Trans Effect of Different Coordinated Atoms of Planar Chiral Ferrocene Ligands with the Same Backbone in Palladium−Catalyzed Allylic Substitutions

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A series of planar chiral P,S-, P,(C═N)-, and S,(C═N)-bidentate ferrocenyl ligands **4**, **5**, **8**, and **9** with the same central and planar chiralities were prepared from the commercially available starting material *N*,*N*-dimethyl-(*S*)-α-ferrocenylethylamine. A Pd-catalyzed asymmetric allylic alkylation reaction was used as a model reaction to study the trans effect of the coordination atoms by these ligands. On the basis of the reaction results and the study of X-ray diffraction as well as ^{1}H and ^{13}C NMR spectra of the complexes (**12**−**15**), the sequence of the trans effect was established as C═N > P > S, which was supported by molecular modeling at the PM3 level.

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Introduction

Catalytic enantioselective substitution reactions have received much attention recently, and significant progress has been made in the carbon−carbon bond-forming reactions using chiral-modified metal complexes.[1] For a catalytic asymmetric reaction, the chiral environment provided by judiciously chosen ligands is critical. In comparison to similar reactions with C_2-symmetrical ligands, heterobidentate ligands allow more permutation[2] and provide selectivity control.

The trans effect of a ligand is a kinetic phenomenon that partially describes the transition state in a substitution reaction.[3,4] For heterobidentate ligands used in catalytic allylic substitution reactions, the trans effects of the donor atoms can be transmitted to the allylic substrate through the metal. In this way, the reactivity and selectivity of the reaction may be fine-tuned.[5c,g] These effects may be monitored via the ^{13}C chemical shift of the allylic complex.[5a,b,f] The lower field allylic ^{13}C chemical shifts are observed with the terminal carbon atom trans to a stronger π-acceptor donor atom; the higher field allylic ^{13}C shifts are observed with the terminal carbon atom trans to a weaker one. Also, the difference of bond distances between metal and allylic carbon termini could be revealed by X-ray crystallography. That is, the bond between the Pd atom and the allylic terminal carbon atom trans to the more powerful π-acceptor will be longer and hence more susceptible to cleavage, as a result of nucleophilic attack.[5d−g] The trans effects of different coordination atoms in P,N-,[6] N,S-[7] and P,S-bidentate[8] Pd complexes had been reported, respectively, but the trans effect of N had only been studied in oxazoline, pyridine, and amine systems. While most ligands contain an imino moiety and have played very important roles in the

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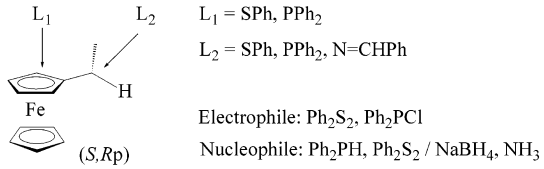
catalysts for olefin polymerization[9] and asymmetric expoxidation,[10] data for the trans effect of the imine system are almost nonexistent. Recently, Anderson studied the trans effect of imino group in N,S-ligands and postulated but did not prove that the nucleophile would attack the terminus trans to the imino donor. The imine group was regarded as a better π-acceptor than thioether.[7a] However, a comparison of trans effects between phosphine and imine systems has not been even studied.

Planar chiral ferrocenyl ligands have been efficient catalysts for asymmetric synthesis in both academic research and industrial processes.[11] In a program aimed at the synthesis and applications of ferrocenyl ligands in asymmetric catalysis,[12,13] we have been interested in the study of trans effects of different coordination atoms in the ligand with the same backbone. To make a better comparison, all ligands have the same planar disposition of the coordination atoms and central chiralities. We report a convenient method to prepare a series of heterobidentate ligands (**4**, **5**, **8**, and **9**) with the above requirements from the commercially available *N*,*N*-dimethyl-(*S*)-α-ferrocenylethylamine. The palladium-catalyzed asymmetric allylic substitution reaction was used as a model reaction to study the trans effect of different coordination atoms. According to the results of the reaction (ee value and configuration of product) and the X-ray diffraction and solution NMR studies of complexes **12**−**15**, a sequence of trans effects of P, S, and C═N was established, which was further supported by molecular modeling at the PM3 level.

Chart 1

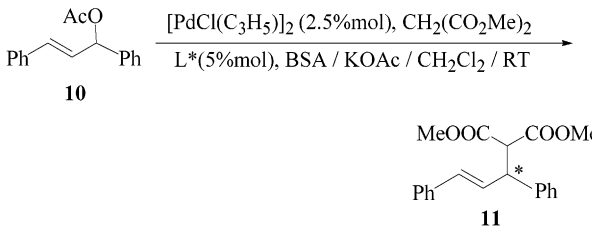


Results and Discussion

Synthesis of Ligands. In 1970, Ugi and co-workers found a diastereoselectively directed ortho-metalation reaction of *N*,*N*-dimethyl-(*S*)-α-ferrocenylethylamine, and a planar chirality was thus induced.[14] They also confirmed that the configuration of the central chiral carbon atom of the ferrocenylethylamine was completely retained after the substitution of the amino group.[15] The different dispositions of the ligating groups on the same backbone is therefore viable (Chart 1).[16]

Taking advantage of the above strategies, we synthesized the four heterobidentate ligands **4**, **5**, **8**, and **9** from *N*,*N*-dimethyl-(*S*)-α-ferrocenylethylamine. Ligands **4**[17] and **8**[18] were synthesized as described in the literature. Using similar methods, compound **5** was conveniently synthesized from the ferrocenyl thioether **3**. When **3** is treated with HOAc at room temperature for $^1/_2$ h followed by direct nucleophilic attack of PPh_2H[19] and then heated to 100 °C for 6 h, ligand **5** can be afforded in 82% yield. **3** was treated with acetic anhydride at 100 °C to give the corresponding acetoxy compound. The acetoxy group was converted to an amino group by reaction with a large excess of ammonia in methanol in an autoclave at 100 °C. Treatment of **7** with benzaldehyde in benzene in the presence of molecular sieves (4 Å) at room temperature gave imine **9** in 97% yield (Scheme 1). Ligands **4**, **5**, **8**, and **9** have the same planar and central chiralities and S,R_p configuration.

Asymmetric Alkylation. The Pd-catalyzed allylic substitution reactions of 1,3-diphenyl-2-propenyl acetate (**10**) was carried out in dry dichloromethane at room temperature in the presence of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ and ligands **4**, **5**, **8**, and **9**. The nucleophile was generated from dimethyl malonate in the presence of *N*,*O*-bis-(trimethylsilyl)acetamide (BSA) and a catalytic amount of potassium acetate[20] (eq 1). The results are compiled



in Table 1, which showed that the ligands with different

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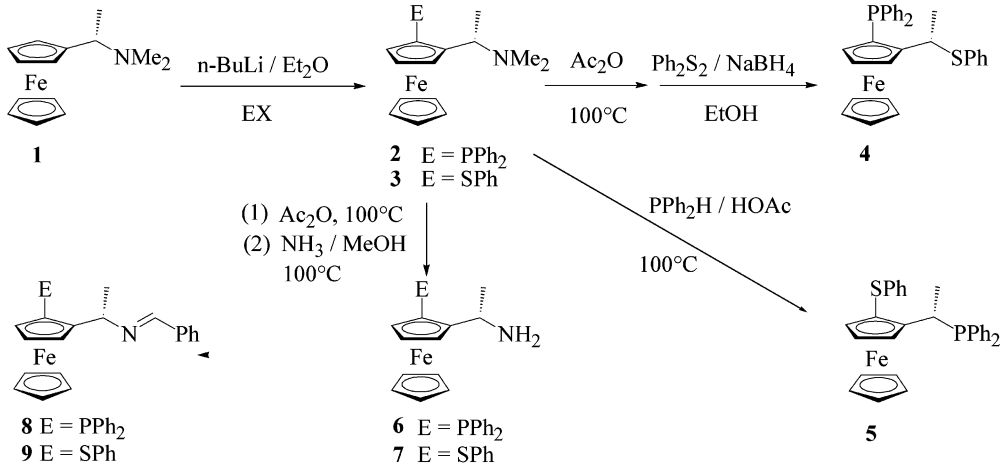
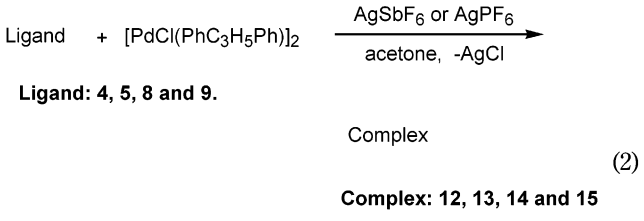
Scheme 1. Syntheses of the Ligands 4, 5, 8, and 9



coordination atoms resulted in different enantioselectivities and absolute configurations of products. For ligand **4**, the PPh_2 group was attached directly on the Cp ring and the SPh group was on the α-carbon atom, while for ligand **5**, the disposition of the two groups was just reversed. The opposite asymmetric induction was observed when ligands **4** and **5** were used in the asymmetric allylic substitution reactions (entries 1 and 2, Table 1). Ligands **5**, **8**, and **9** all gave products with *R* configuration, while for **4**, the *S* configuration was found in the product.

