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Novel Stereochemistry, Reactivity, and Stability of an Arsenic Heterocycle in a Metal-Promoted Asymmetric Cycloaddition Reaction

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The organopalladium complex containing ortho-metalated (*S*)-[1-(dimethylamino)ethyl]phenylene as the chiral auxiliary has been used as the chiral template to promote the asymmetric cycloaddition reaction between diphenylvinylphosphine and 3,4-dimethyl-1-phenylarsole. A diphenylphosphino-substituted asymmetrical heterobidentate arsanorbornene (As–P) ligand was obtained stereoselectively on the chiral palladium template in moderate yield. The chiral benzylamine auxiliary could be removed chemoselectively from the template by treatment with HCl to produce the neutral complex [(As–P)$PdCl_2$]. In contrast to their reported P–P analogue, the arsenic donor in the dichloro complex could be eliminated stereospecifically under mild reaction conditions to generate the corresponding 1-(diphenylphosphino)-3,4-dimethyl-2,4-cyclohexadiene, which remained as a bidentate ligand at the $PdCl_2$ unit via phosphorus and the η^2-C_4–C_5 double bond. The arsenic-elimination process was found to be influenced by the halo ligand in [(As–P)PdX_2]. A similar process was observed with the analogous dibromo complex, but the corresponding diiodo species did not show similar reactivity. All of the novel As–Pd complexes have been characterized by X-ray crystallography.

Introduction

In general, the chemistry of five-membered heterocyclic rings is dramatically affected by the presence of heteroatoms. For instance, the pyrrole rings rarely react in the cycloaddition reaction,[1] but we have previously reported that the analogous phospholes are much more reactive toward various types of dienophiles in the metal-promoted [4 + 2] cycloaddition reactions.[2] In view of the general importance of the heterocycles and the fact that the diversity of heterocyclic chemistry is often unpredictable by the classic periodicity trends, the relatively unexplored arsole system as a building block deserved attention.[3] The pronounced difference in electronic as well as in steric properties between the coordination atoms is vital in many important applications of these ligands including as active catalysts.[4]

Recently, chiral phosphine−olefin hybrid ligands have also received considerable attention in asymmetric catalysis. These ligands display unusual phosphorus and η^2 bonding, with the olefin performing the unconventional role of a "spectator" ligand that stays on the metal during catalysis and influences the metal's catalytic property. However, only a small number of chiral phosphine–olefin hybrid palladium complexes have been reported.[5] These palladium complexes showed high catalytic activity in asymmetric reactions. For example, the phenanthrene-based phosphinepalladium dibenzylidene acetone (dba) complex was successfully used in the

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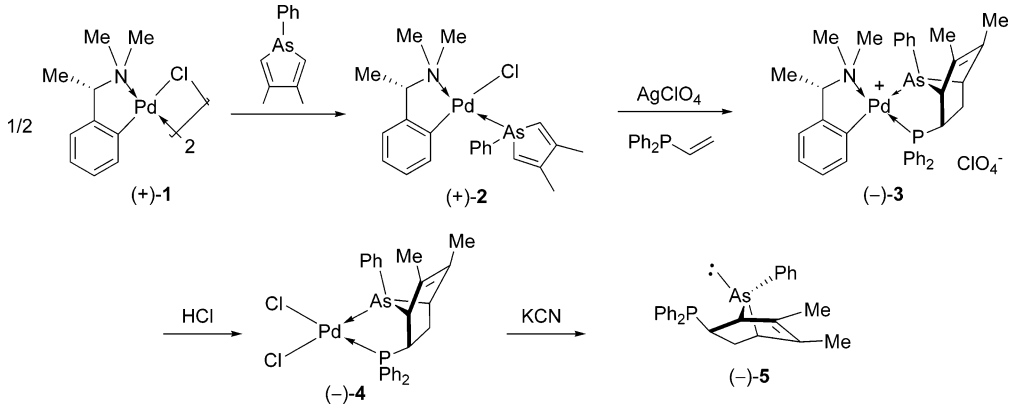
Scheme 1



Suzuki cross-coupling reaction to form sterically hindered tetra-ortho-substituted biaryls in high yields.[5c]

As part of our studies on asymmetric ligand transformation reactions, a series of organometallic reagents containing an orthometalated chiral amine auxiliary have been efficiently utilized as chiral templates to activate cyclic and noncyclic phosphines in cycloaddition, hydroamination, hydrophosphination, and, most recently, hydroarsination reactions. However, the stereoselectivity and reactivity of cyclic arsines in these reactions have been much less studied compared to phospholes. In order to enrich this heterobidentate chemistry, we have decided to explore the chemistry of arsoles. We herein report the metal-promoted cycloaddition reaction of 3,4-dimethyl-1-phenylarsole (DMPA) and the stability of the resulting novel arsanorbornene. A chiral phosphine−olefin hybrid palladium complex was unexpectedly obtained in this work.

Results and Discussion

Asymmetric Cycloaddition of DMPA. Similar to its phosphorus analogue (DMPP), reports on the reactivity of uncoordinated arsoles including DMPA are rare; however, they become reactive when they are coordinated onto a transition-metal ion.[6] As illustrated in Scheme 1, DMPA was coordinated regiospecifically to (+)-**1** to give the monomeric neutral complex (+)-**2** (Figure 1) as yellow prisms. The X-ray structural analysis of (+)-**2** reveals a marked bond ordering within the planar arsole ring in which the C11−C12 and C13−C14 bonds exhibit significant double-bond character [1.320(7) and 1.335(7) Å, respectively; Table 1]. The two As−C bonds [1.910(4) and 1.914(4) Å] within the arsole ring are significantly shorter than the As−Ph bond [1.939(3) Å]. Interestingly, the C−As−C bond angle [86.9(2)°] is dramatically smaller than the other four bond angles [111.0(4)−116.2(4)°] within the arsole ring. It is noteworthy that (+)-**2** is the first complex containing the DMPA ligand that has been characterized by X-ray crystallography.

