DOI: 10.1002/ejic.200700171

Substituent Effects on the Stereoelectronic and Chemical Properties of a Novel Phosphapalladacycle

Joseph Kok-Peng Ng,[a] Shuli Chen,[b] Geok-Kheng Tan,[a] and Pak-Hing Leung*[b]

Keywords: Palladium / Phosphane ligands / Chirality / NMR spectroscopy / Substituent effects

A novel phosphapalladacycle was prepared by direct cyclopalladation of the ligand (diphenylmethyl)diphenylphosphane (**2**). The corresponding μ-chloro five-membered phosphapalladacycle **3** was obtained by heating a toluene solution of **2** and $Pd(OAc)_2$ followed by chloride ion metathesis. An optical resolution procedure was then employed by separation of the (*S*)-prolinato derivatives **4** by fractional crystallization followed by treatment with dilute hydrochloric acid to yield both enantiopodes of the dimers **3** in the optically active forms. The current phosphapalladacycle was noted to display different properties with respect to the analogous phosphapalladacycle prepared from (diphenylmethyl)di-*tert*-butylphosphane. For instance, the phosphapalladacycle based on the (diphenylmethyl)di-*tert*-butylphosphane was shown to be conformationally rigid. In contrast, the analogous five-membered phosphapalladacycle of phosphane **2** was noted to exist in both the δ and λ conformations in the solid state, while a flattened conformation was observed in solution. In addition, the (diphenylmethyl)di-*tert*-butylphosphane-based phosphapalladacycle was noted to exhibit a much more improved regioselectivity towards ancillary ligands such as (*S*)-prolinate and triphenylphosphane than **2**. Furthermore, the μ-chloro dimer **3** of the current palladacycle was shown to be lacking in thermodynamic stability of the Pd–C bond that was noted for the *t*Bu analogue. In contrast, the Pd–C bonds of dimer **3** were immediately ruptured in the presence of concentrated HCl to give rise to the binuclear complex **5**, in which the phosphane was coordinated in the η^1-P coordination mode.

Introduction

Metal complexes of phosphorus-based ligands have played central roles in organometallic and synthetic chemistry.[1] In particular, the chiral forms of these metal complexes have also continued to be invaluable as agents in catalytic asymmetric syntheses.[2] Suitable forms of these ligands may be transformed to give rise to palladacycles.[3–5] The latter (or cyclopalladated complexes) are a well-known class of compounds in organometallic chemistry, and they can be derived from ligands containing other heteroatom donors such as nitrogen and sulfur, apart from those of phosphorus. The syntheses and applications of many of these cyclopalladated complexes are currently being reported.[6] The properties of a ligand could be enhanced as a result of cyclopalladation. For instance, Lewis demonstrated that while a cyclopalladated triarylphosphite was effective as a catalyst for halogenating C=C bonds, the same task could not be accomplished by its non-cyclopalladated analogue.[7] Since then, the synthetic utilities of these systems as homogeneous catalysts were further illustrated.[3a–3j,5a–5e,8]

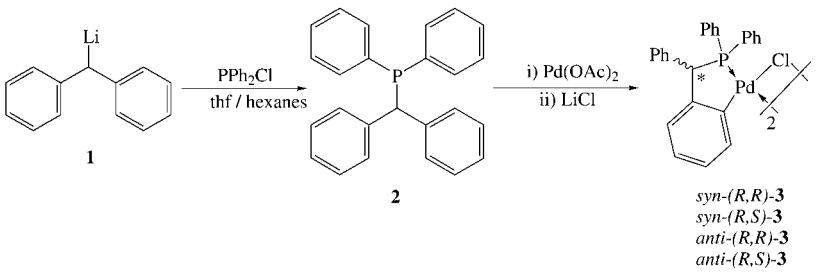
We have previously contributed to the field of palladacycle chemistry by the exploitation of chiral, nitrogen-based palladacycles for the syntheses of optically active phosphanes of various functionalities.[9] To further improve the synthetic efficiency of these invaluable phosphanes in terms of enhanced chemo-, regio-, diastereo- and enantioselectivities, it is essential to develop new variants of this palladacycle motif. Apart from modifying the organic framework of the cyclopalladated ligand,[8m,9d,9e] we have explored the possibility of replacing the original nitrogen atom with its phosphorus and arsenic congeners.[4] The work reported herein serves to describe the development and characteristics of a new phosphorus-based palladacycle that was prepared in the optically active form. The palladacycle was constructed from the ligand (diphenylmethyl)diphenylphosphane and reveals features that are characteristically different from that of the structurally analogous (diphenylmethyl)di-*tert*-butylphosphane.[10]

Results and Discussion

Synthesis of the Phosphapalladacycle in the Optically Active Form

The preparation of the prochiral phosphane **2** was based on the reported procedure that was applied to the synthesis

[a] Department of Chemistry, National University of Singapore
Kent Ridge, Singapore 119260
[b] Division of Chemistry and Biological Chemistry, Nanyang Technological University
Singapore 637616



Scheme 1. Synthesis of compounds **2** and **3**.

of its *t*Bu analogue,[11] i.e. treatment of (diphenylmethyl)-lithium (**1**) with the corresponding chlorodiphenylphosphane (Scheme 1), which afforded the product as a white solid. Earlier attempts had failed to synthesize **2** by the more common methods of halide displacement from either (a) chlorodiphenylphosphane with a Grignard reagent or (b) an alkyl halide by using sodium diphenylphosphanide, which was found to be efficient for structurally analogous phosphanes.[4] The structure of compound **2** was confirmed by the doublet resonance of the α-CH proton in the ^{1}H NMR spectrum ($CDCl_3$). This proton spin couples with the ^{31}P nucleus with $^2J_{P,H}$ = 6.8 Hz. Importantly, this doublet resonance is crucial as an indicator of the successful merging of the diphenylmethyl and diphenylphosphanyl skeletons.

As illustrated in Scheme 1, treatment of the phosphane **2** with palladium(II) acetate followed by chloride ion metathesis led to the chloro-bridged dimeric complex **3** of the phosphapalladacycle. Complex **3** was thus isolated as air-stable pale yellow blocks in 61% yield. The dimer was detected by ^{31}P NMR spectroscopy ($CDCl_3$) as a series of overlapping peaks at δ = 70.4–70.8 ppm at room temperature (300 K). However, upon cooling to 223 K, the resonance was reproduced as four resolved singlets at δ = 70.7, 70.8, 70.9 and 71.4 ppm. This supports the chiral and racemic nature of the phosphapalladacycle in solution, which is exemplified by the presence of the six equilibrating isomers, namely, the chiral *syn*- and *anti*-(*R*,*R*)/(*S*,*S*) and the achiral, *meso syn*- and *anti*-(*R*,*S*) isomers.

In the solid state, an X-ray diffraction study of **3** revealed that the complex was crystallized as the achiral, *meso-anti* isomer. The molecular structure is presented in Figure 1. The structure consists of a symmetrical plane that bisects the ClCl axis, each half of the dimer being the mirror image of the other. Moreover, the central four-membered {$Pd_2(\mu$-$Cl)_2$}cycle is flat, and its four atoms form a perfect plane. The stereogenic states of the two α-C atoms are manifested by the attachments of four different substituents. *ortho*-Palladation generates diastereotopicity on the two PPh rings. One of them is considered "axial", since its P1–C_{ipso} bond subtends an angle of 18.5° with the normal to the m.c.pl. (mean coordination plane), while the value of 62.4° applies to the equivalent bond of the "equatorial" PPh ring.

Addition of the chiral ligand, (*S*)-prolinate, to the dimer **3** gave rise to a mixture of two pairs of diastereomeric derivatives **4** (Scheme 2). The presence of the two extra isomers was a consequence of geometric (*E*,*Z*) isomerism resulting from the nonsymmetrical nature of the (*S*)-prolinate. Four singlets were therefore present in the ^{31}P NMR spectrum ($CDCl_3$). The racemic (and therefore chiral) nature of the phosphapalladacycle was emphasized by categorizing the four singlets into two pairs of resonances with overall equal intensities. These were observed at δ = 62.7, 71.0 and 64.4, 72.1 ppm with relative intensities of 4:9 and 3:10 correspondingly.

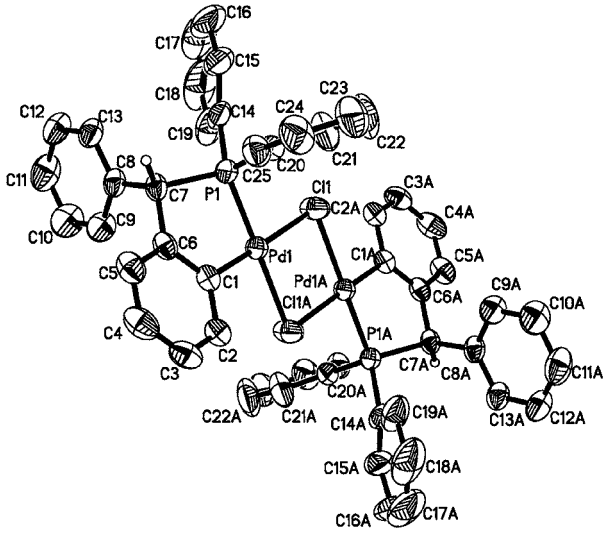
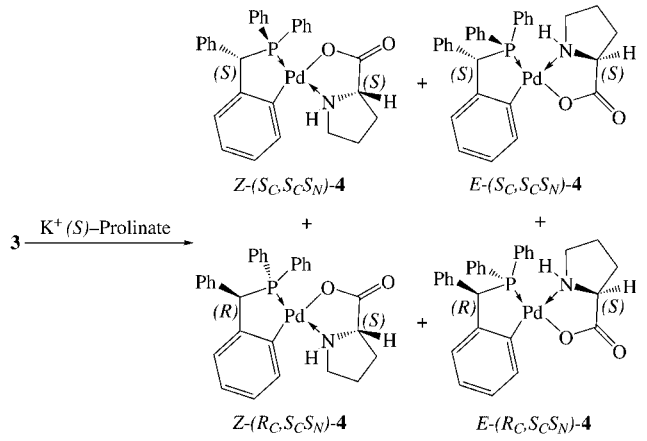


Figure 1. X-ray molecular structure of *meso*-**3**. Selected bond lengths [Å] and bond angles [°]: Pd1–C1, 2.017(3); Pd1–P1, 2.183(1); Pd1–Cl1, 2.441(1); Pd1–Cl1A, 2.407(1); C1–Pd1–P1, 79.43(8); C1–Pd1–Cl1, 174.43(8); C1–Pd1–Cl1A, 97.87(8); P1–Pd1–Cl1, 96.95(3); Cl1–Pd1–Cl1A, 97.87(8); Pd1–Cl1–Pd1A, 94.39(3).