Furthermore, since these four ligands have the same backbone and the same chiralities, and since the new C−Nu bond is formed outside the coordination sphere of the metal center, regioselective attack is often achieved by electronic means.[22] The different configurations of products should be caused by the different trans effects of ligating atoms in these ligands and/or different orientations of the allyl fragment in Pd−π-allyl intermediates (vide infra). To understand further how the trans effect controlled the configuration of products, X-ray diffraction and solution NMR studies were carried out.

The proposed intermediates **12**−**15**, complexes of the ligands with Pd and the substrate, were prepared from bis[(μ-chloro)(η^3-1,3-diphenylallyl)palladium(II)] and the ligands **4**, **5**, **8**, and **9**, respectively. The anion Cl^- was removed by adding $AgSbF_6$ or $AgPF_6$ to the mixture of the chloro-bridged π-allyl compounds and ligand (eq 2).[23]



(2)

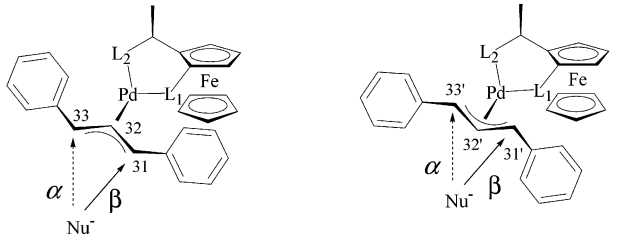
For π-allyl complexes **12**−**15**, there are two possible orientations for the π-allyl moiety with respect to the coordination plane defined by the Pd, L_1, and L_2 atoms, and the structures are designated as W-type and M-type as shown in Chart 2. Because of the differences in electronic character of two donor atoms, the bond length of the palladium−allyl carbon terminus trans to the more powerful π-acceptor atom will be longer and more susceptible to cleavage as a result of nucleophilic attack.[5,24] For the W-type isomer (the allyl moiety has an exo-syn-syn configuration[6a]) as the active catalyst species, if L_1 is a more powerful π-acceptor than L_2, the nucleophile would attack the allylic carbon atom trans to L_1 (as shown by the arrow next to α in structure **a** of Chart 2),and the product with the *S* configuration product could be obtained; however, if L_2 is the more

Table 1. Palladium-Catalyzed Asymmetric Alkylation of 10 with Different Ligands[a]

entry	ligand	yield (%)[b]	ee (%)[c]	config[d]
1	**4**	90	93.8	*S*
2	**5**	93	75.3	*R*
3	**8**	83	71.0	*R*
4	**9**	90	86.3	*R*

[a] Conditions: 2.5 mol % [Pd(η^3-(C_3H_5)Cl]$_2$, 5 mol % ligands, 100 mol % 1,3-diphenyl-2-propenyl acetate (**10**), 3 mol % KOAc, 300 mol % $CH_2(CO_2Me)_2$, 300 mol % BSA. [b] Isolated yield based on 1,3-diphenyl-2-propenyl acetate (**10**). [c] Determined by HPLC (Chiralcel OJ column). [d] The absolute configuration of the product was assigned through comparison of the sign of specific rotations with literature data.[21]

Chart 2. Possible Models of Intermediates Leading to Different Configurations of Products



a. *exo-syn-syn* (W-type) **b.** *endo-syn-syn* (M-type)

12. L_1 = PPh_2, L_2 = SPh; **14**. L_1 = PPh_2, L_2 = N=CHPh;
13. L_1 = SPh, L_2 = PPh_2; **15**. L_1 = SPh, L_2 = N=CHPh.

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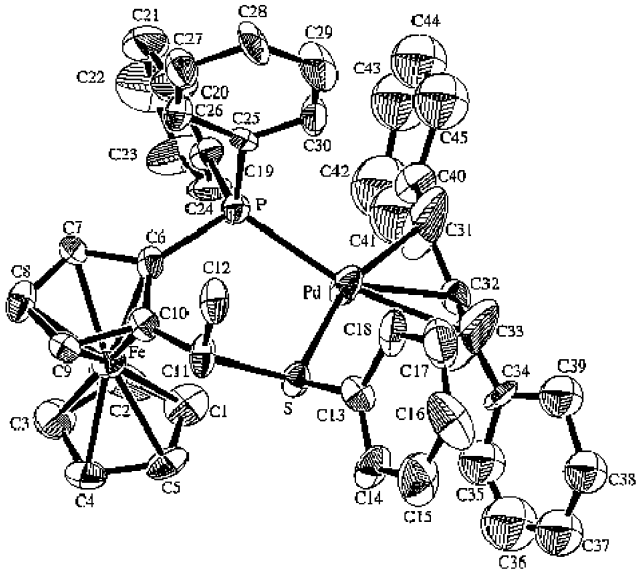

Figure 1. ORTEP drawing of the X-ray crystallographic structure and atom-numbering scheme of the cation **12b**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Complex 12b

Pd−P	2.320(4)	Pd−C(32)	2.18(2)
Pd−S	2.345(4)	Pd−C(33)	2.32(3)
Pd−C(31)	2.23(3)		
S−Pd−P	95.2(2)	P−Pd−C(32)	139.8(5)
S−Pd−C(31)	161.7(8)	P−Pd−C(33)	166.0(1)
S−Pd−C(32)	124.0(5)	Pd−C(31)−C(32)	69(1)
S−Pd−C(33)	92.7(8)	Pd−C(32)−C(33)	77(1)
P−Pd−C(31)	102.9(8)	Pd−C(33)−C(32)	66(1)

powerful π-acceptor, the configuration of the product would be *R*. Conversely, if the allylic moiety adopted the endo-syn-syn configuration (M-type), the result would be opposite to the above statement.

A suitable crystal for complex **12** was obtained from a CH_2Cl_2/ether solution at 0 °C. Figure 1 gives the ORTEP drawing of complex **12**; selected bond lengths and angles are given in Table 2. The allylic moiety adopts an endo-syn-syn configuration (M type), corresponding to the structure **12b** in Chart 2. The six-membered chelating ring is not on a plane; instead, it takes a boatlike conformation. The Pd atom exhibits a pseudo-square-planar coordination geometry. The P−Pd−S angle was 95.2(2)°, suggesting that this ligand has a relatively large bite angle. The pseudo-trans angles P−Pd−C(31) and P−Pd−C(33) were 102.9(8) and 166.0(1)°, respectively, suggesting the usual disposition of allyl ligand. As expected, the Pd−C bond lengths were significantly different. The bond between palladium and the terminal allylic carbon atom, which is trans to phosphorus, was longer (Pd−C(33) = 2.32(3) Å) than that trans to sulfur (Pd−C(31) = 2.23(3) Å), indicating the trans effect of the phosphine moiety was higher than that of thioether.[8a−c] However, if the active species in the reaction was the M-type, the nucleophile would attack the allylic terminus trans to phosphorus and the configuration of the reaction products should be *R*, which is not in agreement with our experimental result (entry 1, Table 1). To identify whether the structure of **12b** in the solid state was also the active catalyst species in the reaction, further NMR studies in solution were carried out.