The chloro ligand in (+)-**2** and indeed in similar orthometalated amine complexes is well-known to be both kinetically and thermodynamically stable.[7] This terminal ligand, however, can be abstracted efficiently by treatment

Table 1. Selected Bond Lengths (Å) and Angles (deg) for (+)-**2**

Pd1−C1	1.982(3)	Pd1−N1	2.141(3)
Pd1−As1	2.343(1)	Pd1−Cl1	2.424 (1)
As1−C11	1.910(4)	As1−C14	1.914(4)
As1−C17	1.939(3)	C11−C12	1.320(7)
C12−C13	1.496(8)	C13−C14	1.335(7)
C12−C16	1.518(8)	C13−C15	1.484(7)
C1−Pd1−N1	81.0 (1)	C1−Pd1−As1	93.9(1)
N1−Pd1−As1	172.9 (1)	C1−Pd1−Cl1	172.8 (1)
N1−Pd1−Cl1	97.4(1)	As1−Pd1−Cl1	88.3(1)
C11−As1−C14	86.9(2)	C11−As1−C17	105.0(2)
C14−As1−C17	103.7(2)	C11−As1−Pd1	118.5(1)
C14−As1−Pd1	123.6(1)	C17−As1−Pd1	114.8(1)

of the complex in dichloromethane with aqueous silver salts. This process allowed DMPA and diphenylvinylphosphine, the incoming dienophile, to coordinate jointly onto the chiral palladium template during the course of the intramolecular cycloaddition reaction. The $^{31}P\{^{1}H\}$ NMR spectroscopic studies indicated that the cycloaddition reaction was completed within 3 h and a 3.2:1 diastereomeric mixture was produced at room temperature. The $^{31}P\{^{1}H\}$ NMR spectrum of the crude product showed a strong singlet at δ 50.1 and a weaker singlet at δ 49.8. The major arsanorbornene complex (−)-**3** was crystallized as colorless prisms from chloroform−diethyl ether in 60% yield, with $[\alpha]_D$ −71.9° (*c* 0.6, CH_2Cl_2). As shown in Figure 2, the structural analysis of (−)-**3** revealed that, in addition to the cycloaddition reaction, a ligand redistribution process was also involved in the formation of (−)-**3**. Because of the distinct electronic-directing effects originating from the σ-donating nitrogen and the π-accepting aromatic carbon of the orthometalated benzylamine ring, it has been well-established that the position trans to the NMe_2 group invariably takes up the softest donor atom available.[8] Therefore, the phosphorus donor in the arsanorbornene ligand is a stronger π acceptor than the arsenic atom.[9] The four new chiral centers have been generated with *R* absolute stereochemistry at As1 and *R*, *R*,

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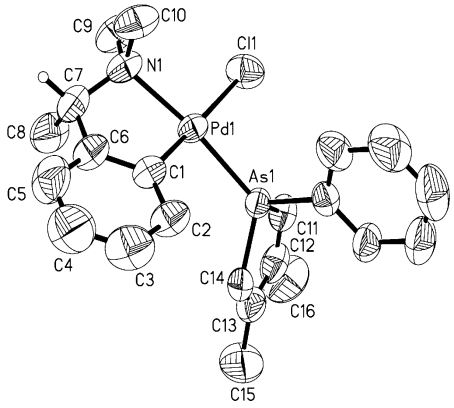


Figure 1. Molecular structure of complex (+)-**2**.

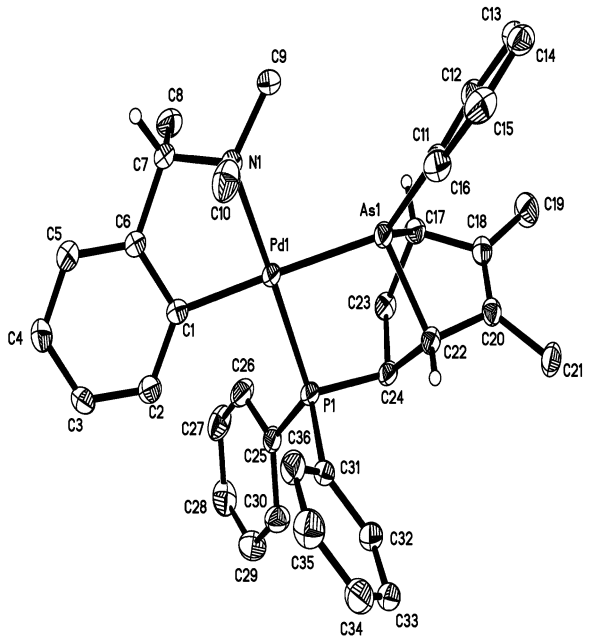


Figure 2. Molecular structure of complex (−)-**3**.

and *S* stereochemistry at C17, C22, and C24, respectively. Similar to its phosphorus analogue,[10] a noticeable feature of the arsanorbornene skeleton is a marked contraction in the C−As−C bridgehead angle to 76.7(1)° that accompanies a significant lengthening of these two As−C bonds [1.978(2) and 1.980(2) Å; Table 2] (compared with those observed in complex (+)-**2**). The chiral amine auxiliary on complex (−)-**3** could be removed chemoselectively by the treatment of the complex with concentrated hydrochloric acid. The neutral dichloro complex (−)-**4** (Figure 3) was thus obtained as stable yellow prisms in high yield, 60%, with $[\alpha]_D$ −40.0° (*c* 0.6, CH_2Cl_2). The structural analysis of the dichloro complex reaffirmed that the arsanorbornene skeleton remained unchanged after the acid treatment. Treatment of a dichloromethane solution of (−)-**4** with aqueous potassium cyanide gave the optically active free ligand (−)-**5** as a white solid in quantitative yield, with $[\alpha]_D$ −70.4° (*c* 0.9, CH_2Cl_2). In $CDCl_3$, the $^{31}P\{^1H\}$ NMR spectrum of (−)-**5** exhibited a singlet at δ −11.1. The optical purity of As−P

