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Optical Resolution and the Study of Ligand Effects on the *Ortho*-Metalation Reaction of Resolved (±)-Diphenyl[1-(1-naphthyl)ethyl]phosphine and Its Arsenic Analogue

Joseph Kok-Peng Ng, Geok-Kheng Tan, Jagadese J. Vittal, and Pak-Hing Leung*

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260

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Two highly air-sensitive asymmetric ligands (±)-diphenyl[1-(1-naphthyl)ethyl]phosphine and its arsenic analogue [(±)-L] have been prepared and resolved by the fractionalization of a pair of diastereomeric palladium complexes containing the appropriate ligand and *ortho*-metalated (*R*)-(1-(dimethylamino)ethyl)naphthylene. X-ray structural analysis revealed that the less soluble isomers in each resolution contained the resolving ligand of the *S* absolute configuration. The resolved ligands coordinated as monodentates with only the phosphorus or arsenic donor coordinated to the resolving organopalladium unit. Due to the steric congestions between the phenyl and the naphthyl rings, the Ph_2E–C distances in both monodentate ligands are unusually long [1.885(2) Å for E = P and 2.035(7) Å for E = As]. The (*R*)-naphthylamine auxiliary could be removed chemoselectively from the resolved complexes by treatment with concentrated hydrochloric acid to give the corresponding bis(μ-chloro) complexes (–)-[(*S*)-$LPdCl_2]_2$. Treatments of these dimeric complexes with sodium acetate in ethanol gave the novel *ortho*-metalated complex bis(μ-chloro)-bis[(*S*)-1-[1-(diphenylphospha)ethyl]naphthylenyl-C^2,*P*]dipalladium(II), with $[\alpha]_D$ +559° (CH_2Cl_2), and the analogous *ortho*-metalated (*S*)-arsa complex, with $[\alpha]_D$ +349° (CH_2Cl_2). The Ph_2E–C distances recorded for the *ortho*-metalated phosphine complex are 1.841(6) and 1.846(5) Å, and those recorded for the organometallic arsa rings are 1.938(9) and 1.945(9) Å. These Ph_2E–C distances are noticeably shorter than those recorded for their analogous monodentate complexes. The intrachelate E–Pd–C angles of the analogous amino, phospha, and arsa complexes involved in the current study are similar [within the range of 80.5(2)–82.1(3)°] although it is noticeable that As > P > N.

Introduction

Since the past decade, there has been a blooming growth in the development of cyclometalated reagents, particularly those with *ortho*-metalated aromatic carbon−metal bonds.[1,2] Such a rapid growth is partly due to the increasing demands for new reagents in catalysis and in synthetic organic reactions.[3] The metal−aromatic carbon bonds in the *ortho*-metalated chelates, being thermodynamically stable and kinetically inert, offer strong and predictable trans electronic influences to the metal ions.[4] Thus, it is unsurprising that *ortho*-metalated complexes are attractive candidates as catalysts or as reaction promoters.

We have been interested in the development of the chiral *ortho*-metalated palladium complexes derived from substi-

* To whom correspondence should be addressed. E-mail: chmlph@nus.edu.sg.

(1) For recent examples, see: Hockness, D. C.; Gugger, P. A.; Leung, P. H.; Mayadunne, R. C,; Pabel, M.; Wild, S. B. *Tetrahedron* **1997**, *53*, 4083.

(2) Doucet, H.; Brown, J. M. *Tetrahedron: Asymmetry* **1997**, *8*, 3775. Albert, J.; Cadena, J. M.; Granell, J.; Muller, G.; Ordinas, J. I.; Panyella, D.; Puerta, C.; Sanudo, C.; Valerga, P. *Organometallics* **1999**, *18*, 8**,** 3511. Zhao, G.; Yang, Q. C.; Mak. T. C. W. *Organometallics* **1999**, *18*, 3623. Bienewald, F.; Ricard, L.; Mercier, F. Mathey, F. *Tetrahedron: Asymmetry* **1999**, *10*, 4701. Zhao, G.; Wang, Q. G.; Mak. T. C. W. *Organometallics* **1998**, *17*, 3437. Dunina, V. V.; Kuzmina, L. G.; Kazakova, M. Y.; Grishin, Y. K.; Veits, Y. A.; Kazakova, E. I. *Tetrahedron: Asymmetry* **1997**, *8*, 2537. Tresoldi, G.; DeMunno, G.; Nicolo, F.; LoSchiavo, S.; Piraino, P. *Inorg. Chem.* **1996**, *35*, 1377.

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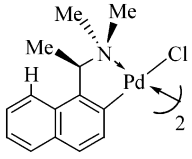
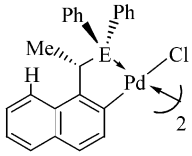
tuted benzyl-,[5] naphthyl-,[6] and phenanthrylamines.[7] All these organometallic complexes are efficient promoters for various types of asymmetric ligand transformation reactions.[8] Among the three types of *ortho*-metalated amine complexes, the enantiomers of the naphthylamine complex **1**, being readily prepared from the commercially available primary precursors, have been utilized most frequently. Similar to other *ortho*-metalated complexes, the organometallic ring in **1** is kinetically and thermodynamically stable. Furthermore, due to the repulsive steric interaction between the methyl group on the chiral carbon center and the adjacent naphthylene proton, the absolute conformation of the five-membered ring is fixed and not interconvertable, both in the solid state and in solution.[9] Thus, the prochiral *N*-methyl groups, which are located on the chiral carbon stereocenter, are able to project efficiently the chirality of the asymmetric organometallic ring to the neighboring coordinate position, which is a potential site in the asymmetric template reactions.[10] A series of functionalized P-chiral phosphines have been generated stereoselectively by using **1** as the chiral reaction template.[8] We believe that by systematically varying the electronic properties of the ligands and the nature of the metal centers, chiral *ortho*-metalated complexes could be applied to a wide spectrum of asymmetric synthesis. In this article, we report the optical resolution of (±)-diphenyl[1-(1-naphthyl)ethyl]-phosphine and its arsenic analogue, followed by the subsequent *ortho*-metalations of these resolved ligands. The corresponding *ortho*-palladated complexes **2** and **3** exhibit the key stereochemical features of their analogous amine complex **1**. Therefore, a comparison of the three complexes should reveal systematically the electronic contributions of the three group-15 elements toward the cyclopalladated rings. It is interesting to note that while a number of chiral cyclopalladated phosphine ligands have been prepared recently,[11] the analogous cyclopalladation reaction involving chiral arsines has not been reported hitherto.



(*R*)-**1**



(*S*)-**2** E = P
(*S*)-**3** E = As

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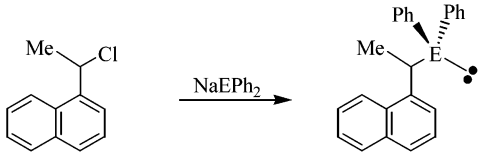
Scheme 1



(±)-**4** (±)-**5** E = P (±)-**6** E = As

Results and Discussion

Synthesis and Optical Resolution of Ligands. As illustrated in Scheme 1, both the racemic arsine and phosphine ligands could be prepared by using the chloro species (±)-**4** as the starting material. Treatments of (±)-**4** with sodium diphenylphosphide and sodium diphenylarsenide at room temperature gave the racemic ligands (±)-**5** and (±)-**6**, respectively, as air-sensitive low melting white solids. The $^{31}P\{^{1}H\}$ NMR spectrum of the phosphine ligand (±)-**5** in $CDCl_3$ showed a singlet at δ 2.1. The ^{1}H NMR spectrum of (±)-**5** in the same solvent exhibited a doublet of doublet signal at δ 1.49 ($^{3}J_{HH}$ = 6.8 Hz, $^{3}J_{PH}$ = 13.7 Hz) for the CH*Me* group and a doublet of quartet resonance pattern at δ 4.42 ($^{3}J_{HH}$ = 6.8 Hz, $^{2}J_{PH}$ = 7.2 Hz) for the C*H*M*e* proton. The ^{1}H NMR spectrum of the arsine ligand in $CDCl_3$ showed a doublet at δ 1.65 ($^{3}J_{HH}$ = 7.2 Hz) for the CH*Me* group while a simple quartet was recorded at δ 4.48 ($^{3}J_{HH}$ = 7.2 Hz) for the C*H*M*e* proton. It is noteworthy that both the arsine and phosphine ligands were found to be highly air-sensitive. Indeed, they would be oxidized spontaneously to the corresponding oxides when brought in contact with water or other aqueous solutions that had been previously deoxygenated by the standard bubbling procedures. Thus, it was necessary to reflux water and all solvents vigorously under argon before they were used in the ligand synthesis. The striking air-sensitivity of (±)-**5** and (±)-**6** is somewhat