Using the standard approach for allylic species,[25] NMR assignments for both stereoisomers were made, which are given in the Experimental Section. According to ^{31}P NMR, the ratio of the two stereoisomers **12a** and **12b** in CD_2Cl_2 (to reflect the reaction medium) was about 1:1 at ambient temperature. $^{13}C-^{1}H$ NMR correlation pinpointed the four allylic termini: δ 81.9 (trans to S) and δ 95.0 (trans to P) for one isomer and δ 88.7 (trans to S) and δ 102.7 (trans to P) for the other. Thus, in both isomers, the allylic terminus trans to phosphine was more downfield than that of S in ^{13}C chemical shifts, indicating a stronger trans effect of P relative to S, as shown in the X-ray results. This also confirmed that the trans effect is due to the nature of the ligand and is not related to the orientation of the allylic fragment and the state of the complex (in the solid state or in solution).

Due to signals overlapping, it was difficult to distinguish **12a** and **12b** simply by NOESY; a $^{31}P-^{1}H$ NMR correlation study was then invoked. From the $^{31}P-^{1}H$ NMR correlation (Figure 2), H′(30) and H′(24) could be easily assigned (here, H stands for the hydrogen atom of the W-type isomer, while H′ stands for that of the M-type). For the shielding effect of the allylic phenyl ring, the signal of H′(30) was more upfield than H′(24). According to the ORTEP diagram of **12b**, the distances between H′(30) and the two allylic termini H′(31) and H′(33) were 2.88 and 3.68 Å, respectively; therefore, there should be a strong NOE effect between such hydrogen atoms. The NOESY spectrum showed the existence of such effects (Figure 3). However, in the W-type configuration, H(31) and H(33) point in the same direction as does H′(32) in the M-type isomer (the distance between H′(30) and H′(32) was 5.02 Å in **12b**); thus, the distances of H(30)−H(31) and H(30)−H(33) were rather long (4.43 and 5.66 Å, respectively, in PM3 calculations) and no such effect occurred. Since NOESY (2D nuclear Overhauser and exchange spectroscopy) contains not only NOE cross-peak signals but also exchange signals,[26] Cyclo-NOEDS was involved to confirm such NOE. When the signal at 6.95 ppm was irradiated (H′(30)), the signal of the multiplet at 4.95 ppm (H′(31) and H′(33)) was enhanced. When the signal at 5.01 ppm was irradiated (H′(31), the left-hand side of the multiplet at 4.95 ppm), the signal at 6.95 ppm was also enhanced. Howver, when H(30) was irradiated (the right-hand-side signal of the multiplet at 6.64 ppm), no NOE between H(30) and H(31) or H(33) could be found. When the signal at 5.60 ppm was irradiated (H(31)) only the signal at 5.86 ppm (H(33)) and other protons of the phenyl ring were enhanced. Therefore, with the aid of $^{31}P-^{-}H$ NMR, it is easy to distinguish between **12a** and **12b** using NOESY; the downfield isomer was assigned as the W-type.

In addition, we found that the ^{13}C chemical shifts of the carbon atoms trans to phosphine of the two isomers were very different ($\Delta\delta$(trans to P) = 7.7 ppm). It had been rationalized that the steric compression effects in terms of the repulsive forces between closely spaced

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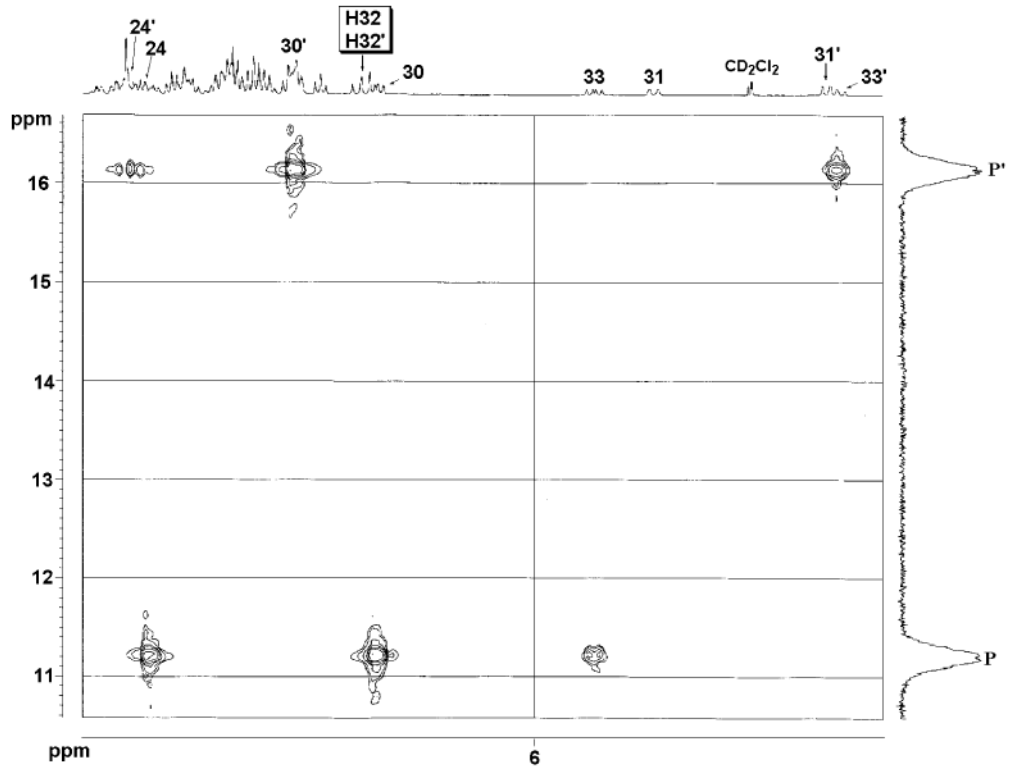

Figure 2. Section of the phase-sensitive $^{31}P-^{1}H$ NMR correlation spectrum of complex **12** (H, exo-syn-syn isomer; H′, endo-syn-syn isomer). The numbers 31, 32, and 33 indicate the three allylic protons; 30 stands for the ortho proton of the phenyl ring attached to phosphine. The arrows show the correlation between the proton and phosphine.

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atoms would generally produce upfield shifts.[27] The X-ray crystallographic study of **12b** (Figure 1) indicated that the allylic phenyl ring attached to C(33) and the phenyl ring of S were parallel but not stacking (the distance between the centroids of two Ph rings is ca. 3.70 Å), the bonds of Pd−C(33) and S−C(13) almost pointing in the same direction. Thus, in such a geometry (M-type), there was a very strong steric compression effect between the C(33) phenyl ring and the phenyl ring of S. However, in the other isomer, **12a** (W-type), the two phenyl rings might be nearly parallel and overlapping, the bonds of Pd−C(33) and S−C(13) pointed in different directions, and thus no such strong steric compression effects could be found. Therefore, the upfield isomer should be M-type (**12b**). This assignment was in accordance with that of the NOESY results.

Furthermore, it was assumed that the carbon terminus of the allyl group pseudo-trans to the P-donor would be attacked preferentially to that trans to the sulfur atom and the nucleophile would attack the highest frequency (most olefin-like) carbon.[28,29] Then one would predict that the product from **12a** was obtained by attacking the carbon atom with δ 102.7, thus giving an *S* configuration for the reaction product, which was in agreement with the experimental result. Considering the different reaction rates of **12a** and **12b**, and the late-transition-state theory,[28b] suggested by Brown and coworkers, the reactive allylic carbon terminus must be trans to the phosphorus atom. The unfavorable equilibrium (**12b** to **12a**) was traversed before the C−C bond-forming step for the Pd−allyl complex **12b**. Although complex **12** adopted an M-type conformation in the solid state, the W-type isomer was the more reactive species in solution (which has a higher heat of formation as found by molecular modeling; entry 1, Table 5). The reacting allylic carbon terminus was placed trans to the P atom; thus, the reaction rate of **12b** was much slower than that of **12a**, where no such preequilibrium was required. Consequently, 93.8% ee was obtained.

