *J. Am. Chem. Soc.* **1979**, *101*, 6938–6946; b) S. E. Jacobson, F. Mares, P. M. Zambri, *J. Am. Chem. Soc.* **1979**, *101*, 6946–6950; c) K. C. Y. Lau, H. S. He, P. Chiu, P. H. Toy, *J. Comb. Chem.* **2004**, *6*, 955–960.

[4] a) V. Farina, B. Krishnan, *J. Am. Chem. Soc.* **1991**, *113*, 9585–9595; b) V. Farina, B. Krishnan, D. R. Marshall, G. P. Roth, *J. Org. Chem.* **1993**, *58*, 5434–5444; c) K. C. Y. Lau, P. Chiu, *Tetrahedron Lett.* **2007**, *48*, 1813–1816.

[5] a) G. W. O'Neil, A. Fürstner, *Chem. Commun.* **2008**, 4294–4296; b) F. Stiemke, M. Gjikaj, D. E. Kaufmann, *J. Organomet. Chem.* **2009**, *694*, 5–13; c) T. Gillmann, T. Weeber, *Synlett* **1994**, 649–650; d) Y. Q. Mu, R. A. Gibbs, *Tetrahedron Lett.* **1995**, *36*, 5669–5672.

[6] a) J. C. Namyslo, D. E. Kaufmann, *Synlett* **1999**, 114–116; b) J. Storsberg, M. L. Yao, N. Öcal, A. de Meijere, A. E. W. Adam, D. E. Kaufmann, *Chem. Commun.* **2005**, 5665–5666; c) A. Kojima, C. D. J. Boden, M. Shibasaki, *Tetrahedron Lett.* **1997**, *38*, 3459–3460; d) S. Y. Cho, M. Shibasaki, *Tetrahedron Lett.* **1998**, *39*, 1773–1776.

[7] a) W. C. Yeo, J. J. Vittal, L. L. Koh, G. K. Tan, P. H. Leung, *Organometallics* **2004**, *23*, 3474–3482; b) P. H. Leung, *Acc. Chem. Res.* **2004**, *37*, 169–177, and references cited therein; c) W. C. Yeo, S. Chen, G. K. Tan, P. H. Leung, *J. Organomet. Chem.* **2007**, *692*, 2539–2547; d) M. Ma, S. A. Pullarkat, Y. Li, P. H. Leung, *Inorg. Chem.* **2007**, *46*, 9488–9494; e) S. A. Pullarkat, Y. L. Cheow, Y. Li, P. H. Leung, *Eur. J. Inorg. Chem.* **2009**, *16*, 2375–2382; f) M. Ma, S. A. Pullarkat, M. Yuan, N.

Zhang, Y. Li, P. H. Leung, *Organometallics* **2009**, *28*, 4886–4889; g) F. Liu, S. A. Pullarkat, Y. Li, K. W. Tan, P. H. Leung, *Organometallics* **2009**, *28*, 6254–6259.

[8] X. Liu, K. F. Mok, P. H. Leung, *Organometallics* **2001**, *20*, 3918–3926.

[9] a) M. L. Bungabong, K. W. Tan, Y. Li, S. V. Selvaratnam, K. G. Dongol, P. H. Leung, *Inorg. Chem.* **2007**, *46*, 4733–4736; b) F. Liu, S. A. Pullarkat, Y. Li, S. Chen, P. H. Leung, *Eur. J. Inorg. Chem.* **2009**, *27*, 4134–4140.

[10] a) W. C. Yeo, S. Y. Tee, H. B. Tan, G. K. Tan, L. L. Koh, P. H. Leung, *Inorg. Chem.* **2004**, *43*, 8102–8109; b) S. A. Pullarkat, Y. Ding, Y. Li, G. K. Tan, P. H. Leung, *Inorg. Chem.* **2006**, *45*, 7455–7463; c) L. Tang, Y. Zhang, D. Luo, Y. Li, K. F. Mok, W. C. Yeo, P. H. Leung, *Tetrahedron Lett.* **2007**, *48*, 33–35; d) Y. Zhang, L. Tang, Y. Ding, J. H. Chua, Y. Li, M. Yuan, P. H. Leung, *Tetrahedron Lett.* **2008**, *49*, 1762–1767; e) M. Yuan, S. A. Pullarkat, M. Ma, Y. Zhang, Y. Huang, Y. Li, A. Goel, P. H. Leung, *Organometallics* **2009**, *28*, 780–786; f) F. Liu, S. A. Pullarkat, Y. Li, S. Chen, M. Yuan, Z. Y. Lee, P. H. Leung, *Organometallics* **2009**, *28*, 3941–3946; g) Y. Zhang, S. A. Pullarkat, Y. Li, P. H. Leung, *Inorg. Chem.* **2009**, *48*, 5535–5539; h) Y. Zhang, L. Tang, S. A. Pullarkat, F. Liu, Y. Li, P. H. Leung, *J. Organomet. Chem.* **2009**, *21*, 3500–3505.