The separation of the two enantiomeric forms of the phosphapalladacycle was then accomplished by the slow fractional crystallization of the mixture of four diastereomers from a solution of CH_2Cl_2/diethyl ether. The (*R*,*S*)- and (*S*,*S*)-**4** complexes were obtained sequentially in 59 and 77% yields. The absolute configurations of these derivatives were determined from their X-ray molecular structures. These are presented in Figure 2 and Figure 3 for (*R*,*S*)-**4** and (*S*,*S*)-**4** [as the (*Z*)-isomers], respectively, while the selected bond lengths and bond angles are presented in Table 1. Their absolute configurations were confirmed from



Scheme 2. Formation of (*S*)-prolinate derivatives **4**.

their respective Flack parameters of 0.02(3) and 0.04(4). Like the previously reported (*S*)-prolinate complexes, the secondary stereogenic nitrogen atom from the (*N*,*O*) chelate was noted to adopt the (*S*) configuration in both diastereomers.[9e,12] Both diastereomers are presented as the (*Z*) geometrical isomer and they are noted to have similar bond lengths and bond angles.

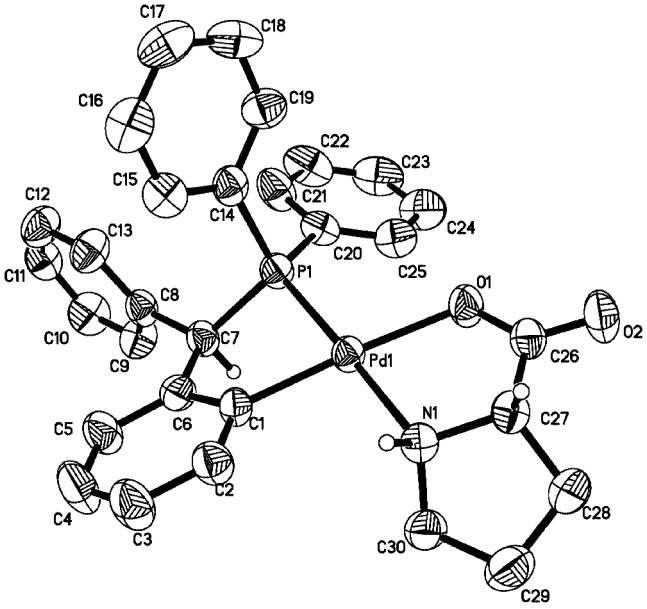


Figure 2. X-ray molecular structure of *Z*-(R_C,S_CS_N)-**4**.

The two optical antipodes of the chloro dimer **3** were then readily obtained by mixing the respective (*S*)-prolinate derivatives **4** with 1 M HCl. Thus, (*R*,*R*)-**3** was isolated as a yellowish-green amorphous powder in quantitative yield (Scheme 3), with $[a]_D$ = –382° (CH_2Cl_2). Notably, such acid treatment did not lead to any loss of optical activity, as verified from the ^{31}P NMR spectroscopic data of the (*S*)-prolinate complexes **4**, obtained by a re-derivatization of the optically resolved forms of **3**. At room temperature (300 K), the $^{31}P\{^1H\}$ spectra ($CDCl_3$) of the optically resolved dimers **3** had an apparent broad singlet at δ = 70.8–70.9 ppm. The variable temperature (VT) $^{31}P\{^1H\}$ NMR spectra of (*R*,*R*)-**3**, summarized in Figure 4, indicate that the appearance of the NMR resonance signals is temperature-dependent, as an additional singlet emerges upon cooling. This resonance is shifted progressively downfield relative to the parent signal. The effect is completely reversible, so that warming the NMR sample causes the signal to coalesce with the latter, albeit rather weakly shifted upfield. The appearance of two sets of singlets indicates the existence of the *syn* and *anti* regioisomers that are possible within the dimeric nature of **3**. The fact that other signals originating from the achiral, *meso syn*- and *anti*-(*R*,*S*) iso-

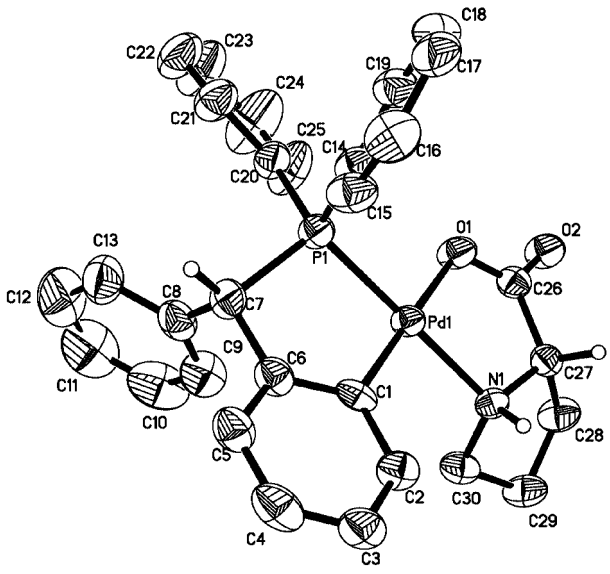
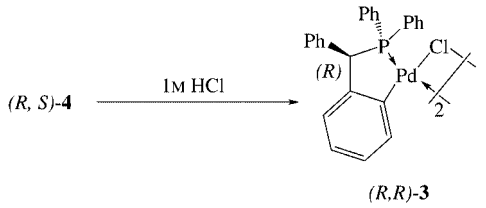


Figure 3.. -ray molecular structure of *Z*-(S_C,S_CS_N)-**4**.

Table 1. Selected bond lengths [Å] and angles [°] of (*Z*)-(R_C,S_CS_N)- and (*Z*)-(S_C,S_CS_N)-**4**.

Z-(R_C,S_CS_N)-**4**		*Z*-(S_C,S_CS_N)-**4**	
Pd1–C1	2.006(4)	Pd1–C1	2.015(4)
Pd1–O1	2.083(3)	Pd1–O1	2.084(3)
Pd1–N1	2.118(3)	Pd1–N1	2.095(4)
Pd1–P1	2.219(1)	Pd1–P1	2.203(1)
P1–C7	1.845(4)	P1–C7	1.849(5)
C6–C7	1.513(6)	C6–C7	1.518(7)
C1–C6	1.408(5)	C1–C6	1.406(6)
P1–C20	1.823(4)	P1–C20	1.815(5)
P1–C14	1.826(5)	P1–C14	1.814(5)
C7–C8	1.514(6)	C7–C8	1.495(7)
C1–Pd1–O1	177.1(2)	C1–Pd1–O1	178.9(2)
C1–Pd1–N1	97.5(1)	C1–Pd1–N1	97.9(2)
O1–Pd1–N1	80.5(1)	O1–Pd1–N1	81.1(1)
C1–Pd1–P1	80.8(1)	C1–Pd1–P1	81.0(1)
O1–Pd1–P1	101.20(8)	O1–Pd1–P1	99.9(1)
N1–Pd1–P1	178.3(1)	N1–Pd1–P1	178.7(1)
C7–P1–Pd1	101.1(1)	C7–P1–Pd1	103.5(2)
C6–C7–P1	103.8(3)	C6–C7–P1	102.5(3)
C1–C6–C7	117.2(4)	C1–C6–C7	118.6(4)
C6–C1–Pd1	120.7(3)	C6–C1–Pd1	120.8(3)
C26–C27–C28	113.2(4)	C26–C27–C28	114.7(4)
N1–C30–C29	104.7(4)	N1–C30–C29	105.0(4)

mers were not observed (but were present for the unresolved parent dimer) points to a good degree of optical purity for the obtained (*R*,*R*)-**3**.



Scheme 3. Regeneration of the dimer **3** in the optically active form.

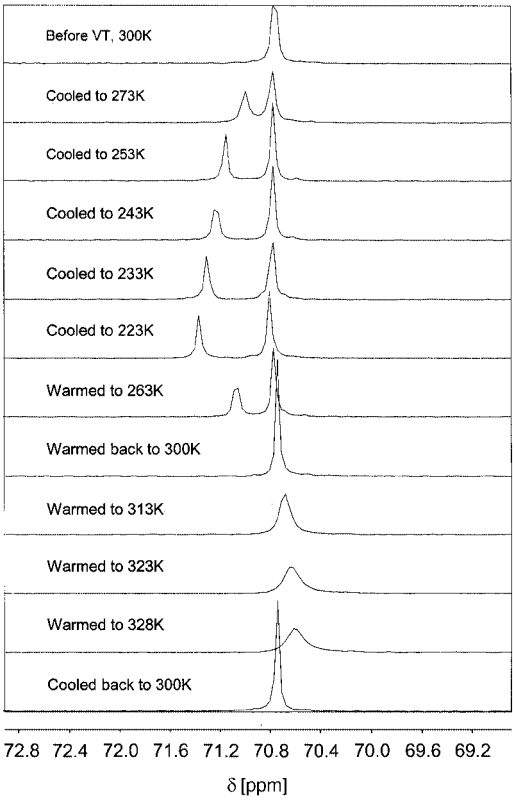
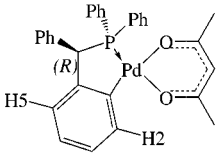


Figure 4. VT ^{31}P NMR spectra of (*R*,*R*)-**3**.

