Synthesis and the Stereoelectronic Properties of Novel Cyclopalladated Complexes Derived from Enantiomerically Pure (*R*/*S*)-*N*,*N*-Dimethyl-1-(9-phenanthryl)ethylamine

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A series of enantiomerically pure organopalladium complexes containing the resolved ortho-metalated (*R*/*S*)-*N*,*N*-dimethyl-1-(9-phenanthryl)ethylamine ligand have been prepared. The absolute ring conformations of these novel organometallic phenanthrylamine chelates in the solid state and in solution have been investigated by X-ray structural analyses and 2D ROESY NMR spectroscopy, respectively. All the chiral ortho-metalated rings were found to be stereochemically rigid, with their absolute ring conformations being locked by the repulsive interactions between the methyl group on the chiral carbon and the adjacent aromatic proton H8 of the phenanthrylamine ring. The methyl substituents on the stereogenic carbons invariably take up the axial positions in the skewed five-membered rings such that the static δ and λ ring conformations are adopted by the *R*- and *S*-phenanthrylamine, respectively. Despite the enormous interchelate steric constraints, the monodentates PPh_3 and DMPP are coordinated regiospecially to the ortho-palladated phenanthrylamine unit trans to the NMe_2 group. The organometallic rings are able to adopt distorted tetrahedral geometries around their palladium atoms and even alter their conjugated phenanthryl planarities in order to accommodate bulky ligands including DMPP, PPh_3, and *N*,*N*,*N*′,*N*′-tetramethyl-2,3-butanediamine. Compared with its naphthylamine analogue, the ortho-palladated phenanthrylamine unit shows a much higher stereoselectivity in the chiral template-promoted asymmetric cycloaddition reaction between DMPP and *N*,*N*-dimethylacrylamide.

Introduction

In the last two decades, the optically active palladium(II) complexes **1** and **2** have been considered to be the most efficient classic resolving agents for chiral ligands such as tertiary phosphines and arsines.[2] Recently, both organopalladium complexes have also been used in many other applications including the determination of the enantiomeric purity of chiral 1,2-diamines,[3] phosphines,[4] and amino acids,[5] the NMR assignment of absolute configurations in solution,[6] and asymmetric syntheses of chiral phosphines[7,8] and iminophosphines.[9] All these useful applications of complexes **1** and **2** involve the initial bridge-cleavage reactions and the subsequent binding of the external chiral ligands to the organometallic units.

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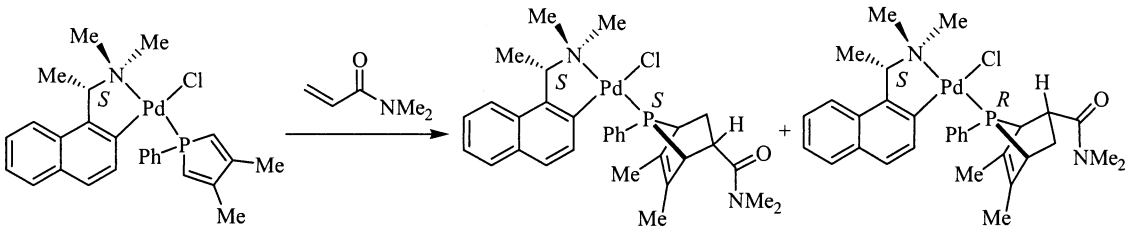
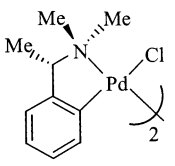
Scheme 1

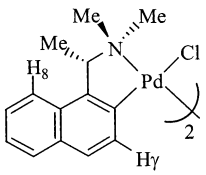


(*S*)-**3** (S_C,S_P)-**4** (S_C,R_P)-**4**

Electronically, complexes **1** and **2** are quite similar. They both contain two readily available coordination sites: one trans to the strong π-accepting aromatic carbon donor and the other trans to the σ-donating nitrogen.[2−9] Hence, when Pd(II) complexes **1** and **2** are treated with external heterobidentate ligands, the resulting complexes are always generated regiospecifically with the softer donor atoms of the heterobidentate ligands invariably taking up the position trans to the NMe_2 group. Despite the fact that the two ortho-metalated complexes show these common electronic properties, the naphthylamine complex **2** has been proven to be superior over its closely related benzyl analogue **1** in most reported applications. This interesting superiority of **2** is attributed to the unique stereochemistry associated with the rigid ortho-metalated naphthylamine ring.[6,10] For example, in complex (*S*)-**2**, the steric interaction between H(8) and the methyl group at the stereogenic carbon center confines the methyl group in the axial position and hence locks the organometallic ring into the stable λ conformation. Due to this unique ring conformation, the chirality of the naphthylamine ring is transmitted efficiently via its prochiral NMe groups onto the neighboring coordination site. On the other hand, the stereochemistry of the five-membered organometallic ring in (*S*)-**1** cannot be well defined, as the puckered benzylamine ring undergoes rapid transformation between the two nonequivalent δ and λ conformations in solution. Upon isolation in the solid state, both the δ and λ conformations were frequently found as diastereomeric mixtures in metal complexes derived from (*S*)-**1**.[11]



(*S*)-**1**



(*S*)-**2**

Recently, we have reported several asymmetric cycloaddition reactions between the cyclic diene 3,4-dimethyl-1-phenylphosphole (DMPP) and a variety of dienophiles using complex **2** as the chiral reaction promoter (Scheme 1).[7,8] These coupling reactions generated a common stable intermediate complex **3** regiospecifically in which the naphthylamine auxiliary, DMPP, and a terminal chloro ligand were coordinated on the metal center. The Pd−Cl bond in **3** is thermodynamically and kinetically stable and remains coordinated onto the palladium template throughout the course of the cycloaddition reaction. Thus the reacting dienophiles do not interact directly with the palladium template, and the reactions proceed via an intermolecular mechanism, leading to the generation of a pair of stereoisomeric *endo*-cycloadducts. For example, when *N*,*N*-dimethylacrylamide was used as the dienophile, the two *endo*-cycloadducts (S_c,R_p)- and (S_c,S_p)-**4** were obtained as a 1:2 diastereomeric mixture.[8] The cycloaddition reaction, however, could not be activated efficiently by the benzylamine complex (*S*)-**1**.

Unlike the other successful applications in which bidentate chelates are involved,[7] the above *endo*-cycloaddition reaction is activated and stereochemically controlled by the naphthylamine template via a single and rotatable P→Pd bond. The DMPP group is bound electronically to the template site that is cis to the aromatic carbon donor. Evidently, the naphthylamine auxiliary does not exert a clear stereochemical effect in directing groups toward this particular site. Unsurprisingly, therefore, a poor stereoselectivity is observed in this intermolecular process. In this paper, we report the design and the evaluation of a chiral phenanthrylamine complex **5**.[12] This new ortho-metalated complex retains all the unique electronic and steric features of its naphthylamine counterpart. However, the rigid organometallic ring carries an additional aromatic ring, which is designed to project the stereochemistry of the chiral auxiliary to the template site that is located cis to the aromatic carbon donor. In contrast to complexes **1** and **2**, therefore, both potential template sites in **5** are stereochemically controlled by the chiral auxiliary. Thus, among the three similar chiral templates, **5** should offer the best chiral inductive effect in various applications. On the other hand, the extra rigid aromatic projecting group in the new phenanthrylamine complex may hinder incoming ligands approaching its neighbor-

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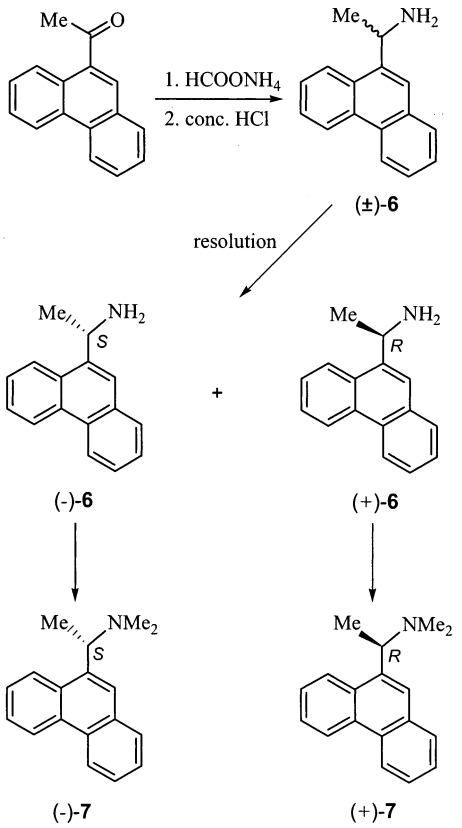
(12) See ref 13 for a preliminary account of the synthesis and resolution of complex **5**. In this preliminary communication, the catalytic activities of complexes **1**, **2**, and **5** in the asymmetric Claisen rearrangement were reported.