For complexes **12** and **13**, except for the fact that the dispositions of the two coordination atoms were reversed, their structural skeletons and chiralities (both planar and central) were the same. Therefore, the argument for complex **12** may also be applied to complex **13**. In the CD_2Cl_2 solution of complex **13**, two isomers were observed in the ratio 5:6 by ^{31}P NMR, the chemical shifts of which were 51.7 and 44.5 ppm, respectively. The ^{13}C NMR chemical shift for the allylic carbon termini trans to phosphorus was δ 95.3 ppm, and that trans to S was δ 87.9 ppm in the major isomer; the corresponding shifts in the minor isomer were 100.7 ppm (trans to P) and 83.3 ppm (trans to S), respectively, with $\Delta\delta$(trans to P) = 5.4 ppm. Accordingly, the W-type isomer with a downfield chemical shift of the carbon terminus trans to the P atom was the reactive species and the configuration of the reaction product should be *R*, which also agrees with the experimental result (entry 2, Table 1). Because ligands **4** and **5** have the same skeleton, the opposite configuration of products with

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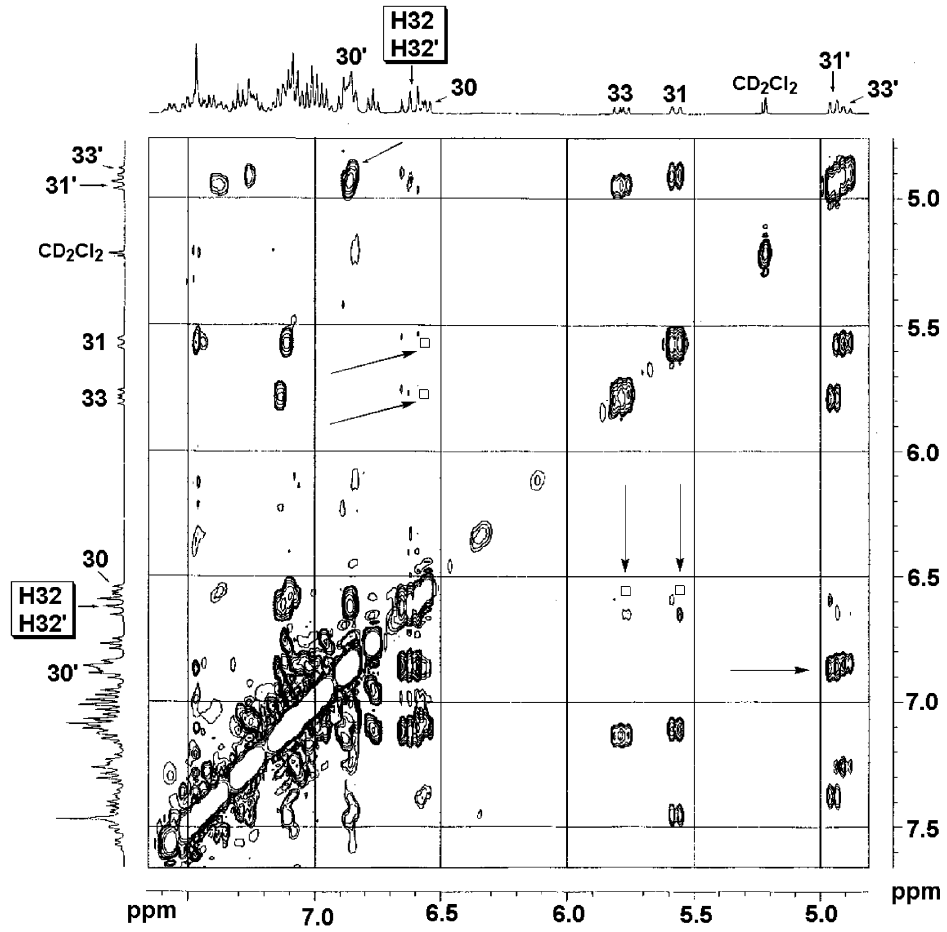
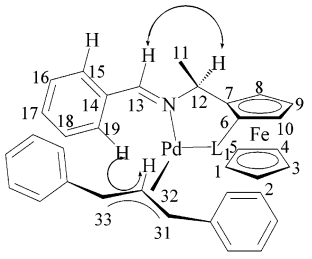


Figure 3. Section of the phase-sensitive ^{1}H 2D NOESY (400 MHz, CD_2Cl_2, 298 K) spectrum of complex **12** (H, exo-syn-syn isomer; H′, endo-syn-syn isomer). The numbers 31, 32, and 33 indicate the three allylic protons; 30 stands for the ortho proton of the phenyl ring attached to phosphine. The arrows show the NOEs between the protons, and square boxes mark the absence of crossing signals.

ligands **4** and **5** were easily explained by the fact that P has a stronger trans effect than S.

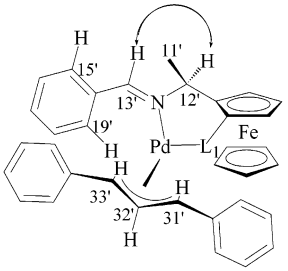
For complex **14**, two isomers in the ratio 5:6 were found in the ^{31}P NMR, which was also confirmed by ^{1}H NMR by the imine proton, which was characteristically downfield. The chemical shifts of the imine proton for the two isomers were 8.62 and 8.75 ppm. According to the strong NOEs between H(13) (proton of imine) and H(12) (the methine proton of central chirality) and the weak cross-peak between H(13) and the proton of the ferrocene, C═N was extrapolated to have the *E* configuration, as shown in Chart 3, which was also in accordance with molecular modeling. Taking into account the position, NOE effect, and COSY with H(13), the signals at 8.06 and 8.27 ppm could be assigned to H(15,19) and H′(15,19). (These are the ortho protons of the phenyl ring attached to the imine group, which are equal due to the free rotation of that phenyl group; the signal of H(15) and H(19) is just the average value of two protons.) When the signal at 8.07 ppm (H(15,19)) was irradiated, the signal at 6.31 ppm, which might be the central allylic proton H(32), was enhanced. H(31) and H(33) then can be assigned by means of COSY. By ^{1}H NMR, NOEDS, COSY, and ^{1}H−^{31}C NMR (HMQC), we found that the ^{13}C chemical shifts of the six allylic carbon atoms are δ 75.8 (trans to P), δ 95.0 (trans to C═N), and δ 109.1 (central) in the major isomer and δ 72.4 (trans to P), δ 101.2 (trans to C═N), and δ 111.2

Chart 3. Configuration and NOE Correlation from NOESY Spectra of Complexes 14 and 15



a. *exo-syn-syn* (W-type)

14a L_1 = PPh_2;
15a L_1 = SPh.



b. *endo-syn-syn* (M-type)

14b
15b

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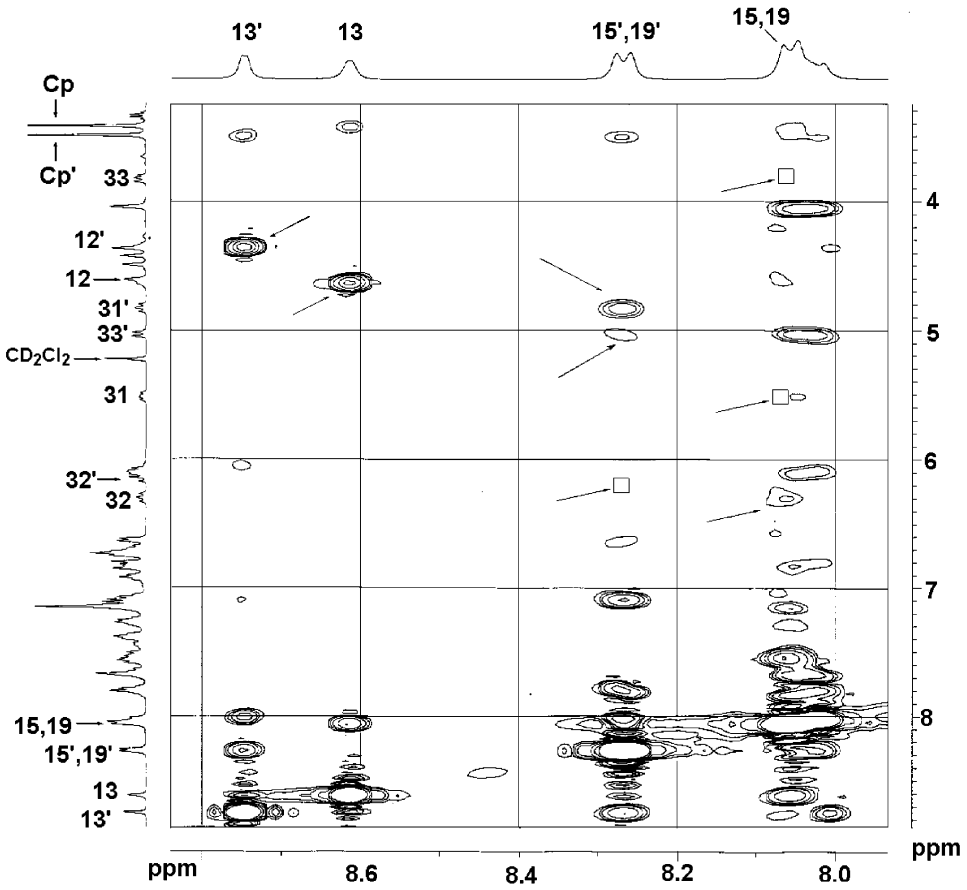

