Backbone Effect of MAP Ligands on Their Coordination Patterns with Palladium(II)

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The allylpalladium complexes (*R*)-**4** and (*R*)-**5** of chiral P, N auxiliaries (*R*)-**1** and (*R*)-**3** have been prepared. The X-ray structures of the complexes have been determined, and the results clearly show that two different chelating modes (P, N vs P, C_σ) are involved. The coordination patterns of donating atoms were dependent on the binaphthyl backbone of the chiral ligands. The isodesymmetrization revealed that the reaction occurs without regiochemical memory effect, which demonstrates a full dynamic equilibrium has been attained before nucleophilic attack. These results, combined with the solution behaviors of the complexes revealed by NMR studies, provided a further understanding of their asymmetric induction in allylic substitution of 1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate. The dramatic enhancement of enantioselectivity with (*R*)-**3** as a chiral inducer can be related to the different chelating mode of catalyst (*R*)-**5** from that of (*R*)-**4**. The change of bite angles of the two donors with palladium in the complexes (*R*)-**4** and (*R*)-**5** was considered as a direct reason for their dramatically different enanatioselectivities in the catalysis.

Introduction

Homogeneous enantioselective catalysis with chiral transition metal complexes is an attractive synthetic methodology since it is able to generate large quantities of enantiopure products using only a small amount of chiral catalyst.[1] Many well-known chiral metal catalysts containing palladium salts and chiral P, N auxiliaries show good asymmetric induction in the reactions such as Heck,[2] Michael,[3] cross-coupling,[4] and allylic substitution.[5] Recently, a novel class of aminophosphine ligand **1** (MAP) containing an sp^3 nitrogen donor, which could be regarded as a nitrogen analogue of Hayashi's MOP,[6] was developed by Kocovsky's and our group independently.[7] This ligand exhibited a dramatic acceleration of the amination of aryl halide,[8] but only moderate asymmetric induction in Pd(0)-catalyzed allylic substitution of 1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate.[7a] Kocovsky also demonstrated by X-ray crystal structural analysis that MAP and MOP ligands coordinated to Pd via unusual P, C_σ-chelation and P, η^2-coordination modes,[9,10] respectively, rather than a P, N- or P, O-chelation pattern. Buchwald et al. reported that the palladium complex of the similar aminophosphine ligand **2** showed excellent reactivity and enantioselectivity in asymmetric cross-coupling reactions.[11] Our previous work on the backbone effect of MAP ligands in Pd-catalyzed allylic substitution revealed that an octahydro analogue (H_8-MAP, **3**) of **1** provided much better asymmetric induction (82.5% ee vs 73% ee).[12a] We speculated that an P, N-chelated Pd complex was responsible for the catalysis and the enhanced enantioselectivity may be attributed to the

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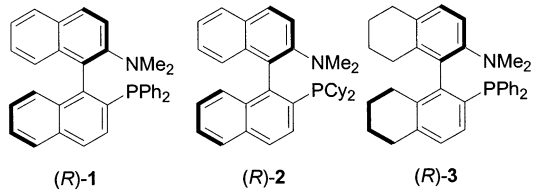
change of bite angle of the Pd complex after partial reduction of binaphthyl backbone. All these distinct results prompted us to elucidate what happened to our catalyst system containing (*R*)-**3**. In this article, we report our results on the structural study of allyl complexes of (*R*)-**1**/Pd and (*R*)-**3**/Pd. The possible pathway of asymmetric induction was proposed on the basis of structural and ^{1}H NMR information of catalysts and of the results of stoichiometric alkylation.

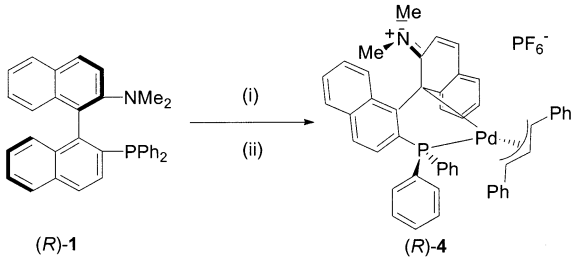


(*R*)-**1** (*R*)-**2** (*R*)-**3**

Results and Discussion

Preparation of the Allyl Complexe (*R*)-4. The reactions of ligand (*R*)-**1** with [$PdCl_2$ ($PhCN)_2$] and [Pd(η^3-C_3H_3) $(MeCN)_2]^+OTf^-$ have been demonstrated by Kocovsky to give P, C_σ-chelated palladium complexes. However, the structure of the real catalyst for asymmetric allylation of 1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate remains unknown. To mimic the catalytic system, a diphenylallyl Pd precursor, [Pd(Ph(η^3-C_3H_3)Ph)Cl]$_2$, was reacted with ligand (*R*)-**1**. As shown in Scheme 1, (*R*)-**1** and palladium dimer

Scheme 1[a]



(*R*)-**1** (*R*)-**4**

[a] (i) [Pd(Ph(η^3-C_3H_3)Ph)Cl]$_2$, CH_2Cl_2, rt; (ii) $AgPF_6$, 62%.

[Pd(Ph(η^3-C_3H_3)Ph)Cl]$_2$ were dissolved in dichloromethane and stirred at room temperature for 10 min. After the addition of $AgPF_6$, the reaction mixture was stirred in the dark at room temperature for an additional 1 h. The resulting AgCl was filtered off through Celite and washed with dichloromethane. The filtrate was concentrated under reduced pressure, and the residue was recrystallized from CH_2Cl_2/heptane to afford (*R*)-**4** as dark red crystals in 62% yield.

