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Synthesis of a Chiral Palladacycle and Its Application in Asymmetric Hydrophosphanation Reactions

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A novel amine ligand, 1-(2,5-dimethylphenyl)-*N*,*N*,2,2-tetramethylpropan-1-amine, was synthesized in six steps from commercially available *p*-xylene. Direct *ortho*-palladation of this amine ligand proceeded readily to form the racemic dimeric complex. The palladacycle structure and ring conformations of its triphenylphosphane derivative were thoroughly investigated by X-ray structural analysis in the solid state and 2D ^{1}H–^{1}H ROESY NMR spectroscopy in solution. This racemic palladacycle was efficiently resolved through the formation of its (*S*)-prolinato derivatives and an efficient separation of the resulting diastereomeric complexes was achieved by slow crystallization with the use of different solvent systems. 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 could be obtained chemoselectively by treating the corresponding prolinato derivatives with 1 M hydrochloric acid. The asymmetric hydrophosphanation reaction between diphenylphosphane and diethyl acetylenedicarboxylate was promoted by this newly synthesized palladacycle and resulted in the formation of a single isomer according to the ^{31}P NMR spectrum. The amine auxiliary could be subsequently removed chemoselectively from the palladium center by treatment with concentrated HCl. An optically pure C_2-symmetrical diphosphane ligand containing two ester functional groups at the two chiral carbon stereogenic centers was prepared by ligand displacement.

Introduction

The *ortho*-palladation of N-donor ligands has been extensively studied and has acquired great interest because of the applications of palladacycles in many areas. Over the past decades, chiral cyclopalladated amine complexes[1] have generated interests for their many roles as resolving agents for chiral ligands,[2] agents for NMR assignment of unknown compound absolute configurations,[3] agents for determination of optical purity of organic compounds,[4] and chiral catalysts for asymmetric reactions.[5] In our group, we have reported the application of *ortho*-palladated dimethyl-[1-(α)-naphthyl]ethylamine complex (*R*)-**1** (Figure 1) and its (*S*)-enantiomer as reaction promoters for various asymmetric reactions including Diels–Alder and hydroamination reactions.[6]

To study the asymmetric synthesis of chiral diphosphanes through the addition of P–H bonds to unsaturated C–C bonds, we have also applied chiral cyclopalladated amine complex **1** in the synthesis of phosphane ligands in asymmetric hydrophosphanation reactions.[7] Our previous studies on asymmetric reactions have given us insight into the influence of the chiral amine auxiliary on the stereo- and regioselectivities observed. The unique stereochemical feature of complex (*R*)-**1** lays in the internal steric repulsion between the methyl substituent on the stereogenic carbon and its neighboring naphthylene proton H8. This particular interaction confines the methyl group in the axial position, and hence, the δ absolute conformation of the five-membered ring is fixed and not interconvertable in both the solid state and in solution.[8] Due to this unique ring conformation, the chirality of the naphthylamine ring is transmitted efficiently through its prochiral NMe groups onto the neighboring coordination site. In pursuit of our interest in the design of new chiral palladacycles[9] and to further improve the stereoselectivity in asymmetric hydrophosphanation reactions, novel palladacycle **2** was designed and synthesized (Figure 1). Palladacycle **2** was designed to improve three aspects: Firstly, the interaction between the aromatic methyl group Me5 and the *tert*-butyl group would more effectively lock the conformation of the five-membered pal-

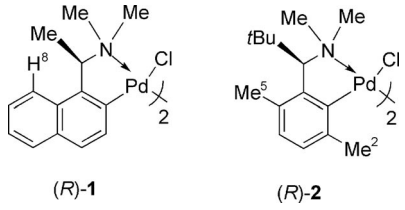

Figure 1. Stereochemical features of complexes (*R*)-**1** and (*R*)-**2**.

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ladacycle in a fixed conformation in solution, hence locking the *tert*-butyl group in the axial position. Secondly, an additional methyl group Me2 was introduced on the aromatic ring next to the Pd–C bond; through this introduction the stereochemistry of the coordination site *trans* to the N donor atom would be controlled more efficiently as compared to palladacycle **1**.[9a,9c,9h,9i] Thirdly, and most importantly, the axially located *tert*-butyl group on the prochiral carbon is expected to further enhance the interaction between itself and the NMe groups, which would translate to a stronger steric influence on the reaction site *cis* to the N donor atom. To evaluate the above design rationale, target chiral cyclopalladated complex **2** was synthesized and its application in asymmetric hydrophosphanation reactions was examined.

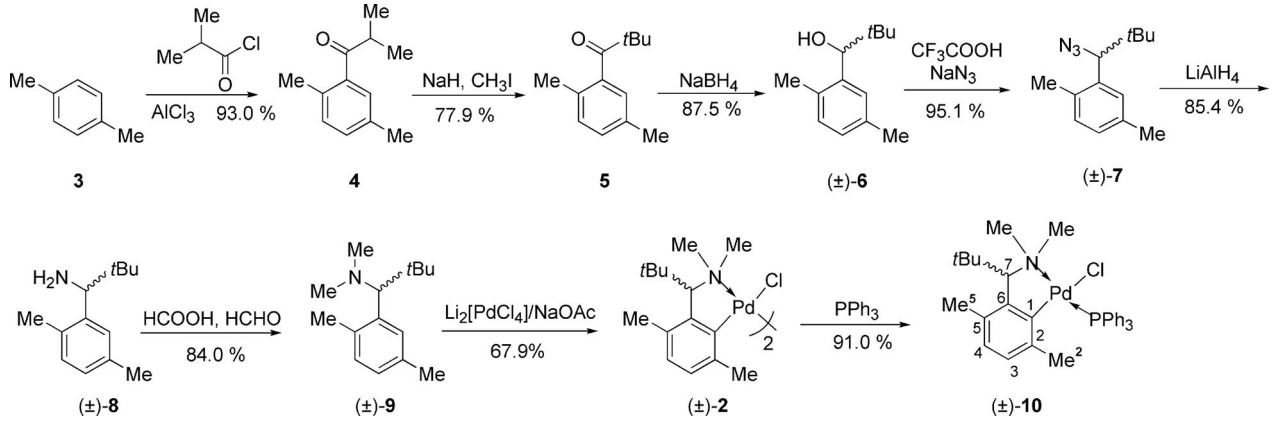
Results & Discussion

Synthesis and Characterization of *ortho*-Palladated Complex (±)-2

The preparation of *ortho*-palladated complex (±)-**2** is illustrated in Scheme 1. The first step involved a reaction between *p*-xylene **3** and isobutyryl chloride in the presence of aluminum(III) chloride, which afforded ketone compound **4** in 93.0% yield. Further treatment of compound **4** with iodomethane in sodium hydride led to the formation of the *tert*-butyl group in compound **5**.[10] Reduction of ketone **5** by sodium borohydride in ethanol resulted in racemate alcohol (±)-**6** in 87.5% yield. The alcohol was then converted into azide (±)-**7** in the presence of sodium azide and trifluoroacetic acid with a yield of 95.1%.[11] Reduction of compound (±)-**7** by lithium aluminum hydride in dry THF yielded amine compound (±)-**8** in 85.4% yield, which was subjected to subsequent methylation to form target *N*,*N*-dimethylamine ligand (±)-**9** as an oil in 84.0% yield. The molecular ion peak (ESI mode) of complex (±)-**9** can be further observed at m/z = 220.2059 $[M + H]^+$ by high-resolution mass spectrometry. *N*,*N*-Dimethylamine (±)-**9** was *ortho*-palladated to give racemic dimeric complex (±)-**2** in 67.9% yield by using $Li_2[PdCl_4]$/NaOAc as the palladation reagents. However, failure of amine (±)-**9** to undergo *ortho*-palladation was observed when $Pd(OAc)_2$ or $Pd(NCMe)_4(ClO_4)_2$/Et_3N was employed as the palladation reagent.[9]

Racemic μ-chlorido dimer (±)-**2** exists as a dynamic mixture of two regioisomers interconverting in solution. This fluxional behavior rendered characterization and confirmation of the palladacycle difficult, as clustered ^1H and ^{13}C NMR spectra were obtained. For example, the multiplet resonance exhibited at δ = 1.64–1.69 ppm in the ^1H NMR spectrum, which is indicative of the *tert*-butyl group, suggests the presence of preferential arrangements in solution due to the variation in peak intensities. Several attempts were made to crystallize the dimeric complex out fractionally in a series of solvent systems. However, none of the above attempts resulted in the formation of crystals that were suitable for single-crystal X-ray crystallography. Thus, racemic dimer (±)-**2** was converted into its mononuclear phosphane derivative (±)-**10** by treatment with triphenylphosphane. Reaction of complex (±)-**2** with two molar equivalents of triphenylphosphane in dichloromethane gave a bright yellow solid that was slowly crystallized in dichloromethane/hexane in 91.0% yield (Scheme 1). Through the formation of phosphane derivative (±)-**10**, thorough examination of the chemical properties and structural characterization in both the solid state and solution became possible.

In the solid state, the structure of complex (±)-**10** was reaffirmed crystallographically. The single-crystal X-ray molecular structure and selected bond lengths and angles are presented in Figure 2 and Table 1, respectively. In complex (±)-**10**, the PPh_3 group is located *trans* to the nitrogen donor and the palladium center has a distorted square-planar coordination geometry. Analysis of the extent of the tetrahedral distortion on the central Pd atom reveals that it is located in a highly congested environment: the dihedral angle between the {N1–Pd1–C1} and {Cl1–Pd1–P1} planes have a large value of 19.5°. The torsion angle P1–Pd1–C1–C2 is 52.0°, and such a twisting can be partially attributed to the repulsive interaction between the methyl spacer C3 and the phenyl group (C22–C27). The five-membered palladacycle, in this case, adopts a single conformation and the *tert*-butyl substituent attached to the α-carbon stereocenter remains axially located. The distance between C10 and C15



Scheme 1.

was found to be 3.060 Å, which is less than 3.4 Å, the sum of the van der Waals radii of the two atoms. This implies that the bulky *tert*-butyl group must be projected away from C15 to relieve steric repulsion in the crowded local environment, which is the main driving force for this group to assume the axial position. Thus, the ring conformation is effectively locked. Furthermore, the distance between C15 and Cl1 was found to be 3.190 Å, which is also smaller than the van der Waals radii of the two atoms (3.5 Å). This is also indicative of a highly crowded localized environment, which hence explains the stereochemical influence exhibited by the organopalladium complex as well as the regioselectivity observed.

