DOI: 10.1002/ejic.200701234

Design, Synthesis, and Stereochemical Evaluation of a Novel Chiral Amine–Palladacycle

Yi Ding,[a] Yongxin Li,[a] Yi Zhang,[a] Sumod A. Pullarkat,[a] and Pak-Hing Leung*[a]

Keywords: Asymmetric synthesis / Palladacycles / Chiral resolution / Cycloaddition / X-ray diffraction

A novel chiral palladacycle containing *ortho*-metallated (±)-1-(3,6-dimethylnaphthalen-2-yl)-*N*,*N*-dimethylethylamine was designed and synthesized by a multi-step synthesis by using 2,7-dimethylnaphthalene as the starting material. The structure and palladacycle ring conformation of the triphenylphosphane derivative was investigated by X-ray structural analysis in the solid state and by 2D ROESY NMR spectroscopy in solution. Through a designed intramolecular steric interaction, the five-membered naphthylamine chelate can be locked into a fixed conformation, both in the solid state and in solution. The racemic cyclopalladated complex could be efficiently resolved through the formation of its (*S*)-prolinato and (*S*)-alaninato derivatives. The structure and absolute configuration of the two optically resolved palladium complexes were determined by X-ray diffraction. Both the (*R*,*R*) and (*S*,*S*)-di-μ-chlorido dimeric palladium complexes containing the resolved amine ligand was obtained chemoselectively by treating the corresponding prolinato and alaninato derivatives with 1 M hydrochloric acid. Despite the severe interchelate steric constraint within these new organopalladium complexes, the bulky monodentate ligand 3,4-dimethyl-1-phenylphosphole (dmpp) was able to split the chlorido bridges regiospecifically in the position *trans* to the NMe_2 group. With the new palladacycle used as the chiral template, the stereoselectivity of Diels–Alder cycloaddition between dmpp and ethyl vinyl ketone significantly improves relative to that of other analogue complexes.

Introduction

Over the past decade, optically active organopalladium compounds, especially those derived from metallated tertiary amines, have proven to be very useful reagents for many synthetic applications. Such complexes have generated interest for their many roles, as catalysts,[1] agents for the determination of enantiomeric excess,[2] resolving agents,[3] and stoichiometric agents for the syntheses of organic compounds.[4]

We have been interested in the development of chiral orthopalladated complexes of substituted benzyl- [(*S*)-**1**] and naphthylamines [(*S*)-**2**] (Figure 1).[4f] It has been proven that (*S*)-**2** is superior over (*S*)-**1** in many applications.[5a,5b] The organometallic ring in (*S*)-**2** is kinetically and thermodynamically stable. The intramolecular steric interaction between H8 and the methyl group at the stereogenic carbon center confines the methyl group in the axial position and hence locks the cyclopalladated ring into the non-interconvertable λ conformation. On the other hand, the ring conformation of (*S*)-**1** is not locked, and the puckered ring adopts both the δ and λ conformations in the solid state and (*S*)-**1** undergoes rapid inversion in solution.[5]

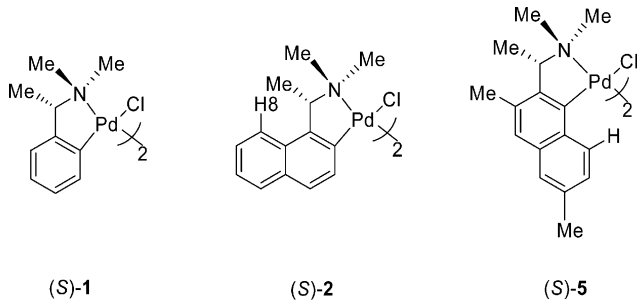
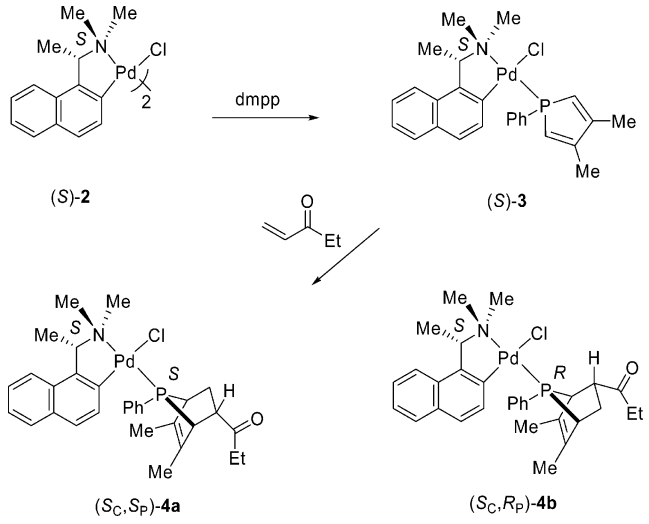


Figure 1. Molecular design for complexes (*S*)-**1**, (*S*)-**2**, and (*S*)-**5**.

Recently, we utilized (*S*)-**2** and its derivatives for the asymmetric syntheses of a series of functionalized mono- and diphosphanes.[4f–4i,6] Complex (*S*)-**3** is generated from the dimeric complex (*S*)-**2** by the regiospecific cleavage reaction with 3,4-dimethyl-1-phenylphosphole (dmpp). The Diels–Alder cycloadditions of this phosphole complex with a series of dienophiles have been extensively studied. For example, when (*S*)-**3** was treated with ethyl vinyl ketone at 70 °C, two *endo*-cycloaddition products were obtained as a 1:1 diastereomeric mixture of complexes **4a** and **4b** (Scheme 1).[6a] This experiment shows that the influence of the chiral naphthylethylamine auxiliary on the reaction site is insignificant. Evidently, in the transition state, the dmpp

[a] Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University,
637371 Singapore
E-mail: Pakhing@ntu.edu.sg

group enjoys a certain degree of free rotation around the P–Pd dative bond thus rendering poor stereoselectivity of the reaction.



Scheme 1.

In several similar syntheses, the separation of the corresponding two *endo*-diastereomeric products was somewhat tedious and resulted in low yields of the target enantiomers because of poor stereoselectivity. To improve the stereoselectivity, we designed and synthesized a new chiral complex (*S*)-**5** (Figure 1). We expect that (*S*)-**5** will retain all the desired stereoelectronic properties of the original naphthylamine template; most importantly, the organometallic ring conformation in (*S*)-**5** can be locked in solution by the interaction between Me12 and Me14 (Scheme 3). Furthermore, the aromatic hydrogen atom H3 is introduced adjacent to the Pd–C bond so as to exert stereochemical influence on the coordination position *trans* to the N donor atom. The application of this new chiral template in asymmetric Diels–Alder reactions was examined.

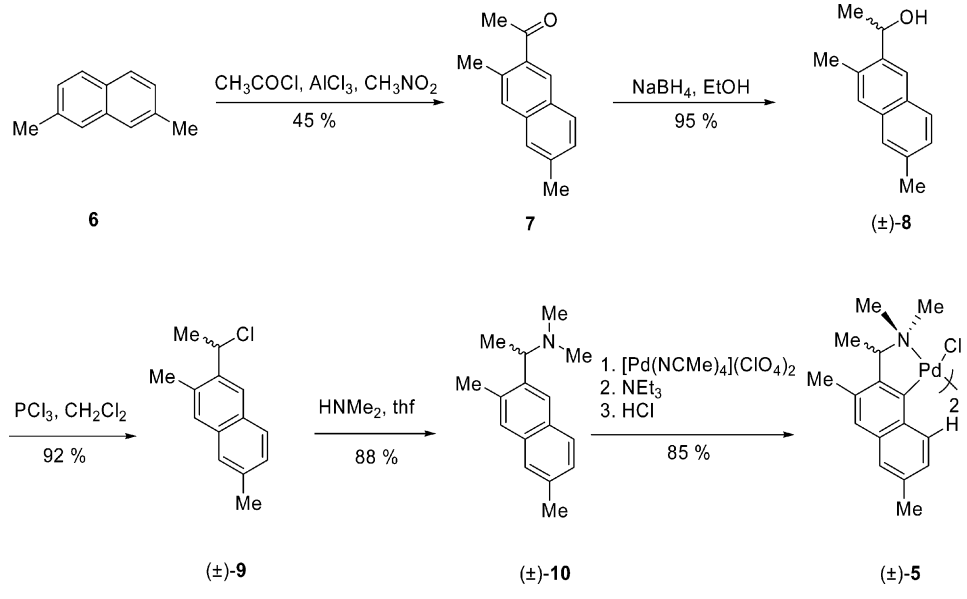
Results and Discussion

Synthesis of the Palladium Complexes (±)-5

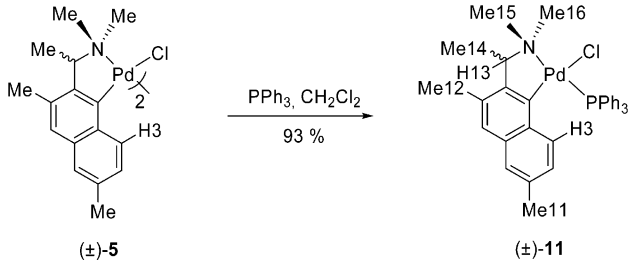
As illustrated in Scheme 2, the disubstituted naphthalene derivative **6**[7] was acetylated with acetyl chloride in the presence of aluminum chloride to give ketone **7** in 45% yield. Reduction of **7** in ethanol by sodium borohydride produced racemic alcohol (±)-**8** in 95% yield, which was then converted to chloride (±)-**9** in 92% yield by treatment with excess PCl_3 in dichloromethane. Reaction between the chloride (±)-**9** and aqueous dimethylamine afforded the target *N*,*N*-dimethylamine (±)-**10** as a white powder in 88% yield. The orthopalladation of (±)-**10** could be achieved in acetonitrile with $[Pd(MeCN)_4](ClO_4)_2$ as the palladium source in the presence of an equimolar amount of triethylamine. Treatment of the reaction mixture with dilute HCl gave (±)-**5** in the form of yellow prisms in an 85% isolated yield.

Stereochemical Investigation of the New Palladacycle

One of the major challenges in the structural design of the auxiliary lies in the introduction of a sterically congestive condition around the template site that is adjacent to the protruding H3 atom. In order to establish a coordination site that is able to accommodate a bulky monodentate ligand in a regiospecific manner, (±)-**5** was treated with triphenylphosphane. Interestingly, the bulky phosphane ligand splits the chlorido bridges of (±)-**5** efficiently and generated the mononuclear complex (±)-**11** as the sole product in 93% yield (Scheme 3).



Scheme 2.



Scheme 3.

The molecular structure of (±)-**11** was studied by single-crystal structural analysis (Figure 2), and the selected bond lengths and angles are listed in Table 1. Complex (±)-**11** adopts a distorted square-planar coordination geometry. The strong steric repulsion between the PPh_3 ligand and the organometallic chelate results in the enlargement of the bond angle C1–Pd1–P1 to 101.7(1)°. With these structural features, the Pd–P bond would not be able to rotate freely, as all the possible rotational motions are blocked by the chlorido ligand and the projecting aromatic proton H3. It is noteworthy that **5** adopts a molecular structure in which the second aromatic ring of the naphthyl group is placed in such a position so as to reduce such Pd–P bond rotations in **11**.[8c] Therefore, among the three P–Ph phenyl rings, the C17–C22 ring experiences the most intramolecular ligand–ligand repulsion. As a result, the bond angle Pd1–P1–C17 is enlarged to 117.9(1)°, which is larger than the two less-affected angles, Pd1–P1–C23 and Pd1–P1–C29 [111.5(1)° and 115.5(1)°]. Most importantly, the ligand–ligand repulsive interactions in complex (±)-**11** also disturb the planarity of the conjugated rings. Thus, the central ring (C1–C2–C7–C8–C9–C10) and the adjacent projecting ring (C2–C7) do not lie within the same plane, and the dihedral angle between these two rings is 5.1°.