[11] a) D. Luo, Y. Li, K. W. Tan, P. H. Leung, *Organometallics* **2009**, *28*, 6266–6274; b) D. Luo, Y. Li, S. A. Pullarkat, K. E. Cockle, P. H. Leung, *Organometallics* **2010**, *29*, 893–903; c) S. Chen, S. A. Pullarkat, Y. Li, P. H. Leung, *Organometallics* **2011**, *30*, 1530–1550.

[12] J. Spencer, M. Pfeffer, N. Kyritsakas, J. Fischer, *Organometallics* **1995**, *14*, 2214–2224, and references cited therein.

[13] a) A. D. Ryabov, *Synthesis* **1985**, 233–252, and references cited therein; b) M. Pfeffer, *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 567–576; c) M. Pfeffer, *Pure Appl. Chem.* **1992**, *64*, 335–342; d) M. Pfeffer, J. P. Sutter, M. A. Rotteveel, A. De Cian, J. Fischer, *Tetrahedron* **1992**, *48*, 2427–2440; e) M. Pfeffer, J. P. Sutter, A. De Cian, J. Fischer, *Organometallics* **1993**, *12*, 1167–1173; f) F. Maassarani, M. Pfeffer, J. Spencer, E. Wehman, *J. Organomet. Chem.* **1994**, *466*, 265–271; g) J. Spencer, M. Pfeffer, *Tetrahedron: Asymmetry* **1995**, *6*, 419–426.

[14] a) J. P. H. Charmant, J. Forniés, J. Gómez, E. Lalinde, M. T. Moreno, A. G. Orpen, S. Solano, *Angew. Chem. Int. Ed.* **1999**, *38*, 3058–3061; b) M. Bernechea, J. R. Berenguer, E. Lalinde, J. Torroba, *Organometallics* **2009**, *28*, 312–320.

[15] P. H. Leung, A. C. Willis, S. B. Wild, *Inorg. Chem.* **1992**, *31*, 1406–1410.

[16] G. J. Grant, D. A. Biggers, D. G. Vanderveer, *Main Group Chem.* **2007**, *6*, 249–261.

[17] a) Y. Li, K. H. Ng, S. Selvaratnam, G. K. Tan, J. J. Vittal, P. H. Leung, *Organometallics* **2003**, *22*, 834–842, and references cited therein; b) Y. Li, S. Selvaratnam, J. J. Vittal, P. H. Leung, *Inorg. Chem.* **2003**, *42*, 3229–3226.

[18] a) S. Y. M. Chooi, T. S. A. Hor, P. H. Leung, K. F. Mok, *Inorg. Chem.* **1992**, *31*, 1494–1500; b) S. Y. M. Chooi, S. Y. Siah, P. H. Leung, K. F. Mok, *Inorg. Chem.* **1993**, *32*, 4812–4818; c) S. Y. M. Chooi, M. K. Tan, P. H. Leung, K. F. Mok, *Inorg. Chem.* **1994**, *33*, 3096–3103; d) S. Selvaratnam, P. H. Leung, A. J. P. White, D. J. Williams, *J. Organomet. Chem.* **1997**, *542*, 61–65.

[19] a) E. G. Samsel, J. R. Norton, *J. Am. Chem. Soc.* **1984**, *106*, 5505–5512; b) P. de Vaal, A. Dedieu, *J. Organomet. Chem.* **1994**, *478*, 121–129.

[20] a) A. D. Ryabov, R. van Eldik, G. Le Borgne, M. Pfeffer, *Organometallics* **1993**, *12*, 1386–1393.

[21] S. M. Y. Chooi, J. D. Ranford, P. H. Leung, K. F. Mok, *Tetrahedron: Asymmetry* **1994**, *5*, 1805–1814.

[22] D. G. Allen, G. M. McLaughlin, G. B. Robertson, W. L. Steffen, G. Salem, S. B. Wild, *Inorg. Chem.* **1982**, *21*, 1007–1014.

[23] D. C. R. Hockless, P. A. Gugger, P. H. Leung, R. C. Mayadunne, M. Pabel, S. B. Wild, *Tetrahedron* **1997**, *53*, 4083–4094.

[24] N. K. Roberts, S. B. Wild, *J. Chem. Soc., Dalton Trans.* **1979**, 2015–2021.

[25] K. W. Tan, *Ph. D. Dissertation*, National University of Singapore, **2005**.

[26] W. Hewertson, I. C. Talyor, S. Trippett, *J. Chem. Soc. C* **1970**, 1835–1839.

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

Received: March 1, 2011
Published Online: June 1, 2011