Substituent Effects on Phosphapalladacycle Characteristics

While the palladacycle obtained from (diphenylmethyl)-di-*tert*-butylphosphane structurally resembles the current one (the two differ only in terms of the substituents on the phosphorus atom), the properties of the two systems were noticeably dissimilar. First, the replacement of the *t*Bu$_2$P with the Ph$_2$P group seems to evoke a conformational flexibility on the phosphapalladacycle ring. Comparison of the *meso*-**3**, (*R*,*S*)- and (*S*,*S*)-**4** molecular structures (Figure 1, Figure 2 and Figure 3) reveals the possibility of the ring to adopt either one of the two conformational states. This is because in *meso*-**3** and (*S*,*S*)-**4**, the phenyl substituent at the stereogenic α-C atom is noted to adopt the axial orientation, as indicated by the respective angles of 7.0 and 9.5° subtended by this substituent to the normal of the m.c.pl. On the other hand, this angle was found to be 96.8° (or 83.2° as the adjacent angle) for (*R*,*S*)-**4** and as such, the phenyl substituent at the α-C atom is considered equatorially disposed. The possibility of the α-C phenyl substituent to adopt two different orientations indicates a lack of crucial intrachelate steric interactions to enforce it to permanently adopt an axial orientation. The absence of such an interaction is due to the rotational ability of this substituent along the C7–C8 bond. Evidently, this could be supported by the diversification of the angle between the mean planes of this phenyl substituent and the palladated {C(1–6)} phenylene ring by 24.6° from 99.2° in *meso*-**3** to 74.6° in ($S_C S_C$)-**4**, despite the common axial disposition of their α-C phenyl substituents. It should be noted from the structure of ($R_C S_C$)-**4** that, when the substituent is equatorially disposed, the mean plane of this phenyl ring is almost perpendicular to that of the palladated phenylene ring, at 83.1°. When the α-C phenyl substituent is in this rotameric state, any unfavourable steric repulsion with the palladated ring may thus be effectively minimized. In support of this statement, the shortest distance between the two aromatic rings, i.e. that between the H5 and H13 protons, at 3.350 Å, may be mentioned. A separation of this magnitude for these two atoms far exceeds the sum of van der Waals radii for two hydrogen atoms (2.4 Å) and is considered too large to generate any kind of instability to the conformational state of the phosphapalladacycle ring when the α-C phenyl substituent is equatorially disposed. For comparison, a close interaction of this kind at 2.148–2.234 Å between the α-C proton and the nearest proton of the palladated naphthylene ring was found for the conformationally rigid *ortho*-palladated [1-(1′-naphthyl)ethyl]diphenylphosphane system.[4a] In other words, in the current phosphapalladacycle, the prevention of any unfavourable steric contacts between the two aromatic rings may be accomplished simply by the adoption of a suitable rotameric state for the equatorially disposed α-C phenyl substituent or by the alternate axial orientation of this substituent. In contrast, the solid state studies of the *t*Bu-based phosphapalladacycle (*S*)-**7** revealed an axial orientation of the α-C phenyl substituent.[10] The alternate equatorially disposed orientation of this substituent was prevented by the close interaction of this phenyl ring with the *t*Bu groups or the H5 atom of the palladated phenyl ring. Any form of steric relief that could be brought about by the adoption of a certain rotameric state of this phenyl ring seems remote, since it is surrounded by three groups in this conformational state.



(*R*)-**6**

The lack of conformational rigidity of the current –PPh$_2$ based phosphapalladacycle is not restricted to the solid state but extends to solution. This was observed in the 2D ^{1}H-^{1}H NOESY NMR spectrum (Figure 5) of the β-dike-

tonate derivative, (*R*)-**6**, which was obtained as an amorphous powder, with $[\alpha]_{436} = -1123°$ (CH_2Cl_2), from the direct treatment of the dimer (*R*,*R*)-**3** with sodium acetylacetonate in acetone. From its ^1H NMR spectrum ($CDCl_3$), two visibly distinguished sets of *ortho*-, *meta*- and *para*-PPh protons appear, as the two PPh rings are diastereotopic. Assignment of the signals was made by a combination of $^1H\{^{31}P\}$, 2D ^1H-^1H COSY and NOESY NMR spectroscopic experiments. The four aromatic protons of the *ortho*-palladated ring form a spin system, as observed from the COSY data. The most upfield aromatic signal was assigned to the H5 proton, in recognition of its NOE contact (interaction C) with the α-CH proton. The latter spin couples with the adjacent ^{31}P nucleus and was presented as a simple doublet resonance ($^2J_{P,H}$ = 13.3 Hz). A rather unexpected long-range coupling with the ^{31}P nucleus was detected for the H2 proton, the corresponding coupling constant being a rather significant 4.0 Hz. The five aromatic protons of the α-C phenyl substituent are collectively represented as an extensively overlapping multiplet at δ = 7.00–7.05 ppm. The 2D ^1H-^1H NOESY NMR spectrum points to a rather flattened palladacycle ring in which each PPh ring was observed to distinctly interact through NOE with only either the methine proton or the phenyl ring at the stereogenic α-C centre (interactions A and D). Such a conformational picture may be satisfied by either one of the two Newman representations in Figure 6.

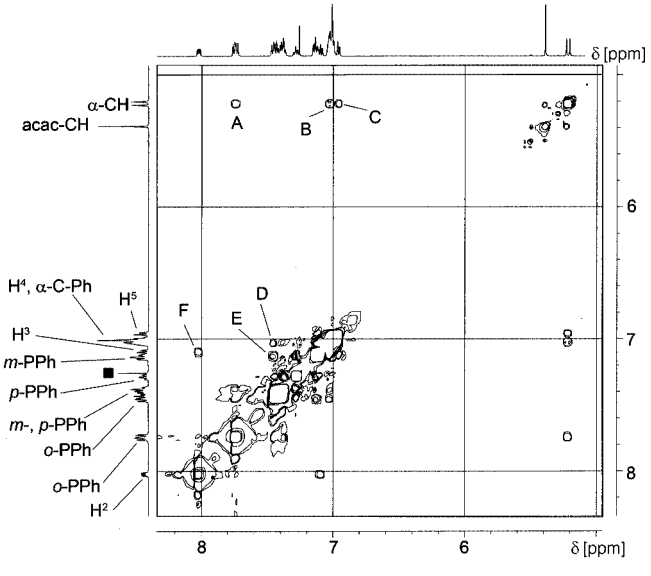


Figure 5. Expanded 2D ^1H-^1H NOESY NMR spectrum of (*R*)-**6** ($CDCl_3$). Selected NOE interactions: A: α-CH–*o*-PPh; B: α-CH–*o*-Ph of α-CPh; C: α-CH–H5; D: *o*-PPh–*o*-Ph of α-CPh; E: *o*-PPh–*m*-PPh; F: H2–H3. Solvent signal: ■, $CDCl_3$.

In contrast, the phosphapalladacycle ring of the tBu_2P equivalent is conformationally rigid, on the basis of a similar 2D ^1H-^1H NOESY NMR study performed on the analogous β-diketonate complex **7** (whose preparation was reported earlier[10]) containing the (*S*) configuration at the α-C centre. The aromatic signals in its ^1H NMR spectrum may be divided into two separate sets of spin patterns accounting for a total of nine aromatic protons. One of these

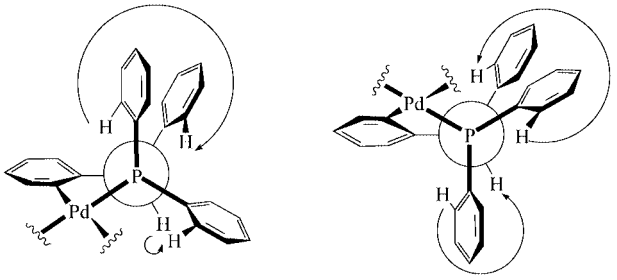
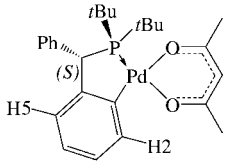


Figure 6. Newman projections for two possible flattened palladacycle conformations for complex (*R*)-**6**. Curved arrows depict NOE contacts.



(*S*)-**7**

comprises the four protons (H2–H5) of the *ortho*-palladated phenylene ring, while the other set of signals is representative of the remaining five aromatic protons belonging to the α-C phenyl substituent. The most upfield aromatic signal was assigned the H5 proton on account of its NOE contact with the α-C methine proton from the 2D ^1H-^1H NOESY NMR spectrum (Figure 7 and Figure 8). Among the (H2–H5) set of aromatic protons, such an NOE interaction is only possible for this proton, given its closest proximity to the α-CH proton. The remaining three aromatic protons of the same set may next be unambiguously assigned by using the H5 proton as a starting point by considering either (i) the coupling information from the COSY data or (ii) the negative, off-diagonal, i.e. NOE signals among these protons from the NOESY NMR spectrum.

As an added peculiarity, the spectral pattern of the five aromatic protons of the α-C phenyl substituent corresponds to a rather complicated ABCDE spin system, in which both *ortho* protons are chemically nonequivalent on the NMR time scale, a characteristic that is also shared by the *meta* protons. The detection of an off-diagonal, opposite-phased EXSY signal (signal I, in Figure 8) between the two *ortho* protons in the 2-D ^1H-^1H NOESY NMR spectrum points to the exchangeability between these two protons, which may be provided by the rotational capability of the C^{α}–C^{i} bond of the phosphapalladacycle, but such capability must be rather restricted even in solution to allow a differentiation and hence signal-doubling of both *ortho* protons (as well as the *meta* protons).