In spite of the severe steric repulsion observed in (±)-**11**, the regiochemistry of this complex remains unchanged in solution. In $CDCl_3$, the ^{31}P NMR spectrum of the complex shows only one singlet resonance at δ = 30.9 ppm, which indicates 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 (2.0 and 3.4 Hz). These $^4J_{(P,H)}$ couplings confirm the *trans* relationship of the phosphorus atom and the nitrogen donor, which can be justified by the "transphobia".[8a,8b] Here, the complex does not undergo the possible ligand redistribution process in solution to form the other possible regioisomer that would be sterically more favorable.

The mononuclear complex (±)-**11** is more suitable for NMR spectroscopic studies of the organopalladium ring conformation because of the improved spectral resolution of the signals with respect to that from its parent dimer, which exists in solution as an equilibrium mixture of two regioisomers. Moreover, the simplicity of the ^1H NMR spectroscopic signals that are presented by the triphenylphosphane ligand is another attractive feature. This ligand only possesses protons from aromatic groups, and the absence of any aliphatic protons will therefore not contribute to the complexity in the aliphatic region of the ^1H NMR spectrum.

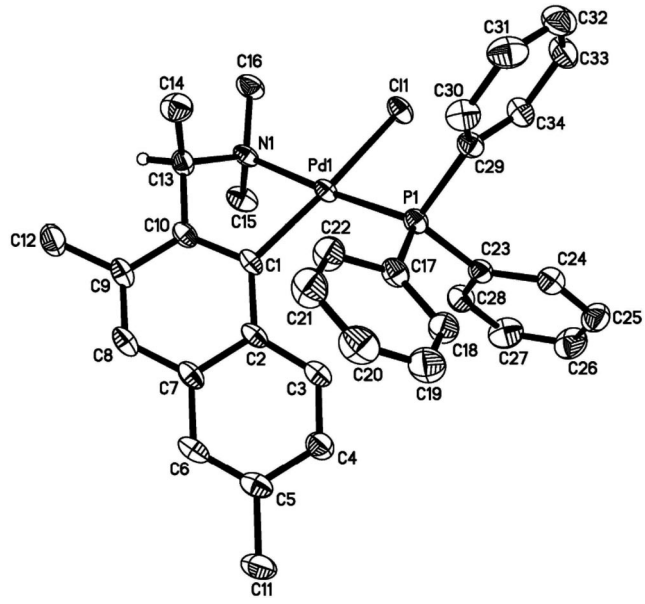


Figure 2. Molecular structure of (±)-**11**.

Table 1. Selected bond lengths [Å] and angles [°] for complex (±)-**11**.

Pd1–C1	2.048(3)	Pd1–N1	2.128(3)
Pd1–P1	2.273(1)	Pd1–Cl1	2.381(1)
P1–C23	1.823(4)	P1–C17	1.827(4)
P1–C29	1.841(4)	P1–Pd1–Cl1	87.9(1)
C1–Pd1–N1	80.0(1)	C1–Pd1–P1	101.7 (1)
N1–Pd1–P1	174.5(1)	C1–Pd1–Cl1	169.4(1)
N1–Pd1–Cl1	91.0(1)		

In solution, the ^1H NMR spectroscopic characterization of (±)-**11** was assisted by a combination of ^1H and 2D ^1H–^1H ROESY NMR spectroscopy experiments. The conformational behavior of the five-membered palladacycle was deduced from NOE data obtained from the 2D ^1H–^1H ROESY NMR spectrum. The labeled structure and the 2D ^1H–^1H ROESY NMR spectrum of (±)-**11** in $CDCl_3$ are shown in Scheme 3 and Figure 3, respectively. In this spectrum, strong NOE signals (A, B) for the interactions between the α-methane proton H13 and the two NMe groups are clearly recorded. On the other hand, the α-Me group interacts strongly with the equatorially disposed NMe group (C), but very weakly with the axially disposed group (D). The driving force for Me14 to assume mainly an axial position, i.e. H13–Me12 (E) and Me14–Me12 (F) repulsive interactions, is prominently reflected. Other expected NOE contacts for H13–Me14(G) and Me16–Me15 (H) are also observed. This set of NOE interactions indicates that the Me14 group is located in the axial position and that the λ and δ conformations are adopted in the (*S*) and (*R*)

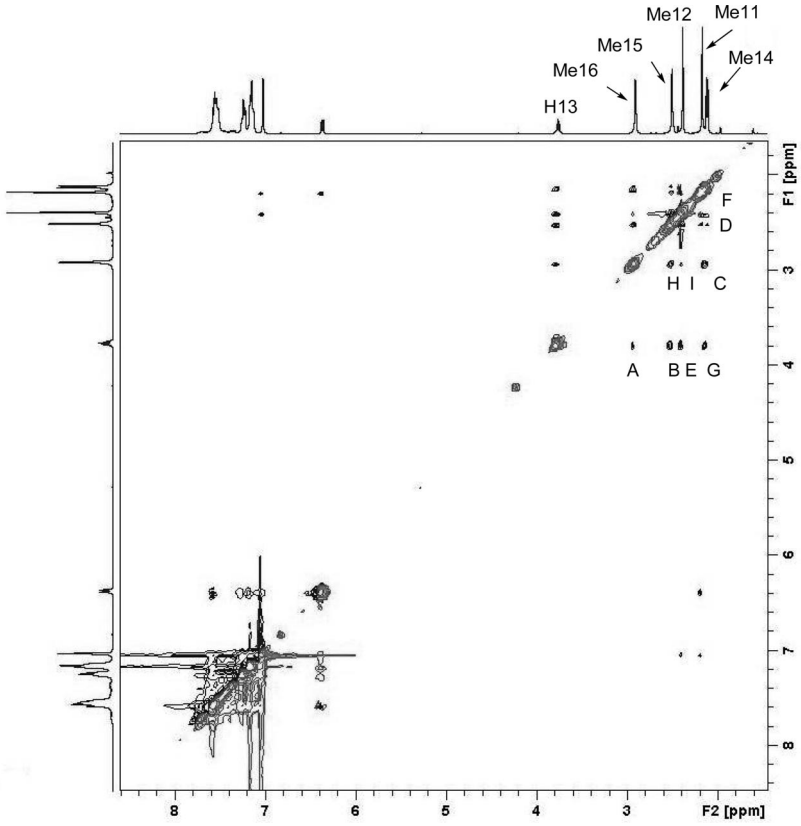


Figure 3. 2D ^{1}H–^{1}H ROESY NMR spectrum of (±)-**11** in $CDCl_3$.

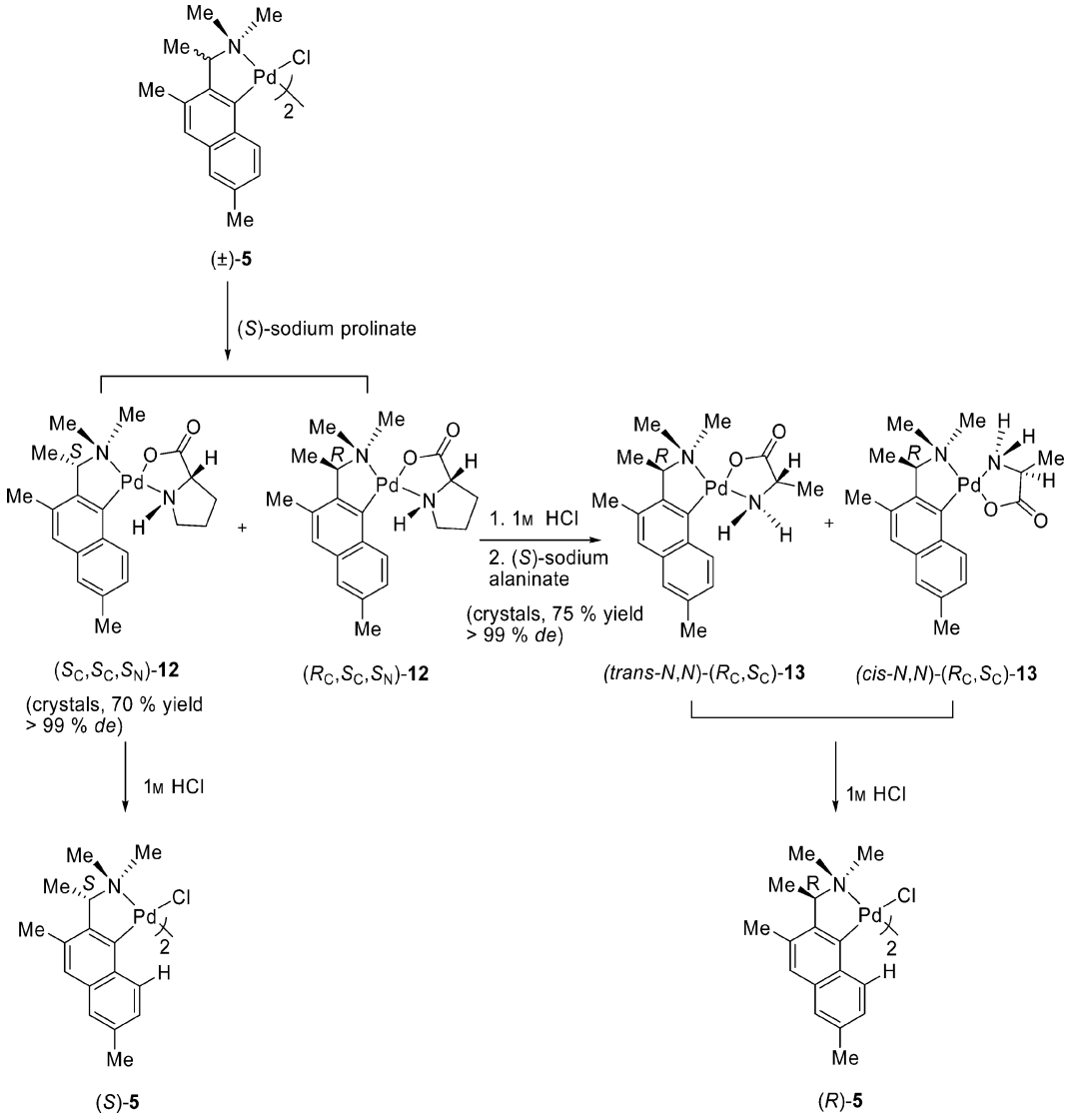
enantiomers, respectively. These spectroscopic results confirm that the five-membered palladacycle exists predominantly in the $\delta(R)$ or $\lambda(S)$ conformation in solution.

Optical Resolution of the Dimeric Complex (±)-5

The resolution of the racemic mixture of complex (±)-**5** was performed by using sodium (*S*)-prolinate and sodium (*S*)-alaninate as resolving reagents, as shown in Scheme 4.[8c] The racemic dimer (±)-**5** was first treated with 2 mol-equiv. sodium (*S*)-prolinate, and the formation of a 1:1 mixture of diastereomeric adducts, (R_C,S_C,S_N)- and (S_C,S_C,S_N)-**12**, was detected by means of ^{1}H NMR spectroscopy. A single crystallization from dichloromethane/diethyl ether afforded the less soluble diastereomer (S_C,S_C,S_N)-**12** in the form of pale-yellow flakes in 70% yield and >99% *de* (according to the ^{1}H NMR spectrum) with a $[\alpha]_D$ value of +331 (c = 0.5, $CHCl_3$). The mother liquor was treated with dilute hydrochloric acid, and the resulting enantiomerically enriched dimer **5** was then cleaved with sodium (*S*)-alaninate to form a mixture of (R_C,S_C)-**13** and (S_C,S_C)-**13**. The less soluble diastereomer (R_C,S_C)-**13** was crystallized as pale-yellow prisms from chloroform/diethyl ether slowly in 75% yield and >99% *de* (according to the ^{1}H NMR spectrum) with a $[\alpha]_D$ value of –300 (c = 0.5, $CHCl_3$).