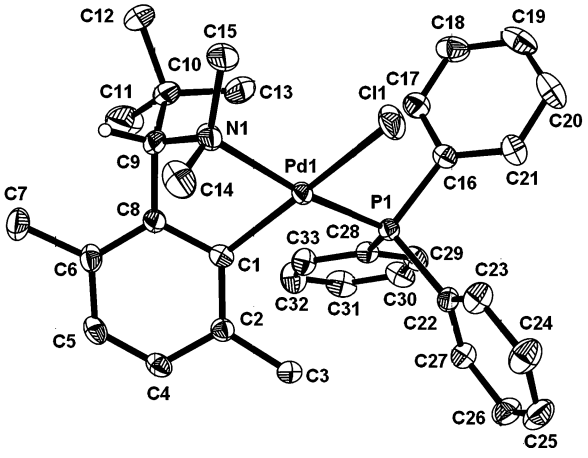


Figure 2. Molecular structure of complex (±)-**10**.

Table 1. Selected bond lengths [Å] and angles [°] for complex (±)-**10**.

Pd1–C1	2.014(2)	Pd1–N1	2.145(2)
Pd1–P1	2.275(5)	Pd1–Cl1	2.392(5)
C1–Pd1–N1	79.06(6)	C1–Pd1–P1	101.8(5)
N1–Pd1–P1	166.0(5)	C1–Pd1–Cl1	164.3(6)
N1–Pd1–Cl1	92.3(4)	P1–Pd1–Cl1	89.8(2)
C2–C1–Pd1	127.1(1)	C8–C1–Pd1	112.6(1)

In solution, the NMR spectroscopic characterization of this racemic palladacycle was achieved by a combination of ^{1}H NMR and 2D ^{1}H–^{1}H ROESY NMR spectroscopy. In $CDCl_3$, the ^{31}P NMR spectrum of complex (±)-**10** shows only a singlet resonance at δ = 30.0 ppm, indicating the presence of a sole isomer in solution. Hence, in comparison with dimeric complex (±)-**2**, mononuclear complex (±)-**10** is more suitable for NMR spectroscopic studies. Furthermore, the absence of aliphatic protons in the triphenylphosphane ligand would not further contribute to the complexity of the aliphatic region of the ^{1}H NMR spectrum. In the ^{1}H NMR spectrum, the two *N*-methyl groups show characteristic P–H couplings (J = 1.5 and 3.4 Hz). These $J_{P,H}$ couplings confirm the *trans* relationship of the phosphorus atom and the nitrogen donor, which could be observed and justified by "transphobia".[12]

NMR study of racemic adduct (±)-**10** has shown that in solution the five-membered palladacycle exists in either the $\delta(R)$ or $\lambda(S)$ conformation with the *tert*-butyl substituent in the axial position. This conclusion can be inferred from the $^4J_{P,H}$ coupling constant of 5.2 Hz for the α-*tert*-butyl proton and further confirmed by 2D ^{1}H–^{1}H ROESY NMR spectroscopy (Figure 3). In the NMR spectrum, the key ROESY interaction is F, which demonstrates that the *tert*-butyl group exhibits a strong interaction only with the equatorial methyl substituent on the nitrogen atom. This interaction confirms that the methyl groups of the nitrogen are fully fixed in position and that the ring is locked in either the $(S)\lambda$ or $(R)\delta$ conformation. Furthermore, the driving forces for the *tert*-butyl group to assume the axial position can also be attributed to the repulsive interactions, (C) Me5–H7 and (G) Me5-*tert*-butyl. Other expected ROESY interactions of NMe(eq)-NMe(ax) (E), *tert*-butyl-H7 (D), Me5–H4 (H), and Me2–H3 (J) are also observed. Interestingly, the interactions of *tert*-butyl-PPh_3 (I) is also observed, which indicates that through the introduction of the bulky *tert*-butyl group, a steric effect will be experienced when the reaction site *trans* to the nitrogen donor is coordinated to a bulky group (for example, PPh_3). The above NMR spectroscopic investigations of complex (±)-**10** in solution indicates that the *tert*-butyl group is located in the axial position and the interaction between the Me7 and *tert*-butyl group can confine the five-membered organometallic ring conformation and therefore λ and δ conformations are adopted in the (*S*) and (*R*) enantiomers, respectively.

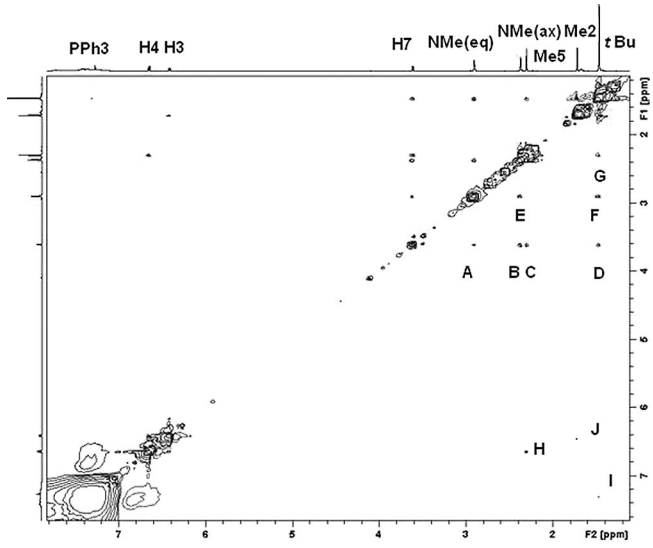
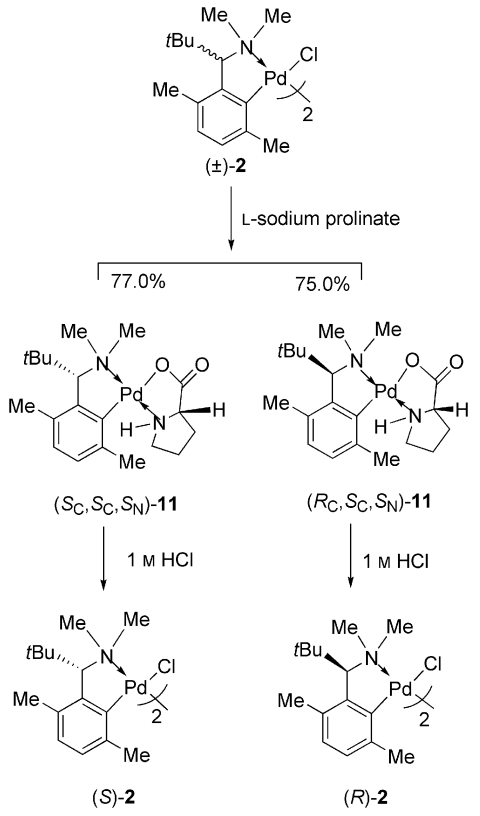


Figure 3. 2D ^{1}H–^{1}H ROESY NMR spectrum of complex (±)-**10** in $CDCl_3$. Refer to Scheme 1 for the numbered structure of complex (±)-**10**. Selected ROESY interactions: (A) NMe(eq)–H7; (B) NMe(ax)–H7; (C) H7–Me5; (D) H7–*tert*-butyl; (E) NMe(eq)–NMe(ax); (F) NMe(eq)–*tert*-butyl; (G) Me5–*tert*-butyl; (H) Me5–H4; (I) PPh_3–*tert*-butyl; (J) Me2–H3.

Optical Resolution of Racemic Dimer (±)-2

The optical resolution of racemic dimeric complex (±)-**2** was achieved through the formation and separation of a pair of diastereomeric (*S*)-prolinate derivatives (Scheme 2).

By treating racemic dimeric complex (±)-**2** with two molar equivalents of sodium (*S*)-prolinate, the expected 1:1 mixture of diastereomeric adducts (R_C,S_C,S_N)-**11** and (S_C,S_C,S_N)-**11** was formed and confirmed by the ^{1}H NMR spectroscopy.



Scheme 2.

Successful optical resolution was achieved by fractional crystallization in dichloromethane/diethyl ether, affording less-soluble diastereomer (S_C,S_C,S_N)-**11** in the form of yellow flakes with $[a]_D$ = +246 (c = 0.5, dichloromethane), >99%*de* (according to ^{1}H NMR spectroscopy). The diastereomerically enriched mother liquor allowed crystallization of remaining diastereomer (R_C,S_C,S_N)-**11** from chloroform/diethyl ether as pale-yellow feather-like crystals with $[a]_D$ = –32 (c = 0.5, dichloromethane), >99%*de* (according to ^{1}H NMR spectroscopy). The absolute configurations of both diastereomers were confirmed from X-ray single-crystal diffractometry.

X-ray diffraction study of diastereomer (R_C,S_C,S_N)-**11** was carried out and there are three crystallographically distinguishable molecules in the unit cell with the same stereochemistry but with slightly different bond lengths and angles. For clarity, only one of them (molecule A) is depicted in Figure 4. Selected bond lengths and angles are provided in Table 2. The X-ray crystal structure revealed the *R* absolute configuration of the stereocenter. The *tert*-butyl group occupied the expected axial position and the conformation of the five-membered palladacycle is *δ*. The coordination geometry of the central palladium atom is in a slightly distorted square plane. The dihedral angle between the planes N1–C1–Pd1 and O1–N2–Pd1 is 6.7°. Worthy to note is that the two coordinated nitrogen atoms are *trans* related, which is in contrast to the *cis*-(*N*,*N*)-relationship for its α-methyl analogue.[9c] This phenomenon can be attributed to severe intramolecular ligand–ligand interaction arising from the presence of the bulky *tert*-butyl group as compared to its α-methyl analogue. Consequently, less steric interactions exist between the *tert*-butyl group and the prolinato ligand when complex (R_C,S_C,S_N)-**11** adopts the favorable *trans*-(*N*,*N*) arrangement.

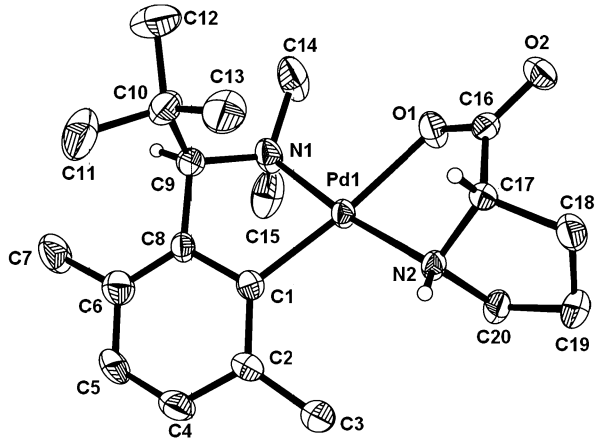


Figure 4. Molecular structure of complex (R_C,S_C,S_N)-**11**.

For diastereomer (S_C,S_C,S_N)-**11**, yellow-colored crystals suitable for X-ray crystallography were achieved from a dichloromethane/diethyl ether solution. There are two crystallographically distinguishable molecules in the asymmetrical unit with the same stereochemistry but slightly different bond lengths and angles and only one of them (molecule A)

Table 2. Selected bond lengths [Å] and angles [°] for complex (R_C,S_C,S_N)-**11**.