In the expanded 2-D ^1H-^1H NOESY NMR spectrum (Figure 7), NOE contacts were observed between the α-CH protons and both sets of the *t*Bu substituents (interactions C and D). Moreover, similar interactions between the two *ortho* protons of the α-C phenyl substituent and only one of the two available *t*Bu substituents were noted (interactions A and B). Consequently, these NOE patterns, together with the absence of similar NOE contacts between the α-C

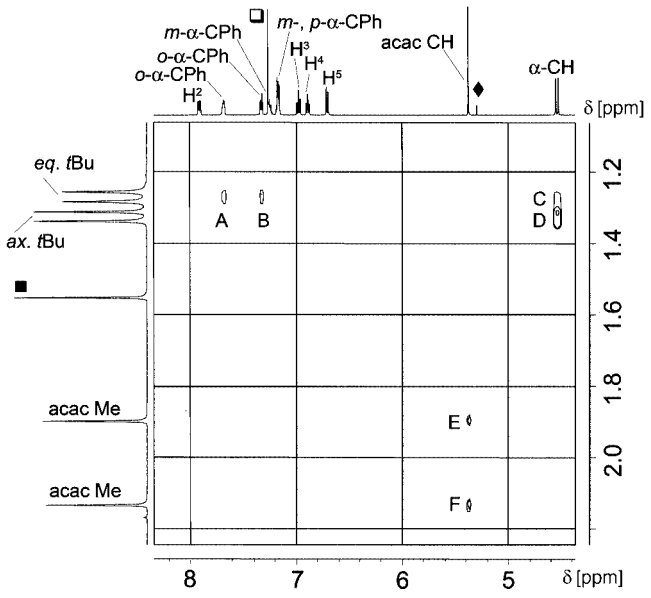


Figure 7. Expanded 2D ^{1}H-^{1}H NOESY NMR spectrum of (*S*)-**7** ($CDCl_3$). Aliphatic–aromatic NOE interactions: A: equatorial *t*Bu–*o*-α-Ph; B: equatorial *t*Bu–*o*-α–Ph; C: equatorial *t*Bu–α–CH; D: axial *t*Bu–α–CH; E: acac CH–acac Me; F: acac CH–acac Me. Solvent signals: ■, H_2O, ♦, CH_2Cl_2, □, $CDCl_3$.

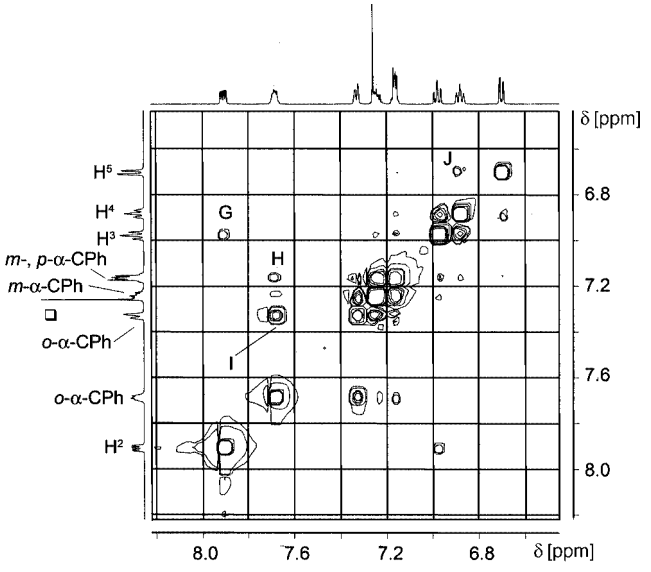


Figure 8. Expanded 2D ^{1}H-^{1}H NOESY NMR spectrum of (*S*)-**7** ($CDCl_3$). Selected aromatic–aromatic NOE interactions: G: H2–H3; H: *o*-α-Ph–*m*-α-Ph; J: H4–H5. EXSY signal: I: *o*-α-Ph–*o*-α-Ph. Solvent signal: □, $CDCl_3$.

phenyl *ortho* protons and the remaining *t*Bu group (i.e. the axially disposed *t*Bu group; the other *t*Bu group must be the equatorially disposed one) must be known in support of the λ conformation and the rigid state of the phosphapalladacycle with (*S*) absolute configuration in solution. As a comparison, this set of NOE interactions is impossible for the case of the δ conformation for the same absolute (*S*) configuration at the α-C centre, as illustrated by the by the Sawhorse and Newman projections along the P–α-C bond in Figure 9.

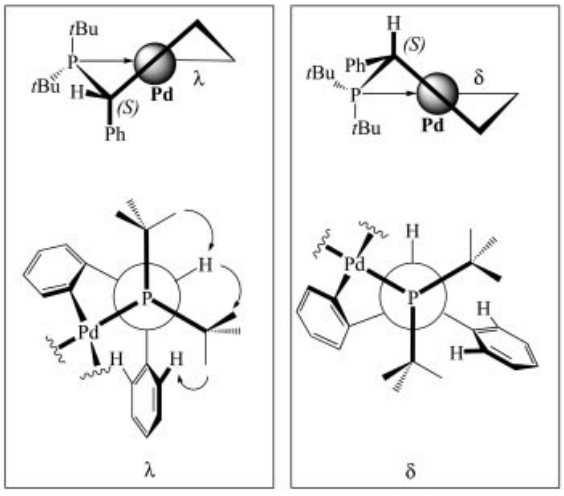
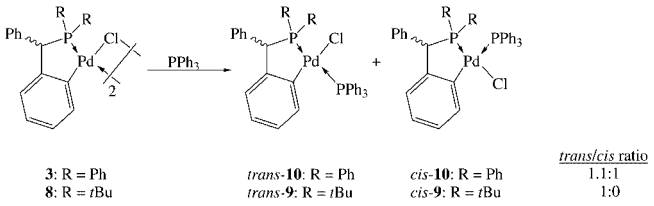


Figure 9. Sawhorse and Newman projections for the λ and δ conformations for complex (*S*)-**7** ($CDCl_3$). Curved arrows depict NOE contacts.

A mentionable observation among these aromatic signals is the presence of the long-range ^{1}H–^{31}P spin-spin couplings for the H2 and H4 protons. A rather significant coupling constant of 3.9 Hz over four bonds was found for the former, while a coupling constant of 2.1 Hz over possibly five bonds was detected for the latter. Such a phenomenon is unusual, when similar couplings for the other two aromatic protons belonging to the same phenylene ring do not exist. A similar feature was also noted for the corresponding H2 proton in (*R*)-**6**.

The large steric bulk of the *t*Bu groups has resulted in a better regioselectivity with respect to the coordination of arriving ancillary ligands to the palladacycle. This was noted in the reaction of the chloro-bridged dimer **8** with (*S*)-prolinate, in which the strong degree of regioselectivity is evident from the product distribution of 99:1 and 98:2 (*E*/*Z*) for its (*S*,*S*) and (*R*,*S*) derivatives, correspondingly.[10] Furthermore, compound **8** reacted with triphenylphosphane to give the *trans* isomer (±)-**9** exclusively (Scheme 4). This is far superior with respect to the current phosphapalladacycle **3**, which generated a mixture of *cis* and *trans* isomers (±)-**10** in 1.1:1 ratio. Both geometrical isomers were readily distinguished from each other by a consideration of the $^2J_{P,P}$ coupling constants. These were determined to be 29.0 Hz for *cis*-**10** and were more pronounced at 418.1 and 390.6 Hz for *trans*-(±)-**10** and *trans*-(±)-**9**, respectively. For *trans*-(±)-**9**, only one set of signals was observed in its ^{1}H NMR spectrum expectedly and the *trans*-(*P*, *P*) geometry was further inferred from the relatively high-field position of the phenylene aromatic proton at δ = 6.24 ppm. The best evidence for this geometry was provided by its molecular structure. The structure (with the accompanying numbering scheme) is presented in Figure 10. The chiral nature of the phosphapalladacycle is obvious from the stereogenic α-C atom, by the *ortho*-palladation of only one of the two available phenyl rings (i.e. the C1–C6 phenyl ring) on the phosphane moiety. 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 {P1–Pd1–C1} and {Cl1–Pd1–P2} planes has a large value of 23.0°. Such a large value is probably an indication of the need to relieve steric repulsion due to the presence of the phosphapalladacycle bulky *t*Bu substituents and the PPh_3 phenyl rings. The overcrowding around the central Pd atom was further demonstrated by the mean vertical displacement of 0.2483 Å from planarity of the five atoms of the m.c.pl.



Scheme 4. Formation of triphenylphosphane adducts (±)-**9** and (±)-**10**.

Notably, the current Ph_2P-based phosphapalladacycle also discloses a profound difference in the Pd–C bond reactivity. To recall, the Pd–C bond of the *t*Bu_2P analogue was noted to be only kinetically unstable and the phosphapalladacycle ring opens and closes reversibly by Pd–C bond cleavage in refluxing acetone containing concentrated HCl.[10] This effect was attributed to the thermodynamic stability imparted to the palladacycle by the steric influence of the bulky *t*Bu substituents. In stark contrast to its *t*Bu_2P analogue, the presence of a few drops of concentrated HCl in a $CDCl_3$ solution of the chloro dimer **3** led to a permanent ring opening of the phosphapalladacycle by cleavage of the Pd–C bond (Scheme 5). The transformation was immediate, as observed from the colour change from pale yellow to orange-red. The fact that the Pd–C bond cleavage of the current phosphapalladacycle was permanent was affirmed by the possibility to even isolate the binuclear product **5** from this procedure and perform an X-ray diffraction study. From Figure 11, the complex has an overall *anti* structure that reveals the occupation of both diagonally opposite terminal ends of the dimer by two additional chloride ligands. Moreover, the η^1-P type of coordination mode adopted by the phosphane ligand is apparent here. Unlike the *ortho*-palladated structure, however, the central four-membered $\{Pd_2(\mu\text{-}Cl)_2\}$cycle is not planar, since each Pd atom deviates from planarity by an angle of 6.45°. It is worth mentioning that the P–Pd bond has weakened as a result of palladacycle ring opening. This bond length has increased from 2.1832(7) Å in the *ortho*-palladated structure

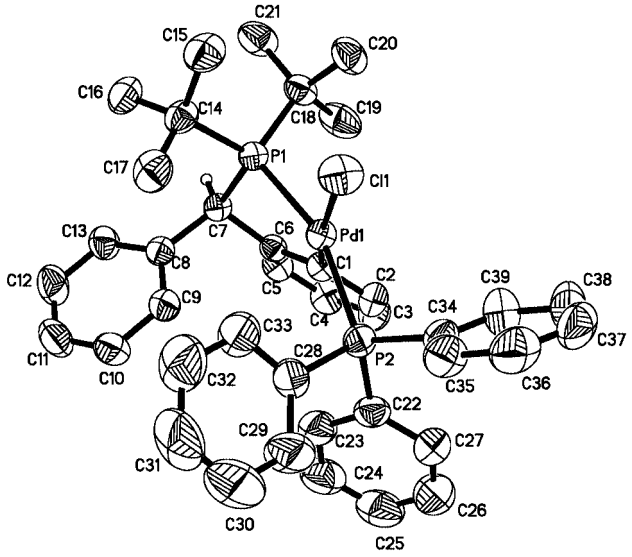


Figure 10. X-ray molecular structure of *trans*-(±)-**9**. Selected bond lengths [Å] and bond angles [°]: Pd1–P1, 2.295(1); Pd1–C1; 2.014(2); Pd1–O1, 2.375(1); Pd1–Cl1, 2.3878(5); C1–Pd1–P1, 80.41(5); C1–Pd1–P2, 96.99(5); P1–Pd1–P2, 161.01(2); C1–Pd1–Cl1, 167.63(5); P1–Pd1–Cl1, 97.77(2); P2–Pd1–Cl1, 88.63(2).