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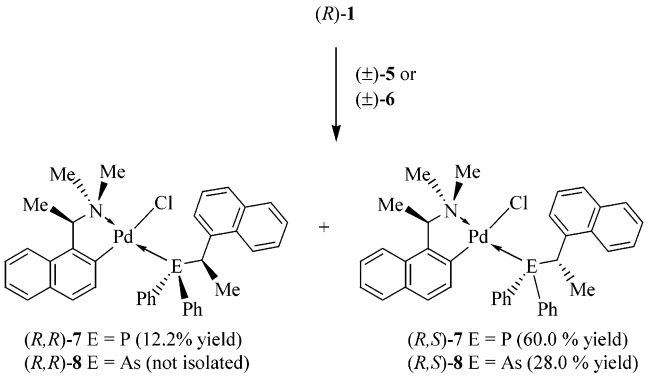
Scheme 2



unexpected as most of the tertiary phosphines and arsines bearing the Ph_2P-C structural feature are either air-stable or only of moderate air-sensitivity. For example, while it is unnecessary that triphenylphosphine and triphenylarsine be stored in inert atmospheres, (2-mercaptoethyl)diphenylarsine,[10] [(2-methylsulfinyl)ethyl]diphenylarsine,[12] and their phosphine analogues can be manipulated in the air for a short period of time. It has also been reported that the enantiomerically enriched form of ethylmethyl-*n*-propylarsine could be transported by a stream of air without being oxidized to the corresponding oxide.[13] In the current ligand synthesis, the tertiary phosphine and arsine ligands are indeed of noticeably higher sensitivity toward air than their secondary diphenylarsine and diphenylphosphine starting materials.

The optical resolutions of (±)-**5** and (±)-**6** were achieved by means of metal complexation (Scheme 2). The resolution processes involved the separation of a pair of internally diastereomeric palladium complexes derived from the resolving agent (*R*)-**1**. The initial mixture of diastereomers in each process was obtained in high yields (85−90%) from the reaction between (*R*)-**1** and 2 equiv each of the appropriate racemic ligand in dichloromethane. In each preparation, the ^1H NMR spectrum of the crude diastereomeric mixture was recorded prior to purification. For the characterization of the phosphine diastereomers (*R*,*R*)- and (*R*,*S*)-**7**, the corresponding $^{31}P\{^1H\}$ NMR spectrum was also recorded. These spectroscopic studies confirmed that a 1:1 mixture of the two stereochemically distinct isomers was formed in each complex synthesis. For instance, the $^{31}P\{^1H\}$ NMR spectrum of **7** in $CDCl_3$ exhibited two singlets of equal intensities at δ 45.1 and 50.5 for the two diasteromers. In both resolutions, the mixtures were separated efficiently into their diastereomerically pure forms by fractional crystallization. Recrystallization of **7** from dichloromethane−ethanol produced the less soluble (*R*,*S*) isomer as bright yellow prisms in 60.0% yield with $[\alpha]_D$ −7.0° (CH_2Cl_2). The $^{31}P\{^1H\}$ NMR spectrum of (*R*,*S*)-**7** in $CDCl_3$ confirmed that the compound is stereochemically pure as only one singlet was observed at δ 50.5. Similarly, the less soluble arsine complex (*R*,*S*)-**8** was isolated in its pure form with a yield of 28.0% and $[\alpha]_D$ +60° (CH_2Cl_2), by fractional crystallization of the original mixture

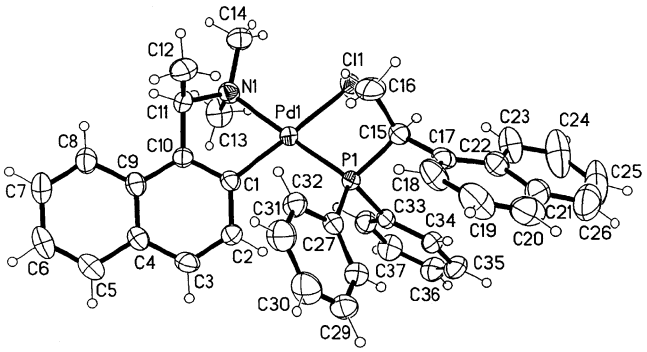


Figure 1. Molecular structure of complex (*R*,*S*)-**7**.

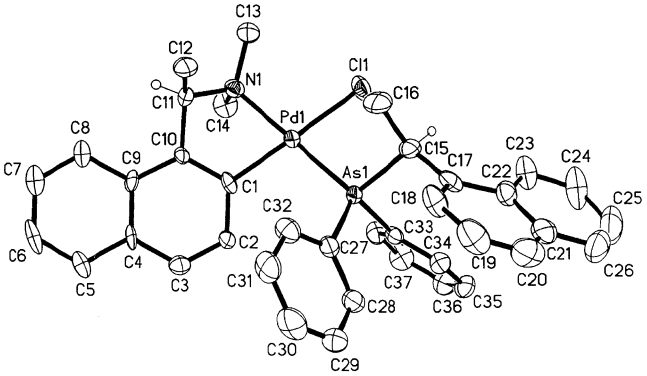


Figure 2. Molecular structure of complex (*R*,*S*)-**8**.

from dichloromethane−ethanol. In the resolution process involving **7**, the remaining mother liquor that has been enriched with the more soluble diastereomer (*R*,*R*)-**7** was purified by silica gel column chromatography. The (*R*,*R*)-**7** diastereomer was thus obtained as a yellow solid in 12.2% yield with $[\alpha]_D$ −12° (CH_2Cl_2) in its optically pure state. This was confirmed by its $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$, which revealed a singlet at δ 45.1. It is noteworthy that the coordinated phosphine and arsine ligands in complexes **7** and **8**, respectively, are air-stable.

The absolute configurations of the two less soluble diastereomeric complexes (*R*,*S*)-**7** and (*R*,*S*)-**8** were confirmed by X-ray crystallography (Figures 1 and 2). The study revealed that the reactions of (*R*)-**1** with (±)-**5** and with (±)-**6** have resulted in the cleavage of the chloro bridges in (*R*)-**1** and that the two novel ligands coordinated to palladium as mondentates via their soft donor atoms at positions trans to the NMe_2 group in each case. The resolved C(15) chiral carbon centers in both coordinated monodentate ligands are of the same *S* absolute configurations. Selected bond distances and bond angles of the complexes are given in Table 1. In each complex, there is a characteristic reduction from 90° in the angle at palladium within the five-membered chelate ring [80.6(1)° in (*R*,*S*)-**7** and 80.5(2)° in (*R*,*S*)-**8**]. It is interesting to note that, in both complexes, the E(1)−C(15) distances are the longest when compared with the other E(1)−C bonds within the same complex. Indeed, the $Ph_2P-CHRR'$ bond distance in (*R*,*S*)-**7** [1.885(2) Å] is clearly longer than that recorded for a similar moiety [1.852(9) Å] in a Ph_2P-substituted phosphanorbornene palladium complex.[14] Similarly, the $Ph_2As-CHRR'$ bond distance in (*R*,*S*)-**8** [2.035(7) Å] is considerably longer than that recorded for a

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Table 1. Selected Bond Lengths (Å) and Angles (deg) of (*R*,*S*)-**7**, (*R*,*S*)-**8**, and (*R*,*S*)-**9**