Scheme 2



ing template site. It is our judgment, therefore, that such structural dilemma should be resolved through experimental investigations.

Results and Discussions

Synthesis of Chiral Ligands and Their Metal Complexes. The racemic form of 1-(9-phenanthryl)-ethylamine, (±)-**6**, was obtained in 70% yield upon the acid hydrolysis of the reaction product between methyl 9-phenanthryl ketone and ammonium formate at 180 °C (Scheme 2). The racemic primary amine could be resolved efficiently using *O*,*O*′-dibenzoyltartaric acid as the resolving agent. Thus, when (+)-*O*,*O*′-dibenzoyl-D-tartaric acid was used as the resolving agent, (−)-**6** was obtained as a white solid in 35% isolated yield, mp 79−81 °C, $[\alpha]_D$ −44.0° (CH_2Cl_2). The enantiomer (+)-**6** was obtained similarly from the equally available (−)-*O*,*O*′-dibenzoyl-L-tartaric acid. Methylation of (+)- and (−)-**6** with formic acid and formaldehyde gave the corresponding *N*,*N*-dimethyl-substituted amines (+)- and (−)-**7**, respectively, as colorless oils with $[\alpha]_D$ ±61° (CH_2Cl_2) in 78% yield.

In contrast to complexes **1** and **2**,[2] complex **5** could not be generated directly from the salt of $[PdCl_4]^{2-}$. Instead, the ortho-metalation reaction between (+)-**7** and $[Pd(MeCN)_4](ClO_4)_2$ in acetonitrile and in the presence of equimolar triethylamine (Scheme 3) resulted in the formation of the monomeric cationic complex (*R*)-**8**, which was obtained as pale yellow prisms in 65% isolated yield, $[\alpha]_D$ −198° (CH_2Cl_2). Recently we have reported the X-ray structural analysis of complex (*R*)-**8** in a preliminary communication.[13] The structural analysis revealed that the five-membered organometallic ring is of the δ absolute configuration, while the methyl

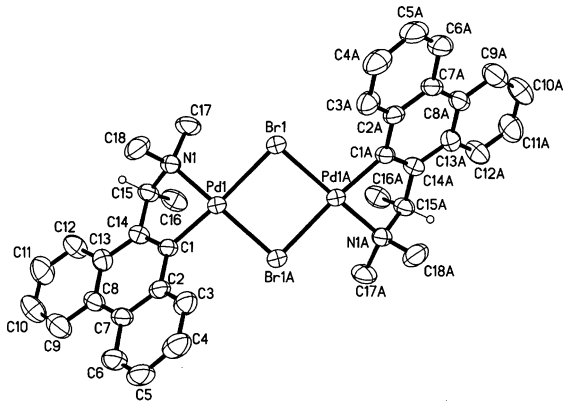
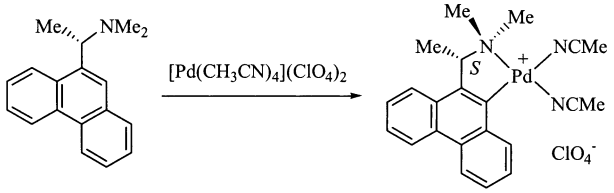
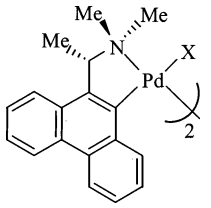


Figure 1. Molecular structure and absolute stereochemistry of the μ-dibromo complex (*S*)-**9**.

Scheme 3



group on the *R*-chiral carbon center is located at the axial position. The enantiomeric complex (*S*)-**8**, with $[\alpha]_D$ +198° (CH_2Cl_2), was prepared similarly from the reaction between (−)-**7** and $[Pd(MeCN)_4](ClO_4)_2$.



(*S*)-**5** X = Cl

(*S*)-**9** X = Br

The optically active μ-chloro dimer **5** could be obtained efficiently by treating the appropriate form of the cationic complex **8** with ammonium chloride. For example, (*S*)-**5** was obtained from (*S*)-**8** as stable orange prisms in 95% yield, $[\alpha]_D$ +393° (CH_2Cl_2). Like complexes **1** and **2**, (*S*)-**5** is stable in solution and in the solid state. However, the dimeric phenanthrylamine complex could not be induced to form single crystals suitable for X-ray structural investigations. In contrast, the μ-bromo analogue (*S*)-**9**, which was readily obtained in 94% yield from the treatment of the cationic complex (*S*)-**8** with ammonium bromide, could be induced to form suitable single crystals from dichloromethane−hexanes, $[\alpha]_D$ +358° (CH_2Cl_2). In the solid state, the X-ray structural analysis revealed that the two organometallic rings in (*S*)-**9** are orientated in the trans geometry with C_2 symmetry (Figure 1). The bond lengths and angles around both palladium atoms are within the normal

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Table 1. Selected Interatomic Distances (Å) and Angles (deg) of the Dibromo Complex (*S*)-9

Pd(1)−C(1)	1.996(4)	Pd(1)−Br(1)	2.593(2)
Pd(1)−N(1)	2.072(4)	Pd(1)−Br(1A)	2.464(2)
C(3)−Br(1A)	3.336(5)	H(12)−C(16)	3.140(5)
C(17)−Br(1)	3.363(5)	H(12)−H(15)	2.087(5)
		C(18)−Br(1)	4.238(5)
C(1)−Pd(1)−N(1)	80.4(1)	C(1)−Pd(1)−Br(1A)	98.8(1)
N(1)−Pd(1)−Br(1A)	166.1(1)	C(1)−Pd(1)−Br(1)	173.4(1)
N(1)−Pd(1)−Br(1)	97.2(1)	Br(1)−Pd(1)−Br(1A)	85.0(1)
Pd(1)−Br(1)−Pd(1A)	93.5(1)		

range (Table 1), and the coordination spheres of both the palladium centers are of distorted square-planar geometry. The bridging Pd−(μ-Br)$_2$−Pd unit in (*S*)-**9** is not planar, with the dihedral angle between the two triangular $PdBr_2$ planes being 18.0°. Similar to the structural findings of the naphthylamine complex (*S*)-**2**,[2] the locked asymmetric λ conformations of the two organometallic rings in (*S*)-**9** are due to the unfavorable interaction between the carbon-methyl group (C16/16A) and H(12/12A). The distances between C(16)−H(12) [3.140(5) Å] and H(12)−H(15) [2.087(5) Å] are similar to those observed in (*S*)-**2**.[2] Accordingly, the methyl groups on both stereogenic carbon centers in (*S*)-**9** are locked into the axial positions. As observed in other similar complexes,[14] the Pd−Br bond trans to carbon [2.593(2) Å] is significantly longer than that trans to nitrogen [2.464(2) Å]. The distances between the bromo ligands and the major steric handles arising from the phenanthrylamine auxiliary are given in Table 1.

It has been reported that, in solution, the dimeric naphthylamine (*S*)-**2** undergoes a facile regiorearrangement to give an equilibrium mixture of both the cis and the trans isomers.[2] A similar dynamic equilibrium mixture was observed when (*S*)-**9** was dissolved in solution. The ^{1}H NMR spectrum of the bromo-bridged complex in $CDCl_3$ showed clearly two distinct pairs of C*Me* doublet resonances at δ 2.44 and 2.52 ($^3J_{HH}$ = 6.4 Hz) in the ratio of ca. 1:1 for the two regioisomers. Upon recrystallization, however, the trans-isomer could always be recovered quantitatively. A similar dynamic process was also observed with the chloro-bridged phenanthrylamine complex (*S*)-**5** in solution.