X-ray and NMR Studies on Complex (*R*)-4. A single crystal of (*R*)-**4** was selected from the crystals obtained above and submitted to X-ray diffraction analysis. A view of the molecular structure is shown in Figure 1, and selected bond lengths and angles are listed in Table 1.

The results of the X-ray diffraction analysis clearly demonstrated that ligand (*R*)-**1** acts as a P, C-ligand in the complex (*R*)-**4** with an unusual C_σ−Pd bonding mode. The distance between Pd and C_{11} was 2.338(11) Å, which is an indication of single C_{11}−Pd bond formation. Moreover, the bond lengths of C_{11}−C_{12} and C_{11}−C_{20} are 1.454 and 1.439 Å, respectively, which show some features of a C−C single bond. The bond length

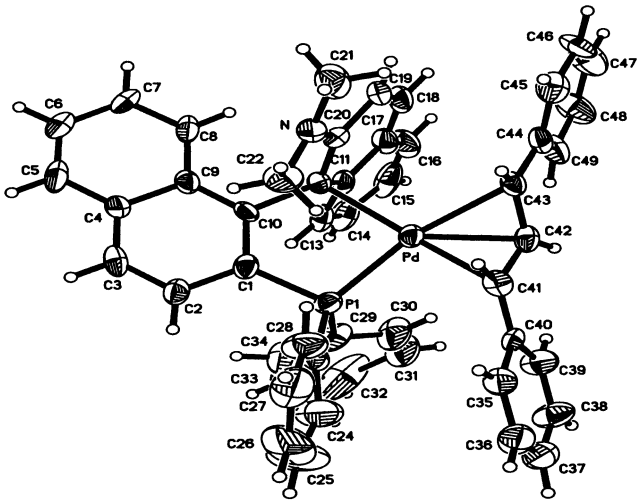


Figure 1. Molecular structure of (*R*)-**4**, showing the atom-numbering scheme. PF_6^- has been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Table 1. Bond Lengths [Å] and Angles [deg] for (*R*)-4

bond lengths	bond angles
Pd−C_{41} 2.214(12)	C_{41}−Pd−C_{43} 66.3(4)
Pd−C_{42} 2.182(10)	P_1−Pd−C_{11} 82.5(2)
Pd−C_{43} 2.320 (10)	C_{43}−Pd−C_{11} 111.8(4)
Pd−C_{11} 2.338(11)	C_{41}−Pd−P_1 99.0(3)
Pd−P_1 2.283(3)	
N−C_{20} 1.365(15)	
N−C_{21} 1.437(18)	
C_6−C_7 1.39(2)	
C_{11}−C_{12} 1.454(15)	
C_{11}−C_{20} 1.439(15)	
C_{18}−C_{19} 1.36(2)	
C_{19}−C_{20} 1.491(18)	

of C_{18}−C_{19} is only 1.36 Å, which is responsible for a conjugated C=C double bond. Particularly, the bond length of C_{20}−N (1.365(15) Å) is much shorter than a normal N−C single bond (1.40 Å), which suggests a partial C=N double-bond feature. Moreover, the planar arrangement of the NMe_2 group (Figure 1) is an alternative demonstration of the sp^2 hybridization at the nitrogen, which again supports the presence of a C=N double bond. The significant difference of bond lengths between C_{11}−Pd (2.338(11) Å) and C_{12}−Pd (2.863 Å) excluded the possibility for the formation of an η^2-coordinated complex. All these results again support the observation by Kocovsky in allylic Pd/**1** complex.[9,10] The stronger *trans* effect of the P atom than that of the C_{11} atom can be observed by comparison of the bond length of C_{43}−Pd (2.320 (10) Å) with that of C_{41}−Pd (2.214 (12) Å). A similar phenomenon was also observed in an analogous allyl Pd complex by Kocovsky.[9,10] The distinct structural feature is that the distances of allyl moiety carbon atoms from Pd in (*R*)-**4** increase by ≥0.1 Å in comparison with those observed in the unsubstituted allyl complex.[9] These differences may be attributed to the increased steric demand of the 1,3-diphenylallyl moiety in the complex. Accordingly, the nucleophile will attack at the allylic C_{43} carbon occupying the position *trans* to the P atom to give the *S* product, as observed experimentally.[12a]

The behavior of (*R*)-**4** in solution was also investigated by ^{1}H NMR and ^{31}P NMR in $CDCl_3$. A mixture of three species (11:9:1) was detected by ^{1}H NMR spectroscopy.

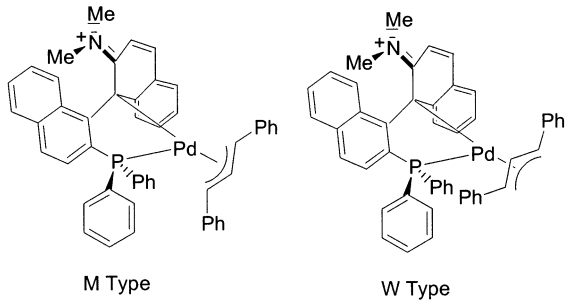
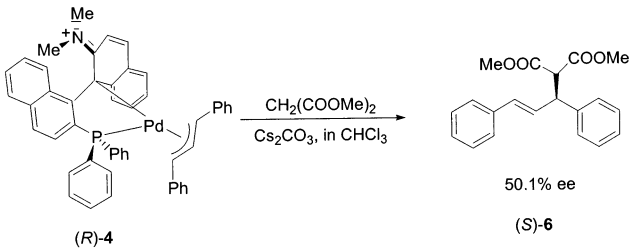


Figure 2. Different orientations (M and W types) of diphenylallyl unit in the complex (*R*)-**4**.