	(*R*,*S*)-**7** [E = P, X(1) = Cl(1)]	(*R*,*S*)-**8** [E = As, X(1) = Cl(1)]	(*R*,*S*)-**9** [E = P, X(1) = O(1)]
Pd(1)−N(1)	2.140(2)	2.144(5)	2.132(2)
Pd(1)−C(1)	2.006(2)	2.005(6)	1.990(3)
Pd(1)−E(1)	2.269(1)	2.394(1)	2.288(1)
Pd(1)−X(1)	2.409(1)	2.427(2)	2.192(2)
N(1)−C(11)	1.512(3)	1.531(8)	1.505(4)
C(10)−C(11)	1.502(3)	1.525(9)	1.513(4)
C(1)−C(10)	1.384(3)	1.399(9)	1.374(4)
E(1)−C(15)	1.885(2)	2.035(7)	1.872(3)
E(1)−C(27)	1.826(2)	1.952(6)	1.819(3)
E(1)−C(33)	1.826(2)	1.963(6)	1.822(3)
C(15)−C(17)	1.522(3)	1.524(9)	1.523(4)
C(17)−C(18)	1.371(4)	1.382(9)	1.373(4)
C(1)−Pd(1)−N(1)	80.6(1)	80.5(2)	80.5(1)
C(1)−Pd(1)−E(1)	97.2(1)	97.1(2)	95.2(1)
N(1)−Pd(1)−E(1)	172.5(1)	171.9(1)	175.2(1)
C(1)−Pd(1)−X(1)	168.4(1)	170.7(2)	171.9(1)
N(1)−Pd(1)−X(1)	93.1(1)	94.6(2)	91.8(1)
E(1)−Pd(1)−X(1)	90.3(1)	88.8(1)	92.4(1)
C(1)−C(10)−C(9)	121.7(2)	122.7(6)	121.7(3)
C(1)−C(10)−C(11)	117.3(2)	115.5(5)	117.3(3)
N(1)−C(11)−C(10)	106.5(2)	106.3(5)	105.8(2)
E(1)−C(15)−C(16)	109.5(2)	106.8(5)	109.4(2)
E(1)−C(15)−C(17)	115.7(2)	114.5(4)	115.4(2)
C(15)−C(17)−C(18)	119.6(2)	120.2(6)	119.4(3)

Ph_2As-substituted arsanorbornene palladium complex [1.950(7) Å].[15] The E−Ph distances in both (*R*,*S*)-**7** and (*R*,*S*)-**8** do not differ significantly from those observed in the Ph_2E-substituted norbornene complexes. Apparently, the lengthening of the E(1)−C(15) distances is attributed to the steric congestion that is present between the naphthyl and the phenyl rings.

It is interesting to note that, in theory, the naphthylene moieties of the monodentate phosphine and arsine ligands in (*R*,*S*)-**7** and (*R*,*S*)-**8**, respectively, may undergo the *ortho*-metalation reaction to form the targeted P−C and As−C organometallic rings. However, attempts to form these bis-bidentates were unsuccessful. As the *ortho*-metalation requires the accessibility of two adjacent coordination sites, the reaction could be kinetically hindered by the Pd−Cl bonds in these metal complexes. It has been well established that the Pd−Cl bonds in this class of *ortho*-metalated amine complexes are inert toward ligand substitution reactions.[16] Therefore the terminal chloro ligand in (*R*,*S*)-**7** was replaced by a highly labile perchlorato counterpart. The conversion of the chloro complex (*R*,*S*)-**7** into its perchlorato analogue (*R*,*S*)-**9** was achieved efficiently by the treatment of a dichloromethane solution of chloro complex with an aqueous solution of silver perchlorate. The perchlorato complex was isolated from dichloromethane−diethyl ether as beautiful yellow prisms with $[\alpha]_D$ +18.0° (CH_2Cl_2). The $^{31}P\{^1H\}$ NMR spectrum of (*R*,*S*)-**9** in $CDCl_3$ recorded a sole singlet

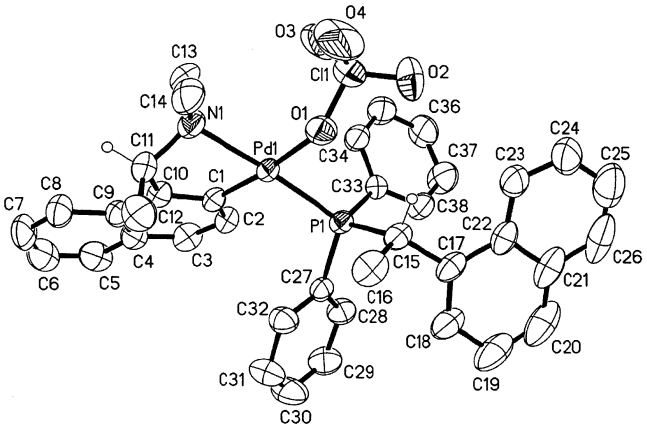
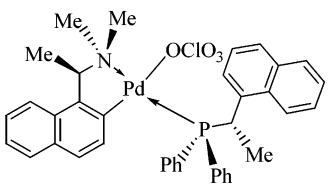


Figure 3. Molecular structure of complex (*R*,*S*)-**9**.

at δ 47.9. The X-ray structural analysis of (*R*,*S*)-**9** confirmed that the intended Pd−$OClO_3$ coordination complex had been formed (Figure 3). The general structural features of (*R*,*S*)-**9** are similar to that observed in its parent chloro complex (*R*,*S*)-**7**. The Pd−$OClO_3$ bond can be displaced readily by most potential donor atoms.[6] Indeed, the perchlorato ligand could be replaced even by means of the very weak keto-oxygen → Pd coordination.[17] Hence, The Pd−$OClO_3$ bond in (*R*,*S*)-**9** may be considered as a readily available vacant site for the coordinated phosphine ligand to undergo the *ortho*-metalation reaction. However, attempts to form the P−C organometallic chelate with complex (*R*,*S*)-**9** under different reaction conditions only resulted in the decomposition of the complex. Clearly, the failure of the *ortho*-metalation reaction with complexes (*R*,*S*)-**7, 8**, and **9** was not simply due to the kinetic predicament. It is likely that the reaction was deterred by the thermodynamic instability of the *ortho*-metalated products. Should the coordinated phosphine or arsine ligands form the corresponding E−C organometallic rings, the resulting product would be a bis-bidentate complex containing the trans aryl−Pd−aryl moiety. The trans geometry, however, is thermodynamically unfavorable as the aryl groups are strong π-acids and the classic competition for electrons would occur between the *trans*-aryl groups.[18] A regio-rearrangement of these complexes to form the corresponding isomeric *trans*-aryl−Pd−P moieties would result in similar adverse electronic properties.[1,10,12] In the attempt to resolve this electronic dilemma, the *ortho*-metalation reaction was carried out in the absence of the orthometalated naphthylamine auxiliary.



(*R*,*S*)-**9**

Removal of the Naphthylamine Auxiliary and Formation of the *Ortho*-*Metalated Complexes*. Similar to the well-documented resolution of phosphine and arsine ligands,[19] the resolved ligands in complexes (*R*,*S*)-**7** and **8** could, in principle, be liberated from palladium prior to the *ortho*-

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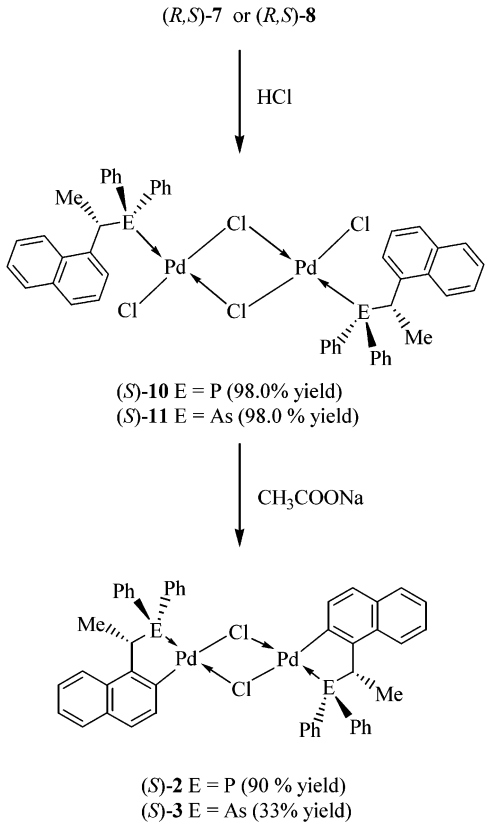
Scheme 3



metalation reaction with another palladium(II) ion. In practice, however, we found that this approach was inefficient when applied to the synthesis of (*S*)-**2** and (*S*)-**3**. Due to their extreme air-sensitivities, large portions of the precious optically active ligands were oxidized into the corresponding oxides during the liberation and recomplexation processes.