Molecule A		Molecule B		Molecule C	
Pd1–C1	2.018(5)	Pd2–C21	2.009(6)	Pd3–C41	2.007(6)
Pd1–N1	2.062(5)	Pd2–N3	2.067(5)	Pd3–N6	2.072(5)
Pd1–N2	2.083(4)	Pd2–N4	2.071(5)	Pd3–N5	2.079(5)
Pd1–O1	2.136(4)	Pd2–O3	2.130(4)	Pd3–O5	2.112(4)
C1–Pd1–N1	80.4(2)	C21–Pd2–N3	81.0(2)	C41–Pd3–N6	105.7(2)
C1–Pd1–N2	106.1(2)	C21–Pd2–N4	105.5(2)	C41–Pd3–N5	81.8(2)
N1–Pd1–N2	173.3(2)	N3–Pd2–N4	173.4(2)	N6–Pd3–N5	171.6(2)
C1–Pd1–O1	174.6(2)	C21–Pd2–O3	173.9(2)	C41–Pd3–O5	174.4(2)
N1–Pd1–O1	95.2(2)	N3–Pd2–O3	95.0(2)	N6–Pd3–O5	79.2(2)
N2–Pd1–O1	78.3 (2)	N4–Pd2–O3	78.4(2)	N5–Pd3–O5	93.2(2)

is depicted in Figure 5, and selected bond lengths and angles are provided in Table 3. The X-ray crystal structure revealed the *S* absolute configuration of the carbon chiral center, with the *tert*-butyl group in the axial position. All the bond lengths and angles at the central palladium atoms are within the normal ranges. Consistent with its α-methyl counterpart, the two nitrogen atoms in each molecule are *trans*-(*N*,*N*) related.[9c]

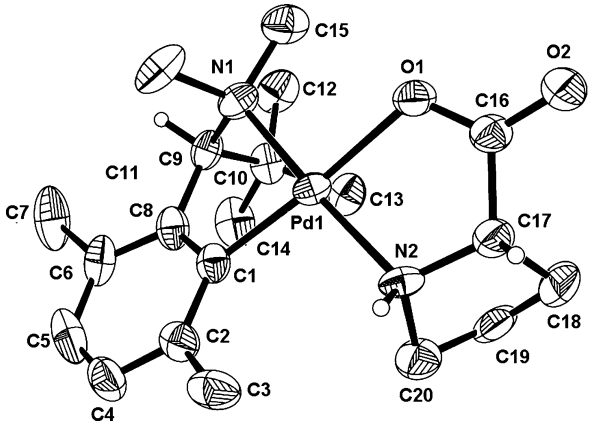


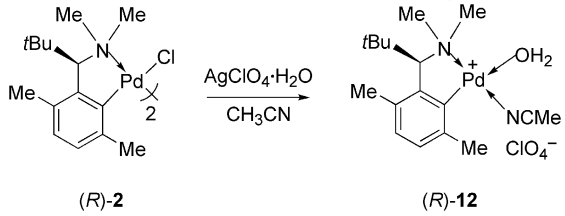
Figure 5. Molecular structure of complex (S_C,S_C,S_N)-**11**.

Table 3. Selected bond lengths [Å] and angles [°] for complex (S_C,S_C,S_N)-**11**.

Molecule A		Molecule B	
Pd1–C1	2.022(7)	Pd2–C21	2.016(7)
Pd1–N1	2.030(1)	Pd2–N3	2.044(1)
Pd1–N2	2.065(1)	Pd2–N4	2.090(1)
Pd1–O1	2.128(6)	Pd2–O3	2.116(5)
C1–Pd1–N1	81.2(4)	C21–Pd2–N3	80.6(3)
C1–Pd1–N2	103.1(3)	C21–Pd2–N4	102.0(3)
N1–Pd1–N2	173.4(3)	N3–Pd2–N4	173.5(3)
C1–Pd1–O1	174.6(3)	C21–Pd2–O3	175.8(3)
N1–Pd1–O1	94.0(3)	N3–Pd2–O3	95.9(3)
N2–Pd1–O1	81.5(3)	N4–Pd2–O3	81.7(3)

Standard protonation of the auxiliary amino acid ligand in complex (R_C,S_C,S_N)-**11** by 1 M hydrochloric acid under two-phase conditions readily yielded the enantiomerically pure palladium complex dimer (*R*)-**2**. The other prolinate derivative, (S_C,S_C,S_N)-**11**, was converted into its respective dichlorido dimer (*S*)-**2** in a similar manner (Scheme 2). Unfortunately, both chiral dimeric palladium complexes, (*R*)-**2** and (*S*)-**2**, could not be crystallized by using an array of solvent systems. Thus, a conversion of dimeric complex (*R*)-**2** to its perchlorate salt derivative (*R*)-**12**, $[\alpha]_D$ = –124 (*c* = 0.5, dichloromethane), by treatment with an excess amount of silver perchlorate monohydrate in acetonitrile (Scheme 3) circumvented this problem.

A single crystal of complex (*R*)-**12** suitable for X-ray crystallography was obtained from a dichloromethane/hexane solution, and it allowed the absolute configuration of



Scheme 3.

the chiral palladacycle to be determined. The molecular structure and its numbering scheme are presented in Figure 6, whereas selected bond lengths and angles are given in Table 4. The (*R*) absolute configuration of the optically active palladacycle was confirmed from the Flack parameter of 0.001(16). X-ray analysis of complex (*R*)-**12** revealed that the *tert*-butyl group at the carbon center is in the axial position. The geometry at palladium is in a distorted square-planar with one molecule of water and one molecule of acetonitrile coordinated *cis* and *trans* to the NMe_2 group, respectively. The dihedral angle between the planes N1–C1–Pd1 and O1–N2–Pd1 is 5.7°.

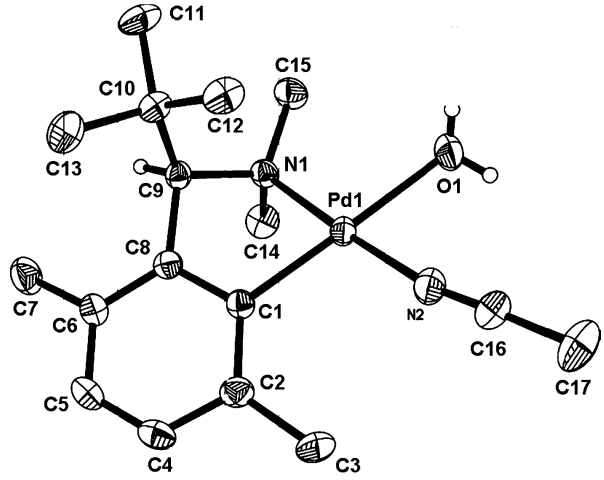


Figure 6. Molecular structure of complex (*R*)-**12**.

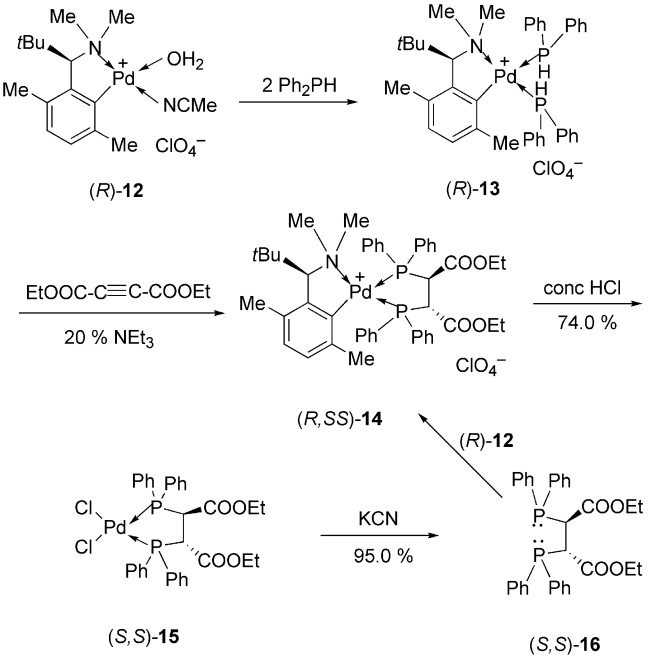
Table 4. Selected bond lengths [Å] and angles [°] for complex (*R*)-**12**.

Pd1–C1	1.989(2)	Pd1–N2	2.015(2)
Pd1–N1	2.052(1)	Pd1–O1	2.207(2)
C1–Pd1–N2	100.2(7)	C1–Pd1–N1	81.7(6)
N2–Pd1–N1	176.1 (6)	C1–Pd1–O1	173.3(7)
N2–Pd1–O1	85.3(6)	N1–Pd1–O1	93.1(6)
C2–C1–Pd1	127.5(1)	C8–C1–Pd1	112.2(1)

Asymmetric Hydrophosphanation Reaction between Diphenylphosphane and Diethyl Acetylenedicarboxylate Promoted by Chiral Palladium Complex (*R*)-2

To evaluate the stereoselectivity of the new palladacycle, the asymmetric hydrophosphanation reaction between diphenylphosphane and diethyl acetylenedicarboxylate promoted by palladacycle (*R*)-**2** was investigated.

As illustrated in Scheme 4, two equivalents of diphenylphosphane ligand was allowed to coordinate to complex (*R*)-**12** in dichloromethane to yield complex (*R*)-**13**, the ^{31}P NMR spectrum of which showed a pair of doublets at δ = –14.8 and 2.0 ppm ($J_{P,P}$ = 42.6 Hz). The hydrophosphanation reaction between diphenylphosphane and diethyl acetylenedicarboxylate was carried out at –78 °C in the presence of 20% equivalent of NEt_3 in dichloromethane. The reaction was monitored by ^{31}P NMR spectroscopy and was found to be complete in 12 h. The ^{31}P NMR spectrum of the reaction mixture in $CDCl_3$ exhibited only one pair of doublets and the resonances were observed at δ = 30.2 and 39.5 ppm ($J_{P,P}$ = 40.5 Hz). This indicated that only one isomer was generated in the hydrophosphanation reaction. However, the cationic product could not be crystallized from a series of solvent systems. Hence a dichloromethane solution of this complex was subsequently treated with concentrated HCl to remove the amine auxiliary, chemoselectively giving dichlorido complex (*S*,*S*)-**15**, which was confirmed by X-ray analysis.



Scheme 4.

In $CDCl_3$, dichlorido palladium complex (*S*,*S*)-**15** exhibited a sharp singlet at δ = 57.7 ppm when monitored by ^{31}P NMR spectroscopy. Crystallization of the dichlorido complex from dichloromethane/diethyl ether resulted in the formation of light-yellow-colored crystals. The molecular structure and the absolute stereochemistry of complex (*S*,*S*)-**15** was determined by X-ray crystallography. There were two crystallographically distinguishable molecules in the asymmetrical unit with the same stereochemistry and only one of them is depicted in Figure 7. Selected bond lengths and angles are given in Table 5. The absolute stereochemistry at C29 and C29A were established to be *S* and both the ester substituents on the chiral carbon centers were in the sterically favorable equatorial position as predicted.

