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Stereochemical Investigations of a Novel Class of Chiral Phosphapalladacycle Complexes Derived from 1-[(2,5-Dimethyl)phenyl]ethyldiphenylphosphine

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The phosphapalladacycle derived from 1-(2′,5′-dimethylphenyl)ethyldiphenylphosphine has been prepared in the optically active and racemic forms. The phosphine was synthesized as a racemate by the treatment of 1-chloro-1-(2′,5′-dimethylphenyl)ethane with sodium diphenylphosphide in THF. The racemic phosphapalladacycle was subsequently obtained as the chloro-bridged dimer by the treatment of the phosphine with palladium(II) acetate followed by anion metathesis with lithium chloride. Alternatively, the phosphine could be optically resolved via metal complexation using (*R*,*R*)-bis(μ-chloro)bis{1-[1-(*N*,*N*-dimethylamino)ethyl]naphthyl-C^2,*N*}dipalladium(II) as the resolving agent. An efficient separation of the resulting diastereomeric complexes was achieved by silica gel chromatography. The obtained optically resolved diastereomers were next subject to chemoselective removal of the (*R*)-*N*,*N*-(dimethylamino)-1-(1-naphthyl)ethylaminate auxiliary by treatment with concentrated hydrochloric acid. This process yielded the binuclear dimer complexes containing the resolved η^1-P ligand. Cyclopalladation of the coordinated phosphine could next be performed by treatment of its η^1-P binuclear dimer with silver(I) hexafluorophosphate(V) in a dichloromethane/water mixture followed by treatment with lithium chloride, giving rise to a pair of optically pure enantiomeric dimers with $[\alpha]_D$ −322 and +319° in CH_2Cl_2. Despite the possibilities of the phosphine to attain a five- membered structure by *ortho*-palladation or a six-membered ring formation by aliphatic C–H bond activation, only the former was observed. X-ray crystallographic data of the *meso* dimer and an acetylacetonate derivative indicated that the phosphapalladacycle α-C* methyl substituent was axially located. The 2-D ^{1}H–^{1}H ROESY spectrum of the acetylacetonate derivative further revealed that the phosphapalladacycle was conformationally rigid in $CDCl_3$.

Introduction

The use of chiral metal−ligand systems as promoters of various asymmetric organic transformations has continued to remain very significant in the field of synthetic chemistry.[1] Among these, the chiral ligand bearing Lewis acid promoted asymmetric Diels−Alder reaction[2] constitutes an extremely remarkable class of stereoselective syntheses, giving rise to molecular structures that could serve as intermediates to more complex structures via additional synthetic procedures.

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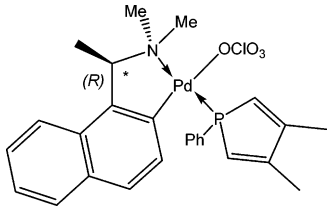
Notably, we have been able to exploit the synthetic utility of the asymmetric Diels−Alder reaction for the construction of optically active *exo*-type diphosphines and functionalized phosphines bearing the norbornene skeleton with high stereoselectivities. These processes commonly employ the optically active cyclopalladated *N*,*N*-(dimethylamino)-1-(naphthyl)ethylaminate derivative **1** as a chiral auxiliary in



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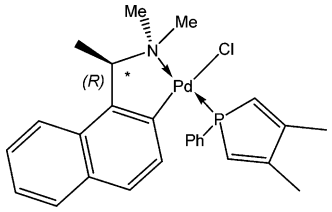
the syntheses.[3] The chiral-inducing ability of this type of palladium(II) complex stems from the various features of the five-membered palladacycle. These include the transmission of vital stereochemical information originating from the conformationally robust palladacycle[3a,g,4] by (i) the dimethylamino group to neighboring coordination site on the Pd atom[5] and (ii) the protruding aromatic proton H′ to the site adjacent to the Pd−C bond.[4e]

Similar asymmetric *endo*-cycloadditions have also been performed for the syntheses of optically active phosphanorbornene ligands.[3a−d,i,6a,b] By this approach, the originally vacant site (from the ready release of the labile, ClO_4^- ligand) in complex **1** can be made unavailable by the substitution of a chloride ligand instead, in the form of the complex **2**.



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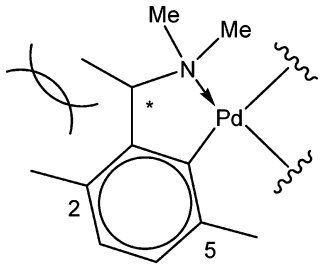
Due to the thermodynamic and kinetic stability of the Pd−Cl bond in the complex of this type,[7] arriving dienophiles become devoid of attachment to the reaction template like they were once capable of as in the case of the perchlorato-bound complex **1**. The implication of this situation is that any [4 + 2] cycloaddition that might take place from this juncture onward could only proceed *inter*molecularly rather than *intra*molecularly, which applies to the complex **1**. As such *endo*-cycloadditions take place at the domain adjacent to and cis with respect to the Pd−C bond of the *N*,*N*-(dimethylamino)-1-(naphthyl)ethylaminate palladacycle, one may expect the aromatic H′ proton to be more influential than the dimethylamino substituents in controlling the stereochemical outcome of the reaction, since the reaction site next to the dimethylamino group has been rendered inactive by the presence of the Pd− Cl bond. It is therefore conceivable that the intermolecular *endo*-cycloaddition has proceeded with relatively low diastereoselectivity, after taking into account the small size of the H′ proton. As a consequence of its steric bulk deficiency, the proton alone is usually ineffectual in conveying any stereochemical information to the reaction site nearby.

A solution to this deficiency was then provided by the introduction of a bulkier spacer methyl group at position 5 on the aromatic ring. The design of this palladacycle complex was aimed at enhancing the chiral-inducing potential of the palladacycle to the reaction site adjacent to the Pd−C bond. With a more pronounced steric bulk, this methyl substituent was shown to exert a more significant influence than the smaller H′ proton of the analogous *N*,*N*-(dimethylamino)-1-(1-naphthyl)ethylaminate palladacycle. Indeed, the derivative **3** was found to be a more efficient chiral promoter for



3

the asymmetric [4 + 2] *endo*-cycloaddition involving ethyl vinyl ketone as the dienophile.[8]

The above complexes **1**−**3** contain instances of cyclopalladated ligands of the N-donor type,[8,9] which represent the most abundant type of palladacycles of other various ligating heteroatom donors[10] that are available. Truly, one can

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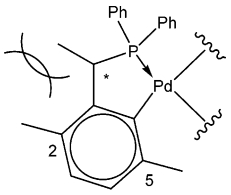
appreciate the importance of cyclopalladated complexes by a consideration of their very diverse applications.[11] In line with our continued interests of expanding the structural diversities of this class of promising organopalladium complexes[8,9a,b,10o] for the purpose of enhancing their efficiencies as promoters for various asymmetric transformations and taking into consideration the above demonstrated potential of the chiral aminate palladacycle **3**, a modification of the structure **3** could be made by the introduction of the phosphine-based palladacycle **4**, as an addition to this rare



4

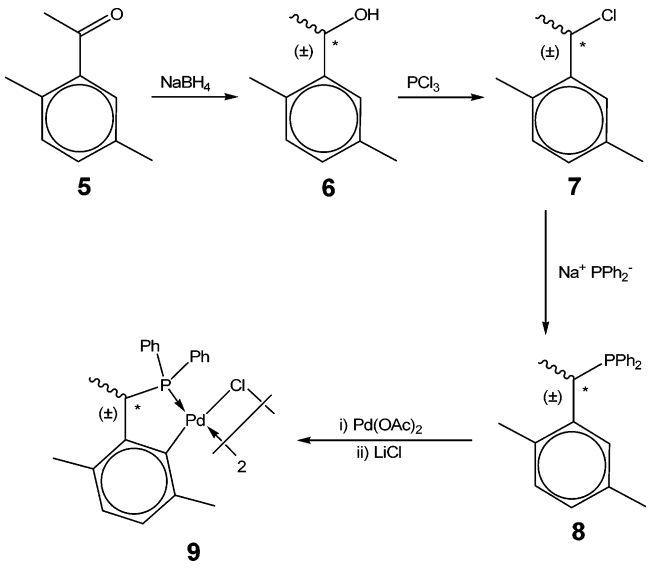
class of P-donor palladacycles that have been prepared in the optically active forms.[10k−o]

In this paper, we report (a) the synthesis of the palladacycle **4** in the optically active form, followed by (b) a stereochemical investigation of the chiral cyclic organopalladium structure. In developing potential chiral Lewis acids for use in future asymmetric transformations, stereochemical properties pertaining to these chiral inductors are fundamental and therefore must be vigorously examined[12] as an avoidance against committing crucial misinterpretations that may further propagate in subsequent research that are built on these interpretations as foundations. Thus, it is in our opinion that an emphasis be placed on point b above, prior to evaluating the effectiveness of the target palladacycle in various applications.

Results and Discussions

Synthesis of the Phosphine Ligand and Its Cyclopalladation. As illustrated in Scheme 1, the synthesis of the key racemic phosphine ligand was accomplished in a sequence of three standard functional group interconversions,

Scheme 1



starting from the ketone **5**. The product of a simple reduction of the ketone **5** using sodium borohydride in ethanol was obtained as a colorless oil after workup in an overall good yield of 89.4%. The ^{1}H NMR spectrum ($CDCl_3$) of the alcohol **6** exhibited a quartet and a doublet resonance at δ 5.11 and 1.46. These characteristic signals are assigned to

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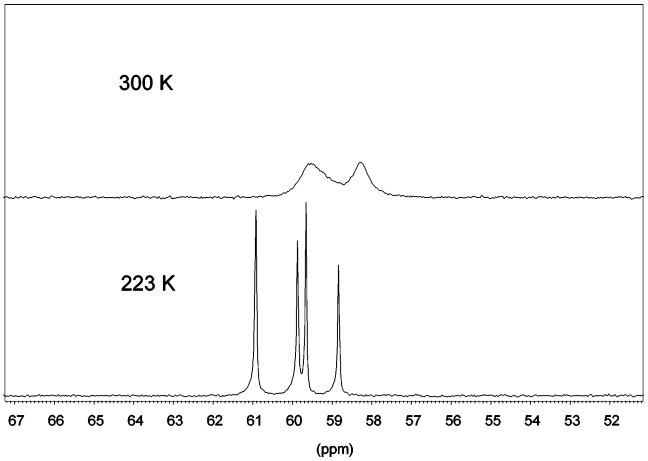


Figure 1. $^{31}P\{^1H\}$ NMR spectra of (±)-**9** at 300 and 223 K.

the methine proton and the protons of the methyl substituent of the α- C* atom correspondingly. The two methyl groups on the aromatic ring are revealed expectedly as two intense, closely spaced individual three-proton singlets at δ 2.30 and 2.34.