Optical Purity and Stereochemical Evaluation of the Resolved Ortho-metalated Phenanthrylamine Auxiliary. To confirm the optical purity of the ortho-metalated phenanthrylamine auxiliary, the bisacetonitrile complex (*S*)-**8** was treated with *N*,*N*,*N*′,*N*′-tetramethyl-(*S*,*S*)-2,3-butanediamine. The 300 MHz ^{1}H NMR spectrum of the crude diamine complex (*S*,*S*,*S*)-**10** in $CDCl_3$ exhibited signals consistent with a single isomer. In this instance, the two nonequivalent C-methyl groups on the diamine chelate each exhibited distinct doublets at δ 1.05 ($^3J_{HH}$ = 6.4 Hz) and 1.19 ($^3J_{HH}$ = 6.4 Hz). However, the treatment of the bisacetonitrile complex (*R*)-**8** with the (*S*,*S*)-butanediamine resulted in a different set of ^{1}H NMR signals for the crude diastereomeric product (*R*,*S*,*S*)-**10**. The two nonequivalent C-methyl groups on the diamine chelate each exhibited two distinct doublets at δ 0.95 ($^3J_{HH}$ = 6.4 Hz) and 1.04 ($^3J_{HH}$ = 6.4 Hz). Signals due to the (*S*,*S*,*S*)-diastereomer were not detected. Thus a simple comparison of the ^{1}H NMR spectra of these two diastereomeric complexes, (*R*,*S*,*S*)- and (*S*,*S*,*S*)-**10**, established the optical purity of the resolved (±)-phenanthrylamine auxiliary.

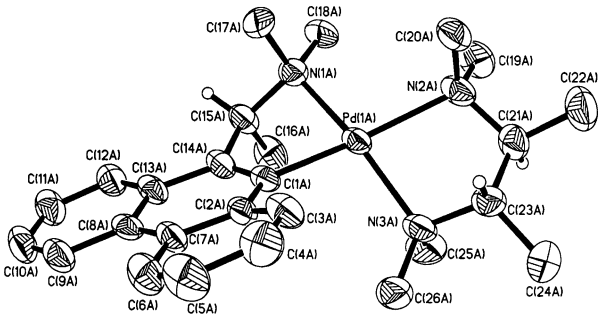

Figure 2. Molecular structure and absolute stereochemistry of (*S*,*S*,*S*)-**10**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of (*S*,*S*,*S*)-10

	molecule A	molecule B
Pd(1)−C(1)	2.003(7)	1.991(8)
Pd(1)−N(1)	2.107(7)	2.083(8)
Pd(1)−N(3)	2.106(7)	2.145(7)
Pd(1)−N(2)	2.238(7)	2.239(7)
N(1)−C(15)	1.509(12)	1.552(14)
N(2)−C(21)	1.491(12)	1.472(13)
N(3)−C(23)	1.552(12)	1.496(11)
C(1)−Pd(1)−N(1)	78.2(3)	78.7(4)
N(3)−Pd(1)−N(2)	79.8(3)	80.8(3)
C(1)−Pd(1)−N(3)	101.6(3)	99.6(3)
N(1)−Pd(1)−N(2)	104.3(3)	104.2(3)
C(1)−Pd(1)−N(2)	167.9(3)	168.4(3)
N(1)−Pd(1)−N(3)	161.9(3)	163.3(3)

Complex (*S*,*S*,*S*)-**10** crystallizes as pale yellow prisms from dichloromethane−hexane. The solid state structure of (*S*,*S*,*S*)-**10** was determined by X-ray crystallography (Figure 2). This complex crystallizes with two crystallographically independent molecules in the unit cell. However, they have identical stereochemistry and differ only slightly in bond lengths and angles. For clarity, only molecule A of (*S*,*S*,*S*)-**10** is depicted in Figure 2. The ORTEP plot of molecule B has been deposited as Supporting Information. Selected bond lengths and angles of both molecules are listed in Table 2. The structural investigations confirm that the organometallic ring adopts the λ conformation with the C-methyl group occupying the axial position. The five-membered chelating ring [N(2A)−N(3A)], however, assumes the δ conformation. Due to the severe steric repulsions between the two chiral ligands, the coordination geometry around palladium is greatly distorted toward tetrahedral. The tetrahedral distortion angles for molecules A and B are 24.3° and 22.4°, respectively.

It would be of interest to determine whether the highly constrained δ/λ ring conformations are adopted by (*S*,*S*,*S*)-**10** in solution. Thus the absolute ring conformation and the stereorigidity of the (*S*)-ortho-metalated phenanthrylamine auxiliary were studied in detail by ROESY NMR spectroscopy. We have previously used the 2D rotating frame nuclear Overhauser enhancement (ROESY) ^{1}H NMR technique for the unambiguous absolute stereochemistry assignments of a series of ortho-metalated naphthylamine complexes.[6] The NOE signals are consistent with the staggered orientation of the substituents when the (*S*)-phenanthrylamine ring adopts the λ conformation as in the solid state. The two nonequivalent diamine donors were also readily identi-

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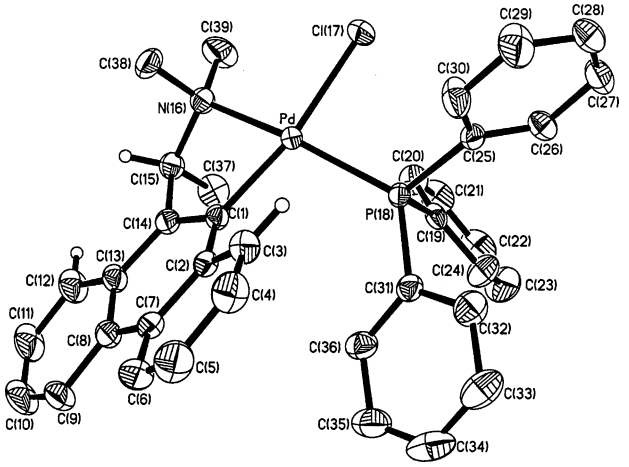


Figure 3. Molecular structure and absolute stereochemistry of the phenanthrylamine complex (*S*)-**11**.

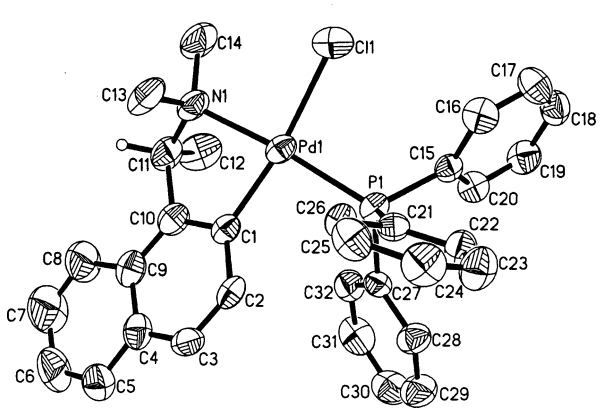


Figure 4. Molecular structure and absolute stereochemistry of the naphthylamine complex (*S*)-**12**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of the Complex (*S*)-11

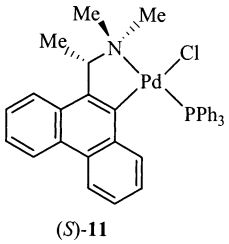
Pd−C(1)	2.016(3)	Pd−N(16)	2.128(2)
Pd−P(18)	2.278(1)	Pd−Cl(17)	2.383(1)
P(18)−C(19)	1.839(3)	P(18)−C(31)	1.828(3)
P(18)−C(25)	1.821(3)		
C(1)−Pd−N(16)	79.3 (1)	C(1)−Pd−P(18)	101.2(1)
N(16)−Pd−P(18)	163.0(1)	C(1)−Pd−Cl(17)	170.4(1)
N(16)−Pd−Cl(17)	93.5(1)	P(18)−Pd−Cl(17)	87.6(1)
Pd−P(18)−C(19)	105.9(1)	Pd−P(18)−C(31)	125.2(1)
		Pd−P(18)−C(25)	114.7(1)

Table 4. Selected Bond Lengths (Å) and Angles (deg) of the Complex (*S*)-12

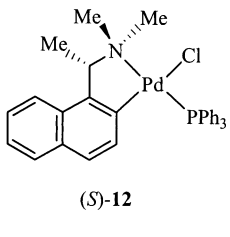
Pd(1)−C(1)	1.987(3)	Pd(1)−N(1)	2.136(3)
Pd(1)−P(1)	2.248(1)	Pd(1)−Cl(1)	2.391(1)
P(1)−C(15)	1.832(4)	P(1)−C(21)	1.822(3)
P(1)−C(27)	1.825(4)		
C(1)−Pd(1)−N(1)	80.3(1)	C(1)−Pd(1)−P(1)	94.0(1)
N(1)−Pd(1)−P(1)	171.4(1)	C(1)−Pd(1)−Cl(1)	168.6(1)
N(1)−Pd(1)−Cl(1)	93.5(1)	P(1)−Pd(1)−Cl(1)	93.1(1)
Pd(1)−P(1)−C(21)	111.9(1)	Pd(1)−P(1)−C(15)	116.5(1)
		Pd(1)−P(1)−C(27)	116.1(1)

fied by the interchelate NOE contacts. It is noteworthy that the NMR signals of complex (*S*,*S*,*S*)-**10** remained unchanged over the temperature range 0 to −60 °C, indicating that the λ conformation of the (*S*)-phenanthrylamine organometallic ring was preserved in solution.