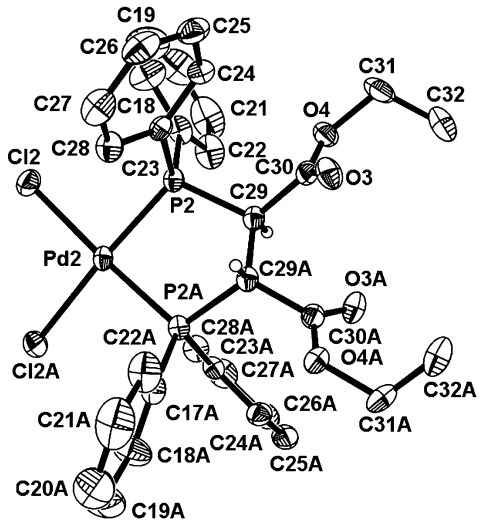


Figure 7. Molecular structure of complex (*S*,*S*)-**15**.

Table 5. Selected bond lengths [Å] and angles [°] for complex (*S*,*S*)-**15**.

Molecule A		Molecule B	
Pd1–P1A	2.233(6)	Pd2–P2	2.229(6)
Pd1–P1	2.233(6)	Pd2–P2A	2.229(6)
Pd1–Cl1	2.355(6)	Pd2–Cl2A	2.348(7)
Pd1–Cl1A	2.355(6)	Pd2–Cl2	2.348(7)
P1A–Pd1–P1	87.4(3)	P2–Pd2–P2A	87.9(3)
P1A–Pd1–Cl1	173.6(2)	P2–Pd2–Cl2A	176.3(2)
P1–Pd1–Cl1	89.0(2)	P2A–Pd2–Cl2A	88.9(2)
P1A–Pd1–Cl1A	89.0(2)	P2–Pd2–Cl2	88.9(2)
P1–Pd1–Cl1A	173.6(2)	P2A–Pd2–Cl2	176.3(3)
Cl1–Pd1–Cl1A	95.1(3)	Cl2A–Pd2–Cl2	94.5(3)

It needs to be noted that optically active diphosphane ligand (*S*,*S*)-**16** could be stereospecifically liberated from complex (*S*,*S*)-**15** by treating the dichlorido complex with aqueous potassium cyanide, liberating compound (*S*,*S*)-**16** as an air-sensitive ligand in 95.0% yield, $[\alpha]_D$ = +280 (*c* = 0.5, dichloromethane), δ = –6.4 ppm (^{31}P NMR, $CDCl_3$). The optical purity of free ligand (*S*,*S*)-**16** was confirmed by the quantitative recoordination of isomer (*R*,*SS*)-**14** from the liberated ligand and complex (*R*)-**12** (Scheme 4). In $CDCl_3$, the ^{31}P NMR spectrum of the crude product exhibited only a pair of doublet signals at δ = 30.2 and 39.5 ppm ($J_{P,P}$ = 40.5 Hz). These signals are identical to those recorded for sole diastereomer (*R*,*SS*)-**14**, which was generated directly from the asymmetric hydrophosphanation reaction. As a further test of the optical purity of the liberated ligand, liberated free ligand (*S*,*S*)-**16** was recoordinated to equally accessible isomer (*S*)-**12**. The ^{31}P NMR spectrum of the crude product in $CDCl_3$ exhibited only a pair of doublets at δ = 45.0 and 34.6 ppm ($J_{P,P}$ = 43.0 Hz). The chemical shifts of these signals were different from the signals for the sole product that was generated from the original hydrophosphanation reaction. Hence, it could be confirmed that liberated diphosphane (*S*,*S*)-**16** is optically pure, and in the asymmetric hydrophosphanation reaction only isomer (*R*,*SS*)-**14** was generated in the presence of new chiral palla-

dacycle (*R*)-**2**. When the widely used naphthylethylamine auxiliary (*R*)-**1** was employed for the asymmetric hydrophosphanation reaction between diphenylphosphane and dimethyl acetylenedicarboxylate under the same reaction condition, two diastereomers were formed in a 1:6 ratio.[7c]

Conclusions

In this article, novel palladacycle **2** was readily prepared from *p*-xylene and then resolved through the separation of its (*S*)-prolinate diastereomeric derivatives. The ability of the newly synthesized palladacycle was demonstrated in the preparation of a new diester-substituted diphosphane ligand through a chiral palladacycle (*R*)-**12** promoted asymmetric hydrophosphanation reaction, which proceeded with excellent selectivity. The superiority of this chiral palladacycle was similarly exhibited when it was used in the preparation of a range of chiral functionalized phosphanes.[13] Further exploration of this novel palladacycle, for example chiral catalysts for asymmetric reactions and resolving agents for chiral ligands, is in progress in our laboratory.

Experimental Section

General: ^{1}H and ^{13}C NMR spectroscopy were performed with Bruker Avance 300, 400, and 500 NMR spectrometers. Multiplicities are given as: s (singlet); br. s (broad singlet), d (doublet), t (triplet), q (quartet), dd (doublets of doublet), m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n* H. Coupling constants are reported as a *J* value in Hz. Nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ = 0.0 ppm) and relative to the signal of [D]chloroform (δ = 77.00 ppm, triplet). 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 with a Thermo Finnigan MAT 95 XP mass spectrometer in the EI mode and a Waters Q-Tof Premimer Mass Spectrometer with ESI mode. Infrared spectra were recorded with a Shimadzu IR Prestige-21, either neat or in $CHCl_3$. Melting points were determined with a SRS-Optimelt MPA-100 apparatus. Optical rotations were measured with a 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.

Caution: Perchlorate salts of metal complexes are potentially explosive compounds and should be handled with care.[14] Care should be taken in handling highly toxic cyanide compounds and azide compounds.

1-Isobutyryl-2,5-dimethylbenzene (4): An isobutyryl chloride (5.30 mL, 50.0 mmol) dichloromethane solution was added to a suspension of anhydrous $AlCl_3$ (7.34 g, 55.0 mmol) in the same solvent (30 mL). A solution of *p*-xylene **3** (5.30 g, 50.0 mmol) was then added dropwise to the mixture. The orange mixture was allowed to stir at room temperature for 3 h and then poured into a mixture of ice water and concentrated HCl (40 mL) and stirred for 10 min. The mixture was extracted with dichloromethane. The organic layers were combined, washed with H_2O, and dried ($MgSO_4$). Removal of the solvent gave product **4** as a yellow oil (8.18 g, 93.0%). IR (NaCl, neat): $\tilde{\nu}$ = 1782 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CHC*H*$_3$), 2.35 (s, 3 H, aryl-C*H*$_3$), 2.37 (s, 3 H, aryl-C*H*$_3$), 3.30–3.37 (m, $^3J_{H,H}$ = 6.8 Hz, 1 H, C*H*CH$_3$), 7.10–7.15 (m, 2 H, aromatic protons), 7.29 (s, 1 H, aromatic proton) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.55 (s, CH*C*H$_3$), 20.21 (s, C_6H_3*C*H$_3$), 20.95 (s, C_6H_3*C*H$_3$), 38.77 (s, *C*HCH$_3$), 127.91 (s, aryl-C), 131.26 (s, aryl-C), 131.47 (s, aryl-C), 134.17 (s, aryl-C), 135.00 (s, aryl-C), 138.68 (s, aryl-C), 209.53 (s, C=O) ppm. HRMS (EI): calcd. for $C_{12}H_{16}O$ 176.1196; found 176.1191.

1-(2,5-Dimethylphenyl)-2,2-dimethylpropan-1-one (5): A solution of compound **4** (16.6 g, 94.4 mmol) in dry THF (100 mL) was added dropwise to a 60% NaH (4.32 g, 108 mmol) solution in the same solvent under an atmosphere of nitrogen, and the pale-yellow solution was heated at reflux for 1 h. The orange-brown solution was cooled to room temperature and CH_3I (15.0 mL, 188 mmol) was added dropwise. The mixture was heated at 50 °C for 1 h then cooled to 0 °C. Ice water was added to quench the excess amount of NaH, and the organic phase was extracted with diethyl ether, washed with H_2O, and dried ($MgSO_4$). Removal of the solvent gave product **5** as a yellow oil (13.9 g, (77.9%). IR (NaCl, neat): $\tilde{\nu}$ = 1685 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (s, 9 H, CC*H*$_3$), 2.18 (s, 3 H, aryl-C*H*$_3$), 2.31 (s, 3 H, aryl-C*H*$_3$), 6.92 (s, 1 H, aromatic proton), 7.04–7.09 (m, 2 H, aromatic protons) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.33 (s, C_6H_3*C*H$_3$), 21.10 (s, C_6H_3*C*H$_3$), 27.25 (s, COC*C*H$_3$), 45.04 (s, CO*C*CH$_3$), 124.94 (s, aryl-C), 129.25 (s, aryl-C), 130.58 (s, aryl-C), 134.33 (s, aryl-C), 140.99 (s, aryl-C), 215.19 (s, C=O) ppm. HRMS (ESI): calcd. for $C_{13}H_{19}O$ [M + H]$^+$ 191.1436; found 191.1437.

1-(2,5-Dimethylphenyl)-2,2-dimethylpropan-1-ol [(±)-6]: A suspension of compound **5** (13.9 g, 73.5 mmol) in ethanol (100 mL) was treated with $NaBH_4$ (5.56 g, 147 mol) in the same solvent and allowed to stir overnight at room temperature followed by treatment with dilute NaOH solution. The resulting clear solution was concentrated under vacuum and extracted with dichloromethane. The organic layers were combined, washed with H_2O, and dried ($MgSO_4$). Removal of the solvent gave product (±)-**6** as a yellow oil (12.4 g, 87.5%). IR (NaCl, neat): $\tilde{\nu}$ = 3454 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.97 (s, 9 H, CC*H*$_3$), 1.72 (s, 1 H, OH), 2.31 (s, 3 H, aryl-C*H*$_3$), 2.33 (s, 3 H, aryl-C*H*$_3$), 4.75 (d, $^3J_{H,H}$ = 3.5 Hz, 1 H, C*H*), 6.98 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, aromatic proton), 7.02 (d, $^3J_{H,H}$ = 7.7 Hz, 1 H, aromatic proton), 7.29 (s, 1 H, aromatic proton) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.00 (s, C_6H_3*C*H$_3$), 21.28 (s, C_6H_3*C*H$_3$), 26.13 (s, *C*H$_3$CCHOH), 36.89 (s, CH$_3$*C*CHOH), 76.75 (s, CH$_3$C*C*HOH), 127.81 (s, aryl-C), 128.16 (s, aryl-C), 130.14 (s, aryl-C), 132.67 (s, aryl-C), 134.77 (s, aryl-C), 140.67 (s, aryl-C) ppm. HRMS (ESI): calcd. for $C_{13}H_{21}O$ [M + H]$^+$ 192.1592; found 192.1603.