The intermediate **7** was obtained as a colorless liquid by the chlorination of the alcohol **6** using the chlorinating agent PCl_3. Treatment of the alkyl chloride **7** with sodium diphenylphosphide gave the racemic phosphine **8** as a viscous and colorless oil in 98.0% yield. While the phosphine was represented as a singlet at δ 3.5 in its $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$), the appearances of the expected $^{31}P-^1H$ spin−spin couplings for the α-methyl ($^3J_{PH} = 14.5$ Hz) and α-methine ($^2J_{PH} = 7.2$ Hz) protons were observed in the ^1H NMR spectrum ($CDCl_3$). We may take note of the more efficient coupling between the α-methyl protons and the attached ^{31}P nucleus, despite the longer distance between these protons and the ^{31}P nucleus. Similar to its 1-(1-naphthyl)ethyldiphenylphosphine analogue,[10o] the phosphine **8** is highly sensitive to air.

The cyclopalladation process was carried out by the treatment of the racemic phosphine with $Pd(OAc)_2$, followed by the in-situ chloride metathesis with LiCl to arrive at the dimer **9** as yellow crystals in 77% yield. As shown in Figure 1, the racemic chloro dimer appeared as two broad, overlapping singlets at δ 58.3 and 59.5 in its $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) at 300 K. However, when the NMR sample was cooled to 223 K, both peaks become resolved into four singlets at δ 58.8, 59.7, 59.9, and 60.9 in unequal amounts. These NMR signals are consistent with the nonchiral form

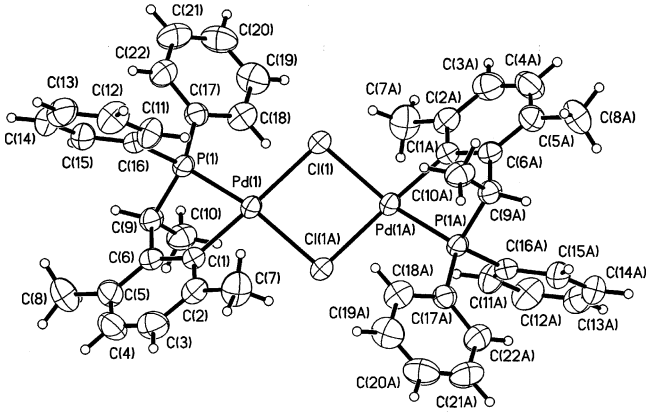


Figure 2. Molecular structure of complex *meso*-**9**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of *meso*-**9**

Pd(1)−C(1)	2.019(3)	Pd(1)−P(1)	2.217(2)
Pd(1)−Cl(1)	2.444(2)	Pd(1)−Cl(1A)	2.441(2)
C(1)−C(6)	1.402(4)	C(6)−C(9)	1.517(4)
P(1)−C(9)	1.848(3)	C(9)−C(10)	1.534(4)
P(1)−C(16)	1.823(3)	P(1)−C(17)	1.825(3)
C(1)−Pd(1)−P(1)	78.1(8)	C(1)−Pd(1)−Cl(1A)	96.5(1)
P(1)−Pd(1)−Cl(1)	102.9(1)	Cl(1)−Pd(1)−Cl(1A)	85.3(1)
Pd(1)−Cl(1)−Pd(1A)	94.7(1)	Pd(1)−C(1)−C(6)	119.3(2)
C(1)−C(6)−C(9)	116.7(2)	C(6)−C(9)−P(1)	99.7(1)

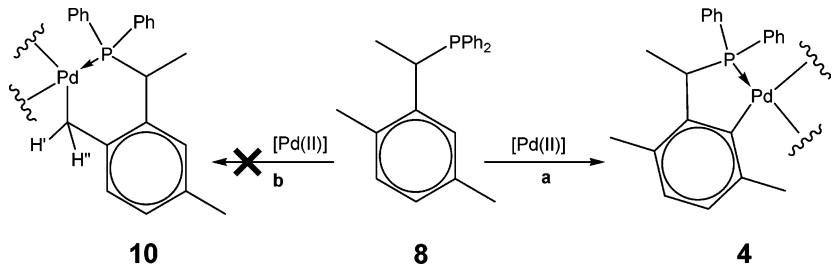
of the cyclopalladated complex, which exists as a mixture of six isomers in solution. These are the chiral *anti*-(*R,R*), *anti*-(*S,S*), *syn*- (*R,R*), and *syn*-(*S,S*) as well as the achiral, *meso anti*-(*R,S*) and *syn*-(*R,S*) isomers, in which both isomers of the first two pairs of are enantiomeric and cannot be distinguished from each other by routine NMR spectroscopy.

It is noteworthy that two modes of phosphapalladacycle formation may be accomplished in this complex synthesis (Scheme 2). In common with the general preference of ligands to assume a five-membered ring when choices of other ring sizes are available, the formation of a six-membered ring **10** (path b) via the activation of the aliphatic C−H bond of C(2) methyl group was not observed.

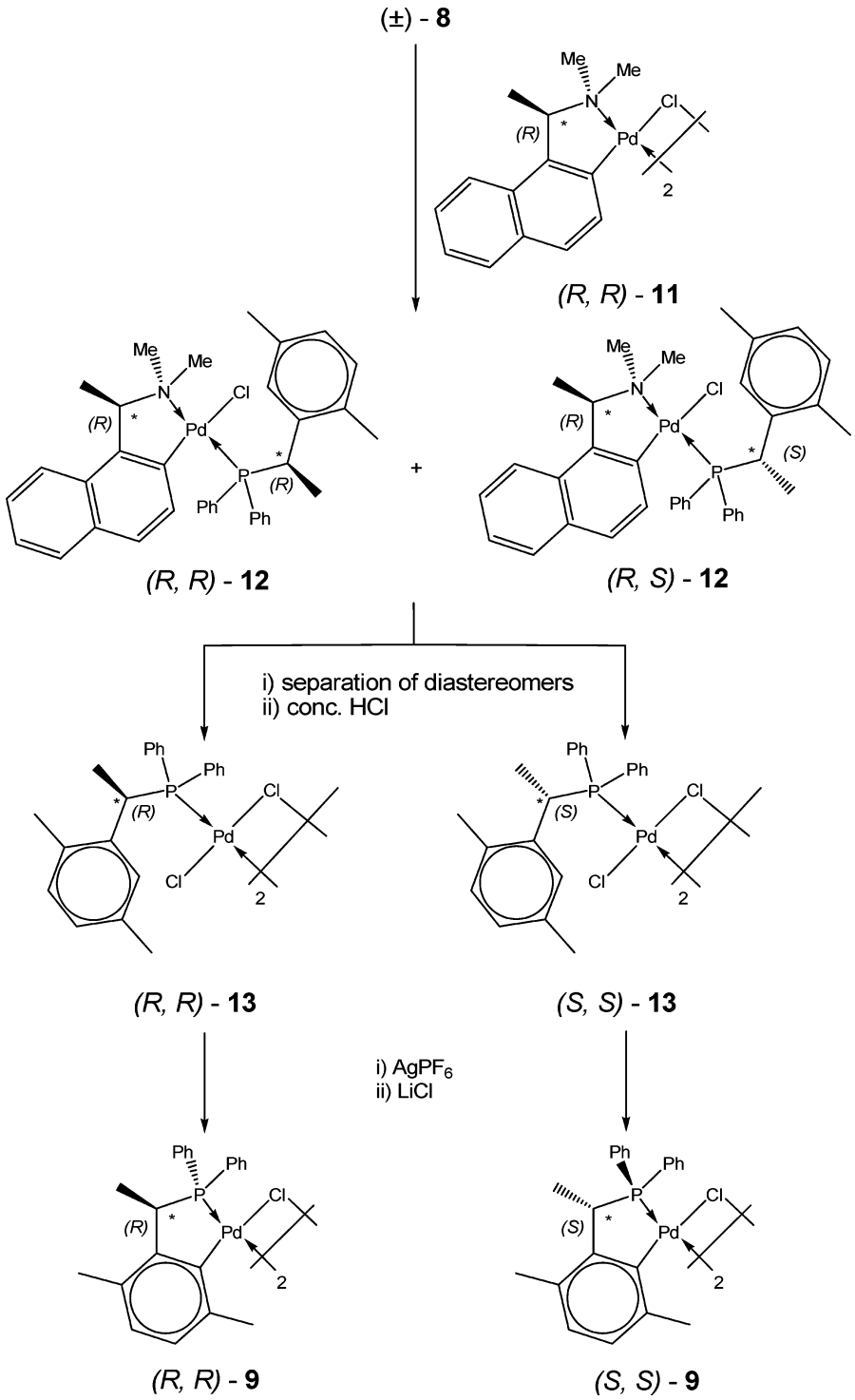
The X-ray crystallographic studies of the racemic dimer **9** reveal that the complex has crystallized in the *meso, anti*-(*S, R*) form (Figure 2). Selected bond lengths and bond angles are given in Table 1. The structure consists of two *anti*-disposed mirror-image halves, and each half of the structure represents an asymmetric unit. The central four-membered $\{Pd_2(\mu\text{-}Cl)_2\}$ cycle forms a regular plane, and the Pd−C, Pd−P, and Pd−Cl bond lengths fall in the expected range of values for a similar phosphapalladacycle complexes.[10l]

In agreement with an anticipated steric effect presented by the introduction of the spacer methyl group at the aromatic