Regioselectivity Originated from the Orthometalated Phenanthrylamine Auxiliary. As intimated above, one of the major challenges in the structural design of the phenanthrylamine auxiliary is the steric congestive condition around the template site that is adjacent to the projecting aromatic ring. To establish that this site is able to accommodate bulky monodentate ligands in a regiospecific manner, the chloro-bridged complex (*S*)-**5** was treated with triphenylphosphine at room temperature. Interestingly, the bulky phosphine ligand split the chloro bridges of (*S*)-**5** efficiently and generated (*S*)-**11** in 86% yield. For comparison purposes, the analogous naphthylamine-PPh_3 complex (*S*)-**12**, containing the less sterically demanding naphthylamine auxiliary, was prepared similarly from (*S*)-**2**. The molecular structures of both complexes (*S*)-**11** and (*S*)-**12** were studied by single-crystal structural analyses (Figures 3 and 4). Selected bond lengths and angles of both complexes are listed in Tables 3 and 4. Both (*S*)-**11** and



(*S*)-**11**



(*S*)-**12**

(*S*)-**12** have distorted square-planar coordination geometry. Between the two complexes, there is a stronger steric repulsion between the PPh_3 ligand and the organometallic chelate in (*S*)-**11**; hence the Pd−C and Pd−P bonds in this complex are longer than those observed in (*S*)-**12**. This steric factor is also manifested in the tetrahedral distortion angles [18.5° for (*S*)-**11** and 11.4° for (*S*)-**12**] of the two complexes. In the absence of a steric projecting group from the aromatic carbon, the steric repulsion between the PPh_3 ligand and the naphthylamine chelate in (*S*)-**12** is relatively insignificant. Thus, the C(1)−Pd(1)−P(1) bond angle [94.01(11)°] in (*S*)-**12** is within the normal range expected for regular square-planar complexes. On the other hand, in (*S*)-**11**, there is significant repulsion between the PPh_3 group and the phenanthrylamine chelate, resulting in the C(1)−Pd−P(18) bond angle in (*S*)-**11** being enlarged to 101.2(1)°. In this phenanthrylamine complex, the Pd−P bond cannot rotate freely, as all the possible rotational motions are blocked by the chloro ligand and the projecting aromatic ring. Hence, among the three P−Ph phenyl rings, the C(31)−C(36) ring suffers the most from the ligand−ligand repulsion. As a result, the bond angle Pd−P(18)−C(31) is enlarged to 125.2(1)°, which is clearly larger than the two less affected Pd−P(18)−C(19) and Pd−P(18)−C(25) angles [110.5(1)° and 116.6(1)°, respectively]. On the other hand, in the absence of such ligand−ligand repulsion in the naphthylamine complex, the three Pd−P−C bond angles in (*S*)-**12** are within the normal range of 111.9(1)−116.5(1)°. Most importantly, the ligand−ligand repulsive interactions in complex (*S*)-**11** also disturb the planarity of the conjugated phenanthryl rings. Thus, the central ring (C1,C2,C7,C8,C13,C14) and the adjacent projecting ring (C2−C7) of the phenanthryl group do not lie in the

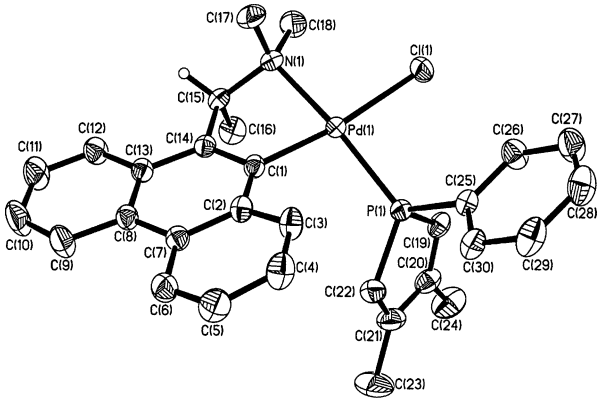


Figure 5. Molecular structure of the *S*-enantiomer in (±)-**13**.

Table 5. Selected Bond Lengths (Å) and Angles (deg) of (±)-13

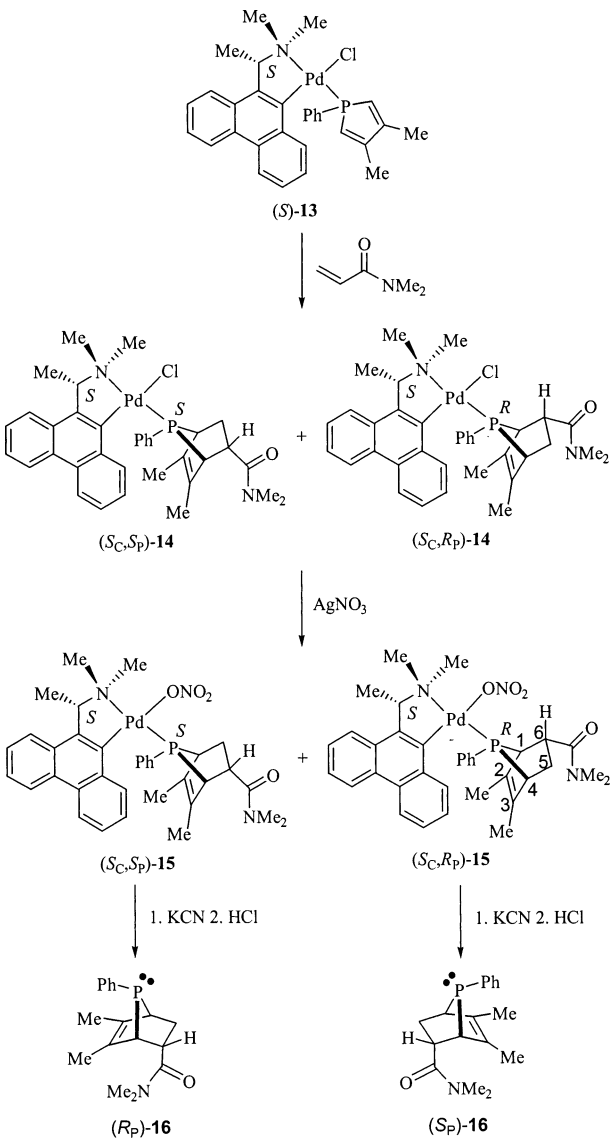
Pd(1)−C(1)	2.022(3)	Pd(1)−N(1)	2.137(2)
Pd(1)−P(1)	2.257(1)	Pd(1)−Cl(1)	2.395(1)
C(1)−Pd(1)−N(1)	80.1(1)	C(1)−Pd(1)−P(1)	98.8(1)
N(1)−Pd(1)−P(1)	169.2(1)	C(1)−Pd(1)−Cl(1)	172.2(1)
N(1)−Pd(1)−Cl(1)	93.2(1)	P(1)−Pd(1)−Cl(1)	88.6(1)
C(22)−P(1)−C(25)	107.1(1)	C(19)−P(1)−C(25)	105.0(1)
C(22)−P(1)−Pd(1)	122.7(1)	C(19)−P(1)−Pd(1)	110.5(1)

same plane, with the dihedral angle between these two rings being 17.6°.