2-(1-Azido-2,2-dimethylpropyl)-1,4-dimethylbenzene [(±)-7]: A mixture of compound (±)-**6** (5.80 g, 30.0 mmol) and sodium azide (3.00 g, 45.0 mmol) in chloroform (30.0 mL) was cooled to below 0 °C. A solution of trifluoroacetic acid (18 mL) in chloroform (15 mL) was added slowly. The mixture was left to stir overnight at ambient temperature and a dilute NaOH solution was added to pH 7. The organic layer was separated, washed with H_2O, and dried ($MgSO_4$). Removal of the solvent gave product (±)-**7** as a yellow oil (6.23 g, 95.1%). IR (NaCl, neat): $\tilde{\nu}$ = 2096 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (s, 9 H, CC*H*$_3$), 2.40 (s, 3 H, aryl-C*H*$_3$), 2.41 (s, 3 H, aryl-C*H*$_3$), 4.70 (s, 1 H, C*H*), 7.05–7.13 (m,

2 H, aromatic protons), 7.22 (s, 1 H, aromatic proton) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.08 (s, $C_6H_3CH_3$), 21.26 (s, $C_6H_3CH_3$), 26.57 (s, CH_3CCHN_3), 37.01 (s, CH_3CCHN_3), 71.20 (s, CH_3CCHN_3), 128.41 (s, aryl-C), 128.91 (s, aryl-C), 130.42 (s, aryl-C), 133.22 (s, aryl-C), 135.09 (s, aryl-C), 136.00 (s, aryl-C) ppm. HRMS (EI): calcd. for $C_{13}H_{19}$ [M – N_3] 175.1481; found 175.1477.

1-(2,5-Dimethylphenyl)-2,2-dimethylpropan-1-amine [(±)-8]: A solution of compound (±)-**7** (5.30 g, 24.4 mmol) in dry THF (50 mL) was added dropwise to a stirred solution of LAH (1.82 g, 48.0 mmol) in the same solvent (100 mL) at 0 °C. The reaction was then heated to reflux for 3 h and then cooled to 0 °C. The excess amount of LAH was quenched by consecutive addition of cold ethyl acetate and ice water. The granular precipitate was removed by filtration under vacuum and the filtrate was dried ($MgSO_4$). Removal of the solvent gave amine product (±)-**8** as a light-yellow oil (3.98 g, 85.4%). IR (NaCl, neat): $\tilde{\nu}$ = 1215, 3447 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (s, 9 H, CCH_3), 1.51 (br. s, 2 H, N*H*), 2.37 (s, 6 H, aryl-CH_3), 4.09 (s, 1 H, C*H*), 6.99 (dd, $^4J_{H,H}$ = 1.6 Hz, $^3J_{H,H}$ = 7.7 Hz, 1 H, aromatic proton), 7.05 (d, $^3J_{H,H}$ = 7.7 Hz, 1 H, aromatic proton), 7.31 (s, 1 H, aromatic proton) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.26 (s, $C_6H_3CH_3$), 21.30 (s, $C_6H_3CH_3$), 26.64 (s, CH_3CCHN), 36.30 (s, CH_3CCHN), 58.60 (s, CH_3CCHN), 127.13 (s, aryl-C), 128.08 (s, aryl-C), 130.08 (s, aryl-C), 132.86 (s, aryl-C), 134.63 (s, aryl-C), 142.30 (s, aryl-C) ppm. HRMS (ESI): calcd. for $C_{13}H_{22}N$ [M + H]$^+$ 192.1752; found 192.1750.

1-(2,5-Dimethylphenyl)-*N*,*N*,2,2-tetramethylpropan-1-amine [(±)-9]: A solution of compound (±)-**8** (13.2 g, 69.1 mmol) in formic acid (24 mL) was treated with formaldehyde (35 mL) at 0 °C. The reaction mixture was heated to 100 °C for 6 h and then cooled to room temperature. Concentrated HCl (10 mL) was added, and the mixture was stirred for 15 min. After removal of the solvent under vacuum, the sticky residual oil was treated with NaOH solution to pH 14, and the liberated amine was extracted with dichloromethane. The organic layers were combined and dried ($MgSO_4$). Removal of the solvent gave product (±)-**9** as a yellow oil (12.7 g, 84.0%). IR (NaCl, neat): $\tilde{\nu}$ = 1215 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (s, 9 H, CCH_3), 2.30 (s, 6 H, NCH_3), 2.34 (s, 3 H, aryl-CH_3), 2.35 (s, 3 H, aryl-CH_3), 3.56 (s, 1 H, C*H*), 6.98 (dd, $^4J_{H,H}$ = 1.3 Hz, $^3J_{H,H}$ = 7.7 Hz, 1 H, aromatic proton), 7.07 (d, $^3J_{H,H}$ = 7.7 Hz, 1 H, aromatic proton), 7.25 (s, 1 H, aromatic proton) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.00 (s, $C_6H_3CH_3$), 21.45 (s, $C_6H_3CH_3$), 29.18 (s, CH_3CCHN), 36.28 (s, CH_3CCHN), 45.44 (s, CH_3N), 71.68 (s, CH_3CCHN), 126.92 (s, aryl-C), 129.37 (s, aryl-C), 130.25 (s, aryl-C), 134.07 (s, aryl-C), 134.26 (s, aryl-C), 137.94 (s, aryl-C) ppm. HRMS (ESI): calcd. for $C_{15}H_{26}N$ [M + H]$^+$ 220.2065; found 220.2059.

(±)-Di-μ-chloridobis{1-[1-(dimethylamino)-2,2-dimethylpropyl]-2,5-dimethyl-6-phenyl-*C*,*N*}dipalladium(II) [(±)-2]: A mixture of palladium(II) chloride (10.3 g, 58.7 mmol) and lithium chloride (9.24 g, 220 mmol) in methanol (100 mL) was stirred at room temperature for 3 h. Sodium acetate trihydrate (8.02 g, 59.0 mmol) was then dissolved into the solution followed by the addition of compound (±)-**9** (12.7 g, 58.0 mmol). The resulting mixture was stirred at room temperature for 5 h and then filtered through Celite. The filtrate was evaporated under vacuum, and the brown residue was dissolved in dichloromethane. The resulting solution was washed with H_2O, dried ($MgSO_4$), and concentrated. The crude product was purified by chromatography (silica gel; dichloromethane/hexane, 1:1) to afford the pure product (14.2 g, 67.9%). M.p. 129–130 °C (dec.). $C_{30}H_{48}Cl_2N_2Pd_2$ (720.46): calcd. C 50.01, H 6.72, N 3.89; found C 50.05, H 6.72, N 3.26. IR (NaCl, $CHCl_3$): $\tilde{\nu}$ = 1217 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.64–1.69 (m, 18 H, CCH_3), 2.24 (s, 6 H), 2.51–2.57 (m, 12 H), 2.70–2.78 (m, 6 H), 3.48–3.50 (m, 2 H, C*H*), 6.58–6.66 (m, 4 H, aromatic protons) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.22 (s, CH_3), 24.97 (s, CH_3), 25.29 (s, CH_3), 25.38 (s, CH_3), 25.49 (s, CH_3), 30.90 (s, CH_3CCHN), 30.98 (s, CH_3CCHN), 36.51 (s, CH_3CCHN), 36.55 (s, CH_3CCHN), 36.65 (s, CH_3), 52.17 (s, CH_3), 52.46 (s, CH_3), 52.77 (s, CH_3), 52.94 (s, CH_3), 56.12 (s, CH_3), 56.17 (s, CH_3), 56.33 (s, CH_3), 87.99 (s, C*H*), 88.05 (s, C*H*), 126.64 (s, aryl-C), 126.75 (s, aryl-C), 127.96 (s, aryl-C), 128.08 (s, aryl-C), 128.24 (s, aryl-C), 130.41 (s, aryl-C), 130.53 (s, aryl-C), 130.59 (s, aryl-C), 139.66 (s, aryl-C), 139.88 (s, aryl-C), 140.05 (s, aryl-C), 140.05 (s, aryl-C), 144.08 (s, aryl-C), 144.31 (s, aryl-C), 144.55 (s, aryl-C), 148.61 (s, aryl-C), 148.65 (s, aryl-C), 148.70 (s, aryl-C) ppm.

(±)-Chlorido{1-[1-(dimethylamino)-2,2-dimethylpropyl]-2,5-dimethyl-6-phenyl-*C*,*N*}(triphenylphosphane-*P*)palladium(II) [(±)-10]: A dichloromethane solution of complex (±)-**2** (0.184 g, 0.250 mmol) and triphenylphosphane (0.131 g, 0.500 mmol) was stirred for 1 h at room temperature and then concentrated to ca. 5 mL. The residue liquid purified by column chromatography (silica gel, dichloromethane) to give a light-yellow powder that was recrystallized (dichloromethane/hexane) to afford (±)-**10** (0.28 g, 91.0%) as light-yellow crystals. M.p. 170–172 °C (dec.). $C_{33}H_{39}ClNPPd$ (621.15): calcd. C 63.67, H 6.31, N 2.25; found C 63.95, H 6.31, N 2.53. IR (NaCl, $CHCl_3$): $\tilde{\nu}$ = 1219 cm^{-1}. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 30.0 (s) ppm. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.46 (s, 9 H, CCH_3), 1.71 (s, 3 H, aryl-CH_3), 2.30 (s, 3 H, aryl-CH_3), 2.37 (s, $^4J_{P,H}$ = 1.5 Hz, 3 H, NCH_3), 2.90 (d, $^4J_{P,H}$ = 3.4 Hz, 3 H, NCH_3), 3.60 (d, $^4J_{P,H}$ = 5.2 Hz, 1 H, CC*H*), 6.41 (dd, $^3J_{H,H}$ = 7.6 Hz, $^5J_{P,H}$ = 1.4 Hz, 1 H, aromatic proton), 6.64 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, aromatic proton), 7.20–8.00 (m, 15 H, aromatic protons) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 23.46 (s, CH_3), 27.75 (d, $J_{C,P}$ = 10.8 Hz, CH_3), 31.68 (s, $NCHCCH_3$), 36.22 (s, $NCHCCH_3$), 51.29 (d, $J_{C,P}$ = 1.4 Hz, CH_3), 53.56 (d, $J_{C,P}$ = 2.7 Hz, CH_3), 88.38 (d, $J_{C,P}$ = 2.5 Hz, C*H*), 126.97 (s, aryl-C), 127.76 (br., aryl-C), 130.11 (br., aryl-C), 131.11 (s, aryl-C), 134.12 (br., aryl-C), 136.52 (br., aryl-C), 139.78 (d, $J_{C,P}$ = 5.3 Hz, aryl-C), 149.92 (d, $J_{C,P}$ = 1.3 Hz, aryl-C), 158.70 (d, $J_{C,P}$ = 3.8 Hz, aryl-C) ppm. HRMS (ESI): calcd. for $C_{33}H_{39}NPPd$ [M – Cl]$^+$ 586.1855; found 586.1874.