Two abundant species with the singlet peaks of NMe_2 at δ 2.80 and 2.60 can be attributed to the P, C_σ-chelated Pd complex with the "M" and "W" rotamers of diphenylallyl moieties (Figure 2), respectively. Two groups of signals at δ 4.71−4.87 and 5.43−5.60 are indicative of allyl protons. Each of them included two broad peaks with a ratio of 11:9, which again demonstrated the presence of different orientations of diphenylallyl moieties in the complex. The minor species with the singlet of NMe_2 at δ 3.45 can be assigned to a P, N-chelated Pd complex, because the coordination of the nitrogen atom to Pd will significantly decrease the shielding of protons at the *N*-methyl group. This can be further verified by the crystal structure and ^{1}H NMR spectrum of (*R*)-**5**. Two singlets in the ^{31}P NMR spectrum at δ 40.21 and 37.23 also confirmed the presence of P−Pd coordination and provided circumstantial evidence for the presence of two rotamers (M and W type) in the complex. These results mirror those observed by Kocovsky and coworkers, although they did not detect the minor P,N-chelate species.[9,10] This may be attributed to the steric bulk of the 1,3-diphenylallyl moiety in (*R*)-**4**, for which the more crowded P,C-chelate may not be as favorable as in the case of the unsubstituted allyl Pd complex of **1**.

Asymmetric Induction with Catalytic and Stoichiometric Amounts of (*R*)-4 in Allylic Substitution. To correlate the crystal and solution structures of complex (*R*)-**4** with its asymmetric induction, the reaction was carried out in $CHCl_3$ in the presence of a stoichiometric amout of (*R*)-**4** (Scheme 2). It was found

Scheme 2



that (*R*)-**4** reacted with malonate smoothly in the presence of Cs_2CO_3 to give the product (*S*)-**6** with 50.1% ee. This result is comparable to that (40.5% ee, *S*) obtained using the catalyst (5 mol %) prepared in situ from the reaction of (*R*)-**1** and $[Pd(C_3H_5)Cl]_2$. This result indicated that the allylic substitution of 1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate most probably took place through a C_σ, Pd-coordinated complex, and the enantioselectivity of the reaction was

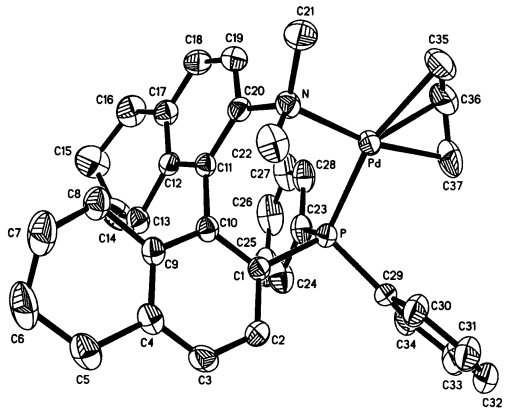
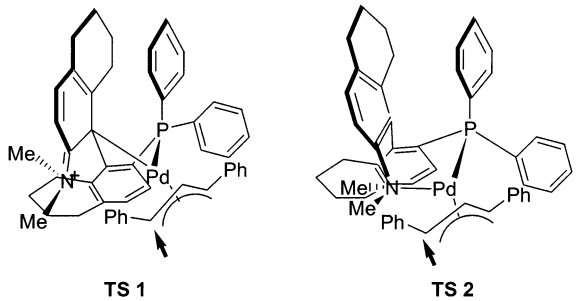


Figure 3. Molecular structure of (*R*)-**5**, showing the atom-numbering scheme. OTf^- and hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

controlled by the reactivity difference between M and W types of (*R*)-**4** complex toward the nucleophile rather than their ratio in solution, because an M/W equilibrium has been reached before the nuleophilic attack occurs (this will be discussed below on the basis of the absence of memory effect in the catalytic system disclosed by isotopical experiment).

Preparation of Allyl Complex (*R*)-5. In our previous work, it was postulated that the Pd complex of (*R*)-**3** would adopt a P, N-chelating pattern because of a higher energy level of the intermediate involved in **TS 1** than that in **TS 2** (1,3-butadiene vs benzene structure).[12a] The significant enhancement of enantioselectivity of the reaction with the catalysis of Pd/(*R*)-**3** in comparison with Pd/(*R*)-**1** may be attributed to the change of bite angle of the Pd complex after partial reduction of the binaphthyl backbone. Therefore, the preparation and X-ray diffraction characterization of the Pd complex of (*R*)-**3** will provide direct evidence for elucidating this problem. Following a similar procedure for the preparation of (*R*)-**4**, complex (*R*)-**5** was obtained by the reaction of (*R*)-**3** with $[Pd(\eta^3\text{-}C_3H_5)(CH_3CN)_2]^+OTf^-$ in dichloromethane at room temperature. Removal of the solvent and recrystallization of the residue from CH_2Cl_2/EtOAc afforded (*R*)-**5** as yellow prisms in 51% yield.