In view of the severe steric repulsion observed within complex (*S*)-**11**, it is interesting to note that the regiochemistry of the complex remains unchanged in solution. In $CDCl_3$, the ^{31}P NMR spectrum of the complex shows only one singlet resonance at δ 29.8, indicating the presence of a single species in solution. In the corresponding ^1H NMR spectrum, the two *N*-methyl groups show the characteristic P−H couplings (2.1 and 3.6 Hz). These ^4J(P−H) couplings confirmed the trans arrangement between the phosphorus and the nitrogen donor. Accordingly, the complex does not undergo the ligand redistribution process in solution to form the corresponding regioisomer, which is sterically more favorable. Despite the severe steric constraints within the metal complex, the electronic properties of the phenanthrylamine auxiliary remain the controlling factors for the regioarrangement of (*S*)-**11** in solution.

A similar treatment of the chloro-bridged complex (*S*)-**5** with the cyclic phosphole ligand DMPP gave the corresponding monomeric neutral complex (*S*)-**13** in quantitative yield. However, complex (*S*)-**13** could not be induced to form single crystals suitable for structural analysis. In contract to its enantiomerically pure analogue, the racemic complex (±)-**13** was readily crystallized as pale yellow prisms from dichloromethane−hexane. This racemic material was prepared by the reaction of (±)-**5** with DMPP. The steric properties of the complex were studied by X-ray structural analyses. For clarity, only the *S* form of complex (±)-**13** is depicted in Figure 5. Selected bond lengths and angles are summarized in Table 5. The complex has the distorted square-planar coordination geometry with the tetrahedral distortion angle of 10.7° (Figure 5). As DMPP is smaller than PPh_3, the C(1)−Pd(1)−P(1) angle in (±)-**13** [98.75(8)°] is somewhat smaller than that observed in (*S*)-**11** [101.2(1)°]. Consistent with this observation, the dihedral angle between the central phenanthryl ring

Scheme 4



and the projecting aromatic ring in (±)-**13** [10.2°] is also smaller than that observed in complex (*S*)-**11** [17.6°]. As with the analogous PPh_3 complex, the ^{31}P NMR spectrum of the DMPP complex (±)-**13** in $CDCl_3$ shows only one singlet resonance at δ 28.6. The corresponding ^1H NMR spectrum showed the ^4J(P−H) coupling in the two nonequivalent N-Me signals to be 2.4 and 3.2 Hz, respectively. These NMR patterns confirm that the regiostereochemistry of the DMPP complex is retained in solution. Apparently, the planarity of the conjugated phenanthryl rings in this class of ortho-metalated complexes is somewhat flexible and can be adjusted slightly to accommodate other bulky ligands.

Asymmetric Diels−Alder Reaction between (*S*)-13 and *N,N*-Dimethylacrylamide. To compare the efficiency of the (*S*)-phenanthrylamine auxiliary and its naphthylamine analogue, the DMPP complex (*S*)-**13** was subjected to the asymmetric Diels−Alder reaction with *N,N*-dimethylacrylamide (Scheme 4). Interestingly, the two chiral auxiliaries appear to exhibit similar reactivity in this intermolecular cycloaddition reaction. Thus, when (*S*)-**13** was treated with the dienophile in 1,2-dichloroethane at 55 °C, the reaction was complete in 4 days. Prior to purification, the ^{31}P NMR spectrum of the

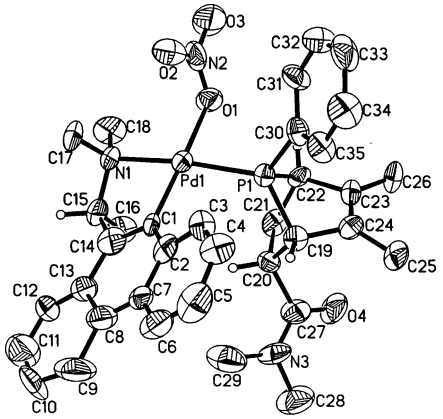


Figure 6. Molecular structure and absolute stereochemistry of (S_c,R_p)-**15**.

Table 6. Selected Bond Lengths (Å) and Angles (deg) of (S_c,R_p)-15

	molecule A	molecule B	molecule C	molecule D
Pd(1)−C(1)	2.011(10)	2.008(11)	2.006(10)	1.965(11)
Pd(1)−N(1)	2.116(9)	2.113(9)	2.125(9)	2.132(10)
Pd(1)−O(1)	2.154(8)	2.161(8)	2.149(11)	2.172(9)
Pd(1)−P(1)	2.241(3)	2.242(3)	2.267(3)	2.258(3)
C(1)−Pd(1)−N(1)	80.2(4)	79.9(4)	80.1(4)	79.2(4)
C(1)−Pd(1)−O(1)	174.2(4)	174.5(5)	173.0(4)	172.0(4)
N(1)−Pd(1)−O(1)	95.2(4)	95.5(4)	95.4(4)	94.7(4)
C(1)−Pd(1)−P(1)	99.2(3)	98.8(3)	97.5(3)	97.5(3)
N(1)−Pd(1)−P(1)	168.8(3)	169.2(3)	169.5(3)	168.5(3)
O(1)−Pd(1)−P(1)	84.6(2)	85.1(2)	87.9(3)	89.4(3)

crude reaction mixture in $CDCl_3$ exhibited two sharp singlets at δ 115.0 and 115.7 in a ratio of 1:6. No other ^{31}P NMR signals were detected in the 202 MHz spectrum, thus confirming that only two stereoisomeric cycloadducts, (S_c,R_p)- and (S_c,S_p)-**14**, were generated from the reaction.

The diastereomeric products could not be efficiently separated by fractional crystallization or silica gel column chromatography. Therefore, the diastereomeric mixture was converted quantitatively to the nitrato analogues (S_c,R_p)- and (S_c,S_p)-**15** by the treatment with silver nitrate (Scheme 4). The major isomer (S_c,R_p)-**15** crystallized readily as yellowish prisms from dichloromethane−hexane with $[\alpha]_D$ +183° (CH_2Cl_2). The molecular structure and the absolute stereochemistry of this major product were determined by X-ray structural analysis. This product crystallizes with four distinct molecules in the unit cell. However, they have identical stereochemistry and differ slightly in bond angles and distances. For clarity, only molecule A is shown in Figure 6. Selected bond distances and bond angles are given in Table 6. Studies revealed that the complex is (S_c,R_p)-**15**, in which the *endo*-cycloadduct coordinates as a typical monodentate via its bridgehead phosphorus donor atom onto the palladium template trans to the NMe_2 group of the (*S*)-phenanthrylamine auxiliary. The absolute configurations of the four newly generated stereogenic centers at P(1), C(19), C(20), and C(22) are *R*, *R*, *S*, and *S*, respectively, with the amide functional group orientated in the *endo* position at C(20). Accordingly, the structural analysis of (S_c,R_p)-**15** confirms that, in the cycloaddition reaction, the diastereomeric products (S_c,R_p)- and (S_c,S_p)-**14** were obtained in the ratio of 6:1. Treatment of (S_c,R_p)-**15** with aqueous potassium cyanide gave the known optically active ligand (S_p)-**16**.[7] Thus the *P*-chiral phosphanorbornene (S_p)-**16** was obtained as the major cycloaddition product when the (*S*)-phenanthrylamine was used as the chiral auxiliary. As mentioned previously, the apparent inversions of configurations at the stereogenic centers during the liberation processes are merely the consequence of the CIP sequence rules.[15]

Finally it should be noted that when the (*S*)-naphthylamine auxiliary was used for the analogous Diels−Alder reaction between DMPP and *N*,*N*-dimethylacrylamide under similar conditions, the cycloadducts (S_p)- and (R_p)-**16** were obtained in the ratio of 1:2.[8] Therefore, we have proven experimentally that the phenanthrylamine complex exerts a greater selectivity than its naphthylamine counterpart for this class of intermolecular cycloaddition reaction. The superiority of the phenanthrylamine auxiliary was similarly exhibited when the two ortho-palladated complexes were used as the chiral catalysts in the asymmetric Claisen rearrangement.[13] Further exploration in the applications of this class of ortho-metalated ligands is in progress in our laboratory.

Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. Proton NMR spectra were recorded at 300.1 or 500.1 MHz on Bruker ACF300 or Bruker AMX500 NMR spectrometers. All the ^{31}P NMR spectra were recorded at 120 MHz on a Bruker ACF300 NMR spectrometer. Melting points were determined on a Büchi melting point B-545 and were uncorrected. Optical rotations were measured on a Perkin-Elmer model 341 polarimeter. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry, National University of Singapore.

2,3-Dimethyl-1-phenylphosphole[16] and the enantiomerically pure forms of the naphthylamine complex **2**[17] and (*S*,*S*)-*N*,*N*,*N*′,*N*′-tetramethyl-2,3-butanediamine[18] were prepared by literature methods. 9-Acetylphenanthrene and *O*,*O*′-dibenzoyl-D-tartaric acid were purchased from Sigma-Aldrich and used without further purification.

Synthesis of (±)-1-(9-Phenanthryl)ethylamine, (±)-6. A mixture of 9-acetylphenanthrene (50 g, 0.23 mol) and ammonium formate (54 g, 0.56 mol) was heated at 180 °C for 4 h before it was treated with toluene (50 mL) and concentrated hydrochloric acid (60 mL) at 100 °C. The mixture was refluxed for another 5 h and then filtered. The creamy solid thus obtained was washed with water (100 mL) and then treated with dilute sodium hydroxide (5 M, 100 mL). The liberated amine was extracted into dichloromethane (100 mL × 2), and the solvent was dried ($MgSO_4$) and removed under reduced pressure. Distillation of the crude product gave the racemic amine as a colorless oil, 37 g (73%), bp 172−174 °C (0.3 mmHg). Anal. Calcd for $C_{16}H_{15}N$: C, 86.8; H, 6.8; N, 6.3. Found: C, 86.5; H, 6.8; N, 6.6. ^{1}H NMR ($CDCl_3$): δ 1.61 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*), 4.96 (q, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*Me), 7.56−8.77 (m, 9H, aromatics).

Optical Resolution of (±)-1-(9-Phenanthryl)ethylamine. Isolation of (*S*)-(−)-6. A solution of the racemic amine (±)-**6** (10.3 g, 46.4 mmol) in ethanol (95%, 200 mL) was neutralized

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with (+)-*O,O′*-dibenzoyl-D-tartaric acid (16.7 g, 46.6 mmol) in the same solvent (95%, 300 mL). The resulting solution was kept at room temperature for 20 h. The resolved product was obtained as colorless crystals from the reaction mixture (16.0 g). Recrystallization of the resolved salt in methanol gave the optically pure salt as colorless prisms (9.4 g) with $[\alpha]_D$ +62.2° (*c* 0.5, MeOH). Treatment of this salt with dilute sodium hydroxide (5 M, 15 mL) liberated (*S*)-(−)-**6**. The optically pure amine was obtained initially as a colorless oil, but it solidified slowly upon storage at room temperature, mp 79−81 °C, 3.58 g (70% yield), $[\alpha]_D$ −44.0° (*c* 0.5, CH_2Cl_2). The ^{1}H NMR spectrum of the resolved amine was identical with that of the initial racemic material. The (*R*)-(+)-form of the amine was obtained similarly by using (−)-*O,O′*-dibenzoyl-L-tartaric acid as the resolving agent.

(*S*)-(−)-*N,N*-Dimethyl-1-(9-phenanthryl)ethylamine, (*S*)-(−)-7. The resolved amine (*S*)-(−)-1-(9-phenanthryl)ethylamine (3.20 g, 14.5 mmol) was dissolved in formic acid (5 mL) and then treated with formaldehyde (37%, 6 mL). The reaction mixture was heated to 100 °C for 6 h. The mixture was cooled to room temperature and treated successively with concentrated hydrochloric acid (10 mL) and dilute sodium hydroxide (5 M, 15 mL). The crude product was extracted into dichloromethane and dried ($MgSO_4$), and the solvent was removed under reduced pressure. Distillation of the crude product gave the product as a colorless oil that slowly solidified, 2.80 g (78%), bp 154−156 °C (0.3 mmHg), mp 68−70 °C, $[\alpha]_D$ −61.3° (*c* 0.5, CH_2Cl_2). Anal. Calcd for $C_{18}H_{19}N$: C, 86.7; H, 7.7; N, 5.6. Found: C, 86.3; H, 7.4; N, 5.9. ^{1}H NMR ($CDCl_3$): δ 1.56 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*), 2.36 (s, 6H, NMe), 4.07 (q, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*Me), 7.58−8.77 (m, 9H, aromatics).

(+)-Bis(acetonitrile)[(*S*)-9-(1-(dimethylamino)ethyl-10-phenanthrenyl)-*C,N*]-palladium(II) Perchlorate, (*S*)-8. A solution of $[Pd(MeCN)_2Cl_2]$ (2.59 g, 10 mmol) in acetonitrile (30 mL) was treated with silver perchlorate (4.14 g, 20 mmol) in the dark for 1 h. The precipitate (AgCl) was removed by filtration through a layer of Celite, and the filtrate was added slowly into a mixture of (*S*)-(−)-*N,N*-dimethyl-1-(9-phenanthryl)ethylamine (2.49 g, 10 mmol) and triethylamine (1.01 g, 10 mmol) in dichloromethane (30 mL). The mixture was stirred for 20 h at room temperature and then filtered through Celite. The residue was dissolved in dichloromethane (100 mL), washed with water, dried ($MgSO_4$), and concentrated to ca. 15 mL. Addition of hexane into the concentrated solution gave the bis(acetonitrile) complex (*S*)-**8** as pale yellow crystals, 3.50 g (64.8%), mp 202−204 °C (dec), $[\alpha]_D$ +198° (*c* 0.5, CH_2Cl_2). Anal. Calcd for $C_{22}H_{24}N_3ClO_4Pd\cdot 0.25H_2O$: C, 48.9; H, 4.6; N, 7.8. Found: C, 48.9; H, 4.3; N, 7.7. ^{1}H NMR ($CDCl_3$): δ 2.07 (s, 3H, N≡C*Me*), 2.25 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH*Me*), 2.31 (s, 3H, N≡C*Me*), 2.80 (s, 3H, N*Me*), 2.87 (s, 3H, N*Me*), 4.29 (q, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*Me), 7.54−7.63 (m, 5H, H_4, H_5, H_{10}, H_{11}, H_{12}), 8.21 (dd, $^3J_{H3H4}$ = 8.4 Hz, $^4J_{H3H5}$ = 1.3 Hz, 1H, H_3), 8.59 (d, $^3J_{H5H6}$ = 7.0 Hz, 1H, H_6), 8.71 (d, $^3J_{H9H10}$ = 8.3 Hz, 1H, H_9).

(+)-Di-μ-chlorobis[(*S*)-9-(1-(dimethylamino)ethyl)-10-phenanthrenyl-*C,N*]dipalladium(II), (*S*)-5. A solution of the cationic complex (*S*)-**8** (2.70 g, 5.00 mmol) in dichloromethane (50 mL) was stirred vigorously with a solution of ammonium chloride (1.07 g, 10.0 mmol) in water (10 mL) for 4 h at room temperature. The organic layer was separated, washed with water (20 mL × 2), dried ($MgSO_4$), and concentrated to ca. 5 mL. Slow addition of hexane to the concentrated solution gave (*S*)-**5** as orange prisms, 1.85 g (95%), mp 200−202 °C (dec), $[\alpha]_D$ +393° (*c* 0.5, CH_2Cl_2). Anal. Calcd for $C_{36}H_{36}N_2Cl_2Pd_2$: C, 55.4; H, 4.7; N, 3.6. Found: C, 55.7; H, 4.4; N, 3.9. ^{1}H NMR ($CDCl_3$): δ 2.39 (d, $^3J_{HH}$ = 6.4 Hz, *trans*-CH*Me*), 2.48 (d, $^3J_{HH}$ = 6.4 Hz, *cis*-CH*Me*), 2.67 (s, *trans*-N*Me*), 2.77 (s, *cis*-N*Me*), 2.85 (s, *trans*- and *cis*-N*Me*), 4.19 (q, $^3J_{HH}$ = 6.4 Hz, *trans*-C*H*Me), 4.27 (q, $^3J_{HH}$ = 6.4 Hz, *cis*-C*H*Me), 7.42−8.90 (m, aromatics). Assignments for cis- and trans-isomers are arbitrary.