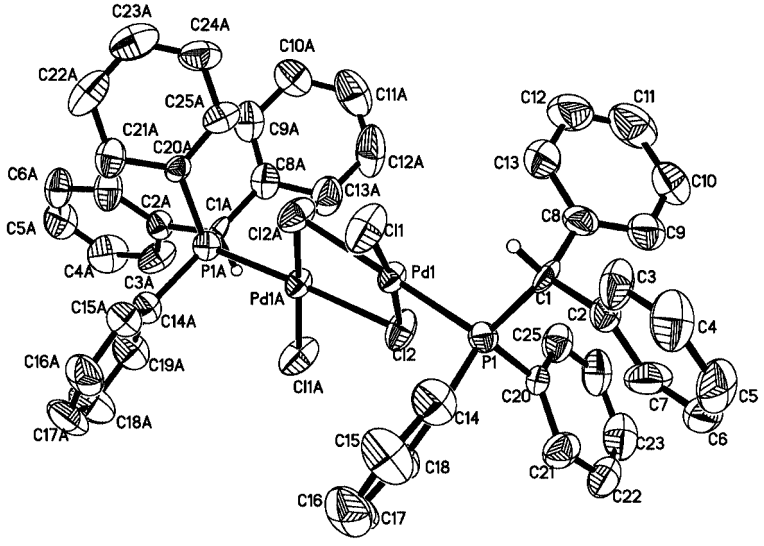
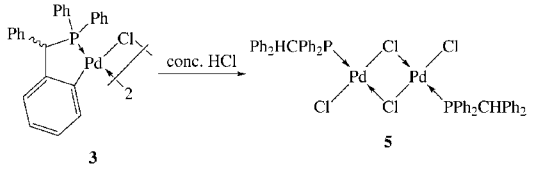


Figure 11. X-ray molecular structure of compound **5**. Selected bond lengths [Å] and bond angles [°]: Pd1–P1, 2.237(3); Pd1–Cl1, 2.260(3); Pd1–Cl2, 2.323(3); Pd1–Cl2A, 2.414(3); P1–Pd1–Cl2, 96.5(1); P1–Pd1–Cl1, 86.9(1); P1–Pd1–Cl2A, 177.4(1); Cl1–Pd1–Cl2, 171.9(1), Cl2–Pd1–Cl2A, 85.8(1); Cl1–Pd1–Cl2A, 90.7(1).

3 to 2.237(3) Å in the monodentate state. Thus, the possibility of stabilizing the P–Pd bond as a result of *ortho*-palladation is noteworthy. The P–C bond strengths have not varied significantly, however.



3 **5**

Scheme 5. Permanent Pd–C bond cleavage to generate the achiral binuclear dimer **5**.

Conclusions

The novel palladacycle based on the ligand (diphenylmethyl)diphenylphosphane was prepared in the optically active forms by optical resolution of its (*S*)-prolinate derivatives. This palladacycle was shown to display properties which were different from those of its bulkier analogue, the (diphenylmethyl)di-*tert*-butylphosphane-based palladacycle. First, the five-membered ring of the current palladacycle assumes both available conformations in solution and in the solid state. From solid-state X-ray structure studies, the conformational flexibility of this system was directly attributed to the absence of intrachelate interactions in either the λ or the δ conformations. Second, the bulkiness of the *t*Bu groups also brings about a more improved regioselectivity with respect to the coordination of ancillary triphenylphosphane and (*S*)-prolinate ligands for the latter palladacycle. Third, in the absence of such steric effects originating from the *t*Bu groups, the Pd–C bond of the former does not possess the type of thermodynamic stability that was observed for the latter. Currently, both palladacycles are being tested in various asymmetric applications.

Experimental Section

General: Reactions involving air-sensitive compounds were performed under a positive pressure of argon. Routine ^{1}H NMR spectra were recorded at 300 MHz or 500 MHz with a Bruker ACF 300 or Bruker AMX 500 NMR spectrometer. All the ^{31}P{^{1}H} NMR spectra were recorded at 120 MHz or 202 MHz with a Bruker ACF 300 or Bruker AMX 500 NMR spectrometer. Unless stated otherwise, all NMR spectroscopic experiments were performed at room temperature (300 K). Melting points were determined with a Büchi melting point B-545 apparatus and are uncorrected. Optical rotations were measured on the specified solution in 1-dm 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.

(Diphenylmethyl)diphenylphosphane (2): A solution of (diphenylmethyl)lithium was prepared by syringing *n*-BuLi in hexanes (3.7 mL, 5.9 mmol, 1.6 M) into a thf solution (5 mL) of diphenylmethane (1.00 g, 5.94 mmol) and allowing the mixture to stir at room temperature for 3 h. The freshly prepared, intensely red solution of (diphenylmethyl)lithium was then added dropwise to an ice-chilled thf solution (5 mL) of chlorodiphenylphosphane (0.98 g, 4.46 mmol) with rapid stirring. The addition led to an immediate decolourization of the (diphenylmethyl)lithium reagent. When decolourization was no longer observed upon further addition of the (diphenylmethyl)lithium reagent, the addition was discontinued, the ice-bath was removed, and the mixture was allowed to stir at room temperature for a further 30 min. It was then concentrated to dryness, washed with freshly deoxygenated water (20 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The organic extracts were combined, dried with $MgSO_4$ and filtered. The product was finally obtained as a white solid upon removal of solvents by distillation and further drying under reduced pressure. Yield: 1.54 g (98.0%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.63 (d, $^2J_{P,H}$ = 6.8 Hz, 1 H, Ph_2CH), 7.03–7.26 (m, 20 H, aromatic protons) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = –3.2 (s) ppm.

Di-μ-chlorobis{[(diphenylphosphanyl)(phenyl)methyl]phenyl-*C*^{2},*P*}-dipalladium(II) (3): The phosphane **2** (1.57 g, 4.46 mmol) and palladium(II) acetate (1.00 g, 4.46 mmol) were suspended in toluene (100 mL), and the reacting mixture was stirred at 50 °C for 2 h to give a deep reddish brown mixture with deposition of palladium black. The mixture was concentrated to dryness by using a rotary evaporator to yield a crude reddish-black residue. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 68.4 (s) ppm. The residue was then suspended in acetone (15 mL), to which a solution of lithium chloride (0.50 g, 11.8 mmol) in acetone/methanol (1:3, v/v) was added. The mixture was then stirred for 90 min, concentrated to dryness and re-suspended in CH_2Cl_2. This suspension was filtered through a plug of Celite to yield an orange solution, which was further washed with water (40 mL). The organic extract was concentrated and chromatographed on a silica gel column from which the chloro dimer was eluted as a pale yellowish-green fraction by using CH_2Cl_2–hexanes (1:2, v/v). Crystallization from CH_2Cl_2/diethyl ether yielded pale yellow blocks; m.p. (decomp.) 232–236 °C. Yield: 1.36 g (61.3%). $C_{50}H_{40}Cl_2P_2Pd_2$ (986.52): calcd. C 60.9, H 4.1; found C 60.6, H 4.1. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.27 (d, $^2J_{P,H}$ = 13.6 Hz, 1 H, α-CH), 6.98–8.11 (br. overlapping m, 19 H, aromatic protons) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 70.4, 70.6, 70.8 (br. overlapping s) ppm; (223 K) four sets of signals at δ = 70.7 (s), 70.8 (s), 70.9 (s) and 71.4 (s) ppm.

***sym*-Dichlorodi-μ-chlorobis[(diphenylmethyl)diphenylphosphane]dipalladium(II) (5):** To a CH_2Cl_2 solution (3 mL) of the racemic complex **3** (0.11 g, 0.12 mmol) was added an excess of conc. HCl (30 μL, 37% wt/wt, spec. gravity 1.19) with a micropipette. The mixture was allowed to stir vigorously for 1 h at room temperature, after which it was diluted with water (5 mL) and CH_2Cl_2 (20 mL). The orange-red organic layer was separated and was washed with water (2 × 5 mL) and dried with $MgSO_4$. The excess CH_2Cl_2 was removed, from which the product was obtained as fine orange-red crystals from CH_2Cl_2/hexanes exhibiting low solubility; m.p. (decomp.) 231–233 °C. Yield: 0.088 g (72.7%). $C_{50}H_{42}Cl_4P_2Pd_2$ (1059.44): calcd. C 56.7, H 4.0; found C 56.3, H 4.3. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.35 (d, $^2J_{P,H}$ = 15.6 Hz, 1 H, α-CH), 7.19–7.48 (m, 20 H, aromatic protons) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 36.8 (s) ppm.

Chloro{[(±)-(diphenylphosphanyl)(phenyl)methyl]phenyl-*C*^{2},*P*}-(triphenylphosphane)palladium(II) [(±)-10]: Triphenylphosphane (0.012 g, 0.045 mmol) was added to a CH_2Cl_2 solution (3 mL) of the dimer **3** (0.022 g, 0.022 mmol), and the mixture was stirred for 30 min, after which the pale yellow solution was concentrated in vacuo, and the product was obtained as pale yellow crystals in CH_2Cl_2/hexanes; m.p. 200–202 °C. Yield: 0.020 g (58.8%).