An alternative approach is to liberate the naphthylamine auxiliary from (*R*,*S*)-**7** and **8** and then perform the *ortho*-metalation reaction with the resolved soft ligands on the palladium ions that were used originally in their resolution processes, the advantage being that, throughout this approach, the resolved ligands are protected by means of metal complexation. As illustrated in Scheme 3, the naphthylamine auxiliary in both complexes could be removed chemoselectively by the treatment of the complexes with concentrated hydrochloric acid. Both neutral complexes (*S*)-**10** and (*S*)-**11** were obtained as orange solids in ca. 98% yield, with $[\alpha]_D$ −215° (CH_2Cl_2) and $[\alpha]_D$ −170° (CH_2Cl_2), respectively. The $^{31}P\{^1H\}$ NMR spectrum of (*S*)-**10** in $CDCl_3$ recorded a sole singlet at δ 43.3. It is noteworthy that the $^{31}P\{^1H\}$ NMR coordination shift recorded for (*S*)-**10** (41.2 ppm) is similar to that observed for (*R*,*S*)-**7** (48.4 ppm) and for (*R*,*S*)-**9** (45.8 ppm). The spectroscopic studies therefore indicated that the resolved phosphine ligand is coordinated as a monodentate to palladium in these three complexes.[20] However, single crystals of complexes (*S*)-**10** and (*S*)-**11** that are suitable for structural investigations could not be obtained. Thus absolute regio orientations of these dimeric complexes could not be unambiguously assigned by X-ray crystallography.

In contrast to complexes for (*R*,*S*)-**7**, **8**, and **9**, the *ortho*-metalation reactions were readily achieved from the chloro-bridged complexes. Thus, treatment of complex (*S*)-**10** with excess sodium acetate in boiling ethanol for 30 min gave the cyclopalladated phosphine complex (*S*)-**2**. The targeted organopalladium complex was isolated from dichloromethane−diethyl ether as pale yellow prisms in 90% yield, $[\alpha]_D$ +559° (CH_2Cl_2). The $^{31}P\{^1H\}$ NMR spectrum of (*S*)-**2** in $CDCl_3$ exhibited two singlets at δ 62.3 and 62.5 indicating that, in solution, the dimeric complex exist as an equilibrium mixture of the two possible cis and trans isomers.[1] It is noteworthy that a similar facile cis and trans rearrangement had been reported when the analogous μ-dichloro-bridged *ortho*-metalated naphthylamine complex was dissolved in chloroform.[1] The relatively large coordination shifts observed for (*S*)-**2** (60.3 and 60.5 ppm) are in agreement with the formation of the five-membered phospha organometallic rings.[20] The *ortho*-metalated arsenic analogue complex (*S*)-**3** was obtained similarly as yellow blocks, $[\alpha]_D$ +349° (CH_2Cl_2), by the treatment of (*S*)-**11** with sodium acetate. Compared with its phosphorus counterpart, however, the cyclopalladated arsine complex was obtained in considerably lower yield (33%). We believe that the low yield obtained in the arsenic complex synthesis is attributed to the kinetic instability of the monodentate As → Pd bondings that are involved in the starting material (*S*)-**11** and in the intermediate complex that was generated during the course of the *ortho*-metalation reaction. Due to its striking air-sensitivity, the uncoordinated diphenylnaphthylarsine would be readily oxidized in the refluxing ethanolic solution. It is noteworthy that, in general, P → Pd bonds are considerably less labile than the As → Pd bonds.[21]

The (*R*,*R*)-**7** diastereomer was similarly subjected to naphthylamine removal to yield the chloro-bridged intermediate (*R*)-**10**. Likewise, subsequent treatment of this intermediate complex in excess sodium acetate led to the formation of the orthopalladated complex (*R*)-**2** with $[\alpha]_D$ −562° (CH_2Cl_2).

The molecular structures of the *ortho*-metalated phosphine and arsine complexes have been studied by X-ray crystallography (Figures 4 and 5). Selected bond distances and bond angles are given in Table 2. The structural analysis reaffirmed that, as desired, the cyclopalladated phospha and arsa organometallic rings have been formed in complexes (*S*)-**2** and (*S*)-**3**, respectively. Both molecules have noncrystallographic C_2 symmetry about an axis passing through the center of, and perpendicular to, the four-membered $Pd_2(\mu\text{-}Cl)_2$ ring. The chiral carbon centers C(11) and C(35) in these complexes are of the *S* absolute configuration. The geometries

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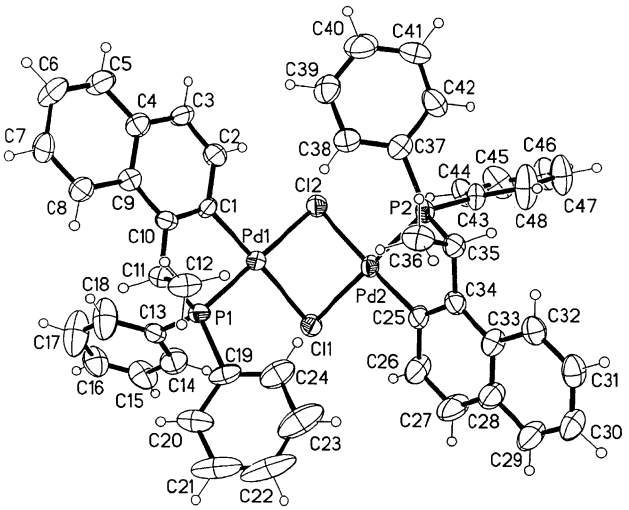


Figure 4. Molecular structure of complex (*S*)-**2**.

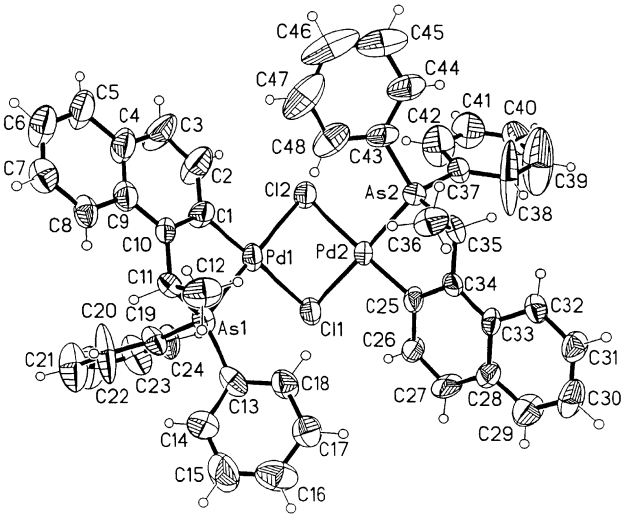


Figure 5. Molecular structure of complex (*S*)-**3**.

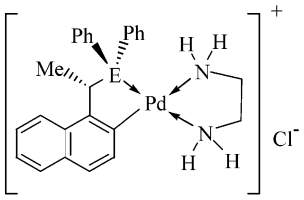
of the *ortho*-metalated phosphine and arsine ligands are similar to that observed in their naphthylamine analogue (see Figures 1−3) with the retention of an axial geometry for the methyl groups at the chiral carbon centers. The five-membered organometallic rings have asymmetric skew conformations of λ helicity. The Ph_2E-C distances [1.841(6) and 1.846(5) Å for (*S*)-**2**; 1.938(9) and 1.945(9) Å for (*S*)-**3**] are dramatically shorter than those observed for their monodentate counterparts in complexes (*R*,*S*)-**7**−**9** (Table 1). It is important to note that the contraction of the Ph_2E-C distances during the course of the *ortho*-metalation reaction might be one of the major kinetic hurdles for the product formation, particularly for the formation of the arsenic complex (*S*)-**3**. During the *ortho*-metalation reaction, the Ph_2As-C bonds have been compressed by ca. 0.1 Å while the Ph_2P-C distances have been shortened only by ca. 0.04 Å. The intrachelate As−Pd−C angles in (*S*)-**3** [81.7(3) and 82.1(3)°] are larger than the P−Pd−C angles in (*S*)-**2** [80.8(2) and 80.9(2)°] which, in turn, are somewhat larger than the N−Pd−C angles observed in complexes (*R*,*S*)-**7**-**9** [80.6(1), 80.5(2), and 80.5(1)°, respectively]. The associated transannular Pd(1)···Pd(2) distances in both *ortho*-metalated complexes are similar [2.985(1) Å for (*S*)-**2** and 2.990 Å for (*S*)-**3**].