(+)-Di-μ-bromobis[(*S*)-9-(1-(dimethylamino)ethyl)-10-phenanthrenyl-*C,N*]dipalladium(II), (*S*)-9. The dibromo complex was prepared similarly by treating (*S*)-**8** with ammonium bromide, 94% yield, mp 193−195 °C, $[\alpha]_D$ +358° (*c* 0.5, CH_2Cl_2). Anal. Calcd for $C_{36}H_{36}N_2Br_2Pd_2$: C, 49.7; H, 4.2; N, 3.2; Br, 18.4. Found: C, 49.6; H, 4.1; N, 3.4; Br, 18.4. ^{1}H NMR ($CDCl_3$): δ 2.44 (d, $^3J_{HH}$ = 6.4 Hz, *trans*-CH*Me*), 2.52 (d, $^3J_{HH}$ = 6.4 Hz, *cis*-CH*Me*), 2.77 (s, *trans*-N*Me*), 2.83 (s, *trans*- and *cis*-N*Me*), 2.90 (s, *cis*-N*Me*), 4.23 (q, $^3J_{HH}$ = 6.4 Hz, *trans*-C*H*Me), 4.31 (q, $^3J_{HH}$ = 6.4 Hz, *cis*-C*H*Me), 7.30−8.95 (m, aromatics). Assignments for cis- and trans-isomers are arbitrary.

{(*S*)-9-[1-(Dimethylamino)ethyl]-10-phenanthrenyl-*C,N*}{(*S,S*)-*N,N,N′,N′*-tetramethyl-2,3-butanediamine)-*N,N′*}palladium(II) Perchlorate, (*S,S,S*)-10. To a solution of (*S*)-**8** (0.65 g, 1.2 mmol) in dichloromethane (10 mL) was added a solution of *N,N,N′,N′*-tetramethyl-(*S,S*)-2,3-butanediamine (0.17 g, 1.2 mmol) in the same solvent (5 mL). The mixture was stirred at room temperature for 0.5 h. Addition of hexane to the solution gave (*S,S,S*)-**10** as pale yellow crystals, 0.53 g (83%), mp 151−153 °C, $[\alpha]_D$ +180° (*c* 0.5, CH_2Cl_2). Anal. Calcd for $C_{26}H_{38}N_3ClO_4Pd\cdot 0.5CH_2Cl_2$: C, 49.7; H, 6.1; N, 6.6. Found: C, 49.7; H, 5.8; N, 6.9. ^{1}H NMR ($CDCl_3$): δ 1.05 (d, $^3J_{H18Me18}$ = 6.4 Hz, 3H, Me_{18}), 1.19 (d, $^3J_{H19Me19}$ = 6.4 Hz, 3H, Me_{19}), 2.15 (s, 3H, $Me_{17(eq)}$), 2.46 (s, 3H, $Me_{16(ax)}$), 2.55 (d, $^3J_{H15Me15}$ = 6.4 Hz, 3H, Me_{15}), 2.78 (s, 3H, $Me_{20(eq)}$), 2.88 (s, 3H, $Me_{16(eq)}$), 2.96 (s, 3H, $Me_{17(ax)}$), 3.01 (s, 3H, $Me_{20(ax)}$), 3.15 (qd, $^3J_{H18H19}$ = 12.0 Hz, $^3J_{H19Me19}$ = 6.0 Hz, 1H, H_{19}), 3.31 (qd, $^3J_{H18H19}$ = 12.0 Hz, $^3J_{H18Me18}$ = 6.0 Hz, 1H, H_{18}), 4.12 (q, $^3J_{H15Me15}$ = 6.4 Hz, 1H, H_{15}), 5.29 (s, 1H, $0.5CH_2Cl_2$), 7.55−7.66 (m, 5H, H_4 + H_5, H_{10} + H_{11} + H_{12}), 8.34 (d, $^3J_{H3H4}$ = 6.8 Hz, 1H, H_3), 8.54 (d, $^3J_{H5H6}$ = 9.2 Hz, 1H, H_6), 8.66 (d, $^3J_{H9H10}$ = 6.8 Hz, 1H, H_9).

Chloro{(*S*)-9-(1-(dimethylamino)ethyl)-10-phenanthrenyl-*C,N*}{(triphenylphosphine)-*P*}palladium(II), (*S*)-11. A solution of (*S*)-**5** (0.78 g, 1.0 mmol) in dichloromethane (10 mL) was treated with triphenylphosphine (0.53 g, 2.0 mmol) in the same solvent (10 mL) for 30 min at room temperature. The reaction mixture was concentrated to ca. 5 mL. Addition of hexane to the concentrated solution gave the product as a yellow powder. Recrystallization of the pure compound from dichloromethane−hexane gave (*S*)-**11** as pale yellow needles, 1.12 g (86%), mp 199 °C (dec), $[\alpha]_D$ +339° (*c* 0.5, CH_2Cl_2). Anal. Calcd for $C_{36}H_{33}ClNPPd$: C, 66.3; H, 5.1; N, 4.8. Found: C, 66.1; H, 4.7; N, 4.6. ^{31}P NMR ($CDCl_3$): δ 29.8 (s, 1P). ^{1}H NMR ($CDCl_3$): δ 2.28 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CH*Me*), 2.63 (d, $^4J_{PH}$ = 2.1 Hz, 3H, N$Me_{(ax)}$), 3.00 (d, $^4J_{PH}$ = 3.6 Hz, 3H, N$Me_{(eq)}$), 4.32 (qn, $^3J_{HH}$ = $^4J_{PH}$ = 6.4 Hz, 1H, C*H*Me), 6.81 (t, $^3J_{H3H4}$ = $^3J_{H4H5}$ = 7.1 Hz, 1H, H_4), 7.10−7.24 (m, 8H, H_5 + P-*Ph*), 7.50−7.58 (m, 6H, H_{10} + H_{11} + P-*Ph*), 7.70 (d, $^3J_{H11H12}$ = 8.2 Hz, 1H, H_{12}), 8.05 (d, $^3J_{H3H4}$ = 8.1 Hz, 1H, H_3), 8.22 (d, $^3J_{H5H6}$ = 8.3 Hz, 1H, H_6), 8.54 (d, $^3J_{H9H10}$ = 8.6 Hz, 1H, H_9).

Chloro{(*S*)-1-(1-(dimethylamino)ethyl)-2-naphthyl-*C,N*}-{(triphenylphosphine)-*P*}palladium(II), (*S*)-12. A solution of (*S*)-**2** (0.38 g, 0.50 mmol) suspended in dichloromethane (5 mL) was treated with triphenylphosphine (0.26 g, 1.0 mmol) in the same solvent (10 mL) for 30 min at room temperature. The reaction mixture was concentrated to ca. 5 mL. Addition of hexane to the concentrated solution gave the product as a yellow powder. Recrystallization of the pure compound from dichloromethane−hexane gave (*S*)-**12** as pale yellow needles, 0.52 g (87%), mp 202−204 °C, $[\alpha]_D$ +40.3° (*c* 0.5, CH_2Cl_2). Anal. Calcd for $C_{32}H_{31}ClNPPd$: C, 63.8; H, 5.2; N, 2.3; P, 5.1. Found: C, 63.7; H, 5.3; N, 2.1; P, 5.0. ^{31}P NMR ($CDCl_3$): δ 40.9 (s, 1P). ^{1}H NMR ($CDCl_3$): δ 2.07 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CH*Me*), 2.75 (s, 3H, N$Me_{(ax)}$), 2.97 (d, $^4J_{PH}$ = 3.2 Hz, 3H, N$Me_{(eq)}$), 4.36 (qn, $^3J_{HH}$ = $^4J_{PH}$ = 6.4 Hz, 1H, C*H*Me), 6.55−7.77 (m, 21H, aromatics).