X-ray and NMR Studies on Complex (*R*)-5. A single crystal of (*R*)-**5** was selected from the crystals obtained above and submitted to X-ray diffraction analysis. A view of the molecular structure is shown in Figure 3, and selected bond lengths and angles are listed in Table 2. The results clearly show that ligand (*R*)-**3** acts as a P, N-ligand in the complex (*R*)-**5** to form a N−Pd coordination bond rather than the case of (*R*)-**4**,

Table 2. Bond Lengths [Å] and Angles [deg] for (*R*)-5

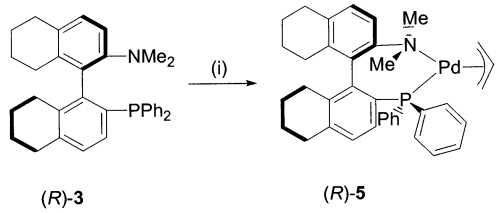
bond length	bond angle
Pd−N 2.193(3)	N−Pd−P 98.90(9)
Pd−C_{35} 2.191(5)	C_{35}−Pd−N 101.4(2)
Pd−C_{36} 2.174 (10)	C_{37}−Pd−P 92.6(2)
Pd−C_{37} 2.105(6)	C_{37}−Pd−C_{35} 67.2(3)
Pd−P 2.2981(10)	
N−C_{20} 1.473(5)	
N−C_{21} 1.460(6)	
C_6−C_7 1.479(9)	
C_{11}−C_{12} 1.413(5)	
C_{11}−C_{20} 1.419(5)	
C_{18}−C_{19} 1.355(6)	
C_{19}−C_{20} 1.373(6)	

with C_σ−Pd bonding. The bond lengths of P−Pd and N−Pd are 2.2981(10) and 2.139(3) Å, respectively, which are indicative of a normal coordination bond between Pd and the P or N atom.[13] The bond distance of N−C_{20} (1.473(5) Å) is longer than that observed in (*R*)-**4** (1.365(15) Å) or that of a normal N−C single bond (1.40 Å) in the 2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN) ligand.[7b] This phenomenon is probably caused by the coordination of lone-pair electrons of N to Pd, which prevents n−π conjugation between the NMe_2 group and the aromatic ring. The bond length of Pd−C_{35} (2.191(5) Å) is longer than that of Pd−C_{37} (2.105(6) Å), which again indicates that the P-donor has a stronger *trans*-influence than the N-donor. Accordingly, the allylation reaction will take place by nucleophilic attack at the carbon atom *trans* to the P-donor in principle. Interestingly, the bite angle of the two donors with palladium (98.90°) was much larger than that of the allyl palladium complex of (*R*)-**1** (84.21°).[9] Although we did not obtain the crystal structure of the 1,3-diphenylallyl palladium complex of (*R*)-**3** (H_8-MAP), it is reasonable to assume that changing the ligand backbone from MAP to H_8-MAP triggers the coordination change from the P, C- to the P, N-pattern, independently of the allyl used (allyl or diphenyl allyl). Therefore, the change of bite angles between the two donors and palladium in (*R*)-**1** and (*R*)-**3** could be an important reason for the dramatic enhancement of the asymmetric induction level with (*R*)-**3** in allylic substitution.[14]

Solution Behavior of Complex (*R*)-5 and Its Asymmetric Induction with Catalytic and Stoichiometric Amounts of Catalysts in Allylic Substitution. The solution behavior of complex (*R*)-**5** was also studied by ^{1}H NMR, ^{31}P NMR, and ^{13}C NMR spectra. The ^{31}P NMR and ^{13}C NMR spectra of (*R*)-**5** indicate that the chemical shifts of ^{31}P (19.90 and 21.23 ppm) and ^{13}C (52.69 ppm for NMe_2) are much higher than those of its free ligand (−14.3 ppm for ^{31}P and 43.32 ppm for NMe_2, respectively), which strongly supports the formation of P, N-chelation with Pd in solution. The signals of NMe_2 in the ^{1}H NMR spectrum of (*R*)-**5** appearing at 3.27 and 3.33 ppm in almost a 1:1 ratio show the presence of two diastereoisomers of (*R*)-**5** in solution because of the spatial orientation of allyl unit. The significant downfield shift of Me_2N in the complex relative to that of free ligand (2.23 ppm) again demonstrates the formation of N−Pd coordination in (*R*)-**5** in solution.

An experiment using the isolated P, N-connected $[Pd(Ph(C_3H_3)Ph)((R)\text{-}\mathbf{3})]^+PF_6^-$ complex ((*R*)-**7**) of H_8-MAP as substrate to react with malonate was carried out in $CDCl_3$ at room temperature in order to compare its asymmetric induction with the case of using a catalytic amount of (*R*)-**3**/Pd complex (Scheme 4). The

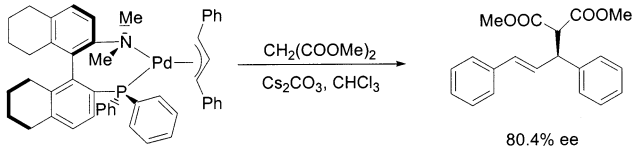
Scheme 3[a]



(*R*)-**3** (*R*)-**5**

[a] (i) $[Pd(\eta^3\text{-}C_3H_5)(CH_3CN)_2]^+OTf^-$, CH_2Cl_2.

Scheme 4



(*R*)-**7** 80.4% ee (*S*)-**6**

allylation product (*S*)-**6** was obtained in 54% yield with 80.4% ee, which is essentially identical to that (82.1% ee) achieved by using 5 mol % of the catalyst prepared in situ from the reaction of (*R*)-**3** and $[Pd(C_3H_5)Cl]_2$. These results reflect that the reaction involves the same asymmetric induction pathway using either catalytic or stoichiometric amount of H_8-MAP/Pd complexes for the reaction.