The X-ray diffraction study of the diastereomer (S_C,S_C,S_N)-**12** was performed (Figure 4), and the selected bond lengths and angles are provided in Table 2. The X-ray crystallographic study reveals the *S* absolute configuration of the α-carbon stereocenter. The α-methyl group occupies the expected axial position, and the conformation of the five-membered palladacycle is λ. This complex adopts a *trans*-(*N*,*N*) arrangement, as observed in similar prolinato complexes.[9] Distortion of the square-planar coordination geometry about the palladium center is minimal. The dihedral angle between the two coordination planes {Pd1C1N1} and {Pd1N2O1} is 10.2°. The bond lengths around the central Pd atom are all in the normal range. However, a slight widening of the angle C1–Pd1–N2 [102.2(6)°] is observed relative to that recorded in the prolinato derivative of (*S*)-**1** [99.9(1)°]. This phenomenon can be attributed to the presence of the spacer group, which imposes a repulsive force onto the adjacent pyrrolidine ring. Consequently, the angle N1–Pd1–O1 is squeezed to 94.9(9)° relative to 98.0(9)° for the prolinato derivative of (*S*)-**1**.[9]

The molecular structure and the absolute stereochemistry of (R_C,S_C)-**13** were also investigated crystallographically. Only one isomer was observed according to the ^{1}H NMR spectrum in $CDCl_3$. Interestingly, two regioisomers, *trans*-(*N*,*N*)-(R_C,S_C)-**13** and *cis*-(*N*,*N*)-(R_C,S_C)-**13**, exist in the asymmetric unit. The molecular structures and selected



Scheme 4.

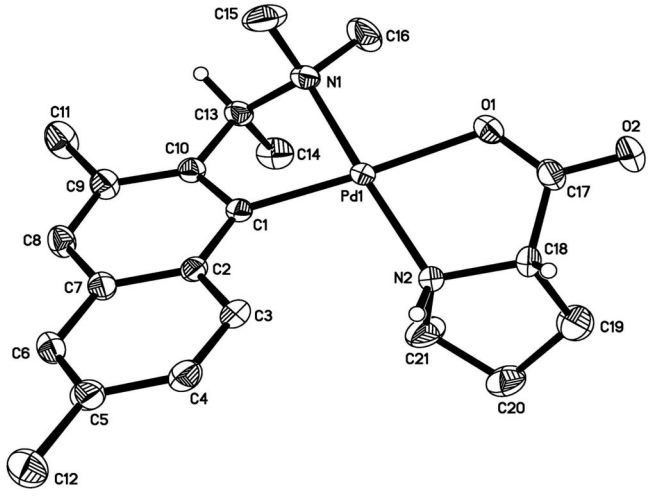


Figure 4. Molecular structure of (S_C,S_C,S_N)-**12**.

Table 2. Selected bond lengths [Å] and angles [°] for complex (S_C,S_C,S_N)-**12**.

Pd1–C1	2.000(2)	Pd1–O1	2.103(1)
Pd1–N1	2.074(2)	Pd1–N2	2.074(2)
N1–C16	1.485(3)	N2–C21	1.496(3)
O1–C17	1.278(3)	O2–C17	1.241(2)
C1–Pd1–N1	81.3(1)	C1–Pd1–N2	102.3(1)
N1–Pd1–O1	95.0(1)	N2–Pd1–O1	81.4(1)
C1–Pd1–O1	176.3(1)	N1–Pd1–N2	169.3(1)

bond lengths and angles of both the *trans*- and *cis* isomers are presented in Figures 5 and 6 as well as in Tables 3 and 4, respectively. These crystallographic studies reveal the *R* absolute configuration of the chiral carbon center at C13 or C32. For *trans*-(*N*,*N*)-(R_C,S_C)-**13**, the coordination geometry of the central palladium atom is slightly distorted square planar. The organopalladium five-membered ring

adopts an envelop-like conformation in which the N3 atom occupies the top point, which is 0.778 Å below the mean plane of C32–C31–C20–Pd2. The torsion angle C35–N3–C32–C33 was found to be –163.1°.

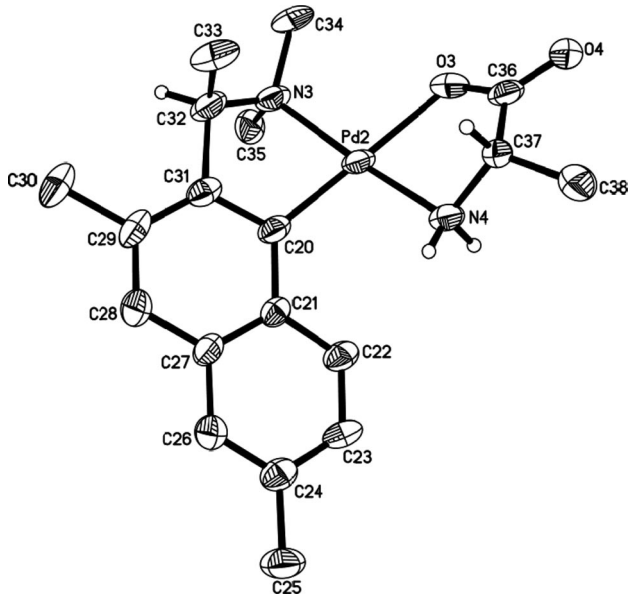


Figure 5. Molecular structure of (*trans*-*N*,*N*)-(R_C,S_C)-**13**.

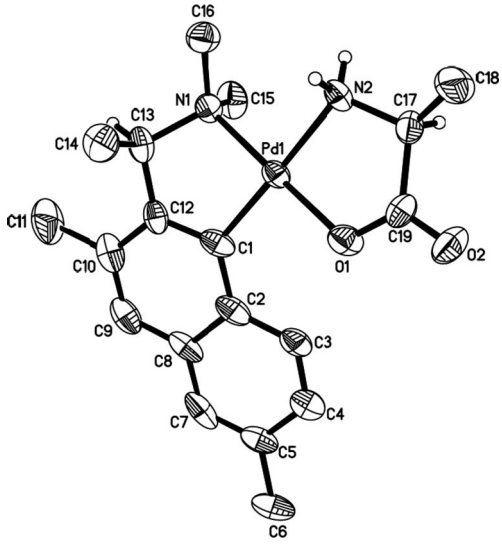


Figure 6. Molecular structure of (*cis*-*N*,*N*)-(R_C,S_C)-**13**.

Table 3. Selected bond lengths [Å] and angles [°] for complex (*trans*-*N*,*N*)-(R_C,S_C)-**13**.

Pd2–C20	1.962(7)	Pd2–O3	2.149(5)
Pd2–N4	2.069(6)	Pd2–N3	2.073(5)
O3–C36	1.269(9)	N3–C35	1.477(1)
N4–C37	1.486(8)	C20–Pd2–N4	99.1(2)
C20–Pd2–N3	81.3(2)	N4–Pd2–N3	170.5(2)
C20–Pd2–O3	174.6(3)	N4–Pd2–O3	78.7(2)
N3–Pd2–O3	100.0(2)	C36–O3–Pd2	112.1(5)

Table 4. Selected bond lengths [Å] and angles [°] for complex (*cis*-*N*,*N*)-(R_C,S_C)-**13**.

Pd1–C1	2.017(7)	Pd1–O1	2.043(5)
Pd1–N1	2.055(6)	Pd1–N2	2.112(5)
O1–C19	1.280(8)	O2–C19	1.225(8)
N1–C13	1.509(8)	N2–C17	1.454(9)
C1–Pd1–O1	101.0(2)	C1–Pd1–N1	81.4(3)
O1–Pd1–N1	176.4(2)	C1–Pd1–N2	177.9(3)
O1–Pd1–N2	79.8(2)	N1–Pd1–N2	97.7(2)

For the *cis* isomer, *cis*-(*N*,*N*)-(R_C,S_C)-**13**, the palladium atom is located in a distorted square-planar coordination sphere as expected. The bond lengths and angles around Pd1 are comparable to those of similar complexes of palladium(II), with the exception of the Pd1–N2 distance [2.112(5) Å], which is significantly longer than the reported values in the range 1.973–2.065 Å and also longer than the Pd2–N4 distance of 2.069(6) Å for *trans*-(*N*,*N*)-(R_C,S_C)-**13**.[9] Such lengthening of a bond is an expected result of the large *trans* influence of the carbon donor atom of the palladacycle. The tetrahedral distortion of the palladium coordination environment is minimal, and the dihedral angle between the two planes {Pd1N1C1} and {Pd1N2O1} is 3.1°.

The observation that there are two regioisomers in the asymmetric unit for (R_C,S_C)-**13** can be attributed to the less severe intramolecular ligand–ligand interaction. In comparison with the prolinato ligand in (S_C,S_C,S_N)-**12**, which possesses a pyrrolidine ring, the alaninato ligand in complex **13** does not have such a bulky group. Consequently, less steric interactions exist between the alaninato resolving unit and the amine auxiliary. The favorable steric environment in complex **13** allows the formation of both the *trans* and *cis* isomers.

Isolation of the Enantiomerically Pure Dimer 5

Treatment of (S_C,S_C,S_N)-**12** with dilute hydrochloric acid gave the enantiomerically pure complex dimer (*S*)-**5** in the form of a yellow powder in 95% yield, with a $[a]_D$ value of +476 (c = 1.0, $CHCl_3$). Single crystals were obtained from dicholoromethane/hexane. The solid-state structure of the dimeric complex (*S*)-**5** was determined by X-ray crystallography. There are four crystallographically distinguishable molecules in the asymmetrical unit with the same stereochemistry but with slightly different bond lengths and angles. For clarity, only one of the four (molecule A) is depicted in Figure 7. Selected bond lengths and angles are listed in Table 5. The X-ray crystallographic study confirms the *S* absolute configuration of the α-carbon stereocenter of the palladacycle. There is a *trans* relationship between the two nitrogen atoms and the two carbon donor atoms. The bond lengths and angles around the palladium atoms are within the normal range, and both palladium centers have a distorted square planar geometry. It is noteworthy that enantiomerically pure (*R*)-**5** could be obtained from (R_C,S_C)-**13** with the same procedure, $[a]_D$ = –471 (c = 0.3, $CHCl_3$). In solution, an equilibrium between the two re-

Table 5. Selected bond lengths [Å] and angles [°] for complex(*S*)-**5**.