Figure 4. Section of the phase-sensitive ^{1}H 2D NOESY (400 MHz, CD_2Cl_2, 296 K) spectrum of complex **14**. The numbers 31, 32, and 33 indicate the three allylic protons, 12 and 13 stand for the proton of the central chirality and the proton of imine, respectively, and 15 and 19 indicate the ortho protons of the phenyl ring attached to imine. The arrows show the NOEs between the protons, and square boxes mark the absence of crossing signals.

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(central) in the minor isomer. There was a selective NOE effect that enabled us to distinguish **14a** and **14b** with a NOESY assignment. Figure 4 shows a very strong cross-peak between H(32) (central allylic proton) and H(15,19) in the minor isomer in the downfield region, while there is no such effect in the major isomer. There was also another selective NOE effect that enabled us to assign **14a** and **14b**. Strong cross-peaks between H′(33)/H′(31) (allylic terminus protons) and H′(15,19) could be found in the major isomer, and no such cross-peaks could be found in the minor isomer. All these NOE effects were confirmed by cyclo-NOE difference Spectroscopy. Therefore, the minor isomer should be W-type (**14a**) and reactive species in the reaction are found in the downfield region. The nucleophile should attack the allylic terminus carbon trans to imine of **14a**; reaction products with *R* configuration could be obtained, which was also in accordance with the experimental results. Because the ^{13}C chemical shifts of the allylic terminus carbon trans to C═N were much more downfield than that trans to P in the two isomers and $\Delta\delta$(trans to C═N) was 6.2 ppm, the trans effect sequence of P and C═N could be regarded as C═N > P.

Although ^{31}P NMR data for complex **15** are absent, a 10:3 ratio of the two isomers can also be obtained from ^{1}H NMR, with the imine protons of the two isomers at 8.59 and 8.77 ppm. By a method (NOESY; Figure 5) similar to the assignment of complex **14** (Chart 3), the configuration of the imino group was also found to be *E* and the downfield isomer was assigned as W-type through a combination of ^{1}H NMR, COSY, ^{1}H−^{13}C NMR, and NOESY studies. Figure 5 shows a very strong cross-peak between H(32) and H(15,19) of the major isomer in the downfield region, while no such signal appears for the minor isomer. This NOE effect was also confirmed by cyclo-NOE difference spectroscopy. ^{13}C NMR chemical shifts for the four allylic termini were δ 79.0 (trans to S) and δ 91.8 (trans to C═N) in the W-type isomer (**15a**) and δ 86.8 (trans to S) and δ 83.3 (trans to C═N) in the M-type isomer (**15b**). By the same argument used for complex **14**, the reactive species was **15a** (W-type) in the downfield region; the nucleophile would attack the allylic carbon terminus trans to imine in **15a**, and a product with an *R* configuration would be obtained. The $\Delta\delta$(trans to C═N) value was 8.5 ppm, and the sequence of trans effects of C═N and S was C═N > S. Although in the M-type isomer the allylic terminus trans to C═N is more upfield than that trans to S, this may be explained by the steric influence of the phenyl ring of SPh toward the allylic terminus trans to C═N.[7a]

To test whether the complexes of **12**−**15** are true intermediates of the allylic alkylation reactions, the complexes **12**−**15** were used directly as the source of chiral catalysis in this reaction. Table 3 shows that complexes **12**−**15** did catalyze this reaction, giving results similar to those described in Table 1. This

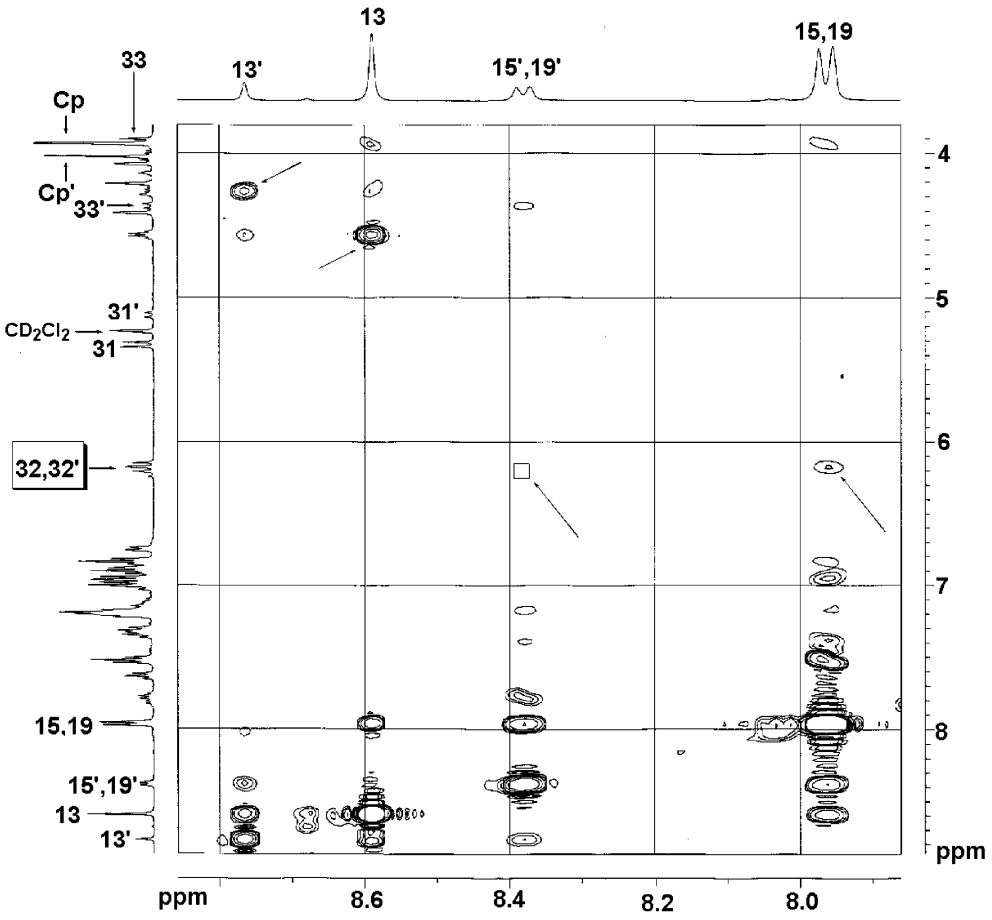

Figure 5. Section of the phase-sensitive ^{1}H 2D NOESY (400 MHz, CD_2Cl_2, 298 K) spectrum of complex **15**. The numbers 31, 32, and 33 indicate the three allylic protons, 12 and 13 stand for the proton of the central chirality and the proton of imine, respectively, and 15 and 19 indicate the ortho protons of the phenyl ring attached to imine. The arrows show the NOEs between the protons, and square boxes mark the absence of crossing signals.