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Complexes (*S*)-**2** and (*S*)-**3**

	(*S*)-**2** (E = P)	(*S*)-**3** (E = As)
Pd(1)−C(1)	2.022(5)	1.978(9)
Pd(1)−E(1)	2.188(2)	2.288(1)
Pd(1)−Cl(1)	2.455(2)	2.417(3)
Pd(1)−Cl(2)	2.459(2)	2.426(2)
C(1)−C(10)	1.391(8)	1.447(11)
C(10)−C(11)	1.501(7)	1.481(12)
E(1)−C(11)	1.841(6)	1.938(9)
E(1)−C(13)	1.805(6)	1.898(4)
E(1)−C(19)	1.811(6)	1.927(4)
Pd(2)−C(25)	2.015(6)	2.010(10)
Pd(2)−E(2)	2.201(2)	2.271(2)
Pd(2)−Cl(2)	2.436(2)	2.450(2)
Pd(2)−Cl(1)	2.442(2)	2.433(3)
C(25)−C(34)	1.399(8)	1.389(12)
C(34)−C(35)	1.505(7)	1.512(11)
E(2)−C(35)	1.846(5)	1.945(9)
E(2)−C(37)	1.820(6)	1.912(5)
E(2)−C(43)	1.820(6)	1.902(4)
Pd(1)···Pd(2)	2.985(1)	2.990(1)
C(1)−Pd(1)−E(1)	80.8(2)	81.7(3)
C(1)−Pd(1)−Cl(1)	176.7(2)	177.1(3)
E(1)−Pd(1)−Cl(1)	96.4(1)	95.4(1)
C(1)−Pd(1)−Cl(2)	100.4(2)	98.9(3)
E(1)−Pd(1)−Cl(2)	177.9(1)	177.7(1)
Cl(1)−Pd(1)−Cl(2)	82.4(1)	84.0(1)
C(11)−E(1)−Pd(1)	107.0(2)	100.6(3)
C(10)−C(11)−E(1)	103.7(4)	105.1(6)
C(1)−C(10)−C(11)	119.0(5)	117.7(8)
C(10)−C(1)−Pd(1)	123.0(4)	124.0(7)
C(2)−C(1)−C(10)	119.1(5)	116.3(9)
C(9)−C(10)−C(1)	120.2(5)	120.5(9)
C(25)−Pd(2)−E(2)	80.9(2)	82.1(3)
C(25)−Pd(2)−Cl(2)	178.4(2)	175.7(3)
E(2)−Pd(2)−Cl(2)	97.7(1)	94.4(1)
C(25)−Pd(2)−Cl(1)	98.4(2)	100.5(3)
E(2)−Pd(2)−Cl(1)	177.6(1)	176.6(1)
Cl(2)−Pd(2)−Cl(1)	83.2(1)	83.2(1)
C(35)−E(2)−Pd(2)	104.3(2)	103.6(3)
C(34)−C(35)−E(2)	103.5(4)	103.0(6)
C(25)−C(34)−C(35)	118.2(5)	121.4(9)
C(34)−C(25)−Pd(2)	122.0(4)	123.8(7)
C(26)−C(25)−C(34)	118.8(6)	117.2(9)
C(25)−C(34)−C(33)	120.6(5)	120.2(8)

All the *ortho*-metalated complexes involved in the current study are air-stable. Addition of a drop of concentrated hydrochloric acid (12.2 M) to each of the above cyclopalladated complexes (*S*)-**2** and (*S*)-**3** dissolved in $CDCl_3$ led to the immediate rupture of the Pd−C bonds thus converting them to their palladacycle precursors, (*S*)-**10** and (*S*)-**11** respectively, as observed from the NMR spectroscopic studies. Both experiments have demonstrated that the phosphine and arsine ligands retain their binding via their respective phosphorus and arsenic donors to Pd as monodentates. However, the $CDCl_3$ solutions of both cyclopalladated complexes (*S*)-**2** and (*S*)-**3** are stable toward glacial acetic acid or dilute hydrochloric acid (1 M). Both complexes undergo the reaction of μ-chloro bridge cleavage the chelating agent 1, 2-diaminoethane to afford their mononuclear complexes (*S*)-**12** and (*S*)-**13**. The complexes (*S*)-**12** and (*S*)-**13** were isolated as water soluble solids with $[\alpha]_D$ +438° (H_2O) and $[\alpha]_D$ +260° (H_2O), respectively. Their ability to dissolve in water also highlights the stabilities of the five-

membered palladacycles in aqueous media. Investigations on the synthetic applications of the enantiomerically pure forms of **2** and **3** are currently in progress.



(*S*)-**12** E = P
(*S*)-**13** E = As

Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of argon. Routine ^{1}H NMR spectra were recorded at 300.1 or 500.1 MHz on a Bruker ACF 300 or Bruker AMX 500 NMR spectrometers. All the ^{31}P{^{1}H} NMR spectra were recorded at 120 MHz on the Bruker ACF 300 MHz NMR spectrometer. Optical rotations were measured on the specified solution in 1 and 0.1 dm cells at 25 °C with a Perkin-Elmer model 341 polarimeter. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore. The enantiomerically pure form of bis(μ-chloro)bis[(*R*)-1-[(dimethylamino)ethyl]naphthylenyl-*C*^{2},*N*]dipalladium(II), (*R*)-**1**,[22] and the racemic chloro compound (1-naphthyl)ethyl chloride, **4**,[23] were prepared according to reported procedures.

Caution! *All the complexes described as perchlorate salts should be handled as potentially explosive compounds*.

(±)-Diphenyl[1-(1-naphthyl)ethyl]phosphine ((±)-5). A solution of sodium diphenylphosphide in tetrahydrofuran was prepared from diphenylphosphine (3.09 g, 16.6 mmol) and sodium (0.5 g, 21.7 mmol) over 1 h. The excess sodium was filtered off, and the phosphide solution was added slowly into a stirring solution of (1-naphthyl)ethyl chloride, **4** (3.16 g, 16.6 mmol), in tetrahydrofuran (20 mL). The addition of sodium diphenylphosphide was carried out over a period of 0.5 h. The solvent was removed by distillation, and the residue was treated with water (50 mL). The product was then extracted into diethyl ether, dried ($MgSO_4$), and evaporated to dryness, affording a colorless liquid which crystallized upon standing as a white solid (4.78 g, 85%). ^{1}H NMR ($CDCl_3$): δ 1.49 (dd, 3H, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 13.7 Hz, CH*Me*), 4.42 (dq, 1H, $^3J_{HH}$ = 6.8 Hz, $^2J_{PH}$ = 7.2 Hz, MeC*H*), 6.93−7.28 (m, 17H, aromatic). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 2.1 (s).

(±)-Diphenyl[1-(1-naphthyl)ethyl]arsine ((±)-6). The ligand was prepared as described above using diphenylarsine as the starting material. Upon standing at room temperature for 3 days, the product was obtaining as a white solid, 10.4 g, 88% yield. ^{1}H NMR ($CDCl_3$): δ 1.65 (d, 3H, $^3J_{HH}$ = 7.2 Hz, CH*Me*), 4.48 (q, 1H, $^3J_{HH}$ = 7.2 Hz, MeC*H*), 7.00−8.07 (m, 17H, aromatic).