Regiochemical Memory Effect of the Catalysis. An important question arises regarding the regiochemical memory effect in the catalysis of the allylic substitution. The study of such memory effect can be an indication of the situation of dynamic equilibrium before nucleophilic attack. Kocovsky reported that Pd complexes of MAP did not exhibit a regiochemical memory effect in the reaction of isocinnamyl acetate with $[NaCR(CO_2Me)_2]$ (R = H or Me). However, the reaction of cyclopentenyl pivalate proved that the reaction occurs with powerful stereochemical memory effects. To investigate whether the memory effect is involved in the present catalytic system, the α-D labeled (±)-1,3-diphenylprop-2-en-1-yl acetate, (±)-**8**, was taken as the substrate for the reaction (Scheme 5). The reaction was carried out in dichloromethane with 5 mol % of Pd catalyst bearing (*R*)-**1** or (*R*)-**3** prepared in situ in the presence of Cs_2CO_3 as the base at room temperature (25 °C). The reaction proceeded smoothly to give allylic substitution product (*S*)-**6** in quantitative yields. The ^{1}H NMR spectrum of the product (Figure 4) shows that (*S*)-α-D-**6** and (*S*)-γ-D-**6** was formed in a 1:1 molar ratio, which clearly demonstrates that there is no regiochemical memory effect in the present catalytic system. The reaction of isocinnamyl acetate (±)-**9** with dimethyl malonate with the catalysis of (*R*)-**3**/Pd in the presence of Cs_2CO_3 gives the branched product **10** as the major isomer, which mirrors the result obtained by Kocovsky using (*R*)-**1**/Pd catalyst (i.e., no memory effect).[10] All

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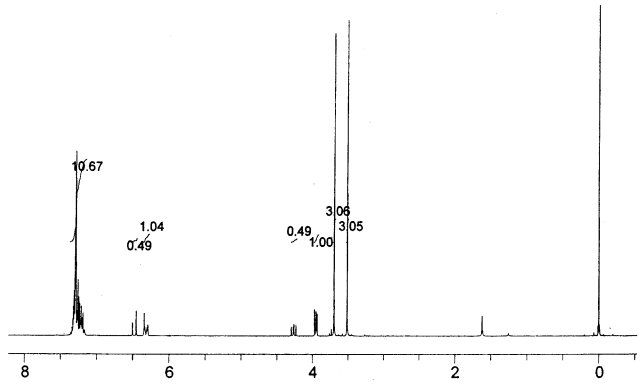
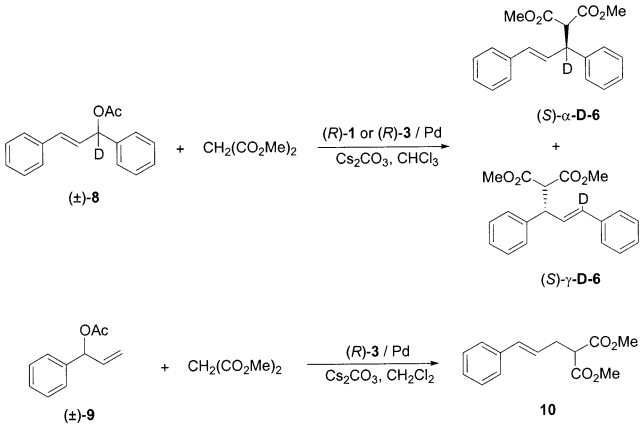


Figure 4. ^{1}H NMR spectrum of product (*S*)-**6** showing a 1:1 mixture of (*S*)-α-D-**6** and (*S*)-γ-D-**6**.

Scheme 5



these results indicated that in the reaction of (±)-1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate in the presence of (*R*)-**1**- or (*R*)-**3**-modified Pd complex the nuleophilic attack takes place after the full dynamic equilibrium has been attained. The enantioselectivity of the reaction was controlled by the reactivity difference between M- and W-type rotamers of the 1,3-diphenylallyl palladium complexes (*R*)-**4** and (*R*)-**5** with the nucleophile rather than their ratio in solution.

Conclusion

In conclusion, the allylpalladium complexes (*R*)-**1** and (*R*)-**3** have been prepared and characterized by X-ray single crystal diffraction analyses. The results clearly demonstrate that two kinds of chelating modes (P, N vs P, C_σ) of coordination donors with the Pd atom have been involved in two kinds of complexes. The coordination patterns of donating atoms were dependent on the binaphthyl backbone of the chiral ligands. The isodesymmetrization experiments revealed that the reaction occurs without regiochemical memory effect, which demonstrates a full dynamic equilibrium has been attained before nucleophilic attack. These results, combined with the solution behaviors of the complexes revealed by NMR studies, provide a further understanding of their asymmetric induction in allylic substitution of 1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate. The dramatic enhancement of enantioselectivity with (*R*)-**3** as a chiral inducer can be related to the different chelating mode of catalyst (*R*)-**5** from that of (*R*)-**4**. The change of bite angle of the two donors with palladium in the complexes (*R*)-**4** and (*R*)-**5** was considered as a direct reason for their dramatically different enanatioselectivities in the catalysis.