Table 3. Asymmetric Alkylation of 10 Catalyzed by Complexes 12−15[a]

entry	complex	yield (%)[b]	ee (%)[c]	config[d]
1	**12**	96.3	96.5	*S*
2	**13**	98.0	73.6	*R*
3	**14**	90.0	64.0	*R*
4	**15**	88.0	80.0	*R*

[a] Conditions: 2.5 mol % complex, 100 mol % 1,3-diphenyl-2-propenyl acetate (**10**), 3 mol % KOAc, 300 mol % $CH_2(CO_2Me)_2$, 300 mol % BSA. [b] Isolated yield based on 1,3-diphenyl-2-propenyl acetate. [c] Determined by HPLC (Chiralcel OJ column). [d] The absolute configuration of the product was assigned through comparison of the sign of specific rotations with literature data.[21]

experiment verified that the complexes **12**−**15** were intermediates of allylic alkylation reactions catalyzed with ligands **4**, **5**, **8**, and **9**.

The experimental results for the ligands (**4**, **5**, **8**, and **9**) and complexes (**12**−**15**) also supported our conclusion qualitatively. First, ligands **4** and **5** have the same central and planar chiralities; only the disposition of the two coordination atoms (S and P) is reversed. When ligands **4** and **5** (or complexes **12** and **13**) are used in asymmetric allylic alkylation reactions, their intermediates have similar configurations and environments; therefore, the opposite configuration of products may mainly be due to the different trans effects of coordinating atoms (S, P). Second, the sequence of trans effects of P, S, and C=N were P > S, C=N > P, and C=N > S, which could be drawn from the experimental results (Table 4). If the sequences are right, the enantioselectivity of the product catalyzed by ligand **9** with S,(C=N) should be higher than by ligand **8** with P,(C=N), which was in accordance with the experimental results (entries 3 and 4, Tables 1 and 3). Third, because they were drawn from ligands with the same backbone, the sequence of trans effects of P, S, and C=N may be established as C=N > P > S.

To further verify these results, we also calculated the atomic (Mulliken) charges on the allylic termini of the possible intermediates **12**−**15** at the PM3 level using Spartan 5.0. Good agreement with each other was found by comparing the structures from PM3 calculations and the X-ray diffraction structure of the complex **12b**. Heats of formation of different configurations of complexes **12**−**15** can explain the ratio of the two isomers (W- and M-type isomers) in solution. Table 5 shows that the atomic (Mulliken) charges on the termini trans to the coordination atoms, those with stronger trans effects, were less negative and more favorably attacked by nucleophile. It was also found that the Pd−C bond lengths in all complexes were only slightly different, not as significantly as those in the X-ray diffraction structure of the intermediate **12b**. However, the Pd−N, Pd−P, and Pd−S bond distances are successively larger by about 0.2 Å. Therefore, the trans effect sequence of C=N > P > S could be further confirmed.

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Table 4. ^{13}C NMR Data of Complexes 12−15[a]

^{13}C	**12a** (W)	**12b** (M)	**13a** (W)	**13b** (M)	**14a** (W)	**14b** (M)	**15a** (W)	**15b** (M)
C(32)	109.8	108.5	110.6	110.6	111.2	109.1	109.2	105.8
C(31)	88.7	81.9	100.7	95.3	101.2	95.0	91.8	83.3
trans to L_2	S	S	P	P	C=N	C=N	C=N	C=N
C(33)	102.7	95.0	83.3	87.9	72.4	75.8	79.0	86.8
trans to L_1	P	P	S	S	P	P	S	S
Δ(C(31)−C(33))	−14	−13.1	17.4	7.4	28.8	19.2	12.8	−3.5

[a] Conditions: 25 °C, CH_2Cl_2. Chemical shifts are given in ppm. The letters "M" and "W" after the compound number refer to the M- and W-type isomers.

Table 5. Heats of Formation, Bond Distances between Palladium and Coordinated Atoms, and Atomic (Mulliken) Charges on the Trans-Effect Allylic Terminal Carbons of the Complexes 12−15[a]

complex (isomer)	heat of formation (kcal/mol)	bond dist between Pd and L (Å)		trans-effect charge	
		L_1	L_2	C33 (L_1)	C31 (L_2)
12a (W)	−14.657	2.266	2.409	−0.0936	−0.1052
12b (M)	−15.278	2.267	2.413	−0.1057	−0.1078
13a (W)	−14.409	2.431	2.285	−0.0951	−0.0945
13b (M)	−14.555	2.425	2.282	−0.1052	−0.0954
14a (W)	1.588	2.286	2.041	−0.1676	−0.1268
14b (M)	4.662	2.263	2.042	−0.1715	−0.1334
15a (W)	−25.667	2.455	2.024	−0.0961	−0.0779
15b (M)	−19.365	2.421	2.024	−0.0987	−0.0818

[a] Calculated by the PM3 method using the Spartan 5.0 program on an O_2 workstation.

Conclusions

A series of chiral ligands with the same skeleton and chiralities but different dispositions of coordinated atoms were synthesized. Palladium-catalyzed allylic substitution reactions showed that they are effective catalysts, and good to excellent ee values were obtained. It was found that the ligands with different coordination atoms showed different enantioselectivities and absolute configurations. From the reaction results as well as the X-ray and NMR studies of complexes **12**−**15**, the overall sequence of trans effects P > S, C=N > P, and C=N > S could be obtained, respectively, which was supported by calculation of the atomic charge at the PM3 level using Spartan 5.0. Because they were drawn from ligands with the same skeleton, the sequence of trans effects of P, S, and C=N is established as C=N > P > S. These results may be used as a reference in the ligand design of the asymmetric reactions.

Experimental Section

General Considerations. Unless otherwise stated, all ^1H NMR spectra were recorded on a Bruker AMX-400 (400 MHz) spectrometer in $CDCl_3$ or CD_2Cl_2 and the chemical shifts were referenced to $CHCl_3$ (δ 7.27 ppm) in $CDCl_3$ and $CHDCl_2$ (δ 5.32 ppm) in CD_2Cl_2. ^{31}P NMR spectra were recorded on a Bruker AMX-400 (162 MHz) spectrometer, and the chemical shifts were referenced to external 85% H_3PO_4. ^{13}C NMR spectra were recorded on a Bruker AMX-100 (100.6 MHz) spectrometer, and the chemical shifts were referenced to $CHDCl_2$ in CD_2Cl_2. Standard pulse sequences were employed for ^1H-2D-NOESY, ^1H-H, and $^{13}C-^1H$ correlation studies; optical rotations were measured on a Perkin-Elmer 241 MC polarimeter with a thermally jacketed 10 cm cell at 20 °C (concentration *c* given as g/100 mL). IR spectra were recorded in KBr and measured in cm^{-1}, using a Shimadzu IR-440 infrared spectrophotometer. Mass spectra and high-resolution mass spectra were obtained by using HP5989A and Finnigan Mat mass spectrometers, respectively. Elemental analyses were performed on a Fross-Heraeus Vario EL instrument. ee values were determined by chiral HPLC on a chiral OJ column.

All reactions were performed under a dry argon atmosphere; diethyl ether was freshly distilled from sodium under an argon atmosphere. Dichloromethane and TMEDA were distilled from CaH_2. Bis(μ-chloro)(1,3-diphenyl-η^3-allyl)dipalladium was prepared by a known method.[19] The commercially available reagents were used as received without further purification.

Compounds **2**,[30b] **3**,[30a] **4**,[17] and **8**[18] were synthesized according to the literature procedures.

1-(Diphenylphosphino)-1-[2′-(phenylthio)ferrocenyl]-ethane (5). To a solution of ferrocene thioether **3** (730 mg, 2 mmol) and 12 mL of acetic acid, Ph_2PH (0.383 mL, 2.2 mmol) was added under argon. The mixture was heated to 100 °C for 6 h, after removal of solvent; the residue was purified by column chromatography under an argon atmosphere. Product **5** was obtained as a thick orange oil (830 mg, yield 82%). $[\alpha]_D^{20} = 163.7$ (*c* 0.7, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.43 (m, 3H), 3.62 (dd, J = 7.0 Hz, 1.4 Hz, 1H), 3.95 (m, 1H), 4.02 (m, 1H), 4.19 (m, 5H), 4.47 (m, 1H), 7.30 (m, 15H). MS: *m*/*z* 506 (M^+, 13.76), 337 (33.19), 320 (100), 319 (16.15), 255 (13.76), 212 (25), 200 (26.89), 199 (16.73). IR (cm^{-1}): 3072, 3055, 1583, 1479, 1069, 740. HRMS for $C_{30}H_{27}FePS$: calcd, 506.0921; found, 506.0914. Anal. Calcd for $C_{30}H_{27}FePS$ (506.09): C, 71.15; H, 5.37. Found: C, 70.90; H, 5.41.