Resolution of (±)-Diphenyl[1-(1-naphthyl)ethyl]phosphine ((±)-5). Isolation of Chloro{(*R*)-1-[1-(dimethylamino)ethyl]-naphthyl-*C*^{2},N}{(S)-1-[1-(Diphenylphospha)ethyl]naphthyl-P}-palladium(II) ((R,S)-7) and Chloro{(R)-1-[1-(dimethylamino)-ethyl]naphthyl-C^2,N}{(R)-1-[1-(diphenylphospha)ethyl]naphthyl-P}palladium(II) ((R,R)-7). A mixture of (±)-**5** (5.6 g) and the resolving agent (*R*)-**1** (4.79 g, 7.0 mmol) in dichloromethane (100 mL) was stirred for 2 h at room temperature until all the resolving agent had dissolved. The solvent was removed under reduced pressure. The ^{31}P{^{1}H} NMR ($CDCl_3$) spectrum of the crude product exhibited two singlets of ca. equal intensities at δ 45.1 and 50.5 indicating that a 1:1 mixture of the two stereochemically non-equivalent diastereomers (*R*,*R*)- and (*R*,*S*)-**7** had been formed. Slow recrystallization of the crude product mixture from dichloromethane−ethanol gave (*R*,*S*)-**7** as bright yellow prisms, mp 241−243 °C (dec); $[\alpha]_D$ −7.0° (*c* 1.0, CH_2Cl_2); 3.39 g (60.0% yield). Anal. Calcd for $C_{38}H_{37}ClNPPd$: C, 67.1; H, 5.5; N, 2.1. Found: C, 66.9; H, 5.4; N 2.3. ^{1}H NMR: $CDCl_3$, δ 1.97 (dd, 3H, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 18.7 Hz, PCH*Me*), 2.09 (d, 3H, $^3J_{HH}$ = 6.0 Hz, NCH*Me*), 2.75 (d, 3H, $^4J_{PH}$ = 1.4 Hz, N*Me*$_{axial}$), 3.06 (d, 3H, $^4J_{PH}$ = 3.2 Hz, N*Me*$_{equatorial}$), 4.32 (dq, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.0 Hz, NC*H*Me), 5.84 (dq, 1H, $^3J_{HH}$ = 7.0 Hz, $^2J_{PH}$ = 9.9 Hz, PC*H*Me), 6.24 (dd, 1H, $^3J_{HH}$ = 8.6 Hz, $^4J_{PH}$ = 6.2 Hz, H^2), 6.45 (d, 1H, $^3J_{HH}$ = 7.4 Hz, H^{18}), 6.61 (d, 1H, $^3J_{HH}$ = 8.6 Hz, H^3), 6.92 (ddd, 2H, $^3J_{HH}$ = $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 1.7 Hz, *m*-PPh), 7.04−7.09 (overlapping m, 3H, *m*-PPh, aromatic proton), 7.13−7.31 (overlapping m, 6H, H^6, H^7, H^{19}, *p*-PPh protons, aromatic proton), 7.45 (d, 1H, $^3J_{HH}$ = 7.9 Hz, H^5), 7.47−7.54 (overlapping m, 4H, *o*-PPh protons), 7.69−7.79 (overlapping m, 4H, H^8, H^{20}, H^{23}, H^{26}); CD_2Cl_2, δ 1.99 (dd, 3H, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 18.5 Hz, PCH*Me*), 2.12 (d, 3H, $^3J_{HH}$ = 6.3 Hz, NCH*Me*), 2.76 (d, 3H, $^4J_{PH}$ = 1.8 Hz, N*Me*$_{axial}$), 3.08 (d, 3H, $^4J_{PH}$ = 3.4 Hz, N*Me*$_{equatorial}$), 4.38 (dq, 1H, $^3J_{HH}$ = 6.3 Hz, $^4J_{PH}$ = 6.1 Hz, NC*H*Me), 5.86 (dq, 1H, $^3J_{HH}$ = 7.2 Hz, $^2J_{PH}$ = 10.6 Hz, PC*H*Me), 6.29 (dd, 1H, $^3J_{HH}$ = 8.6 Hz, $^4J_{PH}$ = 6.1 Hz, H^2), 6.54 (d, 1H, $^3J_{HH}$ = 7.2 Hz, H^{18}), 6.64 (d, 1H, $^3J_{HH}$ = 8.6 Hz, H^3), 7.01 (ddd, 2H, $^3J_{HH}$ = 7.9 Hz, $^4J_{PH}$ = 1.7 Hz, *m*-PPh), 7.11−7.17 (overlapping m, 3H, aromatic proton, *m*-PPh), 7.20−7.36 (overlapping m, 6H, H^6, H^7, H^{19}, *p*-PPh protons, aromatic proton), 7.48 (d, 1H, $^3J_{HH}$ = 7.7 Hz, H^5), 7.52−7.61 (overlapping m, 4H, *o*-PPh protons), 7.69−7.79 (overlapping m, 4H, H^8, H^{20}, H^{23}, H^{26}). ^{31}P{^{1}H} NMR: $CDCl_3$, δ 51.0 (s); CD_2Cl_2, δ 50.8 (s). The remaining mother liquor enriched with (*R*,*R*)-**7** was purified by column chromatography on silica gel using dichloromethane−hexanes (in the ratios from 1:4 up to 2:1) as eluents, from which enantiopure (*R*,*R*)-**7** was obtained as a yellow solid after removal of solvents. Complex (*R*,*R*)-**7** could not be crystallized from any of the solvents tried: mp 152−155 °C; $[\alpha]_D$ −12° (*c* 0.5, CH_2Cl_2); 0.691 g (12.2% yield). Anal. Calcd for $C_{38}H_{37}ClNPPd$: C, 67.1; H, 5.5; N, 2.1. Found: C, 67.1; H, 5.5; N, 2.3. ^{1}H NMR ($CDCl_3$): δ 1.71 (dd, 3H, $^3J_{HH}$ = 7.4 Hz, $^3J_{PH}$ = 16.0 Hz, PCH*Me*), 1.74 (d, 3H, $^3J_{HH}$ = 6.3 Hz, NCH*Me*), 2.63 (d, 3H, $^4J_{PH}$ = 1.5 Hz, N*Me*$_{axial}$), 2.93 (d, 3H, $^4J_{PH}$ = 3.4 Hz, N*Me*$_{equatorial}$), 4.22 (dq, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.3 Hz, NC*H*Me), 5.53 (dq, 1H, $^3J_{HH}$ = 7.4 Hz, $^2J_{PH}$ = 9.3 Hz, PC*H*Me), 6.67 (dd, 1H, $^3J_{HH}$ = 8.5 Hz, $^4J_{PH}$ = 5.5 Hz, H^2), 6.76 (br. d, 1H, $^3J_{HH}$ = 7.5 Hz, H^{18}), 6.97−7.01 (overlapping m, 3H, *m*-PPh, H^3), 7.08 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, H^{19}), 7.23 (dt, 1H, $^3J_{HH}$ = 7.4 Hz, $^5J_{PH}$ = 1.5 Hz, *p*-PPh), 7.27−7.37 (m, 2H, H^6, H^7), 7.34−7.48 (overlapping m, 6H, H,[25] *o*-PPh, *m*-PPh, *p*-PPh), 7.52 (m, 1H, H^{24}), 7.60 (d, 1H, $^3J_{HH}$ = 7.4 Hz, H^5), 7.63−7.65 (overlapping m, 2H, H^8, H^{20}), 7.81 (d, 1H, $^3J_{HH}$ = 8.0 Hz, H^{26}), 7.95 (dd, 2H, $^3J_{HH}$ = 7.4 Hz, $^3J_{PH}$ = 8.9 Hz, *o*-PPh), 8.58 (d, 1H, $^3J_{HH}$ = 8.6 Hz, H^{23}). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 45.1, (CD_2Cl_2) δ 45.6.

Chloro{(*R*)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},N}{(S)-1-[1-(diphenylarsa)ethyl]naphthyl-As}palladium(II) ((R,S)-8). The optically pure arsenic complex was prepared as described above using (±)-**6** (11.8 g) as the starting material: yellow prisms; mp 212−214 °C dec; $[\alpha]_D$ +60° (*c* 1.0, CH_2Cl_2); 3.11 g (28.0% yield). Anal. Calcd for $C_{38}H_{37}ClNAsPd$: C, 63.0; H, 5.2; N 1.9. Found: C, 62.7; H, 5.0; N 2.0. ^{1}H NMR (CD_2Cl_2): δ 1.89 (d, 3H, $^3J_{HH}$ =

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7.2 Hz, AsCH*Me*), 2.11 (d, 3H, $^3J_{HH}$ = 6.4 Hz, NCH*Me*), 2.84 (s, 3H, N*Me*$_{axial}$), 3.08 (s, 3H, N*Me*$_{equatorial}$), 4.39 (q, 1H, $^3J_{HH}$ = 6.4 Hz, NC*H*Me), 5.83 (q, 1H, $^3J_{HH}$ = 7.2 Hz, AsC*H*Me), 6.36 (d, 1H, $^3J_{HH}$ = 8.6 Hz, H^2), 6.64 (d, 1H, $^3J_{HH}$ = 8.6 Hz, H^3), 6.88 (d, 1H, $^3J_{HH}$ = 7.2 Hz, H^{18}), 6.99 (dd, 2H, $^3J_{HH}$ = $^3J_{HH}$ = 7.7 Hz, *m*-AsPh), 7.10 (ddd, 1H, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.4 Hz, H^{24}), 7.14 (dd, 2H, $^3J_{HH}$ = $^3J_{HH}$ = 7.7 Hz, *m*-AsPh), 7.19 (m, 1H, *p*-AsPh), 7.23−7.37 (overlapping m, 9H, H^6, H^7, H^{19}, H^{25}, *o*-AsPh$_2$, *p*-AsPh), 7.48 (d, 1H, $^3J_{HH}$ = 8.6 Hz, H^5), 7.69 (d, 1H, $^3J_{HH}$ = 8.4 Hz, H^8), 7.76 (overlapping d, 2H, $^3J_{HH}$ = 8.4 Hz, H^{20}, H^{26}), 7.80 (d, 1H, $^3J_{HH}$ = 8.4 Hz, H^{23}). The (*R*, *R*) diastereomer remaining in the mother liquor could not be induced to crystallize from any of the solvent systems tried.