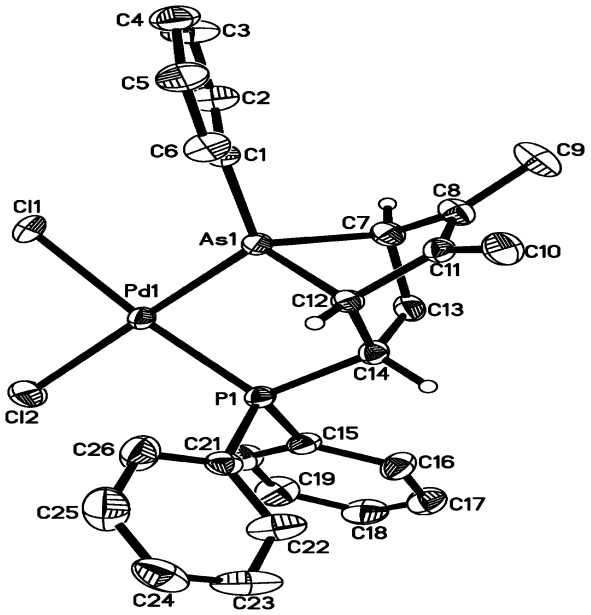


Figure 3. Molecular structure of complex (−)-**4**.

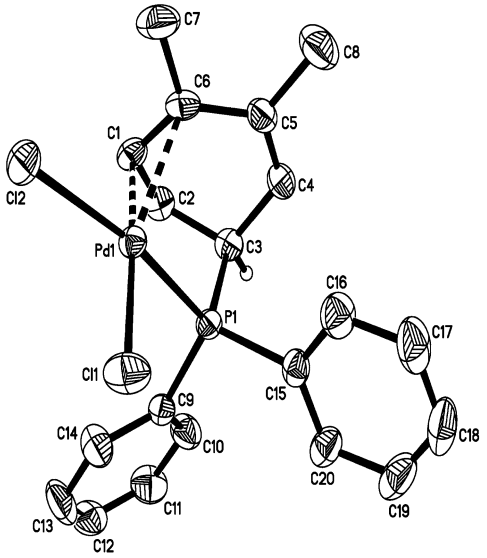
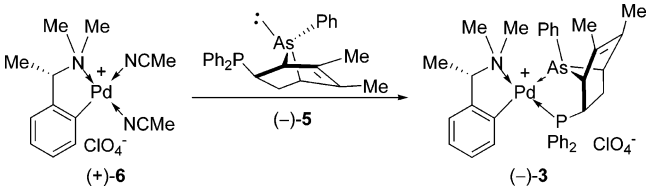


Figure 4. Molecular structure of complex (+)-**7**.

Scheme 2



bidentate ligand (−)-**5** was confirmed by the quantitative preparation of (−)-**3** from the liberated ligand (−)-**5** and bis(acetonitrile)[(*S*)-[(1-(dimethylamino)ethyl]phenyl]palladium(II) perchlorate [(+)-**6**;[11] Scheme 2]: the $^{31}P\{^1H\}$ NMR spectrum of the crude product exhibited only the singlet signal of (−)-**3** at δ 50.1.

When DMPA and DMPP are treated separately with coordinated diphenylvinylphosphine, they both show similar

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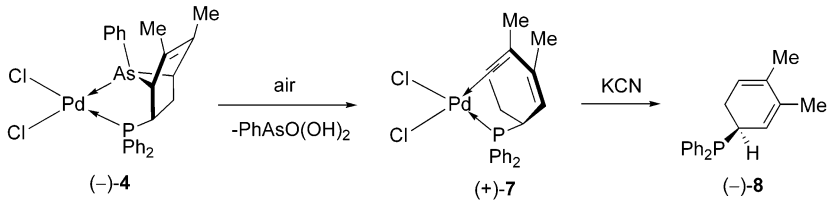
Scheme 3



(–)-**4** (+)-**7** (–)-**8**

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (−)-**3**

Pd1−C1	2.051(2)	Pd1−N1	2.146(2)
Pd1−As1	2.447(1)	Pd1−P1	2.261(1)
P1−C25	1.815(2)	P1−C31	1.820(2)
P1−C24	1.849(2)	As1−C11	1.925(2)
As1−C17	1.978(2)	As1−C22	1.980(2)
C17−C18	1.522(3)	C17−C23	1.557(3)
C18−C20	1.334(3)	C18−C19	1.501(3)
C20−C21	1.492(3)	C20−C22	1.507(3)
C22−C24	1.558(3)	C23−C24	1.567(3)
C1−Pd1−N1	81.8(1)	C1−Pd1−P1	96.8(1)
N1−Pd1−P1	172.8(1)	C1−Pd1−As1	178.7(1)
N1−Pd1−As1	99.5(1)	P1−Pd1−As1	81.9(2)
C11−As1−C17	108.1(1)	C11−As1−C22	107.0(1)
C17−As1−C22	76.7(1)	C11−As1−Pd1	129.1(1)
C17−As1−Pd1	116.8(1)	C22−As1−Pd1	105.7(1)
C18−C17−C23	106.2(2)	C18−C17−As1	101.5(1)
C23−C17−As1	99.6(2)	C20−C18−C19	128.7(2)
C20−C18−C17	111.6(2)	C19−C18−C17	119.5(2)
C18−C20−C21	129.6(2)	C18−C20−C22	111.8(2)
C21−C20−C22	118.5(2)	C20−C22−C24	110.2(2)
C20−C22−As1	103.0(2)	C24−C22−As1	95.9(1)
C17−C23−C24	107.0(2)	C22−C24−C23	105.7(2)
C22−C24−P1	107.8(2)	C23−C24−P1	111.1(1)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for (−)-**4**