Scheme 2



Scheme 3



C(2) atom, the palladium atom was noted to experience a pronounced tetrahedral distortion, provided by the dihedral angle of 23.7° between the P(1)−Pd(1)−C(1) and Cl(1)−Pd(1)−Cl(1A) planes. As a comparison, a similar distortion around the coordination environment of the palladium atom in the chloro (*S*,*S*) dimer of the *ortho*-palladated 1-(1-naphthyl)ethyldiphenylphosphine[10o] has been found to be insignificant, at 2.5−2.7°. The distortion from planarity was further indicated by the mean vertical displacement of 0.2459 Å for the five atoms from the mean coordination plane (m.c.pl.). In addition, the torsion angle for the four atoms of C(2)−C(1)−Pd(1)−Cl(1A) has been dramatically increased from 9.5 to 19.3° to 55.7° involving these four similar atoms for the previously reported analogous complex, in which a spacer group was absent.[10o] Such a significant increment is undoubtedly related to the need of minimizing the interligand repulsions present between the bridging Cl(1A) atom and the spacer methyl group at C(2) atom. The puckering of the five-membered palladacycle ring is significant and is exemplified by the mean intrachelate torsion angle of 31.4° for

the palladacycle ring. As such, the extent of ring puckering is more severe for this system than those derived from the *ortho*- palladated {1-(1-naphthyl)ethyl}diphenylphosphine (16.7−21.0°) and {1-(1-naphthyl)ethyl}diphenylarsine (16.0−20.3°) systems.[10o] The ring puckering generates diastereotopicity on both *P*-phenyl substituents; the chemical nonequivalence between both phenyl rings is thus provided by the positions of these phenyl rings with respect to the m.c.pl. The {C(11−16)} phenyl ring is considered axial while the {C(17−22)} phenyl ring is equatorial. These conclusions are made on the basis of the angles between the P(1)−C(*ipso* carbon atom) bond and the normal to the m.c.pl., in which the values of 9.9 and 58.2° apply to the P(1)−C(16) and P(1)−C(17) bonds, respectively. The C(9) and C(9A) atoms hold opposite absolute configurations and hence opposite ring conformations. The methyl substituents on both atoms were noted to assume axial dispositions: the C(9)−C(10) bond subtends an angle of 27.4° with respect to the normal to the m.c.pl. The need to assume such a conformational state is most probably associated with the necessity to avoid an unfavorable steric repulsion between this methyl group and the spacer methyl group on the aromatic C(5) atom, when it is equatorially oriented instead. This can be supported by the close proximity of 2.630 Å between the equatorially disposed H(9) atom with the C(8) atom of the spacer methyl substituent. The close approach of these two atoms is significant when comparing the above distance with the sum of the van der Waals radii of 3.0 Å for carbon and hydrogen atoms.

Preparation of the Phosphapalladacycle in the Optically Active Form. In principle, the prepared racemic phosphapalladacycle **9** may be optically resolved by the use of suitable resolving agents such as amino acidate salts since this method of obtaining the palladacycle in the optically active forms has been documented.[8,10k−l,9d,q] However, the attempted separation of the (*S*)-prolinate derivatives of **15** by fractional crystallization was rather unsuccessful and, at best, afforded only partially resolved diastereomeric mixtures.

As such, we have performed, according to Scheme 3, an effective optical resolution of the phosphine **8** by metal coordination as a monodentate ligand, followed by a two-step procedure to arrive at the optically active phosphapalladacycle dimer **9**. Thus, the treatment of the racemic phosphine with the resolving agent (*R*,*R*)-**11** led to the expected formation of a pair of diastereomeric adducts (*R*,*R*)- and (*R*,*S*)-**12** in equal amounts. This was revealed from the $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$) of the crude mixture, in which the two diastereomers were presented as two clearly well-separated peaks at δ 45.1 and 49.6 of equal integral intensities. The initial separation of the two diastereomers by fractional crystallization was unsuccessful as crystallization could not be induced despite the use of an array of solvent systems with different polarities. Nevertheless, the neutral nature of these complexes has presented us with the alternate option of diastereomer separation by column chromatography. Thus, the 1:1 diasteromeric mixture was slowly eluted through a silica gel column with hexanes/ethyl acetate (4:1, v/v) as the mobile phase from which the two

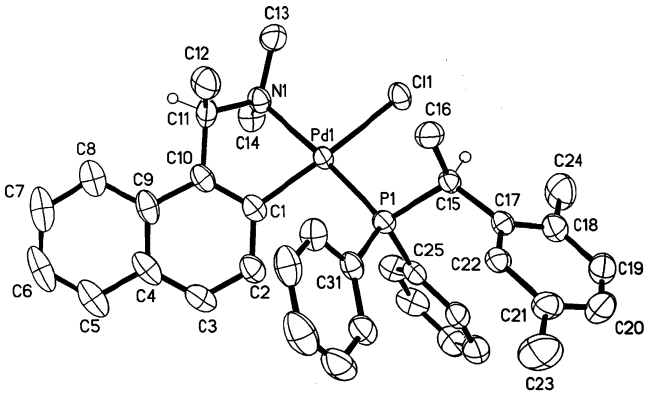


Figure 3. Molecular structure of complex (*R*,*S*)-**12**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of (*R*,*S*)-**12**

Pd(1)−C(1)	1.944(3)	Pd(1)−N(1)	2.152(3)
Pd(1)−P(1)	2.245(1)	Pd(1)−Cl(1)	2.401(1)
N(1)−C(14)	1.470(4)	N(1)−C(13)	1.481(4)
N(1)−C(11)	1.503(4)	P(1)−C(15)	1.867(3)
P(1)−C(25)	1.828(4)	P(1)−C(31)	1.823(3)
C(15)−C(17)	1.511(4)	C(17)−C(22)	1.376(5)
C(1)−Pd(1)−N(1)	80.9(1)	C(1)−Pd(1)−P(1)	93.5(1)
N(1)−Pd(1)−P(1)	170.8(1)	C(1)−Pd(1)−Cl(1)	169.7(1)
N(1)−Pd(1)−Cl(1)	93.0(1)	P(1)−Pd(1)−Cl(1)	93.6(1)
C(31)−P(1)−Pd(1)	115.2(1)	C(25)−P(1)−Pd(1)	112.8(1)
C(15)−P(1)−Pd(1)	109.9(1)	P(1)−C(15)−C(17)	113.8(2)
C(15)−C(17)−C(22)	119.1(3)		

diastereomers were readily distinguished as two different bands with different retention times. The fractions were separately eluted and were further checked by $^{31}P\{^{1}H\}$ NMR spectroscopy for their optical purities. In this manner, both diastereomers were separated efficiently, and thus, the optical purities were revealed by the appearance of only one peak in the $^{31}P\{^{1}H\}$ NMR spectrum of each diastereomer. In its optically pure form, the first eluted diastereomer, (*R*,*S*)-**12**, was readily crystallized from ethyl acetate and hexanes as yellow prisms in an overall yield of 83.6% with $[\alpha]_D$ −135° (CH_2Cl_2). The other diastereomer, (*R*,*R*)-**12**, was isolated as an analytically pure amorphous yellow powder in 71.5% yield with $[\alpha]_D$ +98° (CH_2Cl_2).

The absolute (*R*,*S*) configuration of the diastereomer was confirmed by the X-ray diffraction studies of the complex. The complex exists as two independent molecules in the unit cell, and both molecules are only slightly different in terms of their geometric parameters. For clarity, only one of these is presented (with the accompanying numbering scheme) in Figure 3, and its selected bond lengths and bond angles are given in Table 2. The tetrahedral distortion around the palladium coordination environment is moderate and is provided by the dihedral angle of 9.7° between the {N−Pd−C} and {Cl−Pd−P} planes (and 10.8° for the other molecule).

In accordance with Scheme 3, the next preparative step toward the development of the *ortho*-palladated phosphapalladacycle **9** in the optically active form proceeded with the removal of the homochiral (*R*)-1-(1-naphthyl)ethylaminate auxiliary by hydrolysis in concentrated HCl. The separate transformations of (*R*,*R*)- and (*R*,*S*)-**12** led to the binuclear optical antipodes, (*R*,*R*)- and (*S*,*S*)-**13**, as analytically pure

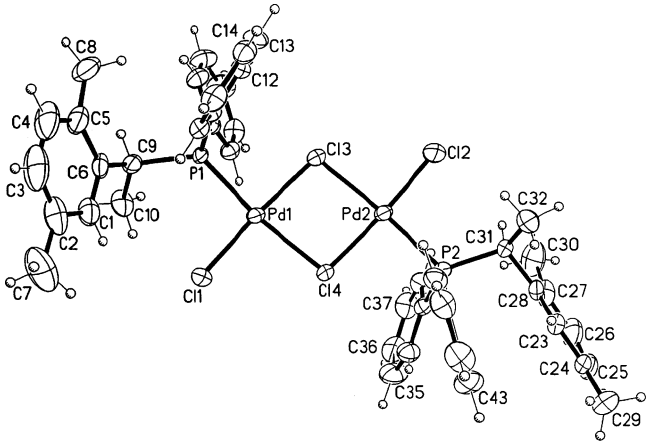


Figure 4. Molecular structure of complex (*S*,*S*)-**13**.