Molecule A		Molecule B		Molecule C		Molecule D	
Pd1–C1	1.99(2)	Pd3–C33	1.99(2)	Pd5–C65	2.00(2)	Pd7–C97	2.00(2)
Pd1–N1	2.069(2)	Pd3–N3	2.066(2)	Pd5–N5	2.065(2)	Pd7–N7	2.08(2)
Pd1–Cl1	2.348(6)	Pd3–Cl3	2.360(6)	Pd5–Cl5	2.361(6)	Pd7–Cl7	2.446(6)
Pd1–Cl2	2.458(6)	Pd3–Cl4	2.469(6)	Pd5–Cl6	2.467(7)	Pd7–Cl8	2.335(6)
Pd2–C17	1.99(2)	Pd4–C49	2.00(2)	Pd6–C81	2.00(2)	Pd8–C113	2.00(2)
Pd2–N2	2.077(2)	Pd4–N4	2.07(2)	Pd6–N6	2.071(2)	Pd8–N8	2.079(2)
Pd2–Cl2	2.351(6)	Pd4–Cl4	2.352(6)	Pd6–Cl6	2.333(6)	Pd8–Cl7	2.347(6)
Pd2–Cl1	2.470(6)	Pd4–Cl3	2.470(6)	Pd6–Cl5	2.457(6)	Pd8–Cl8	2.445(6)
C1–Pd1–N1	80.2(8)	C33–Pd3–N3	80.9(8)	C65–Pd5–N5	80.8(9)	C97–Pd7–N7	81.0(9)
C1–Pd1–Cl1	99.2(6)	C33–Pd3–Cl3	99.2(7)	C65–Pd5–Cl5	100.9(6)	C97–Pd7–Cl8	98.5(7)
N1–Pd1–Cl1	173.5(6)	N3–Pd3–Cl3	170.4(6)	N5–Pd5–Cl5	172.0(6)	N7–Pd7–Cl8	175.1(6)
C1–Pd1–Cl2	176.4(7)	C33–Pd3–Cl4	177.4(7)	C65–Pd5–Cl6	175.9(6)	C97–Pd7–Cl7	176.1(7)
Cl1–Pd1–Cl2	83.3(2)	Cl3–Pd3–Cl4	83.2(2)	Cl5–Pd5–Cl6	82.9(2)	Cl8–Pd7–Cl7	83.9(2)
C17–Pd2–N2	80.0(9)	C49–Pd4–N4	80.6(9)	C81–Pd6–N6	81.2(9)	C113–Pd8–N8	80.5(8)
C17–Pd2–Cl2	98.9(7)	C49–Pd4–Cl4	98.3(7)	C81–Pd6–Cl6	98.6(7)	C113–Pd8–Cl7	98.6(7)
C17–Pd2–Cl1	173.7(7)	C49–Pd4–Cl3	178.3(7)	C81–Pd6–Cl5	176.9(7)	C113–Pd8–Cl8	175.5(7)

gioisomers was observed. The ^{1}H NMR spectrum of (*S*)-**5** in $CDCl_3$ shows clearly two distinct pairs of C*Me* doublet resonances at δ = 2.26 and 2.32 ppm ($^3J_{H,H}$ = 6.3 Hz) in a ratio of ca. 1:1 for the two regioisomers.

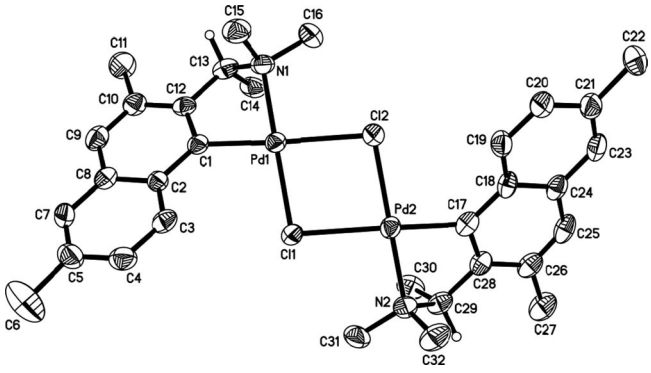
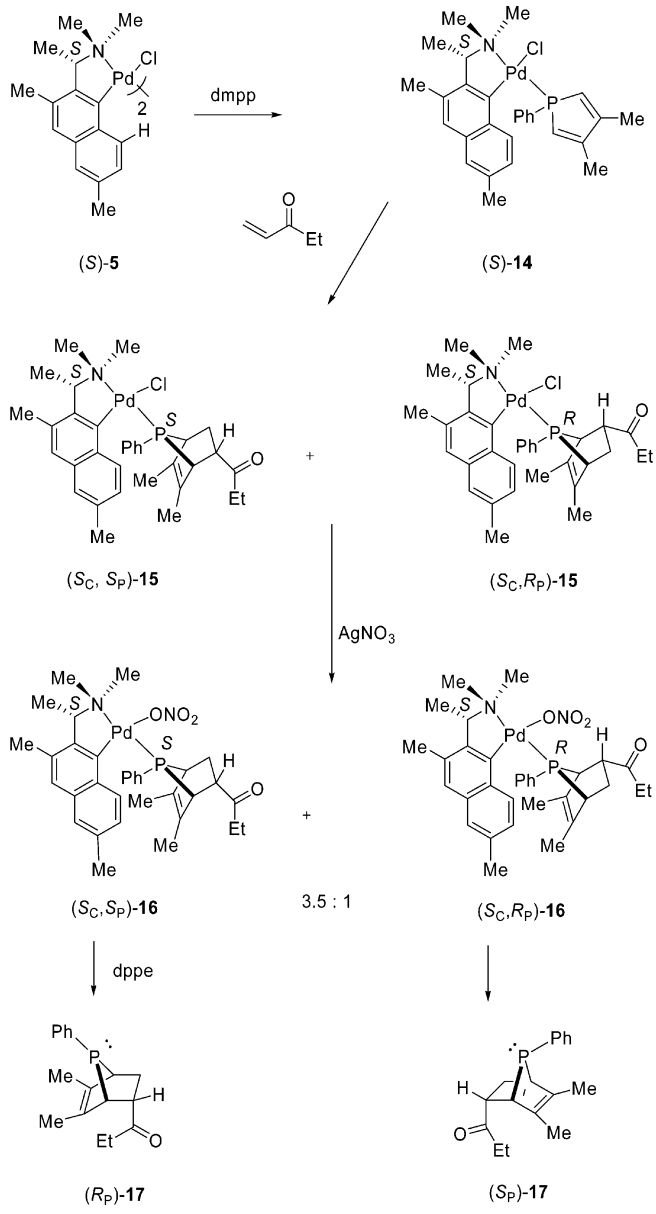


Figure 7. Molecular structure of (*S*)-**5**.

Asymmetric Diels–Alder Reaction Between (*S*)-14 and Ethyl Vinyl Ketone

In order to evaluate the efficiency and stereoselectivity of the new palladacycle **5**, the asymmetric Diels–Alder reaction between dmpp and ethyl vinyl ketone promoted by (*S*)-**5** was investigated (Scheme 5).

The cycloaddition reaction involves the synthesis of the five-membered heterocycle dmpp complex (*S*)-**14**. The structure of this key complex was investigated by X-ray crystallography (Figure 8). Single crystals were obtained by slow evaporation of a solution of dichloromethane and hexane. Selected bond lengths and angles are given in Table 6. The coordination geometry around the Pd center is distorted square planar, and the phosphole is coordinated *trans* to the amine nitrogen atom. The bond lengths and angles around Pd1 atom are all comparable to those of other dmpp complexes of α-arylalkylamine auxiliaries.[10] The complex has a distorted square-planar coordination geometry, with a tetrahedral distortion angle of 8.5°. Due to the fact that dmpp is smaller than PPh_3, the angle C1–Pd1–



Scheme 5.

P1 [99.1(6)°] in (*S*)-**14** is significantly smaller than the corresponding angle observed in (±)-**11** [117.9(6)°]. The dihedral angle between the phenyl ring and the projecting aromatic ring in (*S*)-**14** (4.9°) is also smaller than that observed in (±)-**11** (5.1°]), which is consistent with this observation. The bond angles around P1 are significantly different. The angle C20–P1–Pd1 [111.3(10)°] is significantly smaller than the angles C17–P1–Pd1 [122.7(1)°] and C23–P1–Pd1 [117.6(1)°]. This difference can be attributed to the repulsive interactions between the coordinated dmpp group and the "spacer" H3 (Figure 8). As expected, the five-membered palladacycle adopts a λ configuration, in which the α-methyl group, Me14, is axially disposed.

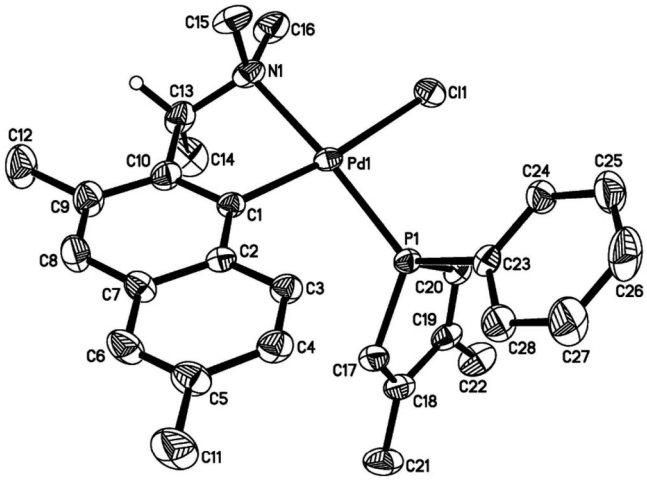


Figure 8. Molecular structure of (*S*)-**14**.

Table 6. Selected bond lengths [Å] and angles [°] for complex (*S*)-**14**.

Pd1–C1	2.035(3)	Pd1–P1	2.252(8)
Pd1–N1	2.132(3)	Pd1–Cl1	2.412(7)
N1–C16	1.487(4)	N1–C13	1.503(4)
P1–C17	1.799(3)	P1–C20	1.797(3)
C1–Pd1–N1	80.1(1)	C1–Pd1–P1	99.2(1)
N1–Pd1–P1	171.0(8)	C1–Pd1–Cl1	172.6(1)
N1–Pd1–Cl1	93.1(8)	P1–Pd1–Cl1	88.0(3)
C16–N1–Pd1	115.9(2)	C13–N1–Pd1	103.6(2)

When (*S*)-**14** was treated with excess ethyl vinyl ketone in chloroform at 50 °C, the reaction was found to be completed in 2 d. The ^{31}P NMR spectrum of the crude reaction mixture in $CDCl_3$ exhibits two singlets at δ = 121.1 ppm (major) and δ = 120.9 ppm (minor) in a ratio of 3.5:1, which indicates that only two stereoisomeric cycloadducts, (S_C,S_P)- and (S_C,R_P)-**15**, were generated from the reaction. The products could not be crystallized from a variety of solvents and were subsequently converted into the nitrato analogues, (S_C,S_P)- and (S_C,R_P)-**16**, by treatment with silver nitrate (Scheme 5). The ^{31}P NMR spectrum of the resultant complex mixture shows two singlets at δ = 121.4 ppm (major) and δ = 120.4 ppm (minor). The major isomer (S_C,S_P)-**16** crystallized readily from ethyl acetate/diethyl ether in the form of pale-yellow prisms with a $[\alpha]_D$ value of +185. The molecular structure and the absolute stereochemistry of this major product were determined by X-ray structural analysis (Figure 9). Selected bond lengths and angles are given in Table 7. Structural investigations reveals that the complex is (S_C,S_P)-**16**, where the *endo*-cycloadduct, *trans* to the NMe_2 group, coordinates to the Pd atom as a typical monodentate ligand through its bridgehead P donor atom. The absolute configurations of the four newly generated stereogenic centers P1, C17, C18, and C23 are *S*, *S*, *R*, and *S*, respectively; the carbonyl group is oriented in the *endo* position at C18. Interestingly, despite the same level of asymmetric induction as that achieved previously,[8c] the geometry of the olefin upon approach is opposite as a result of the steric effect of the newly introduced aromatic ring.