Pd1−Cl1	2.345(1)	Pd1−Cl2	2.353(1)
Pd1−As1	2.325(1)	Pd1−P1	2.260(1)
As1−C1	1.922(3)	As1−C7	1.980(3)
As1−C12	1.961(3)	P1−C14	1.843(3)
P1−C15	1.825(3)	P1−C21	1.820(3)
C7−C8	1.513(5)	C7−C13	1.545(5)
C8−C11	1.342(5)	C8−C9	1.490(5)
C10−C11	1.498(5)	C11−C12	1.522(4)
C12−C14	1.552(4)	C13−C14	1.565(4)
P1−Pd1−As1	83.6(1)	Cl1−Pd1−P1	170.8(1)
As1−Pd1−Cl1	88.6(1)	P1−Pd1−Cl2	94.8(1)
As1−Pd1−Cl2	174.7(1)	Cl1−Pd1−Cl2	92.6(1)
C1−As1−C12	111.1(1)	C1−As1−C7	107.7(1)
C12−As1−C7	77.5(1)	C1−As1−Pd1	124.2(1)
C12−As1−Pd1	106.1(1)	C7−As1−Pd1	120.1(1)
C8−C7−C13	107.3(3)	C8−C7−As1	100.5(2)
C13−C7−As1	99.4(2)	C11−C8−C9	128.3(3)
C11−C8−C7	111.6(3)	C9−C8−C7	119.9(3)
C8−C11−C10	127.8(3)	C8−C11−C12	111.8(3)
C10−C11−C12	120.4(3)	C11−C12−C14	110.7(3)
C11−C12−As1	101.8(2)	C14−C12−As1	95.3(2)
C7−C13−C14	106.8(3)	C12−C14−C13	106.5(3)
C12−C14−P1	109.9(2)	C13−C14−P1	107.8(2)

reactivity and stereoselectivity toward the cycloaddition reaction using the same chiral template.[10] However, the resulting arsanorbornene cycloadduct appeared to be less stable than the corresponding phosphanorbornene. As illustrated in Scheme 3, when a $CDCl_3$ solution of the yellow dichloro complex (−)-**4** was allowed to stand for 3 weeks, an interesting stereospecific arsenic elimination occurred to give the red retrodiene complex (+)-**7** (Figure 4) with $[\alpha]_D$ +395.6° (*c* 0.2, CH_2Cl_2) and phenylarsonic acid. Phenylarsonic acid was subsequently crystallized in quantitative yield and the structure reaffirmed by X-ray crystallography (Table 6). It is interesting to note that the rate of this elimination reaction is affected by the solvent employed. For example, the elimination reaction was found to be completed in 3 weeks in $CDCl_3$ but only 1 week was needed in dichloromethane. Compared with the $^{31}P\{^1H\}$ NMR chemical shift (δ 33.6) of the dichloro complex (−)-**4**, the retrodiene complex (+)-**7** showed an unusually high $^{31}P\{^1H\}$ NMR chemical shift (δ 139.2). The single-crystal X-ray diffraction studies of (+)-**7** revealed the absence of arsine in the palladium complex. One of the double bonds of the six-membered ring coordinated onto the palladium metal center in a η^2 mode. The *S* absolute stereochemistry at C3 remained unchanged, thus reaffirming that the P−C and C−C bonds were not involved in the elimination reaction mechanism (Table 3). Furthermore, it is interesting to note that, under similar or even drastic reaction conditions, the phosphanorbornene analogue of complex (−)-**4** is stable and a similar phenomenon was not observed.[12]

Table 4. Selected Bond Lengths (Å) and Angles (deg) for (+)-**7**

Pd1−Cl1	2.316(1)	Pd1−Cl2	2.370(1)
Pd1−P1	2.226(1)	Pd1−C1	2.190(3)
Pd1−C6	2.409(3)	P1−C3	1.862(3)
C1−C6	1.399(4)	C1−C2	1.506(3)
C2−C3	1.515(3)	C3−C4	1.485(3)
C4−C5	1.326(4)	C5−C6	1.476(4)
C5−C8	1.512(4)	C6−C7	1.493(3)
C1−Pd1−P1	84.6 (1)	C1−Pd1−Cl1	167.5(1)
P1−Pd1−Cl1	87.4(1)	C1−Pd1−Cl2	94.7 (1)
P1−Pd1−Cl2	169.2(1)	Cl1−Pd1−Cl2	91.3(1)
C1−Pd1−C6	35.0(1)	P1−Pd1−C6	91.2(1)
Cl1−Pd1−C6	155.2(1)	Cl2−Pd1−C6	94.5(1)
C6−C1−C2	117.9(2)	C6−C1−Pd1	81.1(2)
C2−C1−Pd1	109.8(2)	C1−C2−C3	108.9(2)
C4−C3−C2	111.1(2)	C4−C3−P1	107.1(2)
C2−C3−P1	103.8(2)	C5−C4−C3	120.8(2)
C4−C5−C6	119.3(2)	C4−C5−C8	121.3(3)
C6−C5−C8	119.4(2)	C1−C6−C5	119.8(2)
C1−C6−C7	120.3(2)	C5−C6−C7	118.0(2)
C1−C6−Pd1	63.9(2)	C5−C6−Pd1	111.3(2)
C7−C6−Pd1	107.0(2)		

It is noteworthy that the η^2 bond in (+)-**7** (Table 4) is chemically inert under normal conditions both in the solid state and in solution. However, the optically pure phosphine ligand (−)-**8** could be liberated from the dichloro complex (+)-**7** by treatment with aqueous potassium cyanide. The phosphine ligand (−)-**8** with $[\alpha]_D$ −10.4° (*c* 0.6, CH_2Cl_2) was obtained as an air-sensitive white solid. The $^{31}P\{^1H\}$ NMR spectrum of (−)-**8** in $CDCl_3$ showed a singlet resonance at δ −11.2. It should be noted that attempts to reprepare the dichloro complex (+)-**7** from the liberated