$C_{43}H_{35}ClP_2Pd$ (755.55): calcd. C 68.4, H 4.7; found C 68.5, H 4.4. ^1H NMR (300 MHz, $CDCl_3$) two sets of signals in 1:0.87 ratio for both geometric isomers in favour of the *cis* isomer, δ = 5.16 (br. d, $^2J_{P,H}$ = 13.7 Hz, 1 H, α- CH of *trans* isomer), 5.31 (d, $^2J_{P,H}$ = 13.3 Hz, 1 H, α-CH of *cis* isomer), 6.32–8.61 (aromatic protons of both isomers) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) two sets of signals in 1:0.87 ratio for both geometric isomers in favour of the *cis* isomer, δ = 18.1 (d, $^2J_{P,P}$ = 29.0 Hz, PPh_3 of *cis* diastereomer), 26.6 (d, $^2J_{P,P}$ = 418.1 Hz, PPh_3 of *trans* diastereomer), 58.6 (d, $^2J_{P,P}$ = 418.1 Hz, palladacycle P of *trans* diastereomer), 71.0 (d, $^2J_{P,P}$ = 29.0 Hz, palladacycle P of *cis* diastereomer) ppm.

[(*S*)-Prolinato-*N*,*O*]{(±)-1-[(diphenylphosphanyl)(phenyl)methyl]-phenyl-*C*^{2},*P*}palladium(II) (4): A methanol solution (9 mL) of potassium (*S*)-prolinate (0.312 g, 0.680 mmol) was added to the dimer **3** (1.00 g, 1.02 mmol) suspended in CH_2Cl_2 (10 mL), and the mixture was stirred for 1 h at room temperature. The resulting white suspension was concentrated to dryness, re-suspended in CH_2Cl_2 (8 mL), washed with water (2 × 10 mL) and dried with $MgSO_4$. The colourless solution was then concentrated to dryness by using a rotary evaporator and was further dried at 70 °C in vacuo for 3 h to yield a flaky white solid; m.p. (decomp.) 225–227 °C. $[\alpha]_D$ = +107°, $[\alpha]_{578}$ = +114°, $[\alpha]_{546}$ = +129°, $[\alpha]_{436}$ = +263°, $[\alpha]_{365}$ = +636° (*c* 1.1, CH_2Cl_2). Yield: 1.15 g (99.1%). $C_{30}H_{28}NO_2PPd$ (571.93): calcd. C 63.0, H 4.9, N 2.5; found C 62.5, H 5.1, N 2.7. ^1H NMR ($CDCl_3$, 500 MHz) four sets of signals in the ratio of 0.4:0.3:0.9:1.0, δ = 1.32–1.44 [overlapping m, γ-H of *E*-(*R*,*S*)- and *E*-(*S*,*S*)-diastereomers], 1.75 [m, γ-H of *E*-(*S*,*S*)-diastereomer], 1.81–1.86 [overlapping m, γ-H of *Z*-(*S*,*S*)-diastereomer, γ-H of *E*- and *Z*-(*R*,*S*)-diastereomers], 2.02–2.41 [series of m, γ-H of *Z*-(*S*,*S*)-and *Z*-(*R*,*S*)-diastereomers, both β-H of *E*-(*R*,*S*)-diastereomers, both β-Hs of *E*-(*S*,*S*)-diastereomers, β-H of *Z*-(*R*,*S*)-diastereomer, both β-H of *Z*-(*S*,*S*)-diastereomers, δ-H of *E*-(*S*,*S*)-diastereomer, N-H of *E*-(*R*,*S*)-diastereomer], 2.44–2.61 [series of m, β-H of *Z*-(*R*,*S*)-diastereomer, δ-H of *E*-(*R*,*S*)-diastereomer, δ-H of *E*-(*S*,*S*)-diastereomer, N-H of *E*-(*S*,*S*)-diastereomer], 2.80 [m, δ-H of *E*-(*R*,*S*)-diastereomer], 3.35 [m, δ-H of *Z*-(*R*,*S*)-diastereomer], 3.41–3.51 [overlapping m, both δ-Hs of *Z*-(*S*,*S*)-diastereomer], 3.55 [δ-H of *Z*-(*R*,*S*)-diastereomer], 3.61–3.69 [overlapping m, N-H of both *Z*-(*R*,*S*)- and *Z*-(*S*,*S*)-diastereomers], 3.92 [m, α-H of *E*-(*R*,*S*)-diastereomer], 3.99 [m, α-H of *E*-(*S*,*S*)-diastereomer], 4.14 [m, α-H of *Z*-(*S*,*S*)-diastereomer], 4.22 [m, α-H of *Z*-(*R*,*S*)-diastereomer], 5.08 [d, $^2J_{P,H}$ = 13.9 Hz, palladacycle α-H of *Z*-(*S*,*S*)-diastereomer], 5.20 [d, $^2J_{P,H}$ = 13.0 Hz, palladacycle α-H of *Z*-(*R*,*S*)-diastereomer], 5.40 [d, $^2J_{P,H}$ = 12.5 Hz, palladacycle α-H of *E*-(*S*,*S*)-diastereomer], 5.49 [d, $^2J_{P,H}$ = 12.5 Hz, palladacycle α-H of *E*-(*R*,*S*)-diastereomer], 6.71 [d, $^2J_{H,H}$ = 7.49 Hz, *o*-α-Ph of *E*-(*R*,*S*)-diastereomer], 6.74 [d, $^2J_{H,H}$ = 7.77 Hz, 2-H of *E*-(*R*,*S*)-diastereomer], 6.78 [m, *o*-α-Ph of *E*-(*S*,*S*)-diastereomer], 6.85 [d, $^2J_{H,H}$ = 6.94 Hz, 5-H of *E*-(*S*,*S*)-diastereomer], 6.93–7.58 [series of m, aromatic protons of all four diastereomers], 7.72–7.85 [partially overlapping m, *o*-PPh of *Z*-(*R*,*S*)-, *o*-PPh of *E*-(*R*,*S*)-and *o*-PPh of *E*-(*S*,*S*)-diastereomers], 8.10–8.15 [partially overlapping m, 2-H proton of *E*-(*R*,*S*)- and *E*-(*S*,*S*)-diastereomers] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz) four signals in relative intensities of 4:3:9:10, δ = 62.7 (s), 64.4 (s), 71.0 (s) and 72.1 (s) ppm respectively.

Separation of (R_C,$S_C$$S_N$) and ($S_C$,$S_C$$S_N$) Diastereomers

Isolation of (R_C,$S_C$$S_N$)-(Prolinato-*N*,*O*){[(diphenylphosphanyl)-(phenyl)methyl]phenyl-*C*^{2},*P*}palladium(II) [(R_C,$S_C$$S_N$)-4]: Diethyl ether was slowly added at regular intervals to a moderately concentrated CH_2Cl_2 solution of the above 1:1 mixture of both diastereomers (1.168 g, 2.04 mmol), from which the less soluble diastereomer (R_C,$S_C$$S_N$)-**4** was isolated after two days as colourless blocks with 97.1% *de* (from $^{31}P\{^1H\}$ NMR spectroscopic data), which gradually desolvated upon standing at room temperature; m.p. 191–193 °C. $[\alpha]_D$ = –109°, $[\alpha]_{578}$ = –114°, $[\alpha]_{546}$ = –131°, $[\alpha]_{436}$ = –242°, $[\alpha]_{365}$ = –397° (*c* 1.1, CH_2Cl_2). Yield: 0.34 g (59.0%, based on the theoretical yield of one diastereomer). $C_{30}H_{28}NO_2PPd$ (571.93): calcd. C 63.0, H 4.9, N 2.5; found C 63.0, H 4.8, N 2.6. ^1H NMR ($CDCl_3$, 500 MHz) two sets of signals in 1:0.28 ratio in favour of the *E*-isomer, δ = 1.41 (m, 1 H, γ-H of *E*-isomer), 1.77–1.87 (overlapping m, γ-H of both isomers), 2.04–2.14 (overlapping m, γ-H of *Z*-isomer, β-H of *E*-isomer), 2.19–2.39 (overlapping m, β-H of *Z*-isomer, β-H and N-H of *E*-isomer), 2.45–2.56 (overlapping m, β-H of *Z*-isomer, δ-H of *E*-isomer), 2.80 (m, 1 H, δ-H of *E*-isomer), 3.36 (m, 1 H, δ-H of *Z*-isomer), 3.56 (br. overlapping m, 2 H, δ-H and N-H of *Z*-isomer), 3.93 (m, 1 H, prolinate α-H of *E*-isomer), 4.21 (m, 1 H, prolinate α-H of *Z*-isomer), 5.20 (d, $^2J_{P,H}$ = 13.0 Hz, 1 H, palladacycle α-H of *Z*-isomer), 5.46 (d, $^2J_{P,H}$ = 12.5 Hz, 1 H, palladacycle α-H of *E*-isomer), 6.70 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H, *o*-α-Ph of *E*-isomer), 6.73 (d, $^3J_{H,H}$ = 7.4 Hz, 1 H, 5-H of *E*-geometrical isomer), 6.92–7.46 (m, aromatic protons of both geometric isomers), 7.52–7.58 (overlapping m, aromatic protons of both geometric isomers), 7.73 (ddd, $^3J_{H,H}$ = 8.5Hz, $^4J_{H,H}$ = 1.6 Hz, $^3J_{P,H}$ = 11.1 Hz, 2 H, *o*-PPh of *Z*-isomer), 7.81 (ddd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.6 Hz, $^3J_{P,H}$ = 11.0 Hz, 2 H, *o*-PPh of *E*-isomer), 8.13 (ddd, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.1 Hz, $J_{P,H}$ = 4.0 Hz, 1 H, 2-H of *E*-isomer) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz) two signals with relative intensities of 2.8:10, δ = 64.5 (s, *Z*-isomer), 72.2 (s, *E*-isomer) ppm.