Chloro{(*S*)-9-(1-(dimethylamino)ethyl)-10-phenanthrenyl-*C,N*}{(3,4-dimethyl-1-phenylphosphole)-*P*}palladium-(II), (*S*)-13. A solution of (*S*)-**5** (0.78 g, 1.0 mmol) in dichlo-

Table 7. Crystallographic Data for Complexes of (*S*)-9, (*S,S,S*)-10, (*S*)-11, (*S*)-12, (±)-13, and (S_c,R_p)-15

	(*S*)-**9**	(*S,S,S*)-**10**	(*S*)-**11**	(*S*)-**12**	(±)-**13**	(S_c,R_p)-**15**
formula	$C_{37}H_{38}Br_2Cl_2N_2Pd_2$	$C_{26.25}H_{39.5}Cl_{1.5}N_3O_4Pd$	$C_{36}H_{33}ClNPPd$	$C_{32}H_{31}ClNPPd$	$C_{30}H_{31}ClNPPd$	$C_{35.13}H_{40.25}Cl_{0.25}$
M	954.21	620.68	652.45	602.40	578.38	714.69
space group	C_2	$P2_1$	$Pna2_1$	$P2_12_12_1$	$Pbca$	$P2_1$
cryst syst	orthorhombic	monoclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic
a/Å	20.274(1)	9.584(1)	31.235(1)	8.132(1)	14.363(1)	13.422(1)
b/Å	11.536(1)	33.900(5)	10.711(1)	14.440(1)	19.053(1)	11.931(1)
c/Å	8.135(1)	9.714(1)	9.129(1)	23.732(1)	19.665(1)	42.215(2)
β/deg	103.591(1)	109.42(1)	90	90	90	98.878(1)
V/Å^3	1849.3(1)	2976.5(7)	3054.2(1)	2786.7(3)	5381.6(1)	6678.9(5)
Z	2	4	4	4	8	8
T/K	293(2)	293(2)	293(2)	223(2)	293(2)	223(2)
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ/mm^{-1}	3.305	0.792	0.773	0.840	0.867	0.666
R_1(obsd data)[a]	0.0352	0.0537	0.0279	0.0420	0.0335	0.0670
wR_2(obsd data)[b]	0.1036	0.1304	0.0638	0.0589	0.0776	0.1646
Flack param	0.02(1)	0.00(0)	−0.01(2)	−0.01(2)		−0.02(3)

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

romethane (10 mL) was added slowly into a solution of 3,4-dimethyl-1-phenylphosphole (0.38 g, 2.0 mmol) in the same solvent (5 mL). The reaction mixture was stirred for 30 min at room temperature and the solvent removed under reduced pressure. The crude product was chromatographed on a silica gel column using ethyl acetate−dichloromethane (1:1, v/v) as the eluent to give (*S*)-**13** as a yellow powder, 1.13 g (97%), mp 133−135 °C, $[\alpha]_D$ +550° (*c* 0.5, CH_2Cl_2). Anal. Calcd for $C_{30}H_{31}ClNPPd$: C, 62.3; H, 5.4; N, 2.4; P, 5.4. Found: C, 62.4; H, 5.6; N, 2.3; P, 5.2. ^{31}P NMR ($CDCl_3$): δ 28.6 (s, 1P). ^{1}H NMR ($CDCl_3$): δ 1.77 (s, 3H, C=C*Me*), 1.92 (s, 3H, C=C*Me*), 2.06 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CH*Me*), 2.70 (d, $^4J_{PH}$ = 2.4 Hz, 3H, N*Me*$_{(ax)}$), 2.93 (d, $^4J_{PH}$ = 3.2 Hz, 3H, N*Me*$_{(eq)}$), 4.29 (qn, $^3J_{HH}$ = $^4J_{PH}$ = 6.4 Hz, 1H, C*H*Me), 5.43 (d, $^2J_{PH}$ = 32.1 Hz, 1H, H_α), 6.71 (d, $^2J_{PH}$ = 31.7 Hz, 1H, H_α), 7.11 (t, $^3J_{H3H4} = {}^3J_{H4H5}$ = 8.0 Hz, 1H, H_4), 7.43−7.52 (m, 4H, H_5 + 2 × (*m*-*Ph*) + *p*-*Ph*), 7.53−7.59 (m, 2H, H_{10} + H_{11}), 7.70 (d, $^3J_{H11H12}$ = 9.2 Hz, 1H, H_{12}), 7.95−8.04 (m, 3H, H_3 + 2 × (*o*-Ph)), 8.59 (d, $^3J_{H5H6}$ = 8.4 Hz, 1H, H_6), 8.71 (d, $^3J_{H9H10}$ = 9.2 Hz, 1H, H_9).

Asymmetric Diels−Alder Reaction between (*S*)-13 and *N,N*-Dimethylacrylamide. Synthesis of (S_c,R_p)- and (S_c,S_p)-14 and Isolation of (S_c,R_p)-15. A mixture of the chloro complex (*S*)-**13** (0.30 g, 0.52 mmol) and *N,N*-dimethylacrylamide (0.15 g, 1.6 mmol) in 1,2-dichloroethane (10 mL) was heated at 55 °C for 4 days. Removal of solvent left a brownish residue. The ^{31}P NMR ($CDCl_3$) spectrum of the crude product prior to purification indicated a 1:6 mixture of the diastereomeric cycloadducts at δ 115.0 and 115.7. This mixture in CH_2Cl_2 (5 mL) was stirred vigorously with excess $AgNO_3$ (0.20 g, 1.2 mmol) in water (5 mL) for 1 h in the dark. The precipitate (AgCl) was removed by filtration through a layer of Celite and the filtrate dried ($MgSO_4$) and the solvent removed. The crude product was chromatographed on a silica gel column using ethyl acetate−dichloromethane (1:1, v/v) as the eluent to give the diastereomeric mixture of (S_c,R_p)- and (S_c,S_p)-**15** as a yellow powder, which exhibited two ^{31}P NMR signals at δ 115.9 (minor) and 116.3 (major). Recrystallization of the mixture from dichloromethane−hexane gave the major isomer (S_c,R_p)-**15** as pale yellow prisms, 0.21 g (57%), mp 200−202 °C (dec), $[\alpha]_D$ +183° (*c* 0.5, CH_2Cl_2). Anal. Calcd for $C_{35}H_{40}N_3O_4PPd\cdot0.125CH_2Cl_2$: C, 59.0; H, 5.7; N, 5.9; P, 4.3. Found: C, 59.1; H, 5.6; N, 5.7; P, 4.3. ^{31}P NMR ($CDCl_3$): δ 116.3 (s, 1P). ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 3H, C=CMe), 1.38 (s, 3H, C=CMe), 1.47 (s, 3H, NMe_{amide}), 2.13 (br, 1H, H_4), 2.15−2.26 (m, 1H, H_6), 2.28 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH*Me*), 2.51 (s, 3H, NMe_{amide}), 2.68 (d, $^4J_{PH}$ = 1.4 Hz, 3H, N*Me*$_{(ax)}$), 2.79 (d, $^4J_{PH}$ = 3.1 Hz, 3H, N*Me*$_{(eq)}$), 2.92 (d, $^4J_{PH}$ = 9.8 Hz, 1H, H_{5endo}), 3.03 (m, 1H, H_{5exo}), 3.28 (m, 1H, H_1), 4.35 (qn, $^3J_{HH} = {}^4J_{PH}$ = 6.2 Hz, 1H, C*H*Me), 7.41−8.67 (m, 13H, aromatics).

X-ray Crystal Structure Determinations of Complexes (*S*)-9, (*S,S,S*)-10, (*S*)-11, (*S*)-12, (±)-13, and (S_c,R_p)-15. Crystallographic data for complexes (*S*)-**9**, (*S,S,S*)-**10**, (*S*)-**11**, (*S*)-**12**, (±)-**13**, and (S_c,R_p)-**15** are summarized in Table 7. The diffraction data were collected on a Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation. SADABS absorption corrections were applied and, except for those of the solvent molecule, all non-hydrogen atoms refined anisotropically by full-matrix least-squares using SHELXL.[19] Hydrogen atoms were introduced at fixed distances from carbon atoms and assigned fixed thermal parameters.

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Supporting Information Available: For (*S*)-**9**, (*S,S,S*)-**10**, (*S*)-**11**, (*S*)-**12**, (±)-**13**, and (S_c,R_p)-**15** 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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