Experimental Section

^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Mercury 300 spectrometer at 25 °C. Chemical shifts are expressed in ppm with TMS as an internal standard ($\delta = 0$ ppm). The ^{31}P NMR spectra were recorded on a Varian Mercury 300 instrument in $CDCl_3$ with 85% H_3PO_4 as an external reference. Optical rotation was measured with a PE-341 automatic polarimeter. Liquid chromatographic analyses were conducted on a JASCO 1580 system. The IR spectra were measured on a Rio-Rad FTS-185 spectrometer in KBr pellets. ESI spectra were obtained on a Mariner LC-TOF spectrometer. Elemental analysis was performed with an Elemental VARIO EL apparatus. Commercial reagents were used as received without further purification unless otherwise noted. Dichloromethane was freshly distilled from calcium hydride. (*R*)-**1** and (*R*)-**3** were prepared according to the literature methods.[7b,12]

Synthesis of (*R*)-4. $[Pd(Ph(\eta^3\text{-}C_3H_3)Ph)Cl]_2$ (100 mg, 0.148 mmol) and (*R*)-**1** (156.8 mg, 0.326 mmol) in dried dichloromethane (10 mL) were stirred at room temperature for 10 min. After the addition of $AgPF_6$ (70.5 mg, 0.729 mmol), the reaction mixture was stirred in the dark at room temperature for an additional 1 h. The AgCl formed was filtered through Celite and washed with dichloromethane. The filtrate was concentrated under reduced pressure, and the residue was recrystallized from CH_2Cl_2/heptane to afford (*R*)-**4** as a dark red crystal (93.2 mg, 62% yield). Mp: 180 °C (dec). $[\alpha]_D^{20} = -2355°$ (*c* 0.03, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.60 (br, 3H), 2.80 (br, 3H), 4.71−4.87 (br, 1H), 5.29 (s, 2H), 5.43−5.60 (br, 1H), 5.89−6.20 (m, 2H), 6.74−7.73 (m, 29H), 7.83 (d, $J = 8.1$ Hz, 1H), 7.91 (d, $J = 8.6$ Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 29.65, 53.43, (other peaks cannot be interpreted clearly). ^{31}P NMR (161.9 MHz): δ 37.2, 40.2. IR (KBr pellet): ν 3053 (w), 1611 (m), 1599 (m), 1539 (m), 1514 (m), 1436 (m), 1097 (m), 838 (vs), 752 (m), 691 (s), 557 (s). ESIMS (*m*/*z*): 780.2 ($[M - PF_6 - CH_2Cl_2]^+$, 100%). Anal. Calcd for $C_{49}H_{41}F_6NP_2Pd\cdot CH_2Cl_2$: C, 59.39; H, 4.29; N, 1.39. Found: C, 59.56; H, 4.32; N, 1.36.

Synthesis of (*R*)-5. $[Pd(\eta^3\text{-}C_3H_5)(CH_3CN)_2]^+OTf^-$ (94.5 mg, 0.25 mmol) and (*R*)-**3** (122.3 mg, 0.25 mmol) in dried dichloromethane (4 mL) were stirred at room temperature for 10 min. The solution was concentrated under reduced pressure. The crude product was recrystallized from CH_2Cl_2/EtOAc to give (*R*)-**5** as yellow prisms (100 mg, 51% yield). Mp: 286−287 °C. $[\alpha]_D^{20} = -31.9°$ (*c* 0.51, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.74 (br, 1H), 0.89−0.94 (m, 1H), 1.24−1.32 (m, 3H), 1.63−1.90 (m, 6H), 2.05−2.29 (m, 3H), 2.50 (br, 1H), 2.84−2.95 (m, 3H), 3.27 (s, 3H), 3.33 (s, 3H), 3.95−4.54 (m, 1H), 4.74−4.77 (m, 1H), 5.76−5.93 (m, 1H), 6.89−7.53 (m, 14H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 21.86, 22.36, 22.61, 27.52, 27.73, 29.16, 29.85, 52.69, 123.00, 123.18, 128.81, 128.95, 129.09, 129.47, 129.58, 130.34, 130.64, 130.67, 130.93, 131.67, 131.70, 132.42, 132.58, 134.74, 134.94, 135.29, 137.81, 142.62, 142.65, 145.52. ^{31}P NMR (161.9 MHz): δ 19.9, 21.2. IR (KBr pellet): ν 3059 (w), 2926 (s), 1589 (w), 1576 (w), 1479 (s), 1461 (m), 1438 (s), 1263 (vs), 1221 (s), 1149 (vs), 1031 (vs), 745 (m), 719 (m), 693 (s), 637 (vs). ESIMS (*m*/*z*): 636.2 ($[M - OTf]^+$, 100%). Anal. Calcd for $C_{38}H_{41}F_3NO_3PPdS$: C, 58.05; H, 5.26; N, 1.78. Found: C, 58.13; H, 5.46; N, 1.72.

X-ray Crystal Structure Determinations of Complexes (*R*)-4 and (*R*)-5. A single crystal of (*R*)-**4** and (*R*)-**5** suitable for X-ray diffraction study was obtained by recrystallization at room temperature from heptane/CH_2Cl_2 and EtOAc/CH_2Cl_2 solutions, respectively. The X-ray diffraction intensity data were collected on a Bruker Smart CCD diffractometer at 20 °C using Mo Kα radiation ($\lambda = 0.71073$ Å) with a $\omega-2\theta$ scan mode.

Table 3. Crystal Data and Experimental Details for Complexes (*R*)-4 and (*R*)-5

	(*R*)-**4**	(*R*)-**5**
formula	$C_{49}H_{41}F_6NP_2Pd$	$C_{38}H_{41}F_3NO_3PPdS$
fw	926.17	786.15
space group	$P2_1$	$P2_12_12_1$
a (Å)	9.717(18)	10.2167(4)
b (Å)	23.259(4)	13.3715(5)
c (Å)	10.320(19)	28.7307(12)
α (deg)		
β (deg)	92.517(3)	
γ (deg)		
V (Å^3)	2330.1(7)	3631.4(3)
Z	2	4
D_{calcd} (g/cm^3)	1.320	1.438
cryst size (mm)	0.15 × 0.20 × 0.20	0.25 × 0.20 × 0.30
μ(Mo Kα) (cm^{-1})	5.23	6.65
orientation reflns: range (2*θ*) (deg)	3.50−50.00	2.84−56.60
no. of unique data, total	6106	8565
with $I > 2.00\sigma(I)$	4712	7742
no. of params refined	547	454
correct. factors, max. min.	0.4695−1.000	0.9366−1.000
R^a	0.0785	0.0469
$R_w{}^b$	0.1849	0.1124
quality of fit indicator^c	1.052	1.057
max. shift/esd final cycle	0.034	0.110
largest peak, e$^-$/Å^3	1.895	0.677
min. peak, e$^-$/Å^3	−0.696	−0.728