Perchlorato{(*R*)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},N}-{(S)-1-[1-(diphenylphosphα)ethyl]naphthyl-P}palladium(II) ((R,S)-9). A solution of (*R*,*S*)-**7** (0.46 g, 0.7 mmol) in dichloromethane (20 mL) was subjected to chloride abstraction using silver perchlorate (0.14 g, 0.67 mmol) in water (5 mL). The reaction mixture was stirred in the dark at room temperature for 30 min and then filtered through a layer of Celite (to remove AgCl), dried ($MgSO_4$), and evaporated to dryness. The product was crystallized from dichloromethane−diethyl ether as shiny yellow blocks: mp 208−210 °C (dec); $[\alpha]_D$ +18° (*c* 1.0, CH_2Cl_2); 0.42 g (83% yield). Anal. Calcd for $C_{38}H_{37}ClNO_4PPd$: C, 61.3; H, 5.0; N, 1.9. Found: C, 61.9; H, 5.0, N, 1.7. ^{1}H NMR (CD_2Cl_2): δ 1.99 (dd, 3H, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 18.5 Hz, PCH*Me*), 2.12 (d, 3H, $^3J_{HH}$ = 6.4 Hz, NCH*Me*), 2.86 (d, 3H, $^4J_{PH}$ = 1.6 Hz, N*Me*$_{axial}$), 3.03 (d, 3H, $^4J_{PH}$ = 3.2 Hz, N*Me*$_{equatorial}$), 4.34 (dq, 1H, $^3J_{HH}$ = 6.4 Hz, $^4J_{PH}$ = 6.4 Hz, NC*H*Me), 5.10 (dq, 1H, $^3J_{HH}$ = 7.2 Hz, $^2J_{PH}$ = 7.2 Hz, C*H*Me), 6.27−7.79 (m, 23H, aromatic). ^{31}P{^{1}H} NMR: CD_2Cl_2, δ 47.6 (s); $CDCl_3$, δ 47.9 (s).

***Ortho*-Metalation Reaction. Isolation of Bis(μ-chloro)bis[(*S*)-1-[1-(diphenylphospha)ethyl]naphthylenyl-*C*^{2},P]dipalladium(II) ((S)-2).** Concentrated HCl (10 M, 2.3 mL) was added slowly to a suspension of the resolved phosphine complex (*R*,*S*)-7 (0.91 g, 1.4 mmol) in acetone (33 mL). The reaction mixture was then refluxed for 90 min to give an orange-red homogeneous solution. The reaction mixture was then cooled to room temperature, and water (200 mL) was added with rapid stirring. After ca. 30 min, the orange product (*S*)-**10** was filtered off, washed with water, and dried under vacuum: mp 167−170 °C (dec); $[\alpha]_D$ −215° (*c* 1.0, CH_2Cl_2); 0.68 g (98% yield). Anal. Calcd for $C_{48}H_{42}Cl_4P_2Pd_2$: C, 55.7; H, 4.1. Found: C, 55.5; H, 4.3. ^{1}H NMR ($CDCl_3$): δ 2.11 (dd, 3H, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 18.9 Hz, PCH*Me*), 5.54 (m, 1H, PC*H*Me), 6.64−7.76 (m, 17H, aromatic). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 43.3 (s).

A mixture of (*S*)-**10** (0.50 g, 0.5 mmol) and sodium acetate trihydrate (1.98 g, 14.5 mmol) in ethanol (50 mL) was boiled for 30 min until a yellow suspension was formed. The resulting pale yellow suspension was cooled to room temperature, and the solvent was removed. The product was extracted into dichloromethane, washed with water (to remove excess sodium acetate), dried ($MgSO_4$), and evaporated to dryness. The crude product was chromatographed on silica gel with chloroform−*n*-hexane (2:1 v/v) as eluent. The *ortho*-metalated complex (*S*)-**2** was collected from the first fraction (R_f = 0.83, 2:1 dichloromethane−*n*-hexane, v/v) and then crystallized from dichloromethane−diethyl ether as pale yellow prisms: mp 250−254 °C (dec); $[\alpha]_D$ +559° (*c* 1.0, CH_2Cl_2); 0.42 g (90% yield). Anal. Calcd for $C_{48}H_{40}Cl_2P_2Pd_2$: C, 59.9; H, 4.2. Found: C, 59.6; H, 4.2. ^{1}H NMR ($CDCl_3$): δ 1.45 (dd, 3H, $^3J_{HH}$ = 6.6 Hz, $^3J_{PH}$ = 18.3 Hz, PCH*Me*), 4.57 (m, 1H, PC*H*Me), 7.30−8.05 (m, 16 H, aromatic). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 62.3 (s), 62.5 (s).

Bis(μ-chloro)bis[(*R*)-1-[1-(diphenylphospha)ethyl]naphthylenyl-*C*^{2},P]dipalladium(II) ((R)-2). The complex (*R*)-**10** was prepared as described above using chromatographically pure (*R*,*R*)-**7** (0.30 g 0.44 mmol) and concentrated HCl (0.8 mL) in acetone (11 mL): mp 168−171 °C (dec); $[\alpha]_D$ +218° (*c* 0.5, CH_2Cl_2); 0.22 g (95% yield). Anal. Calcd for $C_{48}H_{42}Cl_4P_2Pd_2$: C, 55.7; H, 4.1. Found: C, 56.7; H, 4.1. ^{1}H NMR ($CDCl_3$): δ 2.11 (dd, 3H, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 18.9 Hz, PCH*Me*), 5.54 (m, 1H, PC*H*Me), 6.64−7.76 (m, 17H, aromatic). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 43.3 (s). The optically active complex (*R*)-**2** was similarly obtained as described above from (*R*)-**10** (0.13 g, 0.13 mmol) and sodium acetate trihydrate (0.52 g, 3.81 mmol) in boiling ethanol (13 mL): mp 253−255 °C (dec); $[\alpha]_D$ −562° (*c* 0.55, CH_2Cl_2); 0.096 g (79% yield). Anal. Calcd for $C_{48}H_{40}Cl_2P_2Pd_2$: C, 59.9; H, 4.2. Found: C, 59.7; H, 4.2. ^{1}H NMR ($CDCl_3$): δ 1.45 (dd, 3H, $^3J_{HH}$ = 6.6 Hz, $^3J_{PH}$ = 18.3 Hz, PCH*Me*), 4.57 (m, 1H, PC*H*Me), 7.30−8.05 (m, 16 H, aromatic). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 62.3 (s), 62.5 (s).

Bis(μ-chloro)bis[(*S*)-1-[1-(diphenylarsa)ethyl]naphthylenyl-*C*^{2},As]dipalladium(II) ((S)-3). The *ortho*-metalation reaction was conducted in two steps as described above using the resolved arsine complex (*R*,*S*)-**8** (0.85 g, 1.2 mmol) as the starting material. The intermediate complex (*S*)-**11** was obtained as orange solid that could not be induced to crystallize: mp 124−128 °C dec; $[\alpha]_D$ −170° (*c* 0.5, CH_2Cl_2); 0.65 g (98% yield). ^{1}H NMR ($CDCl_3$): δ 2.07 (d, 3H, $^3J_{HH}$ = 6.9 Hz, AsCH*Me*), 5.58 (m, 1H, AsC*H*Me), 7.00−7.80 (m, 17 H, aromatic).