(S_C,S_C,S_N)-Prolinato-{1-[1-(dimethylamino)-2,2-dimethylpropyl]-2,5-dimethyl-6-phenyl-*C*,*N*}palladium(II) [(S_C,S_C,S_N)-11]: A methanol solution of sodium (*S*)-prolinate (0.83 g, 6.00 mmol) was added to a suspension of racemic dimer (±)-**2** (2.18 g, 3.00 mmol) in the same solvent (30 mL). The mixture was stirred at room temperature for 1 h, and the solvent was then removed under pressure. The residue was dissolved in dichloromethane, washed with H_2O, and dried ($MgSO_4$). Removal of the solvent gave a light yellow solid that was dissolved in a minimum amount of dichloromethane. Slow addition of diethyl ether resulted in the crystallization of less-soluble diastereomer (S_C,S_C,S_N)-**11** as yellow needle-like crystals (1.01 g, 77.0%). M.p. 185–187 °C (dec.). $[a]_D$ = +246, $[a]_{578}$ = +256, $[a]_{546}$ = +292, $[a]_{436}$ = +562, $[a]_{365}$ = +890 (*c* = 0.5, dichloromethane). $C_{20}H_{32}N_2O_2Pd$ (438.15): calcd. C 54.73, H 7.35, N 6.38; found C 54.75, H 7.79, N 6.42. IR (NaCl, $CHCl_3$): $\tilde{\nu}$ = 1610, 1110, 1182, 1219 cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.51 (s, 9 H, CCH_3), 1.63–1.73 (m, 1 H, $CHCH_2$), 1.96–2.04 (m, 1 H, $CHCH_2$), 2.13–2.24 (m, 2 H, $CH_2CH_2CH_2$), 2.29 (s, 3 H, aryl-CH_3), 2.38 (s, 3 H, aryl-CH_3), 2.56 [s, 3 H, $NCH_{3(ax)}$], 2.82 [s, 3 H, $NCH_{3(eq)}$], 3.19–3.31 (m, 2 H, $NHCH$, $NHCH_2$), 3.56 (s, 1 H, CC*H*), 4.02–4.07 (m, 1 H, $NHCH_2$), 4.20 (br. s, 1 H, N*H*), 6.67–6.72 (m, 2 H, aromatic protons) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.79 (s, CH_3), 23.78 (s, CH_3), 25.03 (s, CH_2), 29.75 (s, CH_2), 30.09 (s, CH_3CCHN), 35.80 (s, CCH_3), 50.70 (s, CH_3), 53.26 (s, CH_2), 55.12 (s, CH_3), 64.92 (s, NCH), 85.97 (s, $COCH$), 126.00 (s, aryl-C),

127.42 (s, aryl-C), 131.05 (s, aryl-C), 137.96 (s, aryl-C), 147.14 (s, aryl-C), 149.51 (s, aryl-C), 180.17 (s, C=O) ppm. HRMS (ESI): calcd. for $C_{20}H_{33}N_2O_2Pd$ [M + H]$^+$ 439.1577; found 439.1581.

(R_C,S_C,S_N)-Prolinato-{1-[1-(dimethylamino)-2,2-dimethylpropyl]-2,5-dimethyl-6-phenyl-*C*,*N*}palladium(II) [(R_C,S_C,S_N)-11]: The mother liquor of isomer (S_C,S_C,S_N)-**11** was evaporated to dryness, and the residue was dissolved in a minimum amount of $CHCl_3$. The less-soluble diastereomer, (R_C,S_C,S_N)-**11**, was crystallized by slow addition of diethyl ether as pale-yellow feather-like crystals (0.98 g, 75.0%). M.p.182–184 °C (dec.). $[\alpha]_D$ = –32, $[\alpha]_{578}$ = –36, $[\alpha]_{546}$ = –26, $[\alpha]_{436}$ = +22, $[\alpha]_{365}$ = +346 (*c* = 0.5, dichloromethane). $C_{20}H_{32}N_2O_2Pd$ (438.15): calcd. C 54.73, H 7.35, N 6.38; found C 54.75, H 7.79, N 6.42. IR (NaCl, $CHCl_3$): $\tilde{\nu}$ = 1610, 1110, 1182, 1219 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.47 (s, 9 H, CCH_3), 1.70–1.87 (m, 3 H, $CH_2CH_2CH_2$, NCH_2), 2.27 (s, 3 H, aryl-CH_3), 2.34 (s, 3 H, aryl-CH_3), 2.39–2.43 (m, 1 H, CHCH_2), 2.64 [s, 3 H, NC$H_{3(ax)}$], 2.74 [s, 3 H, NC$H_{3(eq)}$], 3.16–3.23 (m, 1 H, CHCH_2), 3.52–3.53 (m, 1 H, NHCH_2), 3.55 (s, 1 H, CC*H*), 3.80 (br. s, 1 H, N*H*), 4.14–4.17 (m, 1 H, COC*H*), 6.67–6.71 (m, 2 H, aromatic protons) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.02 (*C*H_2, *C*H_3), 24.43 (s, *C*H_3), 28.90 (s, *C*H_2), 30.33 (s, *C*H_3CCHN), 36.23 (s, *C*CH_3), 50.84 (s, *C*H_2), 51.01 (s, *C*H_3), 55.69 (s, CH_3*C*CHN), 67.22 (s, *C*H), 86.06 (s, *C*H), 126.46 (s, aryl-C), 127.15 (s, aryl-C), 131.31 (s, aryl-C), 138.02 (s, aryl-C), 145.63 (s, aryl-C), 150.03 (s, aryl-C), 177.80 (s, C=O) ppm. HRMS (ESI): calcd. for $C_{20}H_{33}N_2O_2Pd$ [M + H]$^+$ 439.1577; found 439.1581.

(*S*)-Di-μ-chloridobis{1-[1-(dimethylamino)-2,2-dimethylpropyl]-2,5-dimethyl-6-phenyl-*C*,*N*}dipalladium(II), (*S*)-2: A solution of diastereomer (S_C,S_C,S_N)-**11** (1.01 g, 2.30 mmol) in dichloromethane (15 mL) was treated with aqueous HCl (1 M, 20 mL). After vigorous stirring for 45 min, the organic layer was separated, washed with H_2O, and dried ($MgSO_4$). Removal of the solvent and purification by column chromatography (dichloromethane) gave the product as a light yellow solid (0.78 g, 94.0%). $[\alpha]_D$ = +210, $[\alpha]_{578}$ = +216, $[\alpha]_{546}$ = +228, (*c* = 0.5, dichloromethane). $C_{30}H_{48}Cl_2N_2Pd_2$ (718.13): calcd. C 50.01, H 6.72, N 3.89; found C 50.26, H 6.25, N 4.16. IR (NaCl, $CHCl_3$): $\tilde{\nu}$ = 1217 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.65–1.67 (m, 18 H, CCH_3), 2.22–2.23 (m, 6 H), 2.50–2.56 (m, 12 H), 2.71–2.73 (m, 6 H), 3.47–3.49 (m, 2 H, C*H*CH_3), 6.56–6.64 (m, 4 H, aromatic protons) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.00 (s, *C*H_3), 24.75 (s, *C*H_3), 25.27 (s, *C*H_3), 30.76 (s, *C*H_3), 36.34 (s, 1 *C*), 36.43 (s, 1 *C*), 52.25 (s, *C*H_3), 52.56 (s, *C*H_3), 53.35 (s, *C*H_3), 55.91 (s, *C*H_3), 56.12 (s, *C*H_3), 87.78 (s, *C*H), 126.43 (s, aryl-C), 126.55 (s, aryl-C), 127.75 (s, aryl-C), 128.03 (s, aryl-C), 130.33 (s, aryl-C), 130.39 (s, aryl-C), 139.67 (s, aryl-C), 139.81 (s, aryl-C), 144.10 (s, aryl-C), 144.34 (s, aryl-C), 148.44 (s, aryl-C), 148.49 (s, aryl-C) ppm. Optically pure (*R*)-**2** was prepared from (R_C,S_C,S_N)-**11** in a similar manner: $[\alpha]_D$ = –208, $[\alpha]_{578}$ = –214, $[\alpha]_{546}$ = –224 (*c* = 0.5, dichloromethane).

(*R*)-{1-[1-(Dimethylamino)-2,2-dimethylpropyl]-2,5-dimethyl-6-phenyl-*C*,*N*}palladium(II) Perchlorate [(*R*)-12]: Chiral palladium complex (*R*)-**2** (1.10 g, 1.53 mmol) was dissolved in acetonitrile (20 mL) and $AgClO_4{\cdot}H_2O$ (1.38 g, 6.11 mmol). The mixture was stirred vigorously in the dark at room temperature for 1 h. The mixture was filtered through Celite (to remove AgCl), and the filtrate was concentrated under vacuum. The resulting residue was dissolved in dichloromethane, washed with H_2O, and dried ($MgSO_4$). Removal of the solvent gave (*R*)-**12** (1.28 g, 87.0%) as a yellow powder, and light-yellow crystals were formed by slow evaporation of a (*R*)-**12** dichloromethane/hexane solution. M.p.128–130 °C (dec). $[\alpha]_D$ = –124, $[\alpha]_{578}$ = –128, $[\alpha]_{546}$ = –148 (*c* = 0.5, dichloromethane). $C_{17}H_{29}ClN_2O_5Pd$ (482.08): calcd. C 42.25, H 6.05, N 5.80; found C 42.52, H 5.93, N 6.13. IR (NaCl, $CHCl_3$): $\tilde{\nu}$ = 2299, 3398 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.54 (s, 9 H, CCH_3), 2.27 (s, 3 H, aryl-CH_3), 2.39 (s, 6 H, aryl-CH_3, NCCH_3), 2.61 [s, 3 H, NC$H_{3(ax)}$], 2.77 [s, 3 H, NC$H_{3(eq)}$], 3.06 (br. s, 2 H, OH_2), 3.53 (s, 1 H, CC*H*), 6.78–6.89 (m, 2 H, aromatic protons) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 3.36 (s, *C*H_3), 22.67 (s, *C*H_3), 24.78 (s, *C*H_3), 30.11 (s, NCHC*C*H_3), 36.26 (s, NCH*C*CH_3), 50.66 (s, *C*H_3), 55.74 (s, *C*H_3), 87.36 (s, *C*H), 122.55 (s, CN), 127.63 (s, aryl-C), 128.18 (s, aryl-C), 131.87 (s, aryl-C), 137.92 (s, aryl-C), 140.97 (s, aryl-C), 148.56 (s, aryl-C) ppm. HRMS (ESI): calcd. for $C_{17}H_{29}N_2OPd$ [M – ClO_4]$^+$ 383.1315; found 383.1322.