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum_w|F_o|^2]^{1/2}$; $w = I/\sigma^2(|F_o|)$. ^{c} Quality-of-fit $= [\sum_w(|F_o| - |F_c|)^2/(N_{obs} - N_{params})]^{1/2}$.

The structures of (*R*)-**4** and (*R*)-**5** were solved by direct methods (SHELX-97) and refined by full-matrix least squares. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement gave agreement factors of $R = 0.0785$ and $R_w = 0.1849$ for (*R*)-**4** and $R = 0.0469$ and $R_w = 0.1124$ for (*R*)-**5**.

The details of the crystallographic data and the procedures used for data collection and reduction information for (*R*)-**4** and (*R*)-**5** are given in Table 3. Selected bond lengths and angles are listed in Tables 1 and 2. The atomic coordinates and B_{iso}/B_{eq}, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for them are given in the Supporting Information. The molecular structures of (*R*)-**4** and (*R*)-**5** are given in Figures 1 and 2, respectively.

Asymmetric Allylic Substitution of (*R*)-4 with Dimethyl Malonate. To a solution of (*R*)-**4** (45.0 mg, 0.046 mmol) in dried $CHCl_3$ (1 mL) were added Cs_2CO_3 (30.0 mg, 0.092 mmol) and dimethyl malonate (12.2 mg, 0.092 mmol), respectively. The reaction mixture was stirred at room temperature for 12 h. The mixture was filtered through Celite, and the filtrate was concentrated under reduced pressure. The residue was submitted to chromatographic separation on silica gel with hexane/EtOAc (4:1) as eluent to give (*S*)-**6** as a colorless oil (9.5 mg, 64%) with 50.1% ee (determined by HPLC on Chiralpak AD column, hexane/*i*-PrOH, 90:10, flow rate = 1 mL/min, $t_R = 12.6$ min, $t_S = 18.9$ min). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.52 (s, 3H), 3.69 (s, 3H), 3.97 (d, $J = 10.9$ Hz, 1H), 4.27 (dd, $J = 10.9$, 8.7 Hz, 1 H), 6.34 (dd, $J = 15.4$, 8.4 Hz, 1H), 6.48 (d, $J = 15.8$ Hz, 1H), 7.17−7.24 (m, 10H).

Enantioselective Allylation Catalyzed by in Situ-Generated (*R*)-1/Pd Catalyst. To a Schlenk tube containing 1,3-diphenylprop-2-en-l-yl acetate (46.5 mg, 0.20 mmol), $[Pd(C_3H_5)Cl]_2$ (1.7 mg, 0.0046 mmol), (*R*)-**1** (6.7 mg, 0.014 mmol), and Cs_2CO_3 (120.3 mg, 0.370 mmol) was added 2 mL of $CHCl_3$. The mixture was stirred at room temperature for 20 min, and dimethyl malonate (48.9 mg, 0.37 mmol) was then added. The reaction mixture was stirred at room temperature for 24 h before it was quenched with saturated aqueous NH_4-Cl. The mixture was extracted with EtOAc (3 × 20 mL), and the organic phase was washed with saturated aqueous $NaHCO_3$, water, and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatograghy on silica gel with hexane/EtOAc (4:1) as eluent to give (*S*)-**6** (14.5 mg, 24%) as a colorless oil with 40.5% ee.

Asymmetric Allylic Substitution of [Pd(Ph(C_3H_3)Ph)((*R*)-3)] Complex ((*R*)-7) with Dimethyl Malonate. [Pd(Ph(η^3-C_3H_3)Ph)Cl]$_2$ (62 mg, 0.093 mmol) and (*R*)-**3** (100 mg, 0.204 mmol) in dried dichloromethane (5 mL) were stirred at room temperature for 10 min. After the addition of $AgPF_6$ (45 mg, 0.180 mmol), the reaction mixture was stirred in the dark at room temperature for an additional 1 h. The AgCl formed was filtered through Celite and washed with dichloromethane. The filtrate was concentrated under reduced pressure to give orange solids of (*R*)-**7** in quantitative yield. This complex was taken as a substrate directly without further purification to react with dimethyl malonate. To a solution of (*R*)-**7** (45.0 mg, 0.045 mmol) in dried $CHCl_3$ (1 mL) were added Cs_2CO_3 (30.0 mg, 0.092 mmol) and dimethyl malonate (12.2 mg, 0.092 mmol), respectively. The reaction mixture was stirred at room temperature for 12 h. The mixture was filtered through Celite, and the filtrate was concentrated under reduced pressure. The residue was submitted to chromatographic separation on silica gel with hexane/EtOAc (4:1) as eluent to give (*S*)-**6** as a colorless oil (8.5 mg, 54%) with 80.4% ee.