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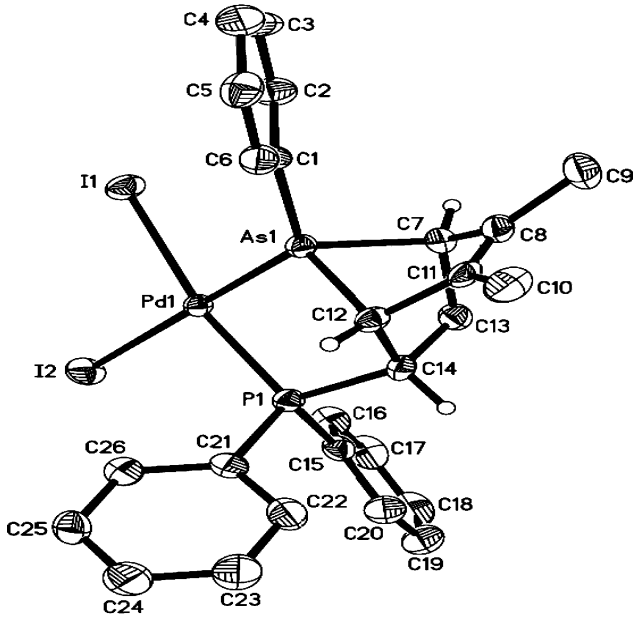

Figure 5. Molecular structure of complex (−)-**11**.

ligand (−)-**8** and $PdCl_2(NCMe)_2$ and indeed many other palladium(II) starting materials were unsuccessful. These observations reveal that, although the dichloro complex (+)-**7** is thermodynamically stable, the formation of the P−η^2−Pd chelate is a kinetically challenging process. It is noteworthy that a synthetic process that involves free ligands and metal ions is not always the most efficient approach to prepare this class of potentially important complexes.

Arsenic-Elimination Reaction. In contrast to the arsenic-elimination reaction observed in [(As−P)$PdCl_2$] [(−)-**4**], the analogous diphosphinepalladium complex [(P−P)$PdCl_2$] cannot be converted to the η^2-complex (+)-**7** under similar or even drastic reaction conditions (Scheme 3).[12] Such an observation is perhaps not surprising because P−C bonds are generally more stable than their As−C counterparts. On the other hand, it is interesting to note that no arsenic-elimination reaction was observed when the complex (−)-**3** containing the same arsanorbornene (As−P) ligand was used. Indeed, complex (−)-**3** is stable, both in the solid state and in solution. Apparently, the other ligands in complexes (−)-**3** and (−)-**4** must play a vital role in the stability of the chelating arsanorbornene (As−P) ligand and the breaking of the two As−C bonds in the elimination process.

In order to gain further insight into this novel arsinic-elimination process, complex (−)-**4** was converted to its analogous derivatives [(As−P)$PdBr_2$] [(−)-**9**] and [(As−P)-PdI_2] [(−)-**11** (Figure 5)] by treatment of the dichloro complex with potassium bromide and sodium iodide, respectively (Scheme 4). The dibromo complex (−)-**9** was isolated as yellow needles in 70% yield with $[\alpha]_D$ −51.7° (*c* 0.6, CH_2Cl_2). The diiodo complex was obtained as red prisms in 62% yield with $[\alpha]_D$ −55.0° (*c* 0.6, CH_2Cl_2). Similar to their dichloro derivative, the dibromo and diiodo complexes are stable in the solid state. In $CDCl_3$, however, the $^{31}P\{^1H\}$ NMR spectroscopic studies showed that the dibromo complex (−)-**9** was converted quantitatively to the retrodiene η^2-dibromo complex (+)-**10** within 25 days with

Scheme 4

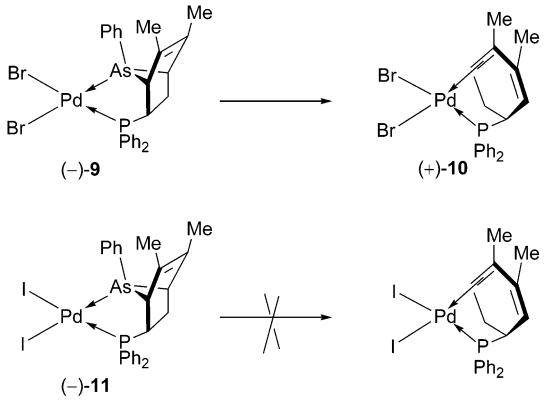

Table 5. Selected Bond Lengths (Å) and Angles (deg) for (−)-**11**

Pd1−I1	2.630(1)	Pd1−I2	2.660(1)
Pd1−As1	2.354(1)	Pd1−P1	2.278(1)
As1−C1	1.931(5)	As1−C7	1.982(5)
As1−C12	1.989(4)	P1−C14	1.846(5)
P1−C15	1.834(5)	P1−C21	1.827(5)
C7−C8	1.520(7)	C7−C13	1.542(7)
C8−C11	1.333(7)	C8−C9	1.502(7)
C10−C11	1.514(7)	C11−C12	1.509(6)
C12−C14	1.560(7)	C13−C14	1.571(7)
P1−Pd1−As1	82.8(1)	I1−Pd1−P1	169.7(1)
As1−Pd1−I1	88.3(2)	P1−Pd1−I2	96.0(1)
As1−Pd1−I2	176.3(1)	I1−Pd1−I2	93.2(1)
C1−As1−C7	106.6(2)	C1−As1−C12	108.8(2)
C7−As1−C12	76.9(2)	C1−As1−Pd1	129.3(1)
C7−As1−Pd1	114.5(2)	C12−As1−Pd1	108.4(1)
C8−C7−C13	108.3(4)	C8−C7−As1	99.4(3)
C13−C7−As1	99.9(3)	C11−C8−C9	128.9(5)
C11−C8−C7	111.5(4)	C9−C8−C7	119.6(5)
C8−C11−C12	112.5(4)	C8−C11−C10	128.4(5)
C12−C11−C10	119.1(5)	C11−C12−C14	112.4(4)
C11−C12−As1	100.6(3)	C14−C12−As1	95.2(3)
C7−C13−C14	107.4(4)	C12−C14−C13	105.6(4)
C12−C14−P1	109.3(3)	C13−C14−P1	109.1(3)