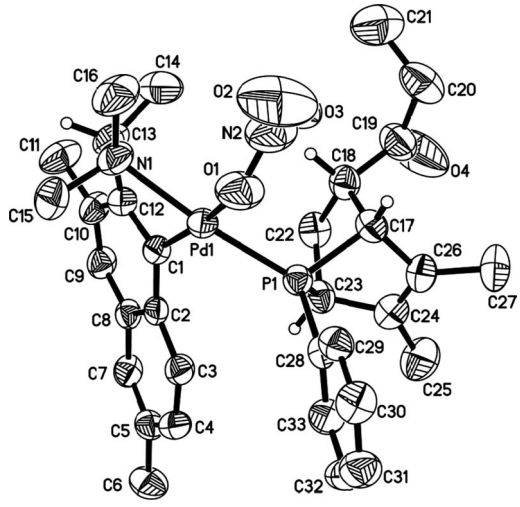


Figure 9. Molecular structure of (S_C,R_P)-**16**.

Table 7. Selected bond lengths [Å] and angles [°] for complex (S_C,S_P)-**16**.

Pd1–C1	2.009(5)	Pd1–N1	2.136(4)
Pd1–O1	2.180(4)	Pd1–P1	2.260(1)
C1–Pd1–N1	79.3(2)	C1–Pd1–O1	170.6(2)
N1–Pd1–O1	93.5(2)	C1–Pd1–P1	95.5(1)
N1–Pd1–P1	169.1(1)	O1–Pd1–P1	92.6(1)

Treatment of (S_C,S_P)-**16** with 1,2-bis(diphenylphosphanyl)ethane (dppe) gave the reported optically active ligand (R_P)-**17**.[6a] Conclusively, the P-chiral phosphanorbornene (R_p)-**17** was obtained as the major cycloaddition product when (*S*)-**5** was used as the chiral auxiliary. The apparent inversion of configuration at the stereogenic centers during the liberation process is merely the consequence of the Cahn–Ingold–Prelog sequence rules.[11]

It is important to note that when the more commonly used chiral reaction promoter (*S*)-**2** was employed for the analogous Diels–Alder reaction between dmpp and ethyl vinyl ketone under similar reaction conditions, the cycloadducts were obtained in the ratio of 1.3:1.[4f] With the new complex (*S*)-**5**, however, the increased ratio (3.5:1) indicates that the stereoselectivity has been improved significantly.

Thus, (*S*)-**5** exerts a greater selectivity for this class of intermolecular cycloaddition reaction. Further exploration in the applications of this class of orthometallated ligands is in progress in our laboratory.

Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen using standard Schlenk techniques. ^{1}H NMR spectra were recorded on a Bruker Advance DPX300 spectrometer at 300 MHz. ^{13}C NMR spectra were recorded at 75 MHz or 100 MHz on a Bruker Advance DPX300 or a Bruker Advance DPX400 spectrometer. The ^{31}P NMR spectra were recorded at 121 MHz on a Bruker Advance DPX300 spectrometer. Unless stated otherwise, all NMR spectroscopic experiments were performed at room temperature (300 K). Chemical shifts (δ) are reported in ppm relative to TMS and referenced to the chemical shifts of residual solvent resonances (^{1}H and ^{13}C NMR) or 85% H_3PO_4 (^{31}P NMR). Mass spectra were recorded on a Finnigan Trace GC Ultra instrument at 70 eV with EI mode. Melting points were determined on a SRS-Optimelt MPA-100 apparatus and were uncorrected. Optical rotations were measured on the specified solution in a 0.1-dm cell at 20 °C with a Perkin–Elmer model 341 polarimeter. Elemental analyses were performed by the Elemental Analysis Laboratory of the Division of Chemistry and Biological Chemistry at the Nanyang Technological University of Singapore.

1-(3,6-Dimethylnaphthalen-2-yl)ethanone (7): A solution of 2,7-dimethylnaphthalene (**6**) (7.3 g, 46.8 mmol) in nitromethane (100 mL) was added whilst stirring to a mixture of anhydrous $AlCl_3$ (7.33 g, 55 mmol) and acetyl chloride (3.34 mL, 46.8 mmol) in nitromethane (20 mL). The resultant red solution was stirred at room temperature for 20 h and poured into a mixture of ice (50 g) and conc. HCl (20 mL). After vigorous stirring for 30 min, the yellowish organic layer was separated, washed with H_2O, dried (Na_2SO_4), and concentrated to dryness. The residue was passed through a SiO_2 column to give product **7** as a colorless solid. Yield: 4.16 g (45%). M.p. 78–80 °C. $C_{14}H_{14}O$ (198.26): C 84.81, H 7.12; found: C 84.98, H 7.09. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.51 (s, 3 H, aryl-CH_3), 2.65 (s, 3 H, aryl-CH_3), 2.69 (s, 3 H, COCH_3), 7.30 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, aromatic proton 7-H), 7.52 (s, 1 H, aromatic proton 5-H), 7.54 (m, 1 H, aromatic proton H_4), 7.76 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, aromatic proton H_8), 8.20 (s, 1 H, aromatic proton 1-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.95 (s, CH_3), 22.08 (s, CH_3), 29.32 (s, CO*C*H$_3$), 125.96 (s, aryl-C), 128.25 (s, aryl-C), 128.42 (s, aryl-C), 129.22 (s, aryl-C), 129.42 (s, aryl-C), 130.75 (s, aryl-C), 134.81 (s, aryl-C), 135.10 (s, aryl-C), 135.28 (s, aryl-C), 138.37 (s, aryl-C), 201.24 (s, CO) ppm. GC-MS (M^+): *m*/*z* (%) = 198.20 (90), 183.33 (100), 155.32(34).

1-(3,6-Dimethylnaphthalen-2-yl)ethanol [(±)-8]: To **7** (1.0 g, 5.05 mmol) in ethanol (20 mL) was added a solution of $NaBH_4$ (0.38 g, 10.1 mmol) in ethanol (20 mL). The mixture was stirred at room temperature for 24 h followed by treatment with dilute NaOH (3%, 20 mL). The resulting solution was concentrated to 10 mL and extracted with CH_2Cl_2. The organic layers were combined, washed with water, and dried with Na_2SO_4. Removal of the solvent gave the product as a colorless oil. Yield: 0.96 g, (95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, CHCH_3), 2.26 (s, 3 H, aryl-CH_3), 2.36 (s, 3 H, aryl-CH_3), 2.61 (s, 1 H, O*H*), 4.94 (q, $^3J_{H,H}$ = 6.2 Hz, 1 H, *CH*CH$_3$), 7.10 (d, $^3J_{H,H}$ = 8.3 Hz, aromatic proton 7-H), 7.29 (s, 1 H, aromatic proton 5-H), 7.33 (s, 1 H, aromatic proton 4-H), 7.53 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, aromatic proton 8-H), 7.71 (s, 1 H, aromatic proton 1-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.44 (s, CH_3), 21.83 (s, CH_3), 24.21 (s, CH*C*H$_3$), 67.03 (s, COH), 123.10 (s, aryl-C), 125.91 (s, aryl-C), 127.58 (s, aryl-C), 127.66 (s, aryl-C), 127.89 (s, aryl-C), 130.57 (s, aryl-C), 133.01 (s, aryl-C), 133.07 (s, aryl-C), 135.34 (s, aryl-C), 142.00 (s, aryl-C) ppm. GC-MS (M^+): *m*/*z* (%) = 182.29 (100), 200.11 (51), 157.30 (70), 142.27 (28).

2-(1-Chloridoethyl)-3,6-dimethylnaphthalene [(±)-9]: A solution of (±)-**8** (1.0 g, 5.0 mmol) in CH_2Cl_2 (30 mL) was slowly added dropwise to a solution of PCl_3 (3.0 g, 22 mmol) dissolved in the same solvent (20 mL). The mixture was stirred overnight at room temperature followed by addition of water. The organic layer was separated, washed with water, and dried with Na_2SO_4. Removal of the solvent gave the product as a white waxy solid. Yield: 1.0 g (92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.07 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CHCH_3), 2.57 (s, 3 H, aryl-CH_3), 2.64 (s, 3 H, aryl-CH_3), 5.51 (q, $^3J_{H,H}$ = 6.8 Hz, 1 H, *CH*CH$_3$), 7.33 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, aromatic proton 7-H), 7.57 (s, 1 H, aromatic proton 5-H), 7.59 (s, 1 H, aromatic proton 4-H), 7.79 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, aromatic proton 8-H), 8.01 (s, 1 H, aromatic proton 1-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.50 (s, CH_3), 21.88 (s, CH_3), 25.04 (s, CH*C*H$_3$), 55.55 (s, *C*HCH$_3$), 124.79 (s, aryl-C), 125.92 (s, aryl-C), 127.78 (s, aryl-C), 127.90 (s, aryl-C), 128.25 (s, aryl-C), 130.38 (s, aryl-C), 133.54 (s, aryl-C), 133.67 (s, aryl-C), 136.21 (s, aryl-C), 138.20 (s, aryl-C) ppm. GC-MS (M^+): *m*/*z* (%) = 183.18 (100), 218.09 (20), 182.28 (55), 168.30 (50), 152.27 (10).

1-(3,6-Dimethylnaphthalen-2-yl)-*N*,*N*-dimethylethanamine [(±)-10]: A solution of **9** (2.18 g, 10 mmol) in CH_2Cl_2 was stirred vigorously with an aqueous solution of dimethylamine (2 M) for 48 h. The solvents were mostly removed, and the residue remained in some CH_2Cl_2. The residue was washed with water and dried and the solvents evaporated. The pure amine was obtained as a colorless oil after column chromatography with ethyl acetate as the eluent. Yield: 2.0 g (88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CHCH_3), 2.22 (s, 6 H, NCH_3), 2.43 (s, 3 H, aryl-CH_3), 2.47 (s, 3 H, aryl-CH_3), 3.52 (q, $^3J_{H,H}$ = 6.5 Hz, 1 H, *CH*CH$_3$), 7.17 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, aromatic protons 7-H), 7.35 (s, 1 H, aromatic proton 5-H), 7.37 (s, 1 H, aromatic proton 4-H), 7.65 (d, $^3J_{H,H}$ = 8.3 Hz,1 H, aromatic proton 8-H), 7.82 (s, 1 H, aromatic proton 1-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.23 (s, CH_3), 20.22 (s, CH_3), 21.81 (s, CH*C*H$_3$), 43.49 (s, N*C*H$_3$), 61.75 (s, *C*HCH$_3$), 124.96 (s, aryl-C), 125.83 (s, aryl-C), 127.38 (s, aryl-C), 127.53 (s, aryl-C), 127.79 (s, aryl-C), 130.71 (s, aryl-C), 132.74 (s, aryl-C), 134.51 (s, aryl-C), 134.99 (s, aryl-C), 141.33 (s, aryl-C) ppm. GC-MS (M^+): *m*/*z* (%) = 212.38 (100), 182.32 (75), 227.12 (70), 168.25 (28), 153.18 (15).