Enantioselective Allylation Catalyzed by in Situ-Generated (*R*)-3/Pd Catalyst. To a Schlenk tube containing 1,3-diphenylprop-2-en-l-yl acetate (54 mg, 0.23 mmol), $[Pd(C_3H_5)Cl]_2$ (2.0 mg, 0.0055 mmol), (*R*)-**3** (7.8 mg, 0.016 mmol), and Cs_2CO_3 (139 mg, 0.37 mmol) was added 2 mL of $CHCl_3$. The mixture was stirred at room temperature for 20 min, and dimethyl malonate (48.9 mg, 0.37 mmol) was then added. The reaction mixture was stirred at room temperature for 24 h before it was quenched with saturated aqueous NH_4Cl. The mixture was extracted with EtOAc (3 × 20 mL), and the organic phase was washed with saturated aqueous $NaHCO_3$, water, and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatograghy on silica gel with hexane/EtOAc (4:1) as eluent to give (*S*)-**6** (64 mg, 86%) as a colorless oil with 82.1% ee.

Synthesis of (±)-1-[$^2H_1$]-1,3-Diphenylprop-2-en-1-yl Acetate (±)-8. 1,3-Diphenylpropenone (3.70 g, 17.8 mmol) in Et_2O (20 mL) was added dropwise to a suspension of LiAl-[$^2H_4$] (0.36 g, 8.60 mmol) in Et_2O (10 mL). After complete addition, water (20 mL) was added dropwise (CAUTION!). The mixture was extracted with Et_2O (7 × 20 mL), and the organic phase was washed with saturated aqueous $NaHCO_3$, water, and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was used for the next step without further purification. To a stirred solution of the residue obtained above (2.12 g, 10 mmol) in Et_3N (10 mL) was added $(Ac)_2O$ (5.60 mL, 0.06 mmol). After 12 h, the reaction mixture was poured into water, extracted with Et_2O (3 × 50 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was submitted to flash chromatography separation on silica gel with ethyl acetate/hexane (1:4) as eluent to give a 1:1 mixture of (±)-1-[$^2H_1$]-1,3-diphenylprop-2-en-1-yl acetate, (±)-**8**, and (±)-1,2,3-[$^2H_3$]-1,3-diphenylpropyl acetate in >99% yield as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.13(s, 1.5H), 2.17 (s, 1.5H), 2.56−2.70 (m, 1H), 6.34 (d, $J = 16.2$ Hz, 0.5 H), 6.64 (d, $J = 16.2$ Hz, 0.5 Hz), 7.13−7.43 (m, 10H).

Search for the Memory Effect in Palladium-Catalyzed Allylic Substitution. The following procedure is typical: To a stirred solution containing (±)-1-[$^2H_1$]-1,3-diphenylprop-2-en-1-yl acetate, (±)-**8** (43.5 mg, 0.18 mmol), $[Pd(C_3H_5)Cl]_2$ (1.6 mg, 0.0044 mmol), (*R*)-**3** (6.3 mg, 0.013 mmol), and Cs_2CO_3 (112.5 mg, 0.34 mmol) was added 2 mL of CH_2Cl_2. The mixture was stirred at room temperature for 20 min, and dimethyl malonate (45.0 mg, 0.34 mmol) was then added. The reaction

mixture was stirred at room temperature for 24 h before it was quenched with saturated aqueous NH_4Cl. The mixture was extracted with EtOAc (3 × 20 mL), and the organic phase was washed with saturated aqueous $NaHCO_3$, water, and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatograghy on silica gel with hexane/EtOAc (4:1) as eluent to give (*S*)-**6** (55 mg, >99%) as a colorless oil with 80% ee. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.51 (s, 3H), 3.70 (s, 3H), 3.93−3.97 (m, 1H), 4.23−4.30 (m, 0.5H), 6.20−6.34 (m, 1H), 6.47 (d, J = 15.9 Hz, 0.5H), 7.19−7.34 (m, 10H). ^{1}H NMR spectrum shows that (*S*)-**6** is a 1:1 mixture of (*S*)-α-D-**6** and (*S*)-γ-D-**6**.

Following the same procedure mentioned above, 5 mol % of (*R*)-**1**/Pd was taken as the catalyst for the same reaction, and a 1:1 mixture of (*S*)-α-D-**6** and (*S*)-γ-D-**6** was obtained in 93% yield with 43.9% ee.

Reaction of Isocinnamyl Acetate (±)-9 with Dimethyl Malonate with the Catalysis of (*R*)-3/Pd. To a Schlenk tube containing isocinnamyl acetate (±)-**9**[10] (60.6 mg, 0.344 mmol), $[Pd(C_3H_5)Cl]_2$ (3.2 mg, 0.0086 mmol), (*R*)-**3** (12.7 mg, 0.026 mmol), and Cs_2CO_3 (225 mg, 0.688 mmol) was added 2 mL of CH_2Cl_2. The mixture was stirred at room temperature for 20 min, and dimethyl malonate (90.8 mg, 0.688 mmol) was then added. The reaction mixture was stirred at room temperature for 24 h before it was quenched with saturated aqueous NH_4Cl. The mixture was extracted with EtOAc (3 × 20 mL), and the organic phase was washed with saturated aqueous $NaHCO_3$, water, and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatograghy on silica gel with hexane/EtOAc (4:1) as eluent to give **10** (75 mg, 88%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.81 (td, J = 1.2, 7.5 Hz, 2H), 3.53 (m, 1H), 3.75 (s, 6H), 6.15 (m, 1H), 6.48 (d, J = 16.5 Hz, 1H), 7.35−7.21 (m, 5H).

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Supporting Information Available: Text giving a full listing of crystallographic data for (*R*)-**4** and (*R*)-**5**, including tables of positional and isotropic equivalent displacement parameters, calculated positions of the hydrogen atoms, anisotropic displacement parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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