(*S*)-1-[(*R*)-2′-(Phenylthio)ferrocenyl]ethylamine (7). Ferrocene thioether **3** (606 mg, 1.66 mmol) was dissolved in 1.1 mL of Ac_2O under argon and heated to 100 °C for 2 h. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure. A dark red oil was obtained. Then, 10 mL of MeOH was added to the residue. The acetoxy group was converted to an amino group by reaction with a large excess of ammonia in methanol in an autoclave at 100 °C. After the mixture was cooled to room temperature, the solvent was removed under vacuum. The resulting residue was chromatographed on silica gel with ethyl acetate/petroleum/Et_3N (2:1:0.01) as an eluent to afford **7** as a yellow solid (313 mg, yield 56%). ^1H NMR ($CDCl_3$): δ 1.45 (d, J = 6.75 Hz, 3H), 1.48 (br, 2H), 4.14 (dd, J = 13.25 Hz, 16.49 Hz, 1H), 4.20 (s, 5H), 4.34 (t, J = 2.64 Hz, 1H), 4.40 (q, J = 2.64 Hz, 1H), 4.46 (q, J = 2.64 Hz, 1H), 7.04 (d, J = 4.99 Hz, 3H), 7.16 (t, J = 8.33 Hz, 2H). MS: *m*/*z* 337 (M^+, 24.79), 336 (100), 228 (34.64), 121 (25.15), 56 (14.57). IR (cm^{-1}): 3267, 3058, 2996, 1664, 1583, 1479, 1107, 739. HRMS for $C_{18}H_{19}FeNS$: calcd, 337.06158; found, 337.05898. Anal. Calcd for $C_{18}H_{19}FeNS$ (337.06): C, 64.10; H, 5.68; N, 4.15. Found: C, 64.11; H, 6.16; N, 4.01.

(*S*)-*N*-Benzylidino-1-[(*R*)-2′-(phenylthio)ferrocenyl]-ethylamine (9). A mixture of **7** (224 mg, 0.665 mmol), 4 Å molecular sieves (250 mg), benzaldehyde (0.07 mL, 0.7 mmol), and 5 mL of benzene was stirred at room temperature under argon overnight. After the mixture was filtered, the solvent was removed under vacuum. A red-orange oil was obtained

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Table 6. Crystal and Structure Refinement Data for Complex 12b

formula	$C_{45}H_{40}FePSbF_6SPd$
fw	1041.83
data collecn *T*, K	293
diffractometer	Rigaku AFC7R
cryst syst	orthorhombic
space group	$P2_12_12_1$ (No. 19)
a, Å	20.091(5)
b, Å	21.622(7)
c, Å	9.664(2)
V, Å^3	4197(1)
Z	4
ρ(calcd), g cm^{-3}	1.648
μ, mm^{-1}	15.49
F(000)	2072.00
radiation	Mo Kα (graphite monochromated, λ = 0.710 69 Å)
scan speed (ω), deg min^{-1}	16.0
2θ range, deg	19 (13.4−23.6)
no. of measd rflns	3743
no. of variables	455
no. of obsd data	2745 ($I > 2.00\ \sigma(I)$)
rfln/param ratio	6.05
R	0.062
R_w	0.067
cryst size (mm)	0.20 × 0.20 × 0.30
GOF	2.12

(275 mg, yield 97%). $[\alpha]_D^{20}$ = 251.0 (*c* 0.25, $CHCl_3$). ^{1}H NMR (300 M, $CDCl_3$): δ 1.67 (d, J = 6.7 Hz, 3H), 4.26 (s, 5H), 4.39 (m, 1H), 4.45 (s, 1H), 4.63 (m, 2H), 6.61 (m, 1H), 6.79 (m, 4H), 7.16 (m, 5H), 7.92 (s, 1H). MS: *m*/*z* 425 (M^+, 100), 320 (38.26), 255 (11.31), 212 (18.24), 159 (13.57), 121 (14.42). IR (cm^{-1}): 3059, 2973, 2864, 1640, 1581, 1479, 1107, 737. HRMS for $C_{25}H_{23}FeNS$: calcd, 425.0927; found 425.0914. Anal. Calcd for $C_{25}H_{23}FeNS$ (425.09): C, 70.59; H, 5.45; N, 3.29. Found: C, 70.28; H, 5.61; N, 3.08.

[Pd(η^3-1,3-diphenylallyl)(4)]$^+$SbF$_6^-$ (12). Bis[(μ-chloro)-(η^3-1,3-diphenylallyl)palladium(II)] (100 mg, 0.148 mmol) was added to a solution of ligand **4** (165 mg, 0.326 mmol) in acetone (10 mL). $AgSbF_6$ (103 mg, 0.299 mmol) was added to the mixture until the solution turned clear again. The solution was stirred for 1 h in the dark at room temperature. The AgCl was removed by filtration through Celite and washed with dichloromethane, and the solvent was evaporated under reduced pressure. On recrystallization from dichloromethane and ether, red crystals of **12** were afforded (271.8 mg, yield 80%). Data for the M-type isomer, **12b**, are as follows. ^{1}H NMR (CD_2Cl_2, 298 K): δ 0.74 (d, J = 6.9 Hz, 3H), 3.60 (d, J = 1.2 Hz, 1H), 4.16 (dq, J = 6.6 Hz, 1.7 Hz, 1H), 4.25 (m, 6H), 4.39 (m, 1H), 5.00 (m, 2H), 6.71 (t, J = 11.9 Hz, 1H), 6.92−7.68 (m, 25H). ^{31}P NMR (CD_2Cl_2, 298 K): δ 16.20 (s). ^{13}C NMR (CD_2Cl_2, 298 K): δ 81.9 (trans to S),, 95.0 (trans to P), 108.5 (central allyl). Data for the W-type isomer, **12a**, are as follows. ^{1}H NMR (CD_2Cl_2, 298 K): δ 0.55 (d, J = 6.9 Hz, 3H), 3.76 (d, J = 1.3 Hz, 1H), 4.35 (dq, J = 6.9 Hz, 1.7 Hz, 1H), 4.47 (m, 6H), 4.57 (d, J = 4.2 Hz, 1H), 5.66 (d, J = 12.6 Hz, 1H), 5.88 (dd, J = 13.5, 8.7 Hz, 1H), 6.64 (m, 1H), 6.71 (t, J = 11.9 Hz, 1H), 6.86 (t, J = 7.7 Hz, 1H), 6.92−7.68 (m, 23H). ^{31}P NMR (CD_2Cl_2, 298 K): δ 11.39 (s). ^{13}C NMR (CD_2Cl_2, 298 K): δ 88.7 (trans to S), 102.7 (trans to P), 109.8 (central allyl). MS (ESI): 805 ($M^+ - SbF_6$) (100). IR (cm^{-1}): 1438, 1099, 1001, 692, 657, 520, 491. Anal. Calcd for $C_{45}H_{40}F_6PSFeSbPd$ (1041.86): C, 51.88; H, 3.87. Found: C, 51.91; H, 3.90.

Crystal and structure refinement data for **12b** are given in Table 6.