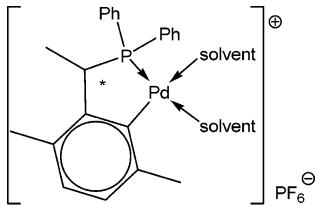
Table 3. Selected Bond Lengths (Å) and Angles (deg) of (*S*,*S*)-**13**

Pd(1)−P(1)	2.239(2)	Pd(2)−P(2)	2.236(2)
Pd(1)−Cl(1)	2.264(2)	Pd(2)−Cl(2)	2.274(2)
Pd(1)−Cl(3)	2.335(2)	Pd(2)−Cl(4)	2.332(2)
Pd(1)−Cl(4)	2.448(2)	Pd(2)−Cl(3)	2.409(2)
P(1)−C(9)	1.889(5)	P(2)−C(31)	1.867(5)
P(1)−C(11)	1.807(7)	P(2)−C(33)	1.821(7)
P(1)−C(17)	1.807(7)	P(2)−C(39)	1.811(6)
C(6)−C(9)	1.487(7)	C(28)−C(31)	1.536(6)
C(1)−C(6)	1.382(7)	C(28)−C(23)	1.392(6)
P(1)−Pd(1)−Cl(1)	96.47(7)	P(2)−Pd(2)−Cl(2)	94.07(7)
P(1)−Pd(1)−Cl(3)	88.1(1)	P(2)−Pd(2)−Cl(4)	90.3(1)
Cl(1)−Pd(1)−Cl(3)	175.2(1)	Cl(2)−Pd(2)−Cl(4)	174.2(1)
P(1)−Pd(1)−Cl(4)	172.3(1)	P(2)−Pd(2)−Cl(3)	175.1(1)
Cl(1)−Pd(1)−Cl(4)	91.0(1)	Cl(2)−Pd(2)−Cl(3)	90.2(1)
Cl(3)−Pd(1)−Cl(4)	84.4(1)	Cl(3)−Pd(2)−Cl(4)	85.3(1)
Pd(1)−Cl(3)−Pd(2)	95.6(1)	Pd(2)−Cl(4)−Pd(1)	94.7(1)
Pd(1)−P(1)−C(11)	103.5(2)	Pd(2)−P(2)−C(33)	103.2(2)
Pd(1)−P(1)−C(17)	109.6(2)	Pd(2)−P(2)−C(39)	109.9(2)
Pd(1)−P(1)−C(9)	125.6(2)	Pd(2)−P(2)−C(31)	117.2(2)
P(1)−C(9)−C(6)	116.8(3)	P(2)−C(31)−C(28)	111.2(3)
C(9)−C(6)−C(1)	121.8(4)	C(31)−C(28)−C(23)	119.1(4)

red crystals in the respective yields of 92.1% and 99.4%, respectively. Their enantiomeric relationship was established from the opposite signs but nearly identical magnitudes of the specific optical rotation measurements: $[\alpha]_D$ +334° for the former and −335° for the latter were recorded in CH_2Cl_2.

An X-ray diffraction study of the (*S*,*S*)-**13** complex was performed, whose molecular structure is presented in Figure 4, and its selected bond lengths and bond angles are provided in Table 3. The structure reveals an *anti* geometrical isomer, in which both phosphine ligands occupy two diagonally opposite ends of the structure. The binuclear complex consists of two crystallographically independent halves with minor variations in the structural parameters. In contrast to the situation in the *ortho*-palladated dimer **9**, both palladium atoms of (*S*,*S*)-**13** are in essentially planar environments. This is indicated by the dihedral angle between the planes {P−Pd−terminal Cl} and {Cl(3)−Pd−Cl(4)} of 2.3−4.4°. The central four-membered $\{Pd_2(\mu\text{-}Cl)_2\}$ ring is planar since an angle of 0.9° was found between the {Cl(3)−Pd(1)−Cl(4)} and {(Cl(3)−Pd(2)−Cl(4)} planes.

The cyclopalladation process comprised of the use of excess $AgPF_6$ as an agent for chloride abstraction from the binuclear complex **13**, in which the process should create available coordination sites for C−H bond activation and hence cyclopalladation.[13] Electronically, the removal of chloride ligands from the coordination sphere of the metal center would also generate a stronger electrophile (Pd^{2+}), which is necessary for the crucial stage of the cyclopalladation reaction, i.e., the presumable electrophilic attack on the *ortho*-palladating aromatic ring.[9f] The cyclopalladation process employed a two-phase reaction mixture comprising a dichloromethane solution of the binuclear complex **13** and aqueous $AgPF_6$ in the absence of an external base. Upon chloride abstraction and subsequent cyclopalladation, a solvated ionic intermediate of the type **14** could be expected. While this intermediate was not isolated, it was presented from its $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) as a series of peaks at δ 62 and a septet resonance at δ −144 corresponding to the PF_6^- counterion. Thus, the conversion of the intermediate species **14** to the dichloro dimer **9** was achieved by the



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addition of LiCl to the reaction mixture. In this manner, the targeted (*R*,*R*)- and (*S*,*S*)-**9** enantiomers were obtained as yellow amorphous solids with $[\alpha]_D$ −322 and +319° (CH_2Cl_2) correspondingly. In solution, the optically active dimer **9** was revealed as a broad singlet only at δ 59.9 from its $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) at room temperature, which represents a contrast to that of the racemate (Figure 1). The spectroscopic appearance of the NMR signal was temperature dependent: below 300 K, the broad resonance was resolved into two singlets in ca. 1.5:1 ratio while the peak width was observed to decrease upon heating, so that, at 328 K, the signal was displayed as a sharp singlet. This behavior was reversible and was correlated to the isomerism of the *syn*/*anti* complexes in solution.

The fact that these phosphapalladacycle complexes were prepared in the optically pure form was further established by derivatizing the racemic and (*R*,*R*)- and (*S*,*S*)-**9** dimers to their corresponding (*S*)-prolinate derivatives **15**. A pair of *E*/*Z* regioisomers was generated from each optical antipode of **9** because of the possibility of geometric isomerism arising from the asymmetrical nature of the (*S*)-prolinate chelate (Figure 5). The $^{31}P\{^1H\}$ spectra of these (*S*)-prolinate derivatives are shown in Figure 6. From Figure 6a,b, the optical purity of each enantiomer of **9** was readily confirmed by the appearance of a pair of singlets corresponding to the pair of *E*- and *Z*-regioisomers, whose formations were specific to the enantiomeric form of the dimer **9**. In fact, the spectrum obtained from the racemate (Figure 6c) represents a direct superimposition of the other two spectra.

(13) Avshu, A.; O'Sullivan, R. D.; Parkins, A. W. *J. Chem. Soc., Dalton. Trans.* **1983**, 1619.

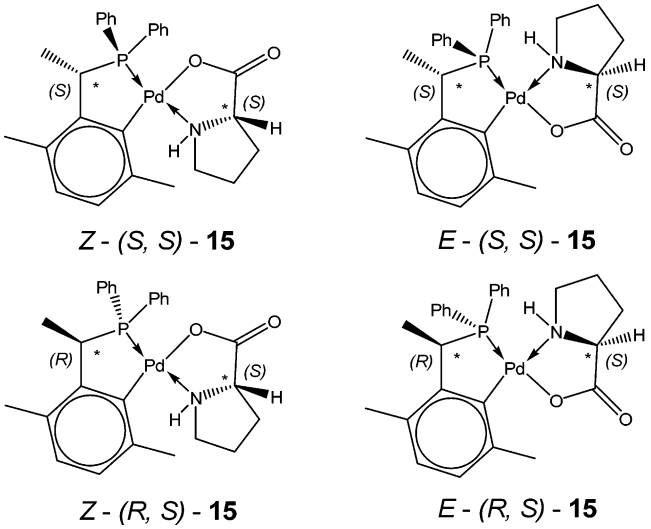


Figure 5. The four diastereomers of **15**.

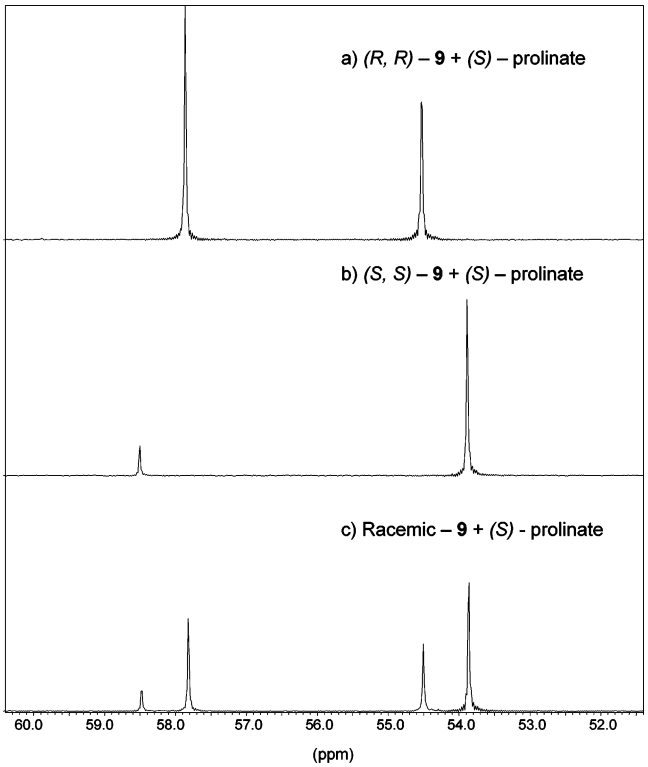


Figure 6. Optical purity determinations of (*R*,*R*)- and (*S*,*S*)-**9**.

Stereochemical Investigations of the Phosphapalladacycle. In solution, the ^{1}H NMR spectroscopic characterization of the chiral phosphapalladacycle was assisted by a combination of ^{1}H{^{31}P} and 2D ^{1}H−^{1}H ROESY NMR spectroscopy experiments performed on the β-diketonate derivative (*S*)-**16**, with $[\alpha]_D$ +502° (CH_2Cl_2). This derivative was prepared efficiently from the reaction between the (*S*,*S*)-**9** dimer and sodium acetylacetonate. The mononuclear complex is more suitable for NMR spectroscopic studies of the organopalladium ring on account of the improved spectral resolution of the signals with respect to that from its parent dimer. Moreover, the simplicity of the ^{1}H NMR spectroscopic signals that are presented by the acetylacetonate ligand is another attractive feature. It possesses only protons from aliphatic groups, and the absence of any aromatic protons within the acetylacetonate framework will therefore not contribute to the complexity at the aromatic region of the ^{1}H NMR spectrum. Most importantly, as the chelated acetylacetonate ring is planar and is nonchiral, we may therefore expect the observed phosphapalladacycle conformational behavior to be intrinsic and not be imposed by that of the adjacent β-diketonate chelate.