(±)-D-μ-Chloridobis{3-[1-(dimethylamino)ethyl]-2,7-dimethyl-4-naphthalenyl-*C*,*N*}dipalladium(II) [(±)-5]: A mixture of *trans*-dichloridobis(acetonitrile)palladium(II) (2.59 g, 10 mmol) and silver perchlorate (4.14 g, 20 mmol) in acetonitrile (30 mL) was stirred at room temperature for 1 h. The precipitate (AgCl) was filtered out, and the filtrate was added dropwise into a mixture of *N*,*N*-dimethyl-1-(2,7-dimethylnaphthalen-5-yl)ethylamine (±)-**10** (2.28 g, 10 mmol) and triethylamine (1.01 g, 10 mmol) in dichloromethane (30 mL) whilst stirring. The mixture was stirred at room temperature for 20 h and filtered through a Celite layer. The filtrate was evaporated, and the residue was dissolved in dichloromethane (100 mL). Dilute HCl (1 M, 50 mL) was then added to the solution, and the mixture was stirred vigorously for 1 h. The organic layer was separated, washed with H_2O, dried (Na_2SO_4), and concentrated to c.a. 10 mL. Dilution of the solution with hexane caused the precipitation of the racemic dimer as yellow prisms. Yield: 3.13 g, (85%). M.p. 150–

152 °C (dec.). $C_{32}H_{40}Cl_2N_2Pd_2$ (736.42): C 52.19, H 5.47, N 3.80; found: C 52.52, H 5.34, N 3.59. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.19–2.28 (m, 6 H, CH_3), 2.26–2.42 (m, 12 H, CH_3), 2.55–2.66 (m, 12 H, CH_3), 3.56–3.70 (m, 2 H, *CH* CH_3), 6.89–7.30 (m, 6 H, aromatic protons), 8.33–8.61 (m, 2 H, aromatic protons) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.61 (s, CH_3), 21.20 (s, CH_3), 21.28 (s, CH_3), 22.53 (s, CH_3), 22.60 (s, CH*C*H$_3$), 22.69 (s, CH*C*H$_3$), 49.17 (s, NCH_3), 49.57 (s, NCH_3), 49.72 (s, NCH_3), 49.88 (s, NCH_3), 75.08 (s, CH_3*C*H), 75.22 (s, CH_3*C*H), 125.06 (s, aryl-C), 125.39 (s, aryl-C), 125.57 (s, aryl-C), 125.63 (s, aryl-C), 125.94 (s, aryl-C), 128.74 (s, aryl-C), 128.79 (s, aryl-C), 130.35 (s, aryl-C), 130.46 (s, aryl-C), 132.58 (s, aryl-C), 132.76 (s, aryl-C), 133.95(s, aryl-C), 134.03 (s, aryl-C), 144.08 (s, aryl-C), 144.39 (s, aryl-C), 147.04 (s, aryl-C), 147.20 (s, aryl-C), 147.37 (s, aryl-C) ppm.

(±)-Chlorido{3-[1-(dimethylamino)ethyl]-2,7-dimethyl-4-naphthalenyl-*C*,*N*}(triphenylphosphane-*P*)palladium(II) [(±)-11]: To a solution of (±)-**5** (0.184 g, 0.250 mmol) in dichloromethane (10 mL) was added triphenylphosphane (0.131 g, 0.500 mmol) dissolved in the same solvent (10 mL). The resulting solution was stirred for 30 min at room temperature and concentrated to ca 5 mL. Addition of hexane to the solution caused the precipitation of the product as yellow fluffy crystals. Yield: 0.29 g (93%). M.p. 200–202 °C (dec.). $C_{34}H_{35}ClNPPd$ (630.45): C 64.77, H 5.60, N 2.22; found: C 64.40, H 5.42, N 2.22. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 30.9 (s) ppm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.11 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, CHCH_3), 2.17 (s, 3 H, aryl-CH_3), 2.38 (s, 3 H, aryl-CH_3), 2.50 (d, $^4J_{P,H}$ = 2.0 Hz, 3 H, NCH_3), 2.90 (d, $^4J_{P,H}$ = 3.4 Hz, 3 H, NCH_3), 3.76 (quint, $^4J_{P,H}$ = $^3J_{H,H}$ = 6.2 Hz, 1 H, C*H*CH$_3$), 6.36 (dd, $^4J_{H,H}$ = 1.3 Hz, $^3J_{H,H}$ = 8.5 Hz, 1 H, aromatic proton 6-H), 7.02–7.58 (m, 18 H, aromatic protons) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.90 (s, CH_3), 21.01 (s, CH_3), 21.14 (s, CH*C*H$_3$), 49.07 (s, NCH_3), 50.75 (d, $^3J_{C,P}$ = 3.0 Hz, NCH_3), 74.99 (d, $^3J_{C,P}$ = 3.3 Hz, CH_3*C*H), 124.55 (s, aryl-C), 125.13 (s, aryl-C), 125.31 (s, aryl-C), 127.66 (d, $^2J_{C,P}$ = 14.7 Hz, aryl-C), 129.45 (s, aryl-C), 129.87 (d, $^3J_{C,P}$ = 2.3 Hz, aryl-C), 131.69 (d, $^1J_{C,P}$ = 47.2 Hz, aryl-C), 132.12 (d, $^2J_{C,P}$ = 11.4 Hz, aryl-C), 133.13 (s, aryl-C), 133.31 (s, aryl-C), 133.53 (d, $^4J_{C,P}$ = 4.1 Hz, aryl-C), 134.80 (d, $^3J_{C,P}$ = 11.1 Hz, aryl-C), 147.86 (d, $^4J_{C,P}$ = 1.9 Hz, aryl-C), 156.53 (s, aryl-C) ppm.

(S_C,$S_C$$S_N$)-Prolinato-{3-[1-(dimethylamino)ethyl]-2,7-dimethyl-4-naphthalenyl-*C*,*N*}palladium(II) [(S_C,S_C,S_N)-12]: To a suspension of the racemic dimer (±)-**5** (3.00 g, 4.07 mmol) in CH_3OH (30 mL) was added a solution of sodium prolinate (1.55 g, 11.3 mmol) dissolved in the same solvent (30 mL). The mixture was stirred at room temperature for 1 h, and the solvent was removed under reduced pressure. The solution of the residue in CH_2Cl_2 (50 mL) was washed with H_2O, dried (Na_2SO_4), and diluted with diethyl ether. The less soluble diastereomer (S_C,S_C,S_N)-**12** crystallized slowly as slightly yellowish flakes. Yield: 1.32 g (73%, based on half of the dimer used), >99% *de*. M.p. 185–187 °C (dec.). $[\alpha]_D$ = +331, $[\alpha]_{578}$ = +350, $[\alpha]_{546}$ = +407, $[\alpha]_{436}$ = +827, $[\alpha]_{365}$ = +1697 (*c* = 0.5, $CHCl_3$). $C_{22}H_{30}Cl_2N_2O_2Pd$ (531.78): C 49.69, H 5.69, N 5.27; found: C 49.85, H 5.32, N 5.39. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.55–1.64 (m, 1 H, C*H*), 1.92–2.03 (m, 1 H, C*H*), 2.07 (d, $^3J_{H,H}$ = 6.2 Hz, 3 H, CHCH_3), 2.34–2.37 (overlapping m, 2 H, CH_2), 2.38 (s, 3 H, aryl-CH_3), 2.46 (s, 3 H, aryl-CH_3), 2.65 (s, 3 H, NCH_3), 2.77 (s, 3 H, NCH_3), 2.81–2.96 (m, 2 H, CH_2), 3.66–3.72 (m, 1 H, C*H*), 4.15 (q, $^3J_{H,H}$ = 7.9 Hz, 1 H, C*H*CH$_3$), 4.50 (br. s, 1 H, N*H*), 7.18 (s, 1 H, aromatic proton 8-H), 7.20 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, aromatic proton 5-H), 7.41 (s, 1 H, aromatic proton 1-H), 7.65 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, aromatic proton 6-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.49 (s, CH_3), 21.31 (s, CH_3), 22.71 (s, CH*C*H$_3$), 25.24 (s, NCH_3), 30.39 (s, NCH_3), 48.17 (s, CH_3*C*H), 53.01 (s, CH_2), 53.25 (s, CH_2), 66.03 (s, CH_2), 74.04 (s, CO*C*H), 124.49 (s, aryl-C), 126.69 (s, aryl-C), 127.74 (s, aryl-C), 129.46 (s, aryl-C), 132.84 (s, aryl-C), 134.01 (s, aryl-C), 134.81 (s, aryl-C), 147.93 (s, aryl-C), 148.58 (s, aryl-C), 181.25 (s, CO) ppm.

(R_C,S_C)-Alaninato-{3-[1-(dimethylamino)ethyl]-2,7-dimethyl-4-naphthalenyl-*C*,*N*}palladium(II) [(R_C,S_C)-13]: The previously described mother liquor of (S_C,$S_C$$S_N$)-**12** was evaporated and treated with aqueous HCl (1 M, 30 mL) to afford a mixture of (±)-**5** (2.00 g, 2.71 mmol). A solution of sodium alaninate (0.90 g, 8.13 mmol) in CH_3OH was added to the mixture of (±)-**5**, which was stirred at room temperature for 1 h, and the solvent was removed under reduced pressure. The solution of the residue in $CHCl_3$ (50 mL) was washed with H_2O, dried (Na_2SO_4), and diluted with diethyl ether. The less soluble diastereomer (R_C,S_C)-**13** crystallized slowly as slightly yellowish crystals. Yield: 1.65 g (75%, based on half of the dimer used), >99% *de*. M.p. 190–192 °C (dec.). $[\alpha]_D$ = –300, $[\alpha]_{578}$ = –314, $[\alpha]_{546}$ = –364, $[\alpha]_{436}$ = –670, $[\alpha]_{365}$ = –1080 (*c* = 0.5, $CHCl_3$). $C_{21}H_{30}N_2O_3Pd$ (464.87): C 54.25, H 6.50, N 6.03; found: C 54.47, H 7.04, N 5.88. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.62 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CHCH_3), 2.01 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H, CHCH_3), 2.37 (s, 3 H, aryl-CH_3), 2.46 (s, 3 H, aryl-CH_3), 2.69 [s, 3 H, NC$H_{3(ax)}$], 2.75 [s, 3 H, NC$H_{3(eq)}$], 3.34 (br. m, 2 H, N*H*), 3.75 (q, $^3J_{H,H}$ = 6.3 Hz, 1 H, COC*H*CH$_3$), 3.78 (q, $^3J_{H,H}$ = 6.3 Hz, 1 H, C*H*CH$_3$), 7.17 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, aromatic proton 5-H), 7.19 (s, 1 H, aromatic proton 1-H), 7.31 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, aromatic proton 6-H), 7.43 (s, 1 H, aromatic proton 8-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.58 (s, CH_3), 21.09 (s, CH_3), 21.39 (s, CH*C*H$_3$), 22.67 (s, CH-*C*H$_3$), 48.06 (s, NCH_3), 53.19 (s, NCH_3), 56.27 (s, CH_3*C*H), 74.14 (s, CO*C*H), 124.79 (s, aryl-C), 127.06 (s, aryl-C), 127.49 (s, aryl-C), 129.92 (s, aryl-C), 132.72 (s, aryl-C), 134.22 (s, aryl-C), 134.98 (s, aryl-C), 145.32 (s, aryl-C), 149.14 (s, aryl-C), 179.31 (s, CO) ppm.