[Pd(η^3-1,3-diphenylallyl)(5)]$^+$PF$_6^-$ (13). Bis[(μ-chloro)(η^3-1,3-diphenylallyl)palladium(II)] (128 mg, 0.189 mmol) was added to a solution of ligand **5** (191 mg, 0.378 mmol) in acetone (10 mL). $AgPF_6$ (90 mg, 0.356 mmol) was added to the mixture until the solution turned clear again. The solution was stirred for 1 h in the dark at room temperature. The AgCl that formed was removed by filtration through Celite and washed with dichloromethane, and the solvent was evaporated under reduced pressure. The crude product **13** was recrystallized from dichloromethane and hexane (316 mg, yield 78%). Data for the M-type isomer, **13b**, are as follows. ^{1}H NMR (CD_2Cl_2, 298 K): δ 1.20 (m, 3H), 3.36 (m, 1H), 3.83 (m, 2H), 4.00 (m, 6 H), 5.05 (dd, J = 12.1, 10.0 Hz, 1H), 5.21 (d, J = 12.7 Hz, 1H), 6.28 (t, J = 12.4 Hz, 1H), 6.72−7.65 (m, 25H). ^{31}P NMR (CD_2Cl_2, 298 K): δ 51.7 (s), −130.7 to −157.0 (m). ^{13}C NMR (CD_2Cl_2, 298 K) δ 87.9 (trans to S), 95.3 (trans to P), 110.6 (central allyl). Data for the W-type isomer, **13a**, are as follows. ^{1}H NMR (CD_2Cl_2, 298 K): δ 1.30 (m, 3H), 3.75 (m, 1H), 4.00 (m, 8H), 4.45 (d, J = 11.5 Hz, 1H), 5.56 (dd, J = 13.5, 8.3 Hz, 1H), 6.44 (dd, J = 13.5, 11.7 Hz, 1H), 6.72−7.65 (m, 25H). ^{31}P NMR (CD_2Cl_2, 298 K): δ 44.5 (s), −130.7 to −157.0 (m). ^{13}C NMR (CD_2Cl_2, 298 K): δ 83.3 (trans to S), 100.7 (trans to P), 110.6 (central allyl). MS (ESI): 805 ($M^+ - PF_6^-$) (100). IR (cm^{-1}): 1438, 1104, 1001, 837, 746, 691, 557, 519. Anal. Calcd for $C_{45}H_{40}F_6P_2SFePd$ (951.08): C, 56.83; H, 4.24. Found: C, 57.04; H, 4.49.

[Pd(η^3-1,3-diphenylallyl)(8)]$^+$SbF$_6^-$ (14). This complex was prepared in a way similar to that described for **12**; a yellow powder was obtained in 85% yield. Data for the M-type isomer, **14b**, are as follows. ^{1}H NMR (CD_2Cl_2, 298 K): δ 1.59 (d, J = 6.4 Hz, 3H), 3.50 (s, 5H), 4.05 (s, 2H), 4.37 (m, 2H), 4.83 (t, J = 11.3 Hz, 1H), 5.05 (d, J = 11.9 Hz, 1H), 6.10 (m, 3H), 6.63−7.83 (m, 21H), 8.27 (d, J = 6.8 Hz, 2H), 8.75 (d, J = 1.7 Hz, 1H). ^{31}P NMR (CD_2Cl_2, 298 K): δ 15.0 (s). ^{13}C NMR (CD_2Cl_2, 298 K) δ 75.8 (trans to P), 95.0 (trans to C═N), 109.1 (central allyl). Data for the W-type isomer, **14a**, are as follows. ^{1}H NMR (CD_2Cl_2, 298 K): δ 2.02 (d, J = 6.2 Hz, 3H), 3.43 (s, 5H), 3.86 (m, 1H), 4.43 (s, 1H), 4.45 (s, 1H), 4.61 (m, 2H), 5.50 (dd, J = 13.4 Hz, 13.5 Hz, 1H), 6.30 (t, J = 12.9 Hz, 1H), 6.63−7.83 (m, 21H), 8.06 (m, 4H), 8.62 (s, 1H). ^{31}P NMR (CD_2Cl_2, 298 K): δ 20.6 (s). ^{13}C NMR (CD_2Cl_2, 298 K): δ 72.4 (trans to P), 101.2 (trans to C═N), 111.2 (central allyl). MS (ESI): 800 ($M^+ - SbF_6$) (100). IR (cm^{-1}): 2965, 1626, 1436, 1262, 801, 755, 693, 657, 521, 491. Anal. Calcd for $C_{46}H_{41}F_6PNFeSbPd$ (1036.82): C, 53.29; H, 3.97; N, 1.35. Found: C, 52.23; H, 3.99; N, 1.28.

[Pd(η^3-1,3-diphenylallyl)(9)]$^+$SbF$_6^-$ (15). This complex was prepared in a fashion analogous to that described for **12**; a yellow powder was obtained in 83% yield. Data for the W-type isomer, **15a**, are as follows. ^{1}H NMR (CD_2Cl_2, 298 K): δ 2.17 (d, J = 6.6 Hz, 3H), 3.90 (m, 1H), 3.94 (m, 5H), 4.08 (s, 1H), 4.21 (t, J = 2.5 Hz, 1H), 4.41 (s, 1H), 4.57 (dd, J = 13.0, 6.4 Hz, 1H), 5.35 (d, J = 12.8 Hz, 1H), 6.17 (dd, J = 12.6 Hz, 1H), 6.63−7.83 (m, 18H), 7.97 (d, J = 7.5 Hz, 2H), 8.59 (s, 1H). ^{13}C NMR (CD_2Cl_2, 298 K): δ 79.0 (trans to S), 91.8 (trans to C═N), 109.2 (central allyl). Data for the M-type isomer, **15b**, are as follows. ^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 1.54 (d, J = 6.6 Hz, 3H), 4.02 (m, 5H), 4.08 (m, 1H), 4.14 (t, J = 2.5 Hz, 1H), 4.25 (m, 1H), 4.28 (s, 1H), 4.38 (m, 1H), 5.13 (d, J = 12 Hz, 1H), 6.21 (m, 1H), 6.65−7.85 (m, 18H), 8.40 (d, J = 7.1 Hz, 2H), 8.77 (s, 1H). ^{13}C NMR (CD_2Cl_2, 298 K, 100.58 MHz): δ 86.8 (trans to S), 83.3 (trans to C═N), 105.8 (central allyl). MS (ESI): 726 ($M^+ - SbF_6^-$) (100). IR (cm^{-1}): 2965, 1628, 1538, 1491, 1444, 1262, 1096, 1023, 800, 755, 691, 697. Anal. Calcd for $C_{40}H_{36}F_6NSFeSbPd$ (960.81): C, 50.00; H, 3.78; N, 1.46. Found: C, 50.00; H, 3.84; N, 1.49.

General Procedure for Palladium-Catalyzed Allylic Alkylations. A mixture of ligand (0.02 mmol) and [Pd(η^3-C_3H_5)Cl]$_2$ (3.7 mg, 0.01 mmol) in 2 mL of dry dichloromethane was stirred at room temperature for 1 h, and to the resulting yellow solution were added potassium acetate (2 mg, 0.02 mmol) and allylic acetate **10** (100 mg, 0.4 mmol). After the mixture was stirred for another 30 min, dimethyl malonate (0.12 mL, 1.2 mmol) and BSA (0.3 mL, 1.2 mmol) were added. The reactions were carried out at room temperature and monitored by TLC for the disappearance of acetate **10**. The reaction mixture was diluted with ether, washed with satu-

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rated aqueous NH_4Cl solution, and then dried over $MgSO_4$. After removal of the solvent, the residue was purified by a chromatography column on silica gel with ethyl acetate/petroleum (1:10) as the eluent to afford pure product **11**. ^1H NMR ($CDCl_3$): δ 3.52 (s, 3H), 3.70 (s, 3H), 3.95 (d, J = 10.8 Hz, 1H), 4.27 (dd, J = 8.8, 10.8 Hz, 1H), 6.30 (dd, J = 8.8, 15.8 Hz, 1H), 6.44 (d, J = 15.8 Hz, 1H), 7.19−7.34 (m, 10H). The enantiomeric excess was determined by HPLC analysis (Chiralcel OD, hexane/2-propanol (80:20); flow rate 0.7 mL/min; t_R = 18.7 min, t_S = 20.4 min). The absolute configuration of the product was assigned by comparing the sign of its specific rotation with literature data.[21]

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Supporting Information Available: Figures giving full spectral characterization data for the new ferrocene compounds and Pd complex and tables giving X-ray data for **12b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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