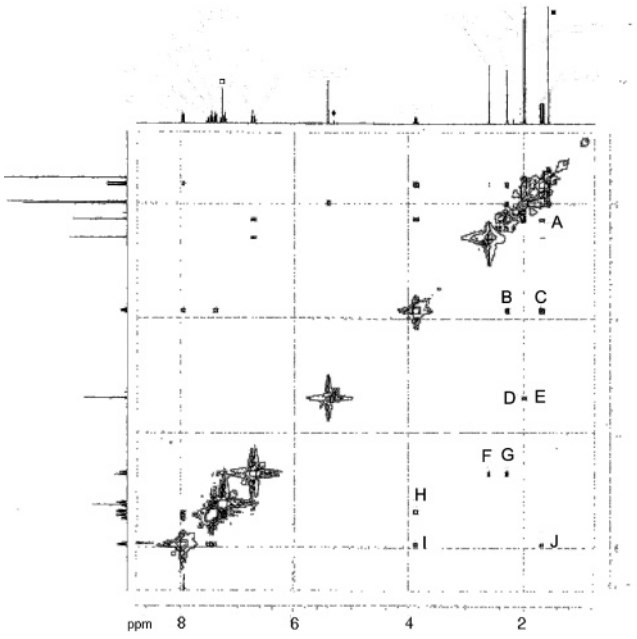


Figure 7. 2D ^{1}H−^{1}H ROESY NMR spectrum ($CDCl_3$) of (*S*)-**16**. Selected NOE interactions: (A) (α-C*Me)−(C^5-Me); (B) (C^5-Me)−(α-C*H); (C) (α-C*Me)−(α- C*H); (D) (acac-Me)−(acac-CH); (E) (acac-Me′)−(acac-CH); (F) (C^2-Me)−H^3; (G) (C^3-Me)−H^4; (H) (α-C*H)−(ax *ortho*-PPh); (I) (α-C*H)−(eq *ortho*-PPh); (J) (α-C*Me)−(eq *ortho*-PPh). Solvent signals: ■, H_2O; ◆, CH_2Cl_2; □, $CDCl_3$.

The ^{1}H and ^{1}H−^{1}H ROESY NMR spectra of (*S*)-**16** are shown in Figure 7. The appearance of the three-proton singlet resonance of the C(5)-methyl substituent immediately rules out the six-membered phosphapalladacycle structure **10** (Scheme 2). This intense singlet resonance was differentiated from the other three-proton singlet resonance attributed to the C(2)-methyl substituent by its NOE signals with the resonance of the α-methyl (interaction A) and methine protons (interaction B) from the 2D ^{1}H−^{1}H ROESY NMR spectrum. The two aromatic H^3 and H^4 protons were distinguished from each other by their selective NOE contacts with either the C(2)- or C(5)-methyl protons (interactions F and G).

The conformational behavior of the five-membered phosphapalladacycle was deduced from NOE data obtained from the ^{1}H−^{1}H ROESY NMR spectrum. The α- methine and methyl protons exhibit characteristic NOE interactions with the *o*- PPh_2 protons that are key indications to the conformational state of the phosphapalladacycle. These comprise the existence of NOE contacts between the α-methine proton and both sets of diastereotopic *o*-PPh protons (interactions H and I) and the observed steric interaction between the α-methyl substituent with only one set of the *o*-PPh protons (interaction J). For the phosphapalladacycle with the (*S*)

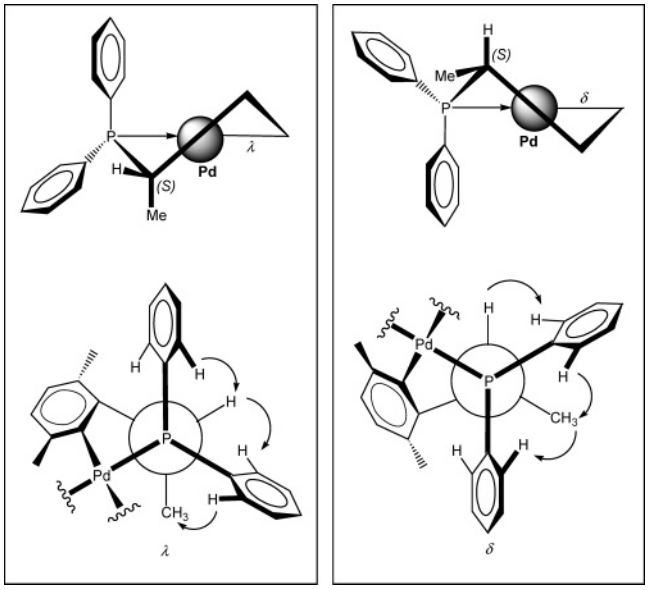


Figure 8. Sawhorse and Newman projections for the λ and δ conformations of the chiral five-membered phosphapalladacycle. (Curved arrows denote possible NOE interactions.)

absolute configuration at the α-C* atom, an agreement with such an observed NOE pattern can only be met by the λ conformation in which the α-methyl substituent is axially disposed. In accordance with the sawhorse and Newman projections (viewed along the P−α*-C bond) illustrated in Figure 8, the *o*-PPh protons which interact with both α-methine and methyl protons must therefore belong to the equatorially oriented phenyl ring of the phosphorus atom. The other PPh ring must hence be axially oriented. For the alternate unobserved δ conformation, it is the methyl substituent that must display NOE contacts with both sets of *o*-PPh protons. As such, the existence of the specific NOE interactions between the α-methyl and only one set of *o*-PPh protons therefore points to the conformational rigidity of the phosphapalladacycle ring in solution.

The above NMR spectroscopic investigations of (*S*)-**16** is in agreement with the following prediction: By the alternate adoption of the δ conformation in which the α-methine proton and the methyl substituent have switched their equatorial or axial orientations, a stronger and hence possibly sterically undesired NOE contact would have developed between the resulting equatorially disposed axial methyl substituent and the C(5)-methyl substituent. It can be foreseen that such a scenario would present a driving force against adopting the diastereomeric δ(*S*) conformation.

In the solid state, the absolute stereochemistry of (*S*)-**16** was investigated crystallographically. The X-ray molecular structure and selected bond lengths and bond angles are presented in Figure 9 and Table 4, respectively. The expected absolute configuration on the phosphapalladacycle α-C* stereogenic center was confirmed from the Flack parameter of 0.03(3), and the geometrical structure of the complex in the solid state resembled that in solution. Moreover, the phosphapalladacycle structural characteristics of the β-diketonate derivative (*S*)-**16** are similar to those of the *meso* dimer **9**, the most important among these being the axial

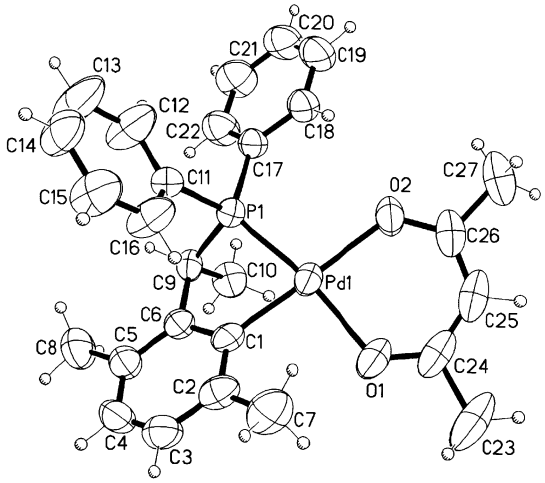


Figure 9. Molecular structure of complex (*S*)-**16**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of (*S*)-**16**

Pd(1)−C(1)	2.019(3)	Pd(1)−O(1)	2.076(3)
Pd(1)−P(1)	2.195(1)	Pd(1)−O(2)	2.100(3)
P(1)−C(17)	1.819(3)	P(1)−C(11)	1.825(3)
P(1)−C(9)	1.827(3)	C(6)−C(9)	1.507(4)
C(1)−C(6)	1.412(5)		
C(1)−Pd(1)−O(1)	93.1(1)	C(1)−Pd(1)−O(2)	178.0(1)
O(1)−Pd(1)−O(2)	88.7(1)	C(1)−Pd(1)−P(1)	77.9(1)
O(1)−Pd(1)−P(1)	165.2(1)	O(2)−Pd(1)−P(1)	100.(1)
P(1)−C(9)−C(6)	101.1(2)	C(1)−C(6)−C(9)	115.5(3)
Pd(1)−P(1)−C(9)	99.0(1)	Pd(1)−C(1)−C(6)	119.0(2)

disposition of the α-C*Me substituent in the solid state. A comparison of the molecular structures of these two complexes points to the steric effect originating from the spacer methyl group at the aromatic C(5) atom as the main factor for the observed conformational state of the palladacycle. This can be supported by the similar distance of 2.630−2.663 Å separating the methyl C(8) and H(9) atoms. The roles of the *P*-phenyl rings as the palladacycle conformation lockers do not seem very significant. While the distances between the H(9) atom and the nearest *ortho* protons of both axial and equatorial *P*-phenyl substituents were found to be 2.347 and 3.658 Å correspondingly for the *meso* dimer **9**; these respective distances were observed to have fluctuated to 3.347 and 2.458 Å for the β-diketonate derivative (*S*)-**16**. Such variations in these distances are indicative of the freely rotating behavior of the these phenyl rings about the P(1)−C(*ipso*) bonds. The possibility of these phenyl substituents to assume different rotameric states is further provided by a consideration of the {axial *P*-phenyl ring/C(1-6)} and {equatorial *P*-phenyl ring/C(1−6)} interplane angles. The values were found to be variable by 10.1 and 111.7° respectively when comparing these angles to those for *meso*-**9** and (*S*)-**16**.

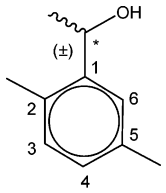
Currently, investigations concerning the synthetic applications of the enantiomeric form of the newly prepared phosphapalladacycle are in progress.

Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of argon. Routine ^{1}H NMR spectra were

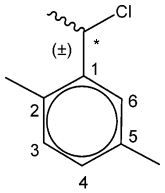
recorded at 300 or 500 MHz on a Bruker ACF 300 or Bruker AMX 500 NMR spectrometer. All the $^{31}P\{^{1}H\}$ NMR spectra were recorded at 120 or 202 MHz on the Bruker ACF 300 or Bruker AMX 500 NMR spectrometer. The ^{13}C NMR spectra were recorded at 126 MHz on the Bruker AMX 500 spectrometer. The phase-sensitive ROESY NMR experiment for (*S*)-**16** was acquired into a 1024 × 512 matrix with a 250 ms spin locking time and a spin lock field strength such that $\gamma B_1/2\pi = 5000$ Hz and then transformed into 1024 × 1024 points using a sine bell weighting functions in both dimensions. Melting points were determined on a Büchi melting point B-545 apparatus and were uncorrected. Optical rotations were measured on the specified solution in 1 or 0.1 dm cells at 25 °C with a Perkin-Elmer model 341 polarimeter. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore. The starting materials 1-acetyl-2,5-dimethylbenzene, **5**,[8] and the enantiomerically pure form of bis-(μ-chloro)bis[(*R*)-1-[(dimethylamino)ethyl]naphthyl-C^2,*N*]dipalladium-(II), (*R*,*R*)-**11**,[4a] were prepared according to reported procedures.