(*S*,*S*)-Dichlorido[diethyl-1,2-bis(diphenylphosphanyl)ethane Dicarboxylate]palladium(II) [(*S*,*S*)-15]: A mixture of complex (*R*)-**12** (0.10 g, 0.20 mmol) and diphenylphosphane (74.0 mg, 0.40 mmol) in dichloromethane was stirred under an atmosphere of nitrogen at room temperature for 1 h. A solution of diethyl acetylenedicarboxylate (34.0 mg, 0.20 mmol) and triethylamine (4.0 mg, 0.04 mmol) in dichloromethane (5 mL) was added dropwise to the reaction above, and the resulting mixture was stirred at –78 °C overnight. After removal of the solvent, yellow-colored solid (*R*,*SS*)-**14** was obtained. $[\alpha]_D$ = –22, $[\alpha]_{578}$ = –24, $[\alpha]_{546}$ = –26, $[\alpha]_{436}$ = –26 (*c* = 0.5, dichloromethane). IR (NaCl, $CHCl_3$): $\tilde{\nu}$ = 1377, 1724 cm^{-1}. ^{31}P NMR (121 MHz, $CDCl_3$) δ = 39.5 (d, $J_{P,P}$ = 40.5 Hz), 30.2 (d, $J_{P,P}$ = 40.5 Hz) ppm. ^{1}H NMR (500 MHz $CDCl_3$): δ = 0.78 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, $COOCH_2CH_3$), 0.82 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, $COOCH_2CH_3$), 1.41 (s, 9 H, CCH_3), 1.86 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 2.73 (s, 3 H, CH_3), 3.49–3.55 (m, 1 H, PC*H*), 3.60–3.66 (m, 1 H, PC*H*), 3.69 (d, $^4J_{P,H}$ = 6.2 Hz, 1 H, NC*H*), 3.73–3.86 (m, 4 H, $COOCH_2CH_3$), 6.51–6.53 (m, 1 H, aromatic proton), 6.68 (d, $^3J_{H,H}$ = 7.7 Hz, 1 H, aromatic proton), 7.18–8.20 (m, 20 H, aromatic protons) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.39 (d, $J_{C,P}$ = 3.6 Hz, *C*H_3), 14.12 (s, *C*H_3), 22.64 (s, *C*H_3), 23.78 (s, *C*H_3), 29.55 (dd, $J_{C,P}$ = 3.6 Hz, $J_{C,P}$ = 9.4 Hz, *C*H), 31.25 (s, *C*H_3CCH), 35.48 (s, CH_3*C*CH), 45.36 (dd, $J_{C,P}$ = 11.8 Hz, $J_{C,P}$ = 15.8 Hz, *C*H), 54.28 (d, $J_{C,P}$ = 4.1 Hz, *C*H_3), 56.98 (d, $J_{C,P}$ = 2.5 Hz, *C*H_3), 62.21 (s, *C*H_2), 62.74 (s, *C*H_2), 91.00 (s, CH_3*C*CH), 123.25, 123.86, 125.74 (d, $J_{C,P}$ = 3.7 Hz, aryl-C), 126.23 (d, $J_{C,P}$ = 3.5 Hz, aryl-C), 127.40 (d, $J_{C,P}$ = 3.6 Hz, aryl-C), 127.74 (d, $J_{C,P}$ = 7.0 Hz, aryl-C), 128.32 (d, $J_{C,P}$ = 11.1 Hz, aryl-C), 128.43 (s, aryl-C), 128.54 (s, aryl-C), 128.59 (s, aryl-C), 128.67 (s, aryl-C), 128.84 (br., aryl-C), 128.94 (br., aryl-C), 130.54 (d, $J_{C,P}$ = 10.9 Hz, aryl-C), 131.85 (br., aryl-C), 131.97 (d, $J_{C,P}$ = 2.6 Hz, aryl-C), 132.04 (d, $J_{C,P}$ = 2.0 Hz, aryl-C), 132.23 (d, $J_{C,P}$ = 6.6 Hz, aryl-C), 133.36 (d, $J_{C,P}$ = 1.9 Hz, aryl-C), 133.47 (d, $J_{C,P}$ = 2.2 Hz, aryl-C), 134.81 (d, $J_{C,P}$ = 14.8 Hz, aryl-C), 136.32 (br., aryl-C), 139.03 (dd, $J_{C,P}$ = 3.2 Hz, $J_{C,P}$ = 6.5 Hz, aryl-C), 149.10 (s, aryl-C), 165.20 (d, $J_{C,P}$ = 7.5 Hz), 166.30 (d, $J_{C,P}$ = 7.3 Hz), 167.11 (dd, $^3J_{C,P}$ = 7.4 Hz, $^2J_{C,P}$ = 26.1 Hz, CO), 167.90 (dd, $^3J_{C,P}$ = 5.6 Hz, $^2J_{C,P}$ = 19.2 Hz, CO) ppm. HRMS (ESI): calcd. for $C_{47}H_{56}NO_4P_2Pd$ [M – ClO_4]$^+$ 866.2719; found 866.2711. Concentrated hydrochloric acid (10 mL) was then added to complex (*R*,*SS*)-**14**, and the mixture was stirred vigorously overnight. The reaction mixture was washed with H_2O, dried ($MgSO_4$), and subsequently crystallized from dichloromethane and diethyl ether to give complex (*S*,*S*)-**15** as yellow crystals (0.11 g, 74.0%). M.p. 251–253 °C (dec). $[\alpha]_{436}$ = –138 (*c* = 0.5, dichloromethane). IR (NaCl, $CHCl_3$): $\tilde{\nu}$ = 1730 cm^{-1}. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 57.3 (s) ppm. ^{1}H NMR (300 MHz $CDCl_3$): δ = 0.91 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, $COOCH_2CH_3$), 3.86–3.92 (m, 4 H, $COOCH_2CH_3$), 4.18 (d, $^3J_{H,H}$ = 5.9 Hz, 2 H, PC*H*$COOCH_2CH_3$), 7.53–7.94 (m, 20 H, aromatic protons) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 13.28 (s, *C*H_3), 48.86 (t, $J_{C,P}$ = 22.3 Hz, *C*H), 62.34 (s, *C*H_2), 123.62 (d, $J_{C,P}$ =

Table 6. Crystallographic data for complexes (±)-**10**, (S_C,S_C,S_N)-**11**, (R_C,S_C,S_N)-**11**, (*R*)-**12**, and (*S*,*S*)-**15**.

	(±)-**10**	(S_C,S_C,S_N)-**11**	(R_C,S_C,S_N)-**11**	(*R*)-**12**	(*S*,*S*)-**15**
Formula	$C_{33}H_{39}ClNPPd$	$C_{20}H_{32}N_2O_2Pd$	$C_{21}H_{33}Cl_3N_2O_2Pd$	$C_{17}H_{29}ClN_2O_5Pd$	$C_{33}H_{34}Cl_4O_4P_2Pd$
Formula weight	622.47	438.88	558.24	483.27	804.74
Space group	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$C2$
Crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic	monoclinic
a [Å]	10.6581(3)	13.4831(4)	10.3779(3)	8.4659(2)	16.0113(4)
b [Å]	15.7791(5)	10.5946(3)	20.8123(8)	10.7872(3)	14.8142(4)
c [Å]	17.6760(5)	15.1086(5)	34.2018(12)	22.7291(6)	16.6228(5)
V [Å^3]	2972.67(15)	2050.72(11)	7387.2(4)	2075.70(9)	3551.99(17)
Z	4	4	12	4	4
T [K]	173(2)	223(2)	223(2)	173(2)	173(2)
$\rho_{calcd.}$ [g cm^{-3}]	1.391	1.421	1.506	1.546	1.505
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	0.790	0.920	1.098	1.051	0.949
Flack parameters	0.044(14)	0.03(5)	0.04(3)	0.001(16)	–0.009(13)
R_1 (obsd. data)[a]	0.0165	0.0468	0.0467	0.0208	0.0280
wR_2 (obsd. data)[b]	0.0418	0.1229	0.1079	0.0508	0.0661

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

2.0 Hz, aryl-C), 124.16 (d, $J_{C,P}$ = 2.0 Hz, aryl-C), 125.74 (d, $J_{C,P}$ = 1.5 Hz, aryl-C), 126.34 (d, $J_{C,P}$ = 1.7 Hz, aryl-C), 128.55 (m, aryl-C), 129.28 55 (m, aryl-C), 132.42 (s, *C*H$_3$), 133.45 (m, aryl-C), 133.71 (s, *C*H$_3$), 135.78 (m, aryl-C), 166.03 (dd, $^3J_{C,P}$ = 9.2 Hz, $^2J_{C,P}$ = 30.5 Hz, C=O) ppm.

Synthesis of (*S*,*S*)-16 by the Liberation of (*S*,*S*)-Diethyl-1,2-bis(diphenylphosphanyl)ethanedicarboxylate: A solution of complex (*S*,*S*)-**15** (20.0 mg) in dichloromethane (20 mL) was stirred vigorously with a saturated aqueous solution of KCN (0.50 g) for 1 h. The colorless organic layer was separated, washed with H_2O (3 × 20 mL), and dried ($MgSO_4$). Upon removal of the solvent, a white solid (14.0 mg, 95.0%) was obtained. $[\alpha]_D$ = +280 (*c* = 0.5, dichloromethane). ^{31}P NMR (121 MHz, $CDCl_3$): δ = –6.4 (s) ppm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, COOCH$_2$C*H*$_3$), 3.41–3.58 (m, 4 H, COOC*H*$_2$CH$_3$), 3.88 (d, $^3J_{H,H}$ = 4.1 Hz, 2 H, PC*H*COOEt), 7.23–7.86 (m, 20 H, aromatic protons) ppm.