Isolation of (S_C,$S_C$$S_N$)-(Prolinato-*N*,*O*){[(diphenylphosphanyl)-(phenyl)methyl]phenyl-*C*^{2},*P*}palladium(II) [(S_C,$S_C$$S_N$)-4]: Subsequent slow evaporation of the remaining mother liquor above afforded the more soluble diastereomer (S_C,$S_C$$S_N$)-**4** as large colourless blocks with 91.0% *de* (from $^{31}P\{^1H\}$ NMR spectroscopic data); m.p. (decomp.) 272–274 °C. $[\alpha]_D$ = +303°, $[\alpha]_{578}$ = +318°, $[\alpha]_{546}$ = +369°, $[\alpha]_{436}$ = +728°, $[\alpha]_{365}$ = +1580° (*c* 1.1, CH_2Cl_2). Yield: 0.45 g (76.8%, based on the theoretical yield of one diastereomer). $C_{30}H_{28}NO_2PPd$ (571.93): calcd. C 63.0, H 4.9, N 2.5; found C 63.2, H 4.7, N 2.6. ^1H NMR ($CDCl_3$, 500 MHz) two sets of signals in 1: 0.43 ratio in favour of the *E*-isomer, δ = 1.34 (m, 1 H, γ-H of *E*-isomer), 1.75 (m, 1 H, γ-H of *E*-isomer), 1.85 (m, 1 H, γ-H of *Z*-isomer), 2.08–2.13 (overlapping m, γ-H of *Z*-isomer, β-H and δ-H of *E*-isomer), 2.23 (m, 1 H, β-H of *E*-isomer), 2.38 (overlapping m, 2 H, both β-H of *Z*-isomer), 2.50–2.61 (overlapping m, 2 H, δ-H and N-H of *E*-isomer), 3.43–3.52 (overlapping m, 2 H, both δ-H protons of *Z*- isomer), 3.65 (br. m, 1 H, N-H of *Z*-isomer), 4.00 (m, 1 H, prolinate α-H of *E*-isomer), 4.14 (m, 1 H, prolinate α-H of *Z*-isomer), 5.08 (d, $^2J_{P,H}$ = 13.8 Hz, 1 H, palladacycle α-H of *Z*-isomer), 5.40 (d, $^2J_{P,H}$ = 12.7 Hz, 1 H, palladacycle α-H of *E*-isomer), 6.78 (m, 2 H, *o*-α-Ph), 6.85 (d, $^3J_{H,H}$ = 7.3 Hz, 1 H, 5-H of *E*-isomer), 7.00–7.58 (overlapping m, aromatic protons of both geometric isomers), 7.78 (ddd, $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,H}$ = 1.4 Hz, $^3J_{P,H}$ = 10.9 Hz, 2 H, *o*-PPh of *E*-geometrical isomer), 8.10 (ddd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.4 Hz, $J_{P,H}$ = 4.1 Hz, 1 H, 2-H of *E*-geometrical isomer) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz) two sets of signals with relative intensities of 4.3:10 in favour of the *E*-isomer, δ = 62.7 (s, *Z*-geometrical isomer), 71.1(s, *E*-geometrical isomer) ppm.

(*R*,*R*)-di-μ-Chlorobis{[(diphenylphosphanyl)(phenyl)methyl]phenyl-*C*^{2},*P*}dipalladium(II) [(*R*,*R*)-3]: Dilute HCl (10 mL, 1 M) was added to a CH_2Cl_2 solution (10 mL) of the diastereomer (R_C,$S_C$$S_N$)-**4** (0.2347 g, 0.410 mmol), and the resulting solution was vigorously stirred for 5 min at room temperature. The aqueous layer was separated, and the procedure was repeated once with the same amount of HCl. The organic layer was then removed, washed with water (2 × 10 mL), dried with $MgSO_4$ and the solvents evaporated to dry-

ness in vacuo to afford the (*R*,*R*)-**3** as a greenish-yellow powder (attempts to crystallize the product by using a variety of solvents have been unsuccessful thus far); m.p. (decomp.) 196–200 °C. $[\alpha]_D$ = –382°, $[\alpha]_{578}$ = –400°, $[\alpha]_{546}$ = –468°, $[\alpha]_{436}$ = –946° (*c* 0.5, CH_2Cl_2). Yield: 0.20 g (99.0%). $C_{50}H_{40}Cl_2P_2Pd_2$ (986.52): calcd. C 60.9, H 4.1; found C 61.2, H 4.0. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.22 (d, $^2J_{P,H}$ = 13.7 Hz, 1 H, α-CH), 6.89–8.03 (br. overlapping m, 19 H, aromatic protons) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 70.8 (s), (253 K) 2 sets of signals with relative intensities of 1: 0.65, δ = 70.8 (s), 71.1(s) ppm.

(*S*,*S*)-di-μ-Chlorobis{[(diphenylphosphanyl)(phenyl)methyl]phenyl-*C*^{2},*P*}dipalladium(II) [(*S*,*S*)-3]: Dilute HCl (7 mL, 1 M) was added to a CH_2Cl_2 solution (10 mL) of the (S_C, S_CS_N)-**4** (0.1642 g, 0.287 mmol), and the resulting solution was vigorously stirred for 5 min at room temperature. The aqueous layer was separated, and the procedure was repeated once with the same amount of HCl. The organic layer was next removed, washed with water (2 × 10 mL), dried with $MgSO_4$ and the solvents evaporated to dryness in vacuo to afford the (*S*,*S*)-**3** as a greenish-yellow powder; m.p. (decomp.) 198–202 °C. $[\alpha]_D$ = +368°, $[\alpha]_{578}$ = +384°, $[\alpha]_{546}$ = +446°, $[\alpha]_{436}$ = +908° (*c* 0.5, CH_2Cl_2). Yield: 0.141 g (99.5%). $C_{50}H_{40}Cl_2P_2Pd_2$ (986.52): calcd. C 60.9, H 4.1; found C 60.9, H 3.9. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.22 (d, $^2J_{P,H}$ = 13.7 Hz, 1 H, α-CH), 6.89–8.03 (br. overlapping m, 19 H, aromatic protons) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 70.9 (s) ppm.

(*R*)-(Acetylacetonato-*O*,*O*′){1-[(diphenylphosphanyl)(phenyl)methyl]-phenyl-*C*^{2},*P*}dipalladium(II) [(*R*)-6]: To an acetone solution (3 mL) of the dimer (*R*,*R*)-**3** (0.139 g, 0.141 mmol) was added Na acac·H_2O (0.040 g, 0.282 mmol), and the mixture was vigorously stirred at room temperature for 2 h until a white suspension was obtained. The suspension was filtered through a short plug of Celite, and the colourless solution was concentrated to dryness in vacuo to yield a white amorphous powder; m.p. 86–89 °C. $[\alpha]_{436}$ = –1123°, $[\alpha]_{365}$ = –2397° (*c* 0.7, CH_2Cl_2). Yield: 0.089 g (56.7%). $C_{30}H_{27}O_2PPd$ (556.92): calcd. C 64.7, H 4.9; found C 64.9, H 4.8. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.84 (s, 3 H, acac-Me), 2.15 (s, 3 H, acac-Me), 5.22 (d, $^2J_{P,H}$ = 13.3 Hz, 1 H, α-CH), 5.39 (s, 1 H, acac-CH), 6.96 (dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.42 Hz, 1 H, 5-H), 7.00–7.05 (m, 6 H, 4-H, *o*-Ph, *m*-Ph, *p*-Ph protons of α-C-Ph substituent), 7.09 (m, 1 H, 3-H), 7.13 (m, 2 H, *m*-PPh), 7.29 (dtt, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.29Hz, $^5J_{P,H}$ = 2.1 Hz, 1 H, *p*-PPh), 7.45 (ddd, ^3J(H,H) = 8.5, $^4J_{H,H}$ = 1.3, $^3J_{P,H}$ = 11.5 Hz, 2 H, *o*-PPh), 7.74 (dddd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.8 Hz, $^4J_{H,H}$ = 1.3 Hz, $^3J_{P,H}$ = 11.2 Hz, 2 H, *o*-PPh), 8.02 (ddd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.3 Hz, $J_{P,H}$ = 4.0 Hz, 1 H, 2-H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 66.4 (s) ppm.

Chloro{(±)-1-[(di-*tert*-butylphosphanyl)(phenyl)methyl]phenyl-*C*^{2},*P*}(triphenylphosphane)palladium(II) [(±)-9]: Triphenylphosphane (0.069 g, 0.262 mmol) was added to a CH_2Cl_2 solution of the corresponding chloro dimer **3** (0.108 g, 0.119 mmol), and the resulting mixture was allowed to stir for 16 h under a positive pressure of argon. The product was isolated as pale yellow blocks from CH_2Cl_2/hexanes upon slow crystallization; m.p. 216–217 °C. Yield: 0.145 g (85.3%). $C_{39}H_{43}ClP_2Pd$ (715.57): calcd. C 65.5, H 6.1; found C 65.4, H 6.1. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.21 (d, $^3J_{P,H}$ = 12.8 Hz, 9 H, axial *t*Bu), 1.40 (d, $^3J_{P,H}$ = 13.1 Hz, 9 H, equatorial *t*Bu), 4.54 (dd, $^2J_{P,H}$ = 11.7 Hz, $^4J_{P,H}$ = 5.1 Hz, 1 H, α-CH), 6.24 (m, 1 H, 2-H), 6.64–6.71 (m, 2 H, 3-H, 4-H), 6.80 (dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.4 Hz, 1 H, 5-H), 6.94 (br. dd, $^3J_{H,H}$ = $^3J_{H,H}$ = 7.5 Hz, 1 H, *m*-α-Ph), 7.17 (m, 1 H, *p*-α-Ph), 7.24–7.40 (m, *m*-PPh_3, *p*-PPh_3, *o*-α-Ph, *m*-α-Ph, signals of free PPh_3), 7.70 (m, 6 H, *o*-PPh_3), 8.46 (br. d, $^3J_{H,H}$ = 7.8 Hz, 1 H, *o*-α-Ph) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ = –5.0 (*s*, free PPh_3), 24.8 (d, $^2J_{P,P}$ = 390.6 Hz, coordinated PPh_3), 100.5 (d, $^2J_{P,P}$ = 390.6 Hz, palladacycle P), four overlapping sets of signals at 111.8, 111.9, 112.1, 112.2 (s, signals of racemic dimer) ppm.

X-ray Diffraction Studies of the Complexes *meso*-3, (*Z*)-(R_C,S_CS_N)-4, (*Z*)-(S_C, S_CS_N)-4, 5 and *trans*-(±)-9: Crystal data for these five complexes and a summary of the crystallographic analyses are given in Table 2. Diffraction data were collected on a Siemens SMART CCD diffractometer with Mo-K_α radiation (graphite monochromator) by using ω-scans. SADABS absorption corrections were applied, and refinements by full-matrix least-squares were based on SHELXL 93.[13] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at fixed distance from carbon atoms and were assigned fixed thermal parameters.