(±)-1-[(2,5-Dimethyl)-1-phenyl]ethanol, (±)-6. A suspension of $NaBH_4$ (2.6 g, 68.42 mmol) in ethanol (70 mL) was added to an ethanol solution (150 mL) of 1-acetyl-2,5-dimethylbenzene, **11** (5.07 g, 34.21 mmol). The mixture was stirred at room temperature for 24 h, followed by the addition of aqueous NaOH (70 mL, 3 wt %/v) with rapid stirring for another 1 h. The solution was then concentrated to a pale yellow oil and was extracted with dichloromethane (3 × 50 mL). The organic extracts were combined, dried with $MgSO_4$, and filtered. The product was finally obtained as a colorless liquid by distillation, bp 78−80 °C, 0.23 mmHg, 4.62 g (89.4% yield). ^1H NMR ($CDCl_3$): δ 1.46 (d, 3H, $^3J_{HH} = 6.4$ Hz, (OH)CH*Me*), 2.30 (s, 3H, *Me*), 2.34 (s, 3H, *Me*), 5.11 (q, 1H, $^3J_{HH} = 6.4$ Hz, (OH)C*H*Me), 6.98 (d, 1H, $^3J_{HH} = 7.6$ Hz, aromatic), 7.02 (d, 1H, $^3J_{HH} = 7.6$ Hz, aromatic), 7.33 (s, 1H, H^6). ^{13}C NMR (126 MHz, $CDCl_3$): δ 18.4 (s), 21.1 (s), 23.9 (s), 66.8 (s, (OH)-CH*Me*), 125.1 (aromatic), 127.8 (aromatic), 130.3 (aromatic), 131.0 (aromatic), 135.8 (aromatic), 143.6 (aromatic). EI MS: *m*/*z* 150, $[M]^+$.



6

(±)-1-Chloro-1-[(2,5-dimethyl)-1-phenyl]ethane, (±)-7. A dichloromethane solution (380 mL) of racemic 1-[(2,5-dimethyl)-1-phenyl]ethanol, **(±)-6** (7.10 g, 47.3 mmol), was added with vigorous stirring to PCl_3 (39 g, 281 mmol) dissolved in the same solvent (250 mL). The mixture was allowed to stir at room temperature for 16 h. Water was then added dropwise to the mixture with stirring (to hydrolyze the excess PCl_3). The organic phase was separated, washed with water (3 × 100 mL), dried with Na_2SO_4, and filtered. The solvent was then removed, and the product was finally obtained as a colorless liquid by distillation under reduced pressure, bp 62−64 °C, 0.23 mmHg, 6.99 g (87.7% yield). ^1H NMR ($CDCl_3$): δ 1.87 (d, 3H, $^3J_{HH} = 6.7$ Hz, ClCH*Me*), 2.34 (s, 3H, *Me*), 2.37 (s, 3H, *Me*), 5.33 (q, 1H, $^3J_{HH} = 6.7$ Hz, ClC*H*Me), 7.01 (d, 1H, $^3J_{HH} = 8.0$ Hz, aromatic H), 7.04 (d, 1H, $^3J_{HH} = 8.0$ Hz, aromatic H), 7.34 (s, 1H, H^6). ^{13}C NMR (126 MHz, $CDCl_3$): δ 18.5 (s), 21.1 (s), 25.3 (s), 55.2 (s, ClCH*Me*), 126.4 (aromatic), 128.9 (aromatic), 130.5 (aromatic), 132.1 (aromatic), 136.0 (aromatic), 140.2 (aromatic). EI MS: *m*/*z* 168 ($[^{35}Cl - M]^+$) and 170 ($[^{37}Cl - M]^+$) in 3:1 relative intensities.



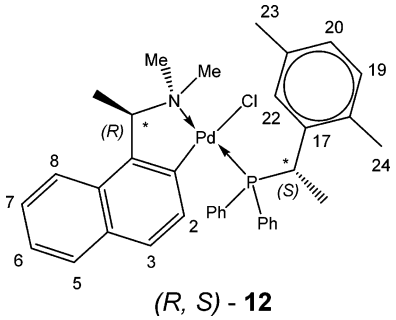
7

{(±)-1-[(2,5-Dimethyl)-1-phenyl]ethyl}diphenylphosphine, (±)-8. A freshly prepared THF solution (20 mL) of sodium diphenylphosphide (22.55 mmol) was added dropwise to a solution of racemic 1-chloro-1-(2,5-dimethylphenyl)ethane, (±)-**7** (3.80 g, 22.55 mmol), in THF (20 mL) with rapid stirring at room temperature. The solvent was removed to give a white residue. Fresh deoxygenated water (40 mL) was added with stirring, and the mixture was extracted with dichloromethane (3 × 40 mL). The combined organic extracts were dried by $MgSO_4$, filtered, and evaporated to give a colorless and air-sensitive liquid. The liquid was further dried under vacuum at 60 °C until a very viscous and colorless oil was obtained, 7.04 g (98.0%). ^1H NMR ($CDCl_3$): δ 1.34 (dd, 3H, $^3J_{HH} = 7.2$ Hz, $^3J_{PH} = 14.5$ Hz, PCH*Me*), 1.92 (s, 3H, aromatic *Me*), 2.32 (s, 3H, aromatic *Me*), 3.78 (dq, 1H, $^3J_{HH} = {}^2J_{PH} = 7.2$ Hz, PC*H*Me), 6.89-6.93 (m, 4H, *aromatic protons*), 7.04−7.17 (m, 3H, *aromatic protons*), 7.32 (br s, 1H, *aromatic*), 7.43−7.45 (m, 3H, *aromatic*), 7.63−7.69 (m, 2H, *aromatic*). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 3.5 (s).

Optical Resolution of {(±)-1-[(2,5-Dimethyl)-1-phenyl]ethyl}-diphenylphosphine. Isolation of Chloro{(*R*)-1-[1-(*N*,*N*-dimethylamino)ethyl]naphthyl-C^2,*N*}{(*R*/*S*)-{1-[(2,5-dimethyl)-1-phenyl]ethyl}diphenylphosphine}palladium(II), (*R*,*R*)- and (*R*,*S*)-12. A dichloromethane solution (50 mL) of the freshly prepared racemic {1-[(2,5-dimethyl)-1-phenyl]ethyl}diphenylphosphine, (±)-8 (9.33 g, 29.29 mmol), was cannulated into a suspension of the resolving agent (*R*,*R*)-11 (9.96 g, 14.65 mmol) in dichloromethane (150 mL) with rapid stirring. The reaction mixture was allowed to stir for 30 min until the resolving agent had entirely dissolved. The mixture was then evaporated to dryness under reduced pressure. At this stage the $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) spectrum of the crude product exhibited two singlets of ca. equal intensities at δ 45.1 and 49.6 indicating the formation of a 1:1 mixture of the two stereochemically nonequivalent (*R*,*R*) and (*R*,*S*) diastereomers. The diastereomeric mixture was redissolved in minimum amount of dichloromethane and was separated using silica gel column chromatography by using hexanes/ethyl acetate (4:1, v/v) as eluent, from which the (*R*,*S*) diastereomer followed by the more polar (*R*,*R*) diastereomer were eluted sequentially.

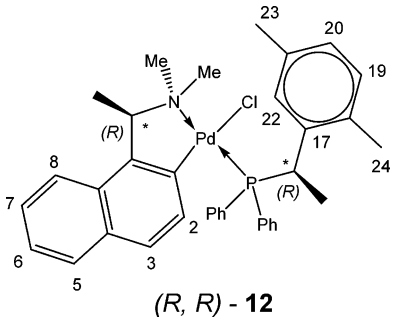
Chloro{(*R*)-1-[1-(*N*,*N*-dimethylamino)ethyl]naphthyl-C^2,*N*}-{(*S*)-{1-[(2,5-dimethyl)-1-phenyl]ethyl}diphenylphosphine}-palladium(II), (*R*,*S*)-12. The optically pure (*R*,*S*)-12 diastereomer was crystallized as yellow blocks from ethyl acetate/hexanes. Mp: 219−221 °C (dec). $[\alpha]_D = -135°$, $[\alpha]_{578} = -141°$, $[\alpha]_{546} = -159°$, and $[\alpha]_{436} = -229°$ (*c* 1.0, CH_2Cl_2). Yield: 8.07 g (83.6%). Anal. Calcd for $C_{36}H_{39}ClNPPd$: C, 65.7; H, 6.0. Found: C, 65.8; H, 6.2. ^1H NMR ($CDCl_3$): δ 1.72 (s, 3H, C^{24}-*Me*), 1.90 (dd, 3H, $^3J_{HH} = 7.2$ Hz, $^3J_{PH} = 19.0$ Hz, PCH*Me*), 2.02 (s, 3H, C^{23}-*Me*), 2.12 (d, 3H, $^3J_{HH} = 6.2$ Hz, NCH*Me*), 2.77 (d, 3H, $^4J_{PH} = 1.3$ Hz, NMe_{ax}), 3.07 (d, 3H, $^4J_{PH} = 3.3$ Hz, NMe_{eq}), 4.36 (dq, 1H, $^3J_{HH} = {}^4J_{PH} = 6.2$ Hz, NC*H*Me), 5.01 (dq, 1H, $^3J_{HH} = 7.2$ Hz, $^2J_{PH} = 10.13$ Hz,

