Crystallographic computing was performed as for **2a**. The systematic absences ($h\ 0\ l$, $h + l \neq 2n$; $0\ k\ 0$, $k \neq 2n$) are consistent with space group $P2_1/n$. The Sn atoms were found on an E-map generated by the program MITHRIL.[23] The Cl, P, and some of the C atoms were located by direct methods (DIRDIF[21]), while the rest of the C atoms were revealed in difference electron density maps. The positions of the hydrogen atoms were idealized (C-H = 0.95 Å) and included in the model as fixed contributors to F_c. Due to the limited number of observed ($I > 3\sigma(I)$) data, the benzyltriphenylphosphonium cation was refined isotropically, except for the P atom. The final refinement was performed on the 2182 unique F_o values with $I > 3\sigma(I)$ and included anisotropic thermal parameters for the Sn, Cl, and P atoms and all the C atoms in the $[Sn_2Cl_2(C_8H_{16})_3 \cdot Cl]$ anion and isotropic thermal parameters for the C atoms in the $[(C_6H_5)_3(C_6H_5CH_2)P]$ cation. The final R values are listed in Table V. The final difference Fourier map and F_o vs F_c analysis were unexceptional.

$[Sn_2Cl_2(C_6H_{12})_3 \cdot F][(C_4H_9)_4N]$ (4). Lattice parameters were determined as for **2a** from the setting angles of 20 reflections ($8° < 2\theta(MoK\alpha_1) < 15°$). Data were collected at room temperature with the use of the ω-scan technique. Due to the weakly diffracting nature of the crystal (i.e., low signal-to-noise for most peaks), a Lehmann-Larsen profile analysis[22] was applied to each of the data in an attempt to maximize the number observed. Even so, as indicated in Table V, the number of observed data is small compared to the total number measured. Three standards, measured at 150 reflection intervals, showed small intensity losses (3-7%) from beginning to end of data collection. The data were not corrected for decay or absorption ($\mu = 14$ cm^{-1}).

All calculations were performed as for **2a**. The systematic absences ($h\ 0\ l$, $h \neq 2n$) are indicative of the space groups Pa and $P2/a$. As the Sn atoms could only be accommodated in the noncentrosymmetric group Pa, this group was selected and is accepted on the basis of the successful structure solution obtained. The structure was solved by direct methods: the Sn atom positions were taken from an E map (MITHRIL[23]), while the Cl, F, N, and C atoms were located by successive phase refinements with the use of the program DIRDIF.[21] Due to the limited number of observed data and the poor quality of the many weak data, refinement of a full anisotropic model was not possible. Consequently, the final refinement performed on the 681 unique F_o values for which $I > 3\sigma(I)$ included anisotropic thermal parameters for the Sn, Cl, F, and N atoms and isotropic thermal parameters for all C atoms. Owing to some rather large distortions in the carbon chains, particularly in the tetrabutylammonium cation, hydrogen atom positions were not included in the model. The final residuals are given in Table V. No unusual trends in F_o vs F_c appear as a function of F_o, $\sin\theta/\lambda$, or Miller indices. There were no significant peaks in the final difference electron density map.

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Supplementary Material Available: Tables containing anisotropic thermal parameters, final positional parameters, and isotropic thermal parameters for the non-hydrogen atoms and hydrogen atom positions for **2b**, **3**, **2a**, and **4** (18 pages); tables containing observed and calculated structure factors (108 pages). Ordering information is given on any current masthead page.

Asymmetric Synthesis Catalyzed by Chiral Ferrocenylphosphine-Transition-Metal Complexes. 8.[1] Palladium-Catalyzed Asymmetric Allylic Amination

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Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan, and the Takatsuki Research Laboratory, Sumitomo Chemical Co., Ltd., 2-10-1 Tsukahara, Takatsuki, Osaka 569, Japan. *Received January 3, 1989*

Abstract: Chiral ferrocenylphosphine ligands, represented by (*R*)-*N*-methyl-*N*-[bis(hydroxymethyl)methyl]-1-[(*S*)-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine ((*R*)-(*S*)-**1a**), which have a pendant side chain bearing a hydroxy group at the terminal position, were designed and used successfully for palladium-catalyzed asymmetric allylic amination of allylic substrates containing a 1,3-disubstituted propenyl structure (RCH=CHCH(X)R: R = Ph, Me, *n*-Pr, *i*-Pr; X = OCOOEt, OCOMe, $OP(O)Ph_2$, etc.). Reaction of the allylic substrates with benzylamine in the presence of a palladium catalyst prepared in situ from $Pd_2(dba)_3$ and (*R*)-(*S*)-**1a** gave high yields of amination products (RCH=CHC*H($NHCH_2Ph$)R: >97% ee (*R*) for R = Ph, 73% ee (*S*) for R = Me, 82% ee (*S*) for R = *n*-Pr, and 97% ee (*S*) for R = *i*-Pr). The allylamines were converted into optically active amino acids and their derivatives. The high stereoselectivity of the ferrocenylphosphine ligand is expected to be caused by an attractive interaction between the terminal hydroxy group on the ligand and the incoming amine, which directs the nucleophilic attack on one of the π-allyl carbons. The key role of the hydroxy group was supported by an X-ray structure analysis of a π-allylpalladium complex and ^{31}P NMR studies. It was demonstrated that the pendant side chain on the ferrocenylphosphine ligand is directed toward the reaction site on palladium and the terminal hydroxy group is located at the position close to one of the π-allyl carbon atoms and that π-allyl group on the palladium coordinated with the ferrocenylphosphine **1a** adopts one of the two possible conformational isomers with high selectivity (20/1) in an equilibrium state.

Of various methods for obtaining optically active compounds by asymmetric reactions, the most efficient is enantioselective synthesis by means of a chiral catalyst, where a small amount of a chiral material can produce a large amount of chiral product.[3] Recently, considerable research has been done on the catalytic

(1) For part 6 and 7 in this series, see: Hayashi, T.; Hayashizaki, K.; Kiyoi, T.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8153 and Hayashi, T.; Yamamoto, A.; Hojo, M.; Kishi, K.; Ito, Y.; Nishioka, E.; Yanagi, K. *J. Organomet. Chem.* In press, respectively.

(2) (a) Kyoto University. (b) Sumitomo Chemical Co., Ltd. (c) Present address: Catalysis Research Center, Hokkaido University, Sapporo 060, Japan.

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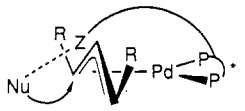