The crude monodentate complex (*S*)-**11** (0.46 g, 0.4 mmol) was treated with sodium acetate trihydrate (1.66 g, 12.2 mmol) in refluxing ethanol. The crude product was evaporated to dryness, washed with water, extracted into dichloromethane, and purified by silica gel chromatography using dichloromethane−*n*-hexane (in 1:4 up to 1:1 v/v) as eluents. The *ortho*-metalated complex (*S*)-**3** was collected from the first fraction (R_f = 0.76, 2:1 dichloromethane−*n*-hexane, v/v) and then crystallized from dichloromethane−*n*-hexane as pale yellow prisms: mp 273−275 °C dec; $[\alpha]_D$ +349° (*c* 1.0, CH_2Cl_2); 0.14 g (33% yield). Anal. Calcd for $C_{48}H_{40}Cl_2As_2Pd_2$: C, 54.9; H, 3.8. Found: C, 54.5; H, 3.8. ^{1}H NMR ($CDCl_3$): δ 1.61 (d, 3H, $^3J_{HH}$ = 6.8 Hz, AsCH*Me*), 4.87 (q, 1H, $^3J_{HH}$ = 6.8 Hz, AsC*H*Me), 7.30−7.91 (*m*, 16 H, aromatic).

[(*S*)-1-[1-(Diphenylphospha)ethyl]naphthylenyl-*C*^{2},P](1,2-ethanediamine-N,N)palladium(II) Chloride ((S)-12). A chloroform solution of an excess of 1,2-diaminoethane (20 mg, 0.033 mmol) was added to (*S*)-**2** (20 mg, 0.021 mmol) dissolved in chloroform (2 mL), and the mixture was stirred for 30 min. The resulting colorless solution was evaporated to dryness and obtained as white crystals from acetononitrile−diethyl ether: mp 211−214 °C dec; $[\alpha]_D$ +438° (*c* 0.5, H_2O); 0.015 g (66.7% yield). Anal. Calcd for $C_{26}H_{28}ClN_2PPd$: C, 57.7; H, 5.2; N, 5.2. Found: C, 57.3; H, 5.6; N, 4.9.

^{1}H NMR: CD_3CN, δ 1.52 (dd, 3H, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 18.5 Hz, PCH*Me*), 2.87 (br m, 2H, C*H*$_2$NH$_2$), 3.07 (br m, 2H, C*H*$_2$NH$_2$), 4.83 (dq, 1H, $^3J_{HH}$ = 7.2 Hz, $^2J_{PH}$ = 18.5 Hz, PC*H*Me), 7.27−7.80 (overlapping m, 15H, aromatic protons), 7.99 (d, 1H, *J* = 8.4 Hz, aromatic); D_2O, δ 1.53 (dd, 3H, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 18.7 Hz, PCH*Me*), 2.83 (m, 2H, C*H*$_2$NH$_2$), 3.11 (m, 2H, C*H*$_2$NH$_2$), 4.82−4.89 (m, 1H, partially overlapped with D_2O signal, PC*H*Me), 7.21−7.73 (overlapping m, 14H, aromatic protons), 7.85 (d, 1H, *J* = 8.0 Hz, aromatic proton), 8.06 (d, 1H, *J* = 8.4 Hz, aromatic proton). ^{31}P{^{1}H} NMR: CD_3CN, δ 59.3; D_2O, δ 58.7.

[(*S*)-1-[1-(Diphenylarsa)ethyl]naphthylenyl-*C*^{2},As]](1,2-ethanediamine-N,N)palladium(II) Chloride ((S)-13). A dichloromethane solution of an excess of 1,2-diaminoethane (20 mg, 0.033 mmol) was added to (*S*)-**3** (20 mg, 0.019 mmol) dissolved in dichloro-

Table 3. Crystallographic Data for Complexes of (*S*)-2, (*S*)-**3**, (*R*,*S*)-**7**, (*R*,*S*)-**8**, and (*R*,*S*)-**9**

	(*S*)-**2**	(*S*)-**3**	(*R*,*S*)-**7**	(*R*,*S*)-**8**	(*R*,*S*)-**9**
formula	$C_{48}H_{40}Cl_2P_2Pd_2$	$C_{48}H_{40}As_2Cl_2Pd_2$	$C_{38}H_{37}ClNPPd$	$C_{38}H_{37}AsClNPd$	$C_{38}H_{37}ClNO_4PPd$
M_r	962.44	1050.34	680.51	724.46	744.51
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
cryst system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
a/Å	12.604(1)	12.670(1)	12.216(1)	12.375(1)	12.944(4)
b/Å	15.195(1)	15.122(1)	15.073(1)	15.150(1)	15.507(5)
c/Å	21.610(1)	21.911(1)	17.445(1)	17.710(1)	17.201(7)
V/Å^3	4138.6(2)	4198.1(5)	3212.2(2)	3320.2(1)	3453(2)
Z	4	4	4	4	4
T/K	223(2)	223(2)	293(2)	223(2)	223(2)
λ/Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
μ/mm^{-1}	1.109	2.581	0.738	1.655	0.702
R_1(obsd data)[a]	0.0606	0.0501	0.0222	0.0485	0.0262
wR_2(obsd data)[b]	0.0740	0.0804	0.0515	0.1143	0.0609
Flack param	−0.04(3)	0.05(1)	−0.01(1)	−0.00(2)	−0.01(2)

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

methane (2 mL), and the mixture was stirred for 30 min. The resulting pale yellow solution was concentrated, from which pale yellow crystals were obtained from dichloromethane−diethyl ether: mp 208−211 °C dec; $[\alpha]_D$ +260° (*c* 0.4, H_2O); 0.010 g (45.5% yield). Anal. Calcd for $C_{26}H_{28}AsClN_2Pd$: C, 53.4; H, 4.8; N, 4.8. Found: C, 53.1; H, 5.2; N, 5.1. ^{1}H NMR: $CDCl_3$, δ 1.58 (d, 3H, $^3J_{HH}$ = 7.2 Hz, AsCH*Me*), 2.94 (br. d, 2H, $^3J_{HH}$ = 8.0 Hz, C*H*$_2$NH$_2$), 3.20 (br d, 2H, $^3J_{HH}$ = 8.0 Hz, C*H*$_2$NH$_2$), 4.74 (q, 1H, $^3J_{HH}$ = 7.2 Hz, AsC*H*Me), 7.04 (t, 2H, $^3J_{HH}$ = 7.6 Hz, aromatic protons), 7.17−7.78 (overlapping m, 13H, aromatic protons), 7.89 (d, 1H, $^3J_{HH}$ = 7.9 Hz, aromatic proton); D_2O, δ 1.65 (d, 3H, $^3J_{HH}$ = 6.8 Hz, AsCH*Me*), 2.84 (br. d, 2H, $^3J_{HH}$ = 8.8 Hz, C*H*$_2$NH$_2$), 3.13 (br d, 2H, $^3J_{HH}$ = 8.8 Hz, C*H*$_2$NH$_2$), 5.06 (q, 1H, $^3J_{HH}$ = 7.2 Hz, AsC*H*Me), 7.23−7.73 (overlapping m, 14H, aromatic protons), 7.87 (d, 1H, J_{HH} = 8.0 Hz, aromatic proton), 8.10 (d, 1H, J_{HH} = 8.4 Hz, aromatic proton).

Crystal Structure Determination of (*R,S*)-7, (*R,S*)-8, (*R,S*)-9, (*S*)-2, and (*S*)-3. Crystal data for all six complexes and a summary of the crystallographic analyses are given in Table 3. Diffraction data were collected on a Siemens SMART CCD diffractometer with Mo Kα radiation (graphite monochromator) using ω-scans. SADABS absorption corrections were applied, and refinements by full-matrix least-squares were based on SHELXL 93.[24] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at fixed distance from carbon and nitrogen atoms and were assigned fixed thermal parameters. The absolute configurations of all chiral complexes were determined unambiguously using of the Flack parameter and by internal reference to the known naphthylamine center.

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Supporting Information Available: For (*S*)-**2**, (*S*)-**3**, (*R*,*S*)-**7**, (*R*,*S*)-**8,** and (*R*,*S*)-**9**, tables of crystal data, data collection, solution and refinement, final positional parameters, bond distances and angles, thermal parameters of non-hydrogen atoms, and calculated hydrogen parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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