Crystal Structure Determination of (±)-10, (S_C,S_C,S_N)-11, (R_C,S_C,S_N)-11, (*R*)-12, and (*S*,*S*)-15: Crystal data for all five complexes and a summary of the crystallographic analyses are given in Table 6. Diffraction data were collected with a Bruker X8 CCD diffractometer with Mo-K_α radiation (graphite monochromator). SADABS absorption corrections were applied. All non-hydrogen atoms were refined anisotropically, whereas 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.[15]

CCDC-728935 [for (±)-**10**], -728936 [for (*S*,*S*)-**15**], -728937 [for (R_C,S_C,S_N)-**11**], -728938 [for (*R*)-**12**], and -728939 [for (S_C,S_C,S_N)-**11**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) J. Vicente, I. Saura-Llamas, M. G. Palin, P. G. Jones, *J. Chem. Soc., Dalton Trans.* **1995**, 2535–2540; b) J. Albert, J. Granell, A. Luque, J. Minguez, R. Moragas, M. Font-Bardia, X. Solans, *J. Organomet. Chem.* **1996**, *522*, 87–95; c) Y. Fuchita, K. Yoshinaga, Y. Ikeda, J. Kinoshita-Kawashima, *J. Chem. Soc., Dalton Trans.* **1997**, 2495–2500; d) V. V. Dunina, L. G. Kuz′mina, M. Y. Kazakova, O. N. Gorunova, Y. K. Grishin, E. I. Kazakova, *Eur. J. Inorg. Chem.* **1999**, 1029–1039; e) B. Calmuschi, U. Englert, *Acta Crystallogr., Sect. C* **2002**, *58*, m545–m548; f) B. Calmuschi, A. Erik, U. Englert, *Acta Crystallogr., Sect. C* **2004**, *60*, m320–m323; g) J. Vicente, I. Saura-Llamas, D. Bautista, *Organometallics* **2005**, *24*, 6001–6004; h) J. Vicente, I. Saura-Llamas, J.-A. Garcia-Lopez, B. Calmuschi-Cula, D. Bautista, *Organometallics* **2007**, *26*, 2768–2776.

[2] For examples, see: a) S. Otsuka, A. Nakamura, T. Kano, K. Tani, *J. Am. Chem. Soc.* **1971**, *93*, 4301–4303; b) K. Tani, L. D. Brown, J. Ahmed, J. A. Ibers, M. Yokota, A. Nakamura, S. Otsuka, M. Yokota, *J. Am. Chem. Soc.* **1977**, *99*, 7976–7886; c) N. K. Roberts, S. B. Wild, *J. Am. Chem. Soc.* **1979**, *101*, 6254–6260; d) R. N. K. Roberts, S. B. Wild, *J. Chem. Soc., Dalton Trans.* **1979**, 2015–2021; e) D. G. Allen, G. M. McLaughlin, G. B. Robertson, W. L. Steffen, G. Salem, S. B. Wild, *Inorg. Chem.* **1982**, *21*, 1007–1014; f) S. Y. M. Chooi, S. Y. Siah, P.-H. Leung, K. F. Mok, *Inorg. Chem.* **1993**, *32*, 4812–4818; g) V. V. Dunina, E. B. Golovan, *Tetrahedron: Asymmetry* **1995**, *6*, 2747–2754; h) M. Pabel, A. C. Willis, S. B. Wild, *Tetrahedron: Asymmetry* **1995**, *6*, 2369–2374; i) M. Pabel, A. C. Willis, S. B. Wild, *Inorg. Chem.* **1996**, *35*, 1244–1249; j) A. Bader, M. Pabel, A. C. Willis, S. B. Wild, *Inorg. Chem.* **1996**, *35*, 3874–3877; k) J. Albert, J. M. Cadena, J. Granell, *Tetrahedron: Asymmetry* **1997**, *8*, 991–994; l) G. He, K. F. Mok, P.-H. Leung, *Organometallics* **1999**, *18*, 4027–4031; m) J. Albert, J. M. Cadena, J. Granell, G. Muller, J. I. Ordinas, D. Panyella, C. Puerta, C. Sanudo, P. Valerga, *Organometallics* **1999**, *18*, 3511–3518; n) J. Albert, J. M. Cadena, J. Granell, G. Muller, D. Panyella, C. Sañudo, *Eur. J. Inorg. Chem.* **2000**, 1283–1286; o) J. Albert, J. M. Cadena, S. Delgado, J. Granell, *J. Organomet. Chem.* **2000**, *603*, 235–239; p) J. Albert, R. Bosque, J. M. Cadena, J. R. Granell, G. Muller, J. I. Ordinas, *Tetrahedron: Asymmetry* **2000**, *11*, 3335–3343; q) E. Duran, E. Gordo, J. Granell, M. Font-Bardia, X. Solans, D. Velasco, F. Lopez-Calahorra, *Tetrahedron: Asymmetry* **2001**, *12*, 1987–1997; r) S. Chatterjee, M. D. George, G. Salem, A. C. Willis, *J. Chem. Soc., Dalton Trans.* **2001**, 1890–1896; s) J. Albert, R. Bosque, J. M. Cadena, S. Delgado, J. Granell, G. Muller, J. I. Ordinas, M. F. Bardia, X. Solans, *Chem. Eur. J.* **2002**, *8*, 2279–2287; t) J.-M. Camus, P. Roy-Garcia, J. Andrieu, P. Richard, R. Poli, *J. Organomet.*

Chem. **2005**, *690*, 1659–1668; u) J. Albert, J. Granell, G. Muller, *J. Organomet. Chem.* **2006**, *691*, 2101–2106.

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

[4] For examples, see: a) R. Schimdt, M. Cereghetti, B. Heiser, P. Schonholzer, H. J. Hausen, *Helv. Chim. Acta* **1988**, *71*, 897–929; b) R. Schimdt, J. Foricher, M. Cereghetti, P. Schonholzer, *Helv. Chim. Acta* **1991**, *74*, 370–389; c) J. S. Giovanett, C. M. Kelly, C. R. Landis, *J. Am. Chem. Soc.* **1993**, *115*, 4040–4057; d) W. McFarlane, J. D. Swarbrick, J. I. Bookham, *J. Chem. Soc., Dalton Trans.* **1998**, 3233–3238; e) G. Uccello-Barretta, R. Bernardini, R. Lazzaroni, P. Salvadori, *Org. Lett.* **2000**, *2*, 1795–1798.

[5] 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) R. Navarro, E. P. Urriolabeitia, C. Cativiela, M. D. Diaz-de-Villegas, M. P. Lopez, E. Alonso, *J. Mol. Catal. A* **1996**, *105*, 111–116; d) J. M. Longmire, X. Zhang, M. Shang, *Organometallics* **1998**, *17*, 4374–4379; e) M. A. Stark, C. J. Richards, *Tetrahedron Lett.* **1997**, *38*, 5881–5884; f) J. Vicente, I. Saura-Llamas, M. C. R. de Arellano, P. G. Jones, *Organometallics* **1999**, *18*, 2683–2693; g) J. Vicente, I. Saura-Llamas, C. Alcaraz, P. G. Jones, D. Bautisda, *Organometallics* **2002**, *21*, 3587–3595; h) W. E. Lindsell, D. D. Palmer, P. N. Preston, G. M. Rosair, R. V. H. Jones, A. J. Whitton, *Organometallics* **2005**, *24*, 1119–1133.

[6] a) P.-H. Leung, *Acc. Chem. Res.* **2004**, *37*, 169–177 and references cited therein; b) S.-K. Loh, G.-K. Tan, L. L. Koh, S. Selvaratnam, P.-H. Leung, *J. Organomet. Chem.* **2005**, *690*, 4933–4938; c) 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; d) M. Ma, S. A. Pullarkat, Y. Li, P.-H. Leung, *Inorg. Chem.* **2007**, *46*, 9488–9494; e) M. Ma, S. A. Pullarkat, Y. Li, P.-H. Leung, *J. Organomet. Chem.* **2008**, *693*, 3289–3294; f) M. Yuan, S. A. Pullarkat, C. H. Yeong, Y. Li, D. Krishnan, P.-H. Leung, *Dalton Trans.* **2009**, 3668–3670; g) 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.

[7] a) W.-C. Yeo, S. Y. Tee, H. B. Tan, G.-K. Tan, L. L. Koh, P.-H. Leung, *Inorg. Chem.* **2004**, *43*, 8102–8109; b) S. A. Pullarkat, D. Yi, Y. Li, G.-K. Tan, P.-H. Leung, *Inorg. Chem.* **2006**, *45*, 7455–7463; c) L. Tang, Y. Zhang, L. Ding, Y. Li, K.-F. Mok, W.-C. Yeo, P.-H. Leung, *Tetrahedron Lett.* **2007**, *48*, 33–35; d) Y. Zhang, S. A. Pullarkat, Y. Li, P.-H. Leung, *Inorg. Chem.* **2009**, *48*, 5535–5339; e) M. Yuan, S. A. Pullarkat, M. Ma, Y. Zhang, Y. Huang, Y. Li, A. Goel, P.-H. Leung, *Organometallics* **2009**, *28*, 780–786; f) F. Liu, S. A. Pullarkat, Y. Li, S. Chen, M. Yuan, Y. Li, P.-H. Leung, *Organometallics* **2009**, *28*, 3941–3946.

[8] B. H. Aw, S. Selvaratnam, P.-H. Leung, N. H. Rees, W. McFarlane, *Tetrahedron: Asymmetry* **1996**, *7*, 1753–1762.

[9] a) Y. Li, K.-H. Ng, S. Selvaratnam, G.-K. Tan, J. J. Vittal, P.-H. Leung, *Organometallics* **2003**, *22*, 834–842; b) J. K.-P. Ng, G.-K. Tan, J. J. Vittal, P.-H. Leung, *Inorg. Chem.* **2003**, *42*, 7674–7682; c) Y. Li, S. Selvaratnam, J. J. Vittal, P.-H. Leung, *Inorg. Chem.* **2003**, *42*, 3229–3236; d) J. K.-P. Ng, Y. Li, G.-K. Tan, L.-L. Koh, J. J. Vittal, P.-H. Leung, *Inorg. Chem.* **2005**, *44*, 9874–9886; e) J. K.-P. Ng, S. Chen, Y. Li, G.-K. Tan, L.-L. Koh, P.-H. Leung, *Inorg. Chem.* **2007**, *46*, 5100–5109; f) J. K.-P. Ng, S. Chen, G.-K. Tan, P.-H. Leung, *Eur. J. Inorg. Chem.* **2007**, *19*, 3124–3134; g) J. K.-P. Ng, S. Chen, G.-K. Tan, P.-H. Leung, *Tetrahedron: Asymmetry* **2007**, *18*, 1163–1169; h) Y. Ding, Y. Li, Y. Zhang, S. A. Pullarkat, P.-H. Leung, *Eur. J. Inorg. Chem.* **2008**, *11*, 1880–1891; i) Y. Ding, Y. Li, S. A. Pullarkat, S. L. Yap, P.-H. Leung, *Eur. J. Inorg. Chem.* **2009**, *2*, 267–276; j) Y. Ding, M. Chiang, S. A. Pullarkat, Y. Li, P.-H. Leung, *Organometallics* **2009**, *28*, 4358–4370.

[10] X. Jiang, C. Zhao, Y. Gong, *Huaxue Xuebao* **1988**, *46*, 900–907.

[11] D. Balderman, A. Kalir, *Synthesis* **1978**, 24–26.

[12] 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.

[13] Y. Huang, S. A. Pullarkat, M. Yuan, Y. Ding, Y. Li, P.-H. Leung, *Organometallics* **2010**, *29*, 536–542.

[14] W. C. Wolsey, *J. Chem. Educ.* **1973**, *50*, A335–A337.

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

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