(*S*)-Di-μ-chloridobis{3-[1-(dimethylamino)ethyl]-2,7-dimethyl-4-naphthalenyl-*C*,*N*}dipalladium(II) [(*S*)-5]: A solution of the diastereomer (S_C,S_C,S_N)-**12** (1.25 g, 2.81 mmol) in CH_2Cl_2 (20 mL) was treated with aqueous HCl (1 M, 30 mL). After vigorous stirring for 30 min, the organic layer was separated, washed with water, dried (Na_2SO_4), and concentrated to dryness to afford an amorphous yellow product. Yield: 1.0 g (97%). M.p. 182–184 °C (dec.). $[\alpha]_D$ = +476, $[\alpha]_{578}$ = +485, $[\alpha]_{546}$ = +562 (*c* = 1.0, $CHCl_3$). $C_{32}H_{40}Cl_2N_2Pd_2$ (736.42): C 52.19, H 5.47, N 3.80; found: C 52.52, H 5.34, N 3.59. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.26 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H, CHCH_3), 2.32 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H, CHCH_3), 2.36–2.45 (m, 12 H), 2.63–2.76 (m, 12 H), 3.62–3.74 (m, 2 H, C*H*CH$_3$), 6.93–7.33 (m, 6 H, aromatic protons), 8.36–8.64 (m, 2 H, aromatic protons) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.24 (s, CH_3), 20.77 (s, CH_3), 21.35 (s, CH_3), 21.43 (s, CH_3), 22.87 (s, CH*C*H$_3$), 22.97 (s, CH*C*H$_3$), 49.47 (s, NCH_3), 50.25 (s, NCH_3), 53.74 (s, NCH_3), 53.90 (s, NCH_3), 75.45 (s, CH_3*C*H), 75.64(s, CH_3*C*H), 125.32 (s, aryl-C), 125.35 (s, aryl-C), 125.53 (s, aryl-C), 125.77 (s, aryl-C), 125.92 (s, aryl-C), 126.25 (s, aryl-C), 128.82 (s, aryl-C), 128.88 (s, aryl-C), 130.43 (br. s, aryl-C), 130.57 (s, aryl-C), 132.80 (s, aryl-C), 133.03 (s, aryl-C), 134.20 (s, aryl-C), 134.32 (br. s, aryl-C), 144.20 (s, aryl-C), 144.50 (s, aryl-C), 147.23 (s, aryl-C), 147.36 (s, aryl-C) ppm.

The optically pure (*R*)-**5** was prepared from (R_C,S_C)-**13** in a similar manner: $[\alpha]_D$ = –471, $[\alpha]_{578}$ = –503, $[\alpha]_{546}$ = –564, $[\alpha]_{436}$ = –587, $[\alpha]_{365}$ = –1187 (*c* = 0.3, $CHCl_3$).

(*S*)-Chlorido{3-[1-(dimethylamino)ethyl]-2,7-dimethyl-4-naphthalenyl-*C*,*N*}{3′,4′-dimethyl-1′-phenylphosphole-P}palladium(II) [(*S*)-14]: To a solution of (*S*)-**5** (0.18 g, 0.25 mmol) in dichloromethane (10 mL) was added a solution of 3,4-dimethyl-1-phenylphosphole

(dmpp) (0.10 g, 0.53 mmol) dissolved in the same solvent (5 mL). The resulting yellow solution was stirred at room temperature for 1 h, and the solvent was removed under reduced pressure. The residue solid was chromatographed on a silica gel column by using dichloromethane/ethyl acetate (1:1, v/v) as the eluent to give a pale yellow powder, which was recrystallized from dichloromethane/hexane as yellow prisms. Yield: 0.24 g (88.9%). $[a]_D$ = +875, $[a]_{578}$ = +920, $[a]_{546}$ = +1090 (c = 0.5, $CHCl_3$). M.p. 190–192 °C (dec). $C_{28}H_{33}ClNPPd$ (556.37): C 60.44, H 5.98, N 2.52; found: C 60.08, H 6.40, N 2.52. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 29.75 (s) ppm. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.82 (s, 3 H, C=CCH_3), 1.90 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, CHCH_3), 1.95 (s, 3 H, C=CCH_3), 2.40 (s, 6 H, aryl-CH_3), 2.54 [d, $^4J_{P,H}$ = 1.7 Hz, 3 H, NC$H_{3(ax)}$], 2.84 [d, $^4J_{P,H}$ = 3.4 Hz, 3 H, NC$H_{3(eq)}$], 3.72 (quint, $^3J_{H,H}$ = $^4J_{P,H}$ = 6.3 Hz, 1 H, CH_3CH), 5.61 (d, $^2J_{P,H}$ = 32.0 Hz, 1 H, C=CH), 6.75 (d, $^2J_{P,H}$ = 32.0 Hz, 1 H, C=CH), 6.76 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, aromatic proton 5-H), 7.19 (s, 1 H, aromatic proton 1-H), 7.37 (s, 1 H, aromatic proton 8-H), 7.40–7.45 (m, 3 H, p-Ph, 2 × m-Ph), 7.60 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, aromatic proton 6-H), 7.97–8.04 (m, 2 H, 2 × o-Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.86 (d, $^3J_{C,P}$ = 12.6 Hz, C=CCH_3), 17.48 (d, $^3J_{C,P}$ = 12.2 Hz, C=CCH_3), 21.07 (s, CH_3), 22.45 (s, CH_3), 27.60 (s $CHCH_3$), 48.15 (s, NCH_3), 50.36 (s, NCH_3), 73.14 (d, $^4J_{C,P}$ = 3.1 Hz, CH_3CH), 122.39 (s, aryl-C), 123.88 (s, aryl-C), 125.44 (d, $^1J_{C,P}$ = 49.0 Hz, aryl-C), 126.49 (s, aryl-C), 126.71 (s, aryl-C), 127.40 (d, $^1J_{C,P}$ = 43.7 Hz, PC=C), 128.16 (d, $^2J_{C,P}$ = 10.8 Hz, aryl-C), 129.14 (d, $^1J_{C,P}$ = 52 Hz, PC=C), 130.22 (s, aryl-C), 131.71 (s, aryl-C), 132.89 (s, aryl-C), 133.06 (d, $^3J_{C,P}$ = 10.5 Hz, aryl-C), 133.12 (s, aryl-C), 140.73 (d, $^4J_{C,P}$ = 5.9 Hz, aryl-C), 147.13 (s, aryl-C), 147.78 (d, $^2J_{C,P}$ = 10.0 Hz, PC=C), 150.93 (s, aryl-C), 153.36 (d, $^2J_{C,P}$ = 10.5 Hz, PC=C) ppm.

Asymmetric Diels–Alder Reaction of (*S*)-14 and Ethyl Vinyl Ketone, Synthesis of (S_C,R_P)-16 and (S_C,S_P)-16 and Isolation of (S_C,S_P)-16: A mixture of the chlorido complex (*S*)-**14** (0.56 g, 1.0 mmol) and ethyl vinyl ketone (0.50 g, 6.0 mmol) in chloroform (10 mL) was left at 50 °C for 2 d. The mixture was filtered through a layer of Celite, and the solvent removed. The ^{31}P NMR ($CDCl_3$) spectrum of the crude product showed signals at δ = 121.1, 120.9 ppm in a ratio of 3.5: 1. This mixture in CH_2Cl_2 (5 mL) was stirred vigorously with excess $AgNO_3$ (0.50 g, 2.9 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 by using ethyl acetate/dichloromethane (1:10, v/v) as the eluent to give the diastereomeric mixture of (S_C,S_P)- and (S_C,R_P)-**16** as a yellow powder, which exhibited two ^{31}P NMR signals at δ = 121.4 (major) and 120.4 ppm (minor) in $CDCl_3$. Recrystallization of the mixture from ethyl acetate/diethyl ether gave the major isomer (S_C,S_P)-**16** as pale yellow prisms. Yield: 0.35 g (52.0%). $[a]_D$ = +185 (c = 0.5, $CHCl_3$). M.p. 198–200 °C (dec). $C_{33}H_{41}N_2O_4PPd{\cdot}H_2O$ (685.10): C 57.85, H 6.33, N 4.09; found: C 57.64, H 6.79, N 4.10. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 121.4 (s) ppm. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.03 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_2CH_3), 1.19 (s, 3 H, C=CCH_3), 1.25–1.32 (m, 1 H, H_{exo}), 1.52 (s, 3 H, C=CCH_3), 1.58–1.74 (m, 1 H, PCHCH), 2.15 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, CHCH_3), 2.41 (s, 3 H, aryl-CH_3), 2.50 (s, 3 H, aryl-CH_3), 2.52 [d, $^4J_{P,H}$ = 1.5 Hz, 3 H, NC$H_{3(ax)}$], 2.61–2.67 (m, 2 H, CH_2CH_3), 2.67–2.71 (m, 1 H, H_{endo}), 2.73 [d, $^4J_{P,H}$ = 3.3 Hz, 3 H, NC$H_{3(eq)}$], 3.49–3.50 (m, 1 H, PCHCH$_2$), 3.77 (quint, $^3J_{H,H}$ = $^4J_{P,H}$ = 5.9 Hz, 1 H, CHCH$_3$), 4.58 (m, 1 H, COCH), 7.02 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, aromatic proton 5-H), 7.23 (s, 1 H, aromatic proton 1-H), 7.40 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, aromatic protons 6-H), 7.41 (s, 1 H, aromatic protons 8-H), 7.50–7.52 (m, 3 H, p-Ph, 2 × m-Ph), 7.64–7.70 (m, 2 H, 2 × o-Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.77 (s, CH_3), 14.29 (s, CH_3), 15.01 (s, CH_3), 20.76 (s, CH_3), 21.46 (s, CH_3), 22.22 (s, CH_3), 25.39 (d, $^2J_{C,P}$ = 18.1 Hz, PCCH_2), 34.76 (s, COCH_2), 45.08 (s, NCH_3), 48.10 (d, $^1J_{C,P}$ = 31.6 Hz, PCCH_2), 50.64 (d, $^2J_{C,P}$ = 22.7 Hz, PCCH), 51.15 (s, NCH_3), 52.74 (d, $^1J_{C,P}$ = 29.0 Hz, PCCH), 73.04 (s, CH_3CH), 125.66 (d, $^2J_{C,P}$ = 17.4 Hz, aryl-C), 126.66 (s, aryl-C), 128.58 (d, $^3J_{C,P}$ = 8.9 Hz, aryl-C), 130.54 (d, $^1J_{C,P}$ = 50.7 Hz, aryl-C), 130.34 (s, aryl-C), 130.67 (s, aryl-C), 131.29 (s, aryl-C), 131.65 (d, $^2J_{C,P}$ = 12.3 Hz, C=C), 132.45 (d, $^2J_{C,P}$ = 8.9 Hz, C=C), 133.21 (s, aryl-C), 134.77 (s, aryl-C), 134.84 (s, aryl-C), 134.90 (s, aryl-C), 135.26 (s, aryl-C), 146.33 (s, aryl-C), 148.89 (s, aryl-C) ppm.

Crystal Structure Determination of (±)-11, (S_C,S_C,S_N)-12, (R_C,S_C)-13, (*S*)-5, (*S*)-14, and (S_C,S_P)-16: Crystal data for all six complexes and a summary of the crystallographic analyses are given in Table 8. Diffraction data were collected on a Bruker X8 CCD diffractometer with Mo-K_α radiation (graphite monochromator). SADABS absorption corrections were applied. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. The absolute configurations of the chiral complexes were determined unambiguously by using the Flack parameter.[12]

Table 8. Crystallographic data for complexes (±)-**11**, (S_C,S_C,S_N)-**12**, (R_C,S_C)-**13**, (*S*)-**5**, (*S*)-**14**, and (S_C,S_P)-**16**.