CCDC-634583 (for *meso*-**3**), -634584 [for (*Z*)-(R_C,S_CS_N)-**4**], -634585 [for (*Z*)-(S_C,S_CS_N)-**4**], -634586 (for **5**), and -634587 [for *trans*-(±)-**9**] 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.

Table 2. Crystallographic data for complexes *meso*-**3**, *Z*-(R_C,S_CS_N)-**4**, *Z*-(S_C,S_CS_N)-**4**, **5** and *trans*-(±)-**9**.

	meso-**3**	*Z*-(R_C,S_CS_N)-**4**	*Z*-(S_C,S_CS_N)-**4**	**5**	*trans*-(±)-**9**
Formula	$C_{50}H_{40}Cl_2P_2Pd_2$	$C_{30}H_{28}NO_2PPd$	$C_{30}H_{28}NO_2PPd$	$C_{50}H_{42}Cl_4P_2Pd_2$	$C_{39}H_{43}ClP_2Pd$
M	986.46	571.90	571.90	1059.38	715.52
Space group	$I4_1/a$	$P2_1$	$P2_12_12_1$	$C2/c$	$P2_1/n$
Crystal system	Tetragonal	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
a [Å]	29.912(2)	9.866(2)	8.7813(7)	10.4912(14)	12.4345(5)
b [Å]	29.912(2)	9.1675(18)	9.6673(7)	16.715(2)	15.4637(6)
c [Å]	10.5243(14)	14.831(3)	31.100(3)	25.710(3)	19.4561(8)
α [°]	90	90	90	90	90
β [°]	90	107.856(4)	90	93.834(4)	106.7020(10)
γ [°]	90	90	90	90	90
V [Å^3]	9416.6(16)	1276.9(5)	2640.1(4)	4498.5(11)	3583.3(2)
Z	8	2	4	4	4
T [K]	223(2)	293(2)	223(2)	295(2)	295(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	0.977	0.817	0.790	1.143	0.707
R_1 (obs. data)	0.0370	0.0382	0.0519	0.0810	0.0360
wR_2 (obs. data)	0.0983	0.0876	0.1029	0.1541	0.0853
Flack parameter	–	0.02(3)	0.04(4)	–	–

Acknowledgments

We thank the National University of Singapore for the financial support of this research and the award of a research scholarship to J. K.-P. N. We also thank the Nanyang Technological University for the research scholarship to S. C.

[1] B. Cornils, W. A. Herrmann (Eds.), *Applied Homogenous Catalysis with Organometallic Compounds*, VCH, Weinheim, **1996**.

[2] a) G. W. Parshall, S. D. Ittel, *Homogenous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed., Wiley, New York, **1992**; b) R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley-Interscience, New York, **1994**; c) I. Ojima (Ed.), *Catalytic Asymmetric Synthesis*, Wiley-VCH, New York, **2000**.

[3] a) W. A. Herrmann, C. Brossmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller, H. Fischer, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1844–1848; b) W. A. Herrmann, C.-P. Reisinger, K. Öfele, C. Broßmer, M. Beller, H. Fischer, *J. Mol. Catal. A* **1996**, *108*, 51–56; c) J. M. Brunel, A. Heumann, G. Buono, *Angew. Chem. Int. Ed.* **2000**, *39*, 1946–1949; d) M. Castella, F. Calahorra, D. Sainz, D. Velasco, *Org. Lett.* **2001**, *3*, 541–544; e) B. L. Shaw, S. D. Perera, E. A. Staley, *Chem. Commun.* **1998**, 1361–1362; f) M. Ohff, A. Ohff, M. E. van der Boom, D. Milstein, *J. Am. Chem. Soc.* **1997**, *119*, 11687–11688; g) K. Kiewel, Y. Liu, D. E. Bergbreiter, G. A. Sulikowski, *Tetrahedron Lett.* **1999**, *40*, 8945–8948; h) J. M. Longmire, X. Zhang, M. Shang, *Organometallics* **1998**, *17*, 4374–4378; i) B. S. Williams, P. Dani, M. Lutz, A. L. Spek, G. van Koten, *Helv. Chim. Acta* **2001**, *84*, 3519–3530; j) D. Morales-Morales, R. E. Cramer, C. M. Jensen, *J. Organomet. Chem.* **2002**, *654*, 44–50; k) V. V. Dunina, O. N. Gorunova, L. G. Kuz′mina, M. V. Livantsov, Y. K. Grishin, *Tetrahedron: Asymmetry* **1999**, *10*, 3951–3961; l) V. V. Dunina, O. N. Gorunova, M. V. Livantsov, Y. K. Grishin, L. G. Kuz′mina, N. A. Kataeva, A. V. Churakov, *Tetrahedron: Asymmetry* **2000**, *11*, 3967–3984.

[4] a) J. K.-P. Ng, G.-K. Tan, J. J. Vittal, P.-H. Leung, *Inorg. Chem.* **2003**, *42*, 7674–7682; b) J. K.-P. Ng, Y. Li, G.-K. Tan, L.-L. Koh, J. J. Vittal, P.-H. Leung, *Inorg. Chem.* **2005**, *44*, 9874–9886.

[5] a) D. A. Albisson, R. B. Bedford, S. E. Lawrence, P. N. Scully, *Chem. Commun.* **1998**, 2095–2096; b) F. Miyazaki, K. Yamaguchi, M. Shibasaki, *Tetrahedron Lett.* **1999**, *40*, 7379–7383; c) R. B. Bedford, S. M. Draper, N. Scully, S. L. Welch, *New J. Chem.* **2000**, *24*, 745–747; d) D. Morales-Morales, C. Grause, K. Kasaoka, R. Redón, R. E. Cramer, C. M. Jensen, *Inorg. Chim. Acta* **2000**, *300–302*, 958–963; e) R. B. Bedford, S. L. Welch, *Chem. Commun.* **2001**, 129–130; f) V. I. Sokolov, L. A. Bulygina, O. Y. Borbulevych, O. V. Shishkin, *J. Organomet. Chem.* **1999**, *582*, 246–251; g) L. L. Troitskaya, S. T. Ovseenko, Y. L. Slovokhotov, I. S. Neretin, V. I. Sokolov, *J. Organomet. Chem.* **2002**, *642*, 191–194.

[6] J. Dupont, C. S. Consorti, J. Spencer, *Chem. Rev.* **2005**, *105*, 2527–2571.

[7] L. N. Lewis, *J. Am. Chem. Soc.* **1986**, *108*, 743–749.

[8] a) M. Beller, H. Fischer, W. A. Herrmann, K. Öfele, C. Brossmer, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1848–1849; b) B. L. Shaw, S. D. Perera, E. A. Staley, *Chem. Commun.* **1998**, 1361–1362; c) M. Beller, T. H. Riermeier, *Eur. J. Inorg. Chem.* **1998**, 29–35; d) D. Morales-Morales, R. Redón, C. Yung, C. M. Jensen, *Chem. Commun.* **2000**, 1619–1620; e) M. Ohff, A. Ohff, D. Milstein, *Chem. Commun.* **1999**, 357–358; f) H. Weissman, D. Milstein, *Chem. Commun.* **1999**, 1901–1902; g) D. E. Bergbreiter, P. L. Osburn, Y.-S. Liu, *J. Am. Chem. Soc.* **1999**, *121*, 9531–9538; h) D. E. Bergbreiter, P. L. Osburn, A. Wilson, E. M. Sink, *J. Am. Chem. Soc.* **2000**, *122*, 9058–9064; i) A. S. Gruber, D. Zim, G. Ebeling, A. L. Monteiro, J. Dupont, *Org. Lett.* **2000**, *2*, 1287–1290; j) X. Gai, R. Grigg, M. I. Ramzan, V. Sridharan, S. Collard, J. E. Muir, *Chem. Commun.* **2000**, 2053–2054; k) S. F. Kirsch, L. E. Overman, *J. Am. Chem. Soc.* **2005**, *127*, 2866–2867; l) L. E. Overman, T. P. Remarchuk, *J. Am. Chem. Soc.* **2002**, *124*, 12–13; m) P.-H. Leung, K.-H. Ng, Y. Li, A. J. P. White, D. J. Williams, *Chem. Commun.* **1999**, 2435–2436; n) S. Gosiewska, S. H. Martinez, M. Lutz, A. L. Spek, G. van Koten, R. J. M. K. Gebbink, *Eur. J. Inorg. Chem.* **2006**, 4600–4607.

[9] a) Y. Qin, H. Lang, J. J. Vittal, G.-K. Tan, S. Selvaratnam, A. J. P. White, D. J. Williams, P.-H. Leung, *Organometallics* **2003**, *22*, 3944–3950; b) X. Liu, K. F. Mok, P.-H. Leung, *Organometallics* **2001**, *20*, 3918–3926; c) G. He, S.-K. Loh, J. J. Vittal, K. F. Mok, P.-H. Leung, *Organometallics* **1998**, *17*, 3931–3936; d) Y. X. Li, K. H. Ng, S. Selvaratnam, G. K. Tan, J. J. Vittal, P.-H. Leung, *Organometallics* **2003**, *22*, 834; e) Y. X. Li, S. Selvaratnam, J. J. Vittal, P.-H. Leung, *Inorg. Chem.* **2003**, *42*, 3229–3236.

[10] J. K.-P. Ng, S. Chen, G.-K. Tan, P-H. Leung, *Inorg. Chem.*, DOI: 10.1021/ic0702320, submitted.

[11] H. Grüetzmacher in *Synthetic Methods of Organometallic and Inorganic Chemistry*, *Vol. 3: Phosphorus, Arsenic, Antimony and Bismuth* (Ed.: H. H. Karsch), Georg Thieme Verlag, Stuttgart, **1996**, pp. 85–88.

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

[13] G. M. Sheldrick, *SHELXL 93, Program for Crystal Structure*, University of Göttingen, Germany **1993**.

Received: February 5, 2007
Published Online: May 10, 2007