the temperature kept at 23 °C. Thus, the arsanorbornene ligand in both the dichloro complex (−)-**4** and the dibromo complex (−)-**9** exhibited similar stability and reactivity. Interestingly, and to our surprise, the arsenic-elimination reaction did not occur when the diiodo complex (−)-**11** was dissolved in solution. At higher temperature, however, (−)-**11** decomposed rapidly. A comparison of the solid-state structures of the complex (−)-**3**, the dichloro complex (−)-**4**, and the diiodo complex (−)-**11** (Table 5) revealed that the structural features of the chiral arsanorbornene (As−P) bidentate in all three complexes are similar; they all suffer from severe intrachelate steric constraints. The torsional strain within these five-membered chelate rings can be observed from the noticeable distortion of the As−C−C angles [95.8-(2), 95.3(2), and 95.2(3)° for (−)-**3**, (−)-**4**, and (−)-**11**, respectively]. All of these angles are seriously distorted from the ideal tetrahedral angle of 109° for tertiary carbon centers. Interestingly, the Pd−As bond distance [2.325(1) Å] in the reactive dichloro complex (−)-**4** is the shortest among the three complexes [2.447(1) and 2.354(1) Å in (−)-**3** and (−)-**11**, respectively]. This structural feature indicates that the Pd−As bond in the dichloro complex is more chemically inert under normal conditions than its counterparts in the other two complexes. It is noteworthy that the observed

Table 6. Crystallographic Data for Complexes (+)-**2**, (−)-**3**, (−)-**4**, (+)-**7**, and (−)-**11**

	(+)-**2**	(−)-**3**	(−)-**4**	(+)-**7**	(−)-**11**
formula	$C_{22}H_{27}AsClNP{\cdot}CHCl_3$	$C_{36}H_{40}AsClNO_4PPd{\cdot}0.5CHCl_3$	$C_{26}H_{26}AsCl_2PPd{\cdot}CHCl_3$	$C_{20}H_{21}Cl_2PPd$	$C_{26}H_{26}AsI_2PPd$
fw	641.58	858.11	741.03	469.64	804.56
space group	$P3_1$	$P1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
cryst syst	trigonal	triclinic	orthorhombic	orthorhombic	orthorhombic
a/Å	10.1936(3)	9.9874(3)	8.6453(3)	7.6291(3)	9.3153(3)
b/Å	10.1936(3)	10.4103(3)	14.7344(6)	14.2545(5)	17.0471(7)
c/Å	22.6287(8)	18.6414(7)	22.8349(9)	17.1460(6)	17.1125(7)
α/deg	90	93.513(2)	90	90	90
β/deg	90	103.462(2)	90	90	90
γ/deg	120	100.6610(10)	90	90	90
V/Å^3	2036.32(11)	1841.32(10)	2908.78(19)	1864.61(12)	2717.45(18)
Z	3	2	4	4	4
T/K	296(2)	173(2)	173(2)	298(2)	273(2)
D_{calcd}/g cm^{-3}	1.570	1.548	1.692	1.673	1.967
λ/Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
μ/mm^{-1}	2.297	1.660	2.298	1.366	4.234
F(000)	960	870	1472	944	1528
Flack param	0.017(7)	0.003(3)	−0.001(8)	0.00(2)	0.022(12)
R1 (obs data)[a]	0.0321	0.0253	0.0296	0.0279	0.0261
wR2 (obs data)[b]	0.0857	0.0623	0.0613	0.0511	0.0714

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

relative stabilities of the Pd−As bonds are consistent with the trend that is derived from the classical electronic trans effects:[13] among the three trans X−Pd−As donors, chloride exhibits the weakest effect on the stability of the Pd−As bond. Furthermore, the structural investigation revealed that, within the five-membered chelate rings, the As−C bond distance in the dichloro complex (−)-**4** [1.961(3) Å] is the shortest when compared with those in complexes (−)-**3** and (−)-**11** [1.980(2) and 1.989(4) Å in (−)-**3**, and (−)-**11**, respectively]. Thus, the structural analysis indicated that the stronger As−Pd coordination effect associated with the dichloro complex is able to transmit to the As−C bond, thus affecting its chemical stability and reactivity. Apparently, the arsenic-elimination reaction from the arsanorbornene (As−P) ligand is therefore controlled by the strength of the As−Pd bonds. In view of the difficulty observed in the subsequent recoordination of the η^2 ligand to palladium(II), we believed that, during the arsenic-elimination reaction, the breaking of the two As−C bonds and the formation of the η^2-Pd coordination must have occurred concertedly. We are currently investigating the general heterocyclic chemistry of DMPA toward other dienophiles, exploring the synthesis of a family of functionalized P−η^2 complexes via similar arsenic-elimination reactions, and also investigating their catalytic potential.

Experimental Section

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 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.

Diphenylvinylphosphine,[14] DMPA,[15] and (+)-**1**[16] were prepared following the literature procedures.