	(±)-**11**	(S_C,S_C,S_N)-**12**	(R_C,S_C)-**13**	(*S*)-**5**	(*S*)-**14**	(S_C,S_P)-**16**
Formula	$C_{34}H_{35}ClNPPd$	$C_{22}H_{30}Cl_2N_2O_2Pd$	$C_{21}H_{30}N_2O_3Pd$	$C_{33}H_{42}Cl_4N_2Pd_2$	$C_{28}H_{33}ClNPPd$	$C_{33}H_{41}N_2O_4PPd$
Formula weight	630.45	531.78	464.87	821.29	556.37	667.05
Space group	$P2_1$	$P2_12_12_1$	$C2$	$P2_1$	$P2_1$	$P2_12_12_1$
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	orthorhombic
a [Å]	11.0844(8)	8.9397(4)	26.346(3)	15.6457(4)	11.7694(7)	11.0169(3)
b [Å]	8.2465(6)	11.3292(5)	9.8051(13)	24.4883(7)	8.3483(5)	14.3105(4)
c [Å]	16.3569(12)	23.2746(10)	18.340(3)	19.2722(6)	13.2810(8)	20.2012(5)
V [Å^3]	1446.69(18)	2357.24(18)	4383.5(10)	7061.1(3)	1289.42(13)	3184.87(15)
Z	2	4	8	8	2	4
T [K]	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
$\rho_{calcd.}$ [g cm^{-3}]	1.447	1.498	1.409	1.545	1.433	1.391
λ [Å]	0.71073(Mo)	0.71073(Mo)	0.71703(Mo)	0.71073(Mo)	0.71073(Mo)	0.71703(Mo)
μ [mm^{-1}]	0.813	1.034	0.868	1.346	0.901	0.671
Flack parameters	–0.01(3)	–0.003(19)	–0.01(4)	–0.03(7)	–0.02(2)	0.01(3)
R_1 (obsd. data)[a]	0.0431	0.0202	0.0366	0.0329	0.0307	0.0443
wR_2 (obsd. data)[b]	0.1052	0.0582	0.0496	0.0772	0.0688	0.0898

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

CCDC-667890 [(±)-**11**], CCDC-667892 [(S_C,S_C,S_N)-**12**], CCDC-667895 [(R_C,S_C)-**13**], CCDC-667894 [(*S*)-**5**], CCDC-667891 [(*S*)-**14**] and CCDC-667893 [(S_C,S_P)-**16**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.cdcc.cam.ac.uk/data_request/cif.

Acknowledgments

We are grateful to Nanyang Technological University for supporting this research and for the research scholarships to Y. D. and Y. Z.

[1] For examples, see: a) T. Mitsudo, W. Fischetti, R. F. Heck, *J. Org. Chem.* **1984**, *49*, 1640–1646; b) L. N. Lewis, *J. Am. Chem. Soc.* **1986**, *108*, 743–749; c) W. A. Herrmann, C. Brossmer, K. Ofele, C. P. Reisinger, T. Piermeier, M. Beller, H. Fischer, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1844–1848; d) B. L. Shaw, S. D. Perera, E. A. Staley, *Chem. Commun.* **1998**, 1361–1362; e) D. A. Albisson, R. B. Bedford, S. E. Lawrence, P. N. Scully, *Chem. Commun.* **1998**, 2095–2096; f) F. Miyazaki, K. Yamaguchi, M. Shibasaki, *Tetrahedron Lett.* **1999**, *40*, 7379–7383; g) D. A. Albisson, R. B. Bedford, P. N. Scully, *Tetrahedron Lett.* **1998**, *39*, 9793–9796; h) M. Nowotny, U. Hanefeld, H. Koningsveld, T. Maschmeyer, *Chem. Commun.* **2000**, 1877–1878; i) X. Gai, R. Grigg, M. I. Ramzan, V. Sridharan, S. Collard, J. E. Muir, *Chem. Commun.* **2000**, 2053–2054; j) D. E. Bergbreiter, P. L. Osburn, Y. S. Liu, *J. Am. Chem. Soc.* **1999**, *121*, 9531–9538; k) D. E. Bergbreiter, P. L. Osburn, A. Wilson, E. M. Sink, *J. Am. Chem. Soc.* **2000**, *122*, 9058–9064; l) M. S. Brody, M. G. Finn, *Tetrahedron Lett.* **1999**, *40*, 415–418; m) P.-H. Leung, K.-H. Ng, Y. Li, A. J. P. White, D. J. Williams, *Chem. Commun.* **1999**, 2435–2436.

[2] For examples, see: a) S. B. Wild, *Coord. Chem. Rev.* **1997**, *166*, 291–311; b) V. V. Dunina, O. N. Gorunova, M. V. Livantsov, Y. K. Grishin, *Tetrahedron: Asymmetry* **2000**, *11*, 2907–2916; c) F. Levrat, H. Stoeckli-Evans, N. Engel, *Tetrahedron: Asymmetry* **2002**, *13*, 2335–2344; d) J. Albert, J. Granell, G. Muller, D. Sainz, M. Font-Bardia, X. Solans, *Tetrahedron: Asymmetry* **1995**, *6*, 325–328; e) V. V. Dunina, E. B. Golovan, N. S. Gulyukina, A. V. Buyevich, *Tetrahedron: Asymmetry* **1995**, *6*, 2731–2746; f) C. Lopez, R. Bosque, D. Sainz, X. Solans, M. Font-Bardia, *Organometallics* **1997**, *16*, 3261–3266; g) J. R. Moncarz, N. F. Laritcheva, D. S. Glueck, *J. Am. Chem. Soc.* **2002**, *124*, 13356–13357; h) S. Y. M. Chooi, P.-H. Leung, C. C. Lim, K. F. Mok, G. H. Quek, K. Y. Sim, M. K. Tan, *Tetrahedron: Asymmetry* **1992**, *3*, 529–532; i) C.-C. Lim, P.-H. Leung, K. Y. Sim, *Tetrahedron: Asymmetry* **1994**, *5*, 1883–1886; j) B.-H. Aw, S. Selvaratnam, P.-H. Leung, N. H. Ress, W. McFarlane, *Tetrahedron: Asymmetry* **1996**, *7*, 1753–1762.

[3] For examples, see: a) S. Chatterjee, M. D. George, G. Salem, A. C. Willis, *J. Chem. Soc., Dalton Trans.* **2001**, 1890–1896; b) N. K. Roberts, S. B. Wild, *J. Am. Chem. Soc.* **1979**, *101*, 6254–6260; c) N. K. Roberts, S. B. Wild, *J. Chem. Soc., Dalton Trans.* **1979**, 2015–2021; d) G. He, K. F. Mok, P.-H. Leung, *Organometallics* **1999**, *18*, 4027–4031; e) V. V. Dunina, E. B. Golovan, *Tetrahedron: Asymmetry* **1995**, *6*, 2747–2754; f) M. Pabel, A. C. Willis, S. B. Wild, *Inorg. Chem.* **1996**, *35*, 1244–1249; g) A. Bader, M. Pabel, A. C. Willis, S. B. Wild, *Inorg. Chem.* **1996**, *35*, 3874–3877; h) M. Pabel, A. C. Willis, S. B. Wild, *Tetrahedron: Asymmetry* **1995**, *6*, 2369–2374; i) S. Y. M. Chooi, S. Y. Siah, P.-H. Leung, K. F. Mok, *Inorg. Chem.* **1993**, *32*, 4812–4818.

[4] For examples, see: a) J. F. van Baar, J. M. Klerks, P. Overbosch, D. J. Stufkens, K. Vrieze, *J. Organomet. Chem.* **1976**, *112*, 95–103; b) Y. Yamamoto, H. Yamazaki, *Inorg. Chim. Acta* **1980**, *41*, 229–232; c) J. Vicente, I. Saura-Llamas, M. C. R. de Arellano, P. G. Jones, *Organometallics* **1999**, *18*, 2683–2693; d) J. Vicente, I. Saura-Llamas, C. Alcaraz, P. G. Jones, D. Bautisda, *Organometallics* **2002**, *21*, 3587–3595; e) W. E. Lindsell, D. D. Palmer, P. N. Preston, G. M. Rosair, R. V. H. Jones, A. J. Whitton, *Organometallics* **2005**, *24*, 1119–1133; f) P.-H. Leung, *Acc. Chem. Res.* **2004**, *37*, 169–177; g) W.-C. Yeo, S. Y. Tee, H.-B. Tan, G.-K. Tan, L. L. Koh, P.-H. Leung, *Inorg. Chem.* **2004**, *43*, 8102–8109; h) S. A. Pullarkat, D. Yi, Y. Li, G.-K. Tan, P.-H. Leung, *Inorg. Chem.* **2006**, *45*, 7455–7463; i) M. L. Bungabong, K. W. Tan, Y. Li, S. V. Selvaratnam, K. G. Dongol, P.-H. Leung, *Inorg. Chem.* **2007**, *46*, 4733–4736; j) W.-C. Yeo, J. J. Vittal, L. L. Koh, P.-H. Leung, *Organometallics* **2006**, *25*, 1259–1269.

[5] For examples, see: a) S. Y. M. Chooi, T. S. A. Hor, P.-H. Leung, K. F. Mok, *Inorg. Chem.* **1992**, *31*, 1494–1500; b) S. Y. M. Chooi, M. K. Tan, P.-H. Leung, K. F. Mok, *Inorg. Chem.* **1994**, *33*, 3096–3103; c) N. W. Alcock, D. I. Hulmes, J. M. Brown, *J. Chem. Soc., Chem. Commun.* **1995**, 395–397; d) N. W. Alcock, J. M. Brown, D. I. Hulmes, *Tetrahedron*: *Asymmetry* **1993**, *4*, 743–756; e) J. L. Bookham, W. McFarlane, *J. Chem. Soc., Chem. Commun.* **1993**, *17*, 1352–1353.

[6] For examples, see: a) P.-H. Leung, S. K. Loh, J. J. Vittal, A. J. P. White, D. J. Williams, *Chem. Commun.* **1997**, 1987–1988; b) W.-C. Yeo, S. Y. Tee, H. B. Tan, G.-K. Tan, L. L. Koh, P.-H. Leung, *Inorg. Chem.* **2004**, *43*, 8102–8109; c) W.-C. Yeo, G.-K. Tan, L. L. Koh, P.-H. Leung, *Eur. J. Inorg. Chem.* **2005**, *23*, 4723–4728; d) W.-C. Yeo, S. Chen, Y. Li, G.-K. Tan, L. L. Koh, P.-H. Leung, *J. Organomet. Chem.* **2007**, *692*, 2539–2547; e) S. A. Pullarkat, K.-W. Tan, M. Ma, G.-K. Tan, L. L. Koh, J. J. Vittal, P.-H. Leung, *J. Organomet. Chem.* **2006**, *691*, 3083–3088; f) W.-C. Yeo, L. Tang, B. Yan, S.-Y. Tee, L. L. Koh, G.-K. Tan, P.-H. Leung, *Organometallics* **2005**, *24*, 5581–5585.

[7] D. Carol, K. Isabelle, G. Marc, *Organic. Synth.* **2002**, *78*, 42–50.

[8] a) J. Vicente, J. A. Abad, A. D. Frankland, M. C. R. Arellano, *Chem. Eur. J.* **1999**, *10*, 3066–3075; b) J. Vicente, A. Arcas, D. Bautista, P. G. Jones, *Organometallics* **1997**, *16*, 2127–2138; c) Y. Li, S. Selvaratnam, J. J. Vittal, P.-H. Leung, *Inorg. Chem.* **2003**, *42*, 3229–3236.

[9] a) R. Urban, R. Kramer, K. Polborn, B. Wagner, W. Beck, *J. Organomet. Chem.* **1996**, *517*, 191–200; b) V. V. Dunina, E. D. Razmyslova, L. G. Kuz′mina, A. V. Churakov, M. Y. Rubina, Y. K. Grishin, *Tetrahedron: Asymmetry* **1999**, *10*, 3147–3155.

[10] S.-K. Loh, K. F. Mok, P.-H. Leung, A. J. P. White, D. J. Williams, *Tetrahedron: Asymmetry* **1996**, *7*, 45–48.

[11] R. S. Cahn, C. K. Ingold, V. Prelog, *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 385–415.

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

Received: November 19, 2007
Published Online: February 26, 2008