PC*H*Me), 5.96 (s, 1H, H^{22}), 6.32 (dd, 1H, $^3J_{HH}$ = 8.7 Hz, $^4J_{PH}$ = 6.3 Hz, H^2), 6.64 (d, 1H, $^3J_{HH}$ = 8.7 Hz, H^3), 6.89−6.94 (2 closely spaced d, 2H, $^3J_{HH}$ = 7.3 Hz, H^{19}, H^{20}), 7.12 (ddd, 2H, $^3J_{HH}$ = $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 1.8 Hz, *m-PPh*), 7.24−7.28 (m, 2H, H^6, *p-PPh*), 7.34−7.37 (m, 3H, H^7, *m-PPh*), 7.48−7.52 (m, 4H, H^5, *o-PPh*, *p-PPh*), 7.68 (d, 1H, $^3J_{HH}$ = 8.5 Hz, H^8), 7.77 (dd, 2H, $^3J_{HH}$ = 7.4 Hz, $^3J_{PH}$ = 10.4 Hz, *o-PPh*). ^{1}H NMR (CD_2Cl_2): δ 1.66 (s, 3H, C^{24}-*Me*), 1.85 (dd, 3H, $^3J_{HH}$ = 7.3 Hz, $^3J_{PH}$ = 18.9 Hz, Ph_2PCH*Me*), 2.00 (s, 3H, C^{23}-*Me*), 2.08 (d, 3H, $^3J_{HH}$ = 6.5 Hz, NMe_2CH*Me*), 2.72 (d, 3H, $^4J_{PH}$ = 1.7 Hz, NMe_{ax}), 3.03 (d, 3H, $^4J_{PH}$ = 3.2 Hz, NMe_{eq}), 4.35 (dq, 1H, $^3J_{HH}$ = 6.5 Hz, $^4J_{PH}$ = 6.1 Hz, NMe_2C*H*Me), 4.94 (dq, 1H, $^3J_{HH}$ = 7.3 Hz, $^2J_{PH}$ = 10.4 Hz, Ph_2PC*H*Me), 6.00 (s, 1H, H^{22}), 6.32 (dd, 1H, $^3J_{HH}$ = 8.5 Hz, $^4J_{PH}$ = 6.2 Hz, H^2), 6.64 (d, 1H, $^3J_{HH}$ = 8.5 Hz, H^3), 6.88−6.93 (m, 2H, H^{19}, H^{20}), 7.13 (ddd, 2H, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.90 Hz, $^4J_{PH}$ = 2.1 Hz, *m-PPh*), 7.21−7.38 (m, 5H, H^6, H^7, *m-PPh*, *p-PPh*), 7.45−7.55 (m, 4H, H^5, *o-PPh*, *p-PPh*), 7.67 (d, 1H, $^3J_{HH}$ = 8.5 Hz, H^8), 7.78 (dtt, 2H, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.2 Hz, $^3J_{PH}$ = 11.0 Hz, *o-PPh*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 49.8 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 49.9 (s).



(R, S) - **12**

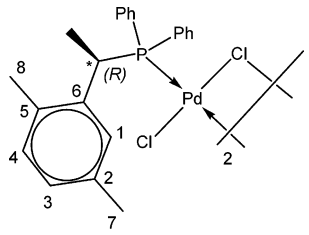
Chloro{(*R*)-1-[1-(*N*,*N*-dimethylamino)ethyl]naphthyl-C^2,*N*}-{(*R*)-{1-[(2,5-dimethyl)-1-phenyl]ethyl}diphenylphosphine}-palladium(II), (*R*,*R*)-12. The solvents from the eluted optically pure (*R*,*R*) diastereomer were evaporated to dryness in vacuo, and the product was obtained as an amorphous yellow powder. Mp: 128−131 °C. $[\alpha]_D$ = +98°, $[\alpha]_{578}$ = +104°, $[\alpha]_{546}$ = +128°, and $[\alpha]_{436}$ =397° (*c* 0.5, CH_2Cl_2). Yield: 6.90 g (71.5%). Anal. Calcd for $C_{36}H_{39}ClNPPd$: C, 65.7; H, 6.0. Found: C, 65.9; H, 6.1. ^{1}H NMR ($CDCl_3$): δ 1.56 (dd, 3H, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 17.6 Hz, PCH*Me*), 1.95 (s, 3H, C^{23}-*Me*), 2.11−2.12 (m, 6H, NCH*Me*, C^{24}-*Me*), 2.71 (d, 3H, $^4J_{PH}$ = 1.2 Hz, NMe_{ax}), 2.99 (d, 3H, $^4J_{PH}$ = 3.2 Hz, NMe_{eq}), 4.35 (dq, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.3 Hz, NCH*Me*), 4.40 (dq, 1H, $^3J_{HH}$ = $^3J_{PH}$ = 7.7 Hz, PCH*Me*), 6.11 (s, 1H, H^{22}), 6.87−6.91 (m, 2H, H^2, H^{20}), 6.99 (d, 1H, $^3J_{HH}$ = 7.8 Hz, H^{19}), 7.12 (d, 1H, $^3J_{HH}$ = 8.6 Hz, H^3), 7.26−7.46 (m, 8H, H^6, H^7, *m-PPh*$_2$, *p-PPh*$_2$), 7.67−7.74 (m, 4H, H^5, H^8, *o-PPh*), 7.77 (dd, 2H, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 10.9 Hz, *o-PPh*). ^{1}H NMR (CD_2Cl_2): δ 1.53 (dd, 3H, $^3J_{HH}$ = 7.3 Hz, $^3J_{PH}$ = 17.5 Hz, Ph_2PCH*Me*), 1.93 (s, 3H, *o*-phenyl-*Me*), 2.10 (d, 3H, $^3J_{HH}$ = 6.5 Hz, NMe_2CH*Me*), 2.13 (s, 3H, *p*-phenyl-*Me*), 2.72 (d, 3H, $^4J_{PH}$ = 1.7 Hz, NMe_{ax}), 3.03 (d, 3H, $^4J_{PH}$ = 3.2 Hz, NMe_{eq}), 4.34−4.41 (partially overlapped m, 2H, $^3J_{HH}$ = 6.5 Hz, $^4J_{PH}$ = 6.5 Hz, NMe_2CH*Me*; $^3J_{HH}$ = 7.3 Hz, Ph_2PC*H*Me), 6.23 (s, 1H, H^{22}), 6.86 (dd, 1H, $^3J_{HH}$ = 8.6 Hz, $^4J_{PH}$ = 5.4 Hz, H^2), 6.90 (d, 1H, $^3J_{HH}$ = 7.6 Hz, H^{19}), 7.00 (d, 1H, $^3J_{HH}$ = 7.6 Hz, H^{20}), 7.10 (d, 1H,$^3J_{HH}$ = 8.6 Hz, H^3), 7.30−7.41 (m, 6H, H^6, H^7, *m-PPh*$_2$), 7.43−7.50 (m, 2H, *p-PPh*$_2$), 7.64−7.68 (m, 3H, H^5, *o-PPh*), 7.73 (d, 1H, $^3J_{HH}$ = 8.1 Hz, H^8), 7.78 (ddd, 2H, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 0.9 Hz, $^3J_{PH}$ = 11.0 Hz, *o-PPh*). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 45.2 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 45.3 (s).



(R, R) - **12**

Attempts to crystallize the (*R*,*R*) diastereomer were unsuccessful despite a range of solvent systems tried.

(*R*,*R*)-*sym*-Dichlorobis(μ-chloro)bis[{1-(2,5-dimethyl-1-phenyl)-ethyl}diphenylphosphine]dipalladium(II), (*R*,*R*)-13. Concentrated HCl (5.4 mL, 65.3 mmol) was added to an acetone solution (43 mL) of the complex (*R*,*R*)-**12** (2.15 g, 3.26 mmol), and the mixture was refluxed for 4 h. Water was then added to the cooled mixture with stirring, and the resulting precipitate was then filtered out, washed successively with water, dried, and redissolved in dichloromethane (20 mL). The reddish solution was further washed with water (3 × 20 mL), dried with $MgSO_4$, and filtered. The solution was then concentrated, and product was crystallized as small red blocks from dichlromethane−hexanes, 1.49 g (92.1% yield). Mp: 196−200 °C (dec). $[\alpha]_D$: +334° (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{44}H_{46}Cl_4P_2Pd_2$: C, 53.3; H, 4.7. Found: C, 53.6; H, 4.7. ^{1}H NMR ($CDCl_3$): δ 1.75 (s, 3H, C^8-*Me*), 1.98 (dd, 3H, $^3J_{HH}$ = 7.1 Hz, $^3J_{PH}$ = 19.3 Hz, PCH*Me*), 2.00 (d, 3H, C^7-*Me*), 4.64 (dq, 1H, $^3J_{HH}$ = 7.1 Hz, $^2J_{PH}$ = 12.3 Hz, PC*H*Me), 6.20 (s, 1H, H^1), 6.88 (d, 1H, $^3J_{HH}$ = 7.8 Hz, H^4), 6.91 (d, 1H, $^3J_{HH}$ = 7.76 Hz, H^3), 7.34−7.39 (m, 4H, *m-PPh* + PPh aromatics), 7.52−7.57 (overlapping m, 4H, *p-PPh* + *PPh* aromatics), 7.80 (dd, 2H, $^3J_{HH}$ = 7.4 Hz, $^3J_{PH}$ = 10.9 Hz, *o-PPh*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 42.5 (s).

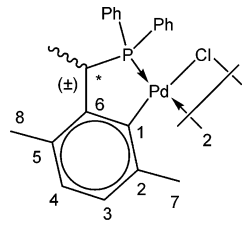


(R, R) - **13**

(*S*,*S*)-*sym*-Dichlorobis(μ-chloro)bis[{1-(2,5-dimethyl-1-phenyl)-ethy}ldiphenylphosphine]dipalladium(II), (*S*,*S*)-13. Complex (*S*,*S*)-**13** was prepared as described above from the chromatographically pure (*R*,*S*)-**12**. Yield: 1.12 g (99.4%). Mp: 196−200 °C (dec). $[\alpha]_D$: −335° (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{44}H_{46}Cl_4P_2Pd_2$: C, 53.3; H, 4.7. Found: C, 53.6; H, 4.6. ^{1}H and ^{31}P{^{1}H} NMR ($CDCl_3$) were identical with those recorded for (*R*,*R*)-**13**.