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

Preparation of Complex (+)-2. A mixture of DMPA (1.50 g, 6.46 mmol) and (+)-**1** (1.87 g, 3.22 mmol) in CH_2Cl_2 (70 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 CH_2Cl_2−*n*-hexane to give a yellow powder, which was recrystallized from $CHCl_3$−*n*-hexane in the form of bright-yellow prisms (2.53 g, 75%). $[\alpha]_D$ = +60.4° (*c* 0.6, CH_2Cl_2). Mp: 110−111 °C. Anal. Calcd for $C_{22}H_{27}AsClNPd$: C, 50.6; H, 5.2; N, 2.7. Found: C, 50.8; H, 5.4; N, 2.8. ^{1}H NMR ($CDCl_3$, δ): 1.64 (d, $^3J_{HH}$ = 6.5 Hz, 3H, $CHCH_3$), 2.09 (s, 6H, DMPA−CH_3), 2.76 (s, 3H, NCH_3), 2.93 (s, 3H, NCH_3), 3.88 (q, $^3J_{HH}$ = 6.5 Hz, 1H, $CHCH_3$), 6.77−7.79 (m, 11H, aromatics).

Cycloaddition Reaction: Preparation of Complex (−)-3. A solution of (+)-**2** (0.91 g, 1.74 mmol) in CH_2Cl_2 (50 mL) was stirred for 2 h in the presence of a solution of silver perchlorate (1.0 g) in H_2O (1 mL). The organic layer, after the removal of AgCl, was then washed with H_2O (3 × 50 mL), dried ($MgSO_4$), and subsequently treated with diphenylvinylphosphine (0.37 g, 1.74 mmol) at room temperature for 3 h. Removal of the solvent gave (−)-**3** as a thick oil, which was then recrystallized from $CHCl_3$−Et_2O to give the complex as colorless prisms (0.77 g, 60%). $[\alpha]_D$ = −71.9° (*c* 0.6, CH_2Cl_2). Mp: 164−165 °C. Anal. Calcd for $C_{36}H_{40}AsClNO_4PPd{\cdot}0.5CHCl_3$: C, 51.1; H, 4.8; N, 1.6. Found: C, 50.9; H, 4.6; N, 1.7. ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 50.1. ^{1}H NMR ($CDCl_3$, δ): 1.40 (s, 3H, DMPA−CH_3), 1.60 (d, $^5J_{PH}$ = 1.0 Hz, 3H, DMPA−CH_3), 1.86 (d, $^3J_{HH}$ = 6.4 Hz, 3H, $CHCH_3$), 1.95 (m, 1H, $H_{6,ax}$), 2.56 (dd, $^2J_{HH}$ = 13.9 Hz, $^3J_{PH}$ = 24.3 Hz, 1H, $H_{6,eq}$) 2.74 (d, $^4J_{PH}$ = 1.5 Hz, 3H, NCH_3), 2.80 (s, 3H, NCH_3), 2.82 (s, 1H, H_4), 3.10 (t, $^3J_{HH}$ = 9.0 Hz, 1H, H_5), 3.64 (qn, $^3J_{HH}$ = $^4J_{PH}$ = 6.0 Hz, 1H, $CHCH_3$), 3.82 (s, 1H, H_1), 6.46−8.19 (m, 19H, aromatics).

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Removal of Chiral Auxiliary: Synthesis of Complex (−)-4. The complex (−)-**3** (0.18 g, 0.16 mmol) was dissolved in CH_2Cl_2 (60 mL) and treated with excess concentrated HCl (4 mL) at room temperature for 0.5 h. The mixture was then washed with H_2O (3 × 50 mL), dried ($MgSO_4$), and subsequently recrystallized from $CHCl_3-Et_2O$ as pale-yellow crystals (−)-**4** (0.06 g, 60%). $[\alpha]_D = -40.0°$ (*c* 0.6, CH_2Cl_2). Mp: 162−163 °C. Anal. Calcd for $C_{26}H_{26}AsCl_2PPd \cdot 0.5CHCl_3$: C, 43.8; H, 3.7. Found: C, 43.6; H, 3.9. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 33.6. ^1H NMR ($CDCl_3$, δ): 1.61 (s, 3H, CH_3), 1.65 (d, $^5J_{PH} = 0.8$ Hz, 3H, CH_3), 1.94 (ddd, $^3J_{HH} = 10.0$ Hz, $^2J_{HH} = 13.2$ Hz, $^3J_{HH} = 19.3$ Hz, 1H, H_3), 2.60 (dd, $^2J_{HH} = 12.8$ Hz, $^3J_{PH} = 23.8$ Hz, 1H, $H_{3'}$), 3.04 (dt, $^3J_{HH} = 6.7$ Hz, $^2J_{PH} = 2.0$ Hz, 1H, H_2), 3.16 (s, 1H, H_1), 3.49 (d, $^3J_{HH} = 3.0$ Hz, 1H, H_4), 7.38−8.26 (m, 15H, aromatics).

Liberation of the As−P Ligand (−)-5. A solution of (−)-**4** (0.13 g, 0.21 mmol) in CH_2Cl_2 (20 mL) was stirred vigorously with a saturated aqueous solution of KCN (1.0 g) for 3 min. The organic layer was separated, then washed with H_2O (3 × 20 mL), and dried ($MgSO_4$). Upon removal of the solvent, the free ligand (−)-**5** was obtained as an air-sensitive white solid (0.08 g, 86%). $[\alpha]_D = -70.4°$ (*c* 0.9, CH_2Cl_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −11.1.

Arsenic-Elimination Reaction: Isolation of Complex (+)-7. The complex (−)-**4** (0.12 g, 0.19 mmol) was dissolved in CH_2Cl_2 and allowed to stand at room temperature for 1 week; red crystals of (+)-**7** were obtained (0.03 g, 34%). $[\alpha]_D = +395.6°$ (*c* 0.2, CH_2Cl_2). Mp: 149−150 °C. Anal. Calcd for $C_{20}H_{21}Cl_2PPd$: C, 51.1; H, 4.5. Found: C, 51.0; H, 4.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 139.2. ^1H NMR ($CDCl_3$, δ): 1.91 (d, $^5J_{PH} = 5.6$ Hz, 3H, CH_3), 2.17 (s, 2H, CH_2), 2.50 (s, 3H, CH_3), 3.29 (t, $^3J_{HH} = 5.5$ Hz, 1H, CH), 5.81 (d, $^3J_{HH} = 4.8$ Hz, 1H, =CH), 6.04 (s, 1H, =CH), 7.45−8.02 (m, 10H, aromatics).

Liberation of Monodentate Phosphine Ligand (−)-8. A solution of (+)-**7** (0.02 g, 0.04 mmol) in CH_2Cl_2 (20 mL) was stirred vigorously with a saturated aqueous solution of KCN (1.0 g) for 3 min. The organic layer was separated, washed with H_2O (3 × 20 mL), and dried ($MgSO_4$). Upon removal of the solvent, the free ligand (−)-**8** was obtained as an air-sensitive white solid (0.01 g, 86%). $[\alpha]_D = -10.4°$ (*c* 0.6, CH_2Cl_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −11.2. ^1H NMR ($CDCl_3$, δ): 1.25 (s, 3H, CH_3), 1.74 (d, 3H, $^5J_{PH} = 1.3$ Hz, CH_3), 2.03−2.17 (m, 2H, CH_2), 3.11 (m, 1H, CH), 5.36 (d, $^3J_{PH} = 5.7$ Hz, 1H, =CH), 5.45 (s, 1H, =CH), 7.31−7.52 (m, 10H, aromatics).

Preparation of the Dibromo Complex (−)-9. The solution of (−)-**4** (0.10 g, 0.16 mmol) in CH_2Cl_2 (50 mL) was added to KBr (0.20 g) in acetone (50 mL) and H_2O (10 mL) and stirred vigorously for 10 min. The solvents were removed, and the residue was extracted with CH_2Cl_2 and H_2O and dried with $MgSO_4$. Removal of the solvent gave (−)-**9** as a solid, which was then recrystallized from $CHCl_3-Et_2O$ to give the product as yellow needle crystals (0.08 g, 70%). $[\alpha]_D = -51.7°$ (*c* 0.6, CH_2Cl_2). Mp: 161−162 °C. Anal. Calcd for $C_{26}H_{26}AsBr_2PPd$: C, 44.0; H, 3.7. Found: C, 43.8; H, 3.8. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 35.8. ^1H NMR ($CDCl_3$, δ): 1.57 (s, 3H, CH_3), 1.64 (s, 3H, CH_3), 1.96 (ddd, $^3J_{HH} = 9.9$ Hz, $^2J_{HH} = 13.1$ Hz, $^3J_{HH} = 19.6$ Hz, 1H, H_3), 2.65 (dd, $^2J_{HH} = 13.0$ Hz, $^3J_{PH} = 25.9$ Hz, 1H, $H_{3'}$), 3.04 (dt, $^3J_{HH} = 4.5$ Hz, $^2J_{PH} = 2.2$ Hz, 1H, H_2), 3.13 (s, 1H, H_1), 3.50 (d, $^3J_{HH} = 3.2$ Hz, 1H, H_4), 7.38−8.27 (m, 15H, aromatics).

Preparation of the Elimination Product (+)-10. A solution of complex (−)-**9** (0.05 g, 0.07 mmol) was dissolved in CH_2Cl_2 and allowed to stand at room temperature for several days. Red crystals of (+)-**10** were obtained (0.02 g, 57%). $[\alpha]_D = +495.0°$ (*c* 0.2, CH_2Cl_2). Mp: 185−186 °C. Anal. Calcd for $C_{20}H_{21}Br_2PPd$: C, 43.0; H 3.79. Found: C, 42.7; H, 3.88. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 141.8. ^1H NMR (CD_2Cl_2, δ): 1.87 (d, $^5J_{PH} = 6.2$ Hz, 3H, CH_3), 2.12 (s, 2H, CH_2), 2.51 (s, 3H, CH_3), 3.29 (t, $^3J_{HH} = 8.0$ Hz, 1H, CH), 5.82 (d, $^3J_{HH} = 7.4$ Hz, 1H, =CH), 6.21 (s, 1H, =CH), 7.46−7.97 (m, 10H, aromatics).

Synthesis of the Diiodo Complex (−)-11. The solution of (−)-**4** (0.10 g, 0.16 mmol) in CH_2Cl_2 (80 mL) was mixed with NaI (0.20 g) in acetone (80 mL) and stirred vigorously for 10 min. The solvents were removed, and the residue was extracted with CH_2Cl_2. Removal of the solvent gave (−)-**11** as a solid, which was then recrystallized from $CHCl_3-Et_2O$ to give the product as red microcrystals (0.08 g, 62%). $[\alpha]_D = -55.0°$ (*c* 0.6, CH_2Cl_2). Mp: 144−145 °C. Anal. Calcd for $C_{26}H_{26}AsI_2PPd$: C, 38.8; H, 3.3. Found: C, 38.5; H, 3.3. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 37.7. ^1H NMR ($CDCl_3$, δ): 1.50 (s, 3H, CH_3), 1.63 (s, 3H, CH_3), 2.00 (ddd, $^3J_{HH} = 9.5$ Hz, $^2J_{HH} = 13.7$ Hz, $^3J_{HH} = 20.8$ Hz, 1H, H_3), 2.70 (dd, $^2J_{HH} = 12.9$ Hz, $^3J_{PH} = 24.8$ Hz, 1H, $H_{3'}$), 2.86 (dt, $^3J_{HH} = 8.2$ Hz, $^2J_{PH} = 2.2$ Hz, 1H, H_2), 3.04 (d, $^3J_{HH} = 1.8$ Hz, 1H, H_1), 3.52 (d, $^3J_{HH} = 3.0$ Hz, 1H, H_4), 7.39−8.24 (m, 15H, aromatics).

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Supporting Information Available: Crystallographic data in CIF format for complexes (+)-**2**, (−)-**3**, (−)-**4**, (+)-**7**, and (−)-**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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