(±)-Bis(μ-chloro)bis{1-[1-(diphenylphosphino)ethyl]-3,6-dimethylphenyl-C^2,*P*}dipalladium(II), (±)-9. A mixture of the racemic phosphine (±)-**8** (7.04 g, 22.1 mmol) and palladium(II) acetate (4.96 g, 22.1 mmol) in toluene (230 mL) was stirred at 50 °C for 10 h, after which a crude brown-black intermediate was obtained upon removal of toluene under reduced pressure. The mixture was dissolved in acetone (30 mL), and a methanol solution (25 mL) of excess LiCl (3.8 g, 89.6 mmol) was added with vigorous stirring for 4 h after which the black-green mixture was filtered through Celite and then evaporated to dryness. The mixture was washed with water (50 mL), extracted with dichloromethane (3 ×

50 mL), dried with $MgSO_4$, and then filtered. The resulting orange solution was then concentrated and purified by silica gel column chromatography using chloroform−*n*-hexane as eluants, from which the bright greenish yellow band was eluted and concentrated. The complex (±)-**9** was crystallized from dichloromethane−hexane as bright yellow prisms, 7.84 g (77.3% yield). Mp: 216−220 °C (dec). Anal. Calcd for $C_{44}H_{44}Cl_2P_2Pd_2$: C, 57.5; H, 4.8. Found: C, 57.4; H, 5.2. ^{1}H NMR ($CDCl_3$, 2 sets of signals in ca. 1:1.5 ratio): δ 1.71 (dd, 3H, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 19.1 Hz, PCH*Me* of minor isomer), 1.86 (dd, 3H, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 19.5 Hz, PCH*Me* of major isomer), 2.24 (s, 3H, aromatic *Me* of minor isomer), 2.31 (s, 3H, aromatic *Me* of major isomer), 2.63 (s, 3H, aromatic *Me* of minor isomer), 2.69 (s, 3H, aromatic *Me* of major isomer), 3.85 (m, 1H, PC*H*Me of both isomers), 6.60−6.69 (m, aromatic signals of both isomers), 7.22−7.50 (m, aromatics of both isomers), 7.81−7.92 (m, aromatic signals of both isomers). ^{31}P{^{1}H} NMR ($CDCl_3$, 300 K): 2 signals in ca. 1:1.5 ratio, δ 58.3 (s), 59.5 (s). ^{31}P{^{1}H} NMR ($CDCl_3$, 223 K): 4 signals, δ 58.8 (s), 59.7 (s), 59.9 (s), 60.9 (s).

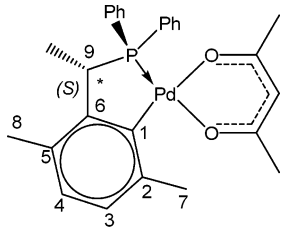


(±) - **9**

(*R*,*R*)-Bis(*μ*-Chloro)bis{1-[1-(diphenylphosphino)ethyl]-3,6-dimethylphenyl-*C*^{2},*P*}dipalladium(II), (*R*,*R*)-9. The complex (*R*,*R*)-**13** (0.64 g, 0.64 mmol) was dissolved in dichloromethane (17 mL) to form a red solution. An aqueous solution (10 mL) of excess $AgPF_6$ (0.65 g, 2.58 mmol) was added to the red solution, and the two-phase mixture was allowed to stir vigorously in the dark for 16 h at room temperature. The reaction mixture was then filtered through a plug of Celite to remove the precipitated AgCl and Pd black. From the filtrate, the aqueous layer was separated from the red dichloromethane layer, and the latter was washed vigorously with water (3 × 50 mL). The combined organic extracts were separated, evaporated to dryness in vacuo, and redissolved in acetone (5 mL). A methanol solution (12 mL) of excess LiCl (1.0 g, 23.6 mmol) was next added to it with vigorous stirring at room temperature for 24 h. The resulting bright yellow solution was subsequently evaporated to dryness and was chromatographed on a silica gel column using chloroform−*n*-hexane as eluants. A greenish yellow band was eluted and evaporated to dryness in vacuo to afford the product as a yellow amorphous powder. Attempts to crystallize the product from a variety of solvents have been unsuccessful, 0.46 g (76.9% yield). Mp: 146−149 °C (dec). $[\alpha]_D$: −322° (*c* 0.5, CH_2Cl_2). Anal. Calcd for $C_{44}H_{44}Cl_2P_2Pd_2$: C, 57.5; H, 4.8. Found: C, 57.9; H, 5.0. ^{1}H NMR ($CDCl_3$): δ 1.72 (dd, 3H, $^3J_{HH}$ = 6.9 Hz, $^3J_{PH}$ = 19.3 Hz, PCH*Me*), 2.32 (s, 3H, C^5-*Me*), 2.70 (s, 3H, C^2-*Me*), 3.86 (dq, 1H, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 13.5 Hz, PC*H*Me), 6.65 (d, 1H, $^3J_{HH}$ = 7.4 Hz, *H*^{3}), 6.69 (d, 1H, $^3J_{HH}$ = 7.4 Hz, *H*^{4}), 7.24-7.39 (m, 6H, *m-PPh*$_2$, *p-PPh*$_2$), 7.48 (ddd, 2H, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.4 Hz, $^3J_{PH}$ = 11.4 Hz, *o-PPh*$_{ax}$), 7.90 (dd, 2H, $^3J_{HH}$ = 7.8 Hz, $^3J_{PH}$ = 10.6 Hz, *o-PPh*$_{eq}$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 59.9 (br s).

(*S*,*S*)-Bis(*μ*-chloro)bis{1-[1-(diphenylphosphino)ethyl]-3,6-dimethylphenyl-*C* ^{2},*P*}dipalladium(II), (*S*,*S*)-9. The complex (*S*,*S*)-**9** was prepared as described above from (*S*,*S*)-**13**, 0.443 g (56.6% yield). Mp: 148−150 °C (dec). $[\alpha]_D$: +319° (*c* 0.9, CH_2Cl_2). Anal. Calcd for $C_{44}H_{44}Cl_2P_2Pd_2$: C, 57.5; H, 4.8. Found: C, 57.4; H, 4.8. ^{1}H and ^{31}P{^{1}H} NMR ($CDCl_3$) were identical with those recorded for (*R*,*R*)-**9**.

(Acetylacetonato-*O*,*O*′){(*S*)-1-[1-(diphenylphosphino)ethyl]-3,6-dimethylphenyl-*C*^{2},*P*}palladium(II), (*S*)-16. Sodium acetylacetonate monohydrate (0.03 g, 0.2 mmol) was added to (*S*,*S*)-**9** (0.110 g, 0.120 mmol) dissolved in acetone (5 mL) with rapid stirring for 4 h at room temperature. The resulting suspension was then filtered through a short plug of Celite, and the filtrate was concentrated. Upon slow evaporation, the product was obtained as pale yellow blocks, 0.087 g (69.2% yield). Mp: 149−150 °C. $[\alpha]_D$ = +502°, $[\alpha]_{578}$ = +531°, $[\alpha]_{546}$ = +620°, and $[\alpha]_{436}$ = +1333° (*c* 0.5, CH_2Cl_2). Anal. Calcd for $C_{27}H_{29}O_2PPd$: C, 62.0; H, 5.6. Found: C, 61.9; H, 5.6. ^{1}H NMR ($CDCl_3$): δ 1.66 (dd, 3H, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 19.2 Hz, Ph_2CH*Me*), 1.97 (s, 3H, acac-*Me*), 2.00 (s, 3H, acac-*Me*), 2.28 (s, 3H, C^5-*Me*), 2.59 (s, 3H, C^2-*Me*), 3.87 (dq, 1H, $^3J_{HH}$ = 7.0 Hz, $^2J_{PH}$ = 13.2 Hz, Ph_2C*H*Me), 5.39 (s, 1H, acac-C*H*), 6.96 (dd, 1H, $^3J_{HH}$ = 7.6 Hz, J_{PH} = 1.2 Hz, C^4-*H*), 6.73 (d, 1H, $^3J_{HH}$ = 7.6 Hz, C^3-*H*), 7.20−7.23 (m, 2H, *m-PPh*$_{ax}$), 7.26−7.30 (m, 1H, *p-PPh*$_{ax}$), 7.35−7.39 (m, 2H, *o-PPh*$_{ax}$), 7.42−7.46 (m, 2H, *m-PPh*$_{eq}$), 7.48−7.52 (m, 1H, *p-PPh*$_{eq}$), 7.93−7.97 (m, 2H, *o-PPh*$_{eq}$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 53.7 (s).



(*S*) - **16**

Table 5. Crystallographic Data for Complexes of *meso*-**9**, (*R*,*S*)-**12**, (*S*,*S*)-**13**, and (*S*)-**16**

param	*meso*-**9**	(*R*,*S*)-**12**	(*S*,*S*)-**13**	(*S*)-**16**
formula	$C_{44}H_{44}Cl_2P_2Pd_2$	$C_{36}H_{39}ClNPPd$	$C_{44}H_{46}Cl_4P_2Pd_2$	$C_{27}H_{29}O_2PPd$
M_r	918.43	658.50	991.35	522.87
space group	$P2_1/c$	$P2_1$	$P1$	$P2_12_12$
cryst system	monoclinic	Monoclinic	triclinic	orthorhombic
a/Å	12.649(11)	11.789(1)	8.790(1)	9.5880(7)
b/Å	12.067(10)	13.128(1)	8.943(1)	26.560(2)
c/Å	13.869(13)	21.367(1)	15.387(1)	9.5467(7)
V/Å^3	2023(3)	3305(1)	1048(1)	2431(1)
Z	2	4	1	4
T/K	223(2)	223(2)	223(2)	295(2)
λ/Å	0.710 73	0.710 73	0.710 73	0.710 73
μ/mm^{-1}	1.130	0.715	1.219	0.850
R_1 (obsd data)[a]	0.0352	0.0424	0.0374	0.0449
wR_2 (obsd data)[b]	0.0794	0.0773	0.0795	0.0838
Flack param		−0.02(1)	0.00(2)	0.03(3)

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

Crystal Structure Determination of *meso*-9, (*R*,*S*)-12, (*S*,*S*)-13, and (*S*)-16. Crystal data for all four complexes and a summary of the crystallographic analyses are given in Table 5. Diffraction data were collected on a Siemens SMART CCD diffractometer with Mo Kα radiation (graphite monochromator) using ω-scans. SADABS absorption corrections were applied, and refinements by full-matrix least squares were based on SHELXL 93.[14] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were intro-

duced at fixed distance from carbon and nitrogen atoms and were assigned fixed thermal parameters.

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(14) Sheldrick, G. M. *SHELXL 93, Program for Crystal Structure*; University of Gottingen: Gottingen, Germany, 1993.

Supporting Information Available: For *meso*-**9**, (*R*,*S*)-**12**, (*S*,*S*)-**13**, and (*S*)-**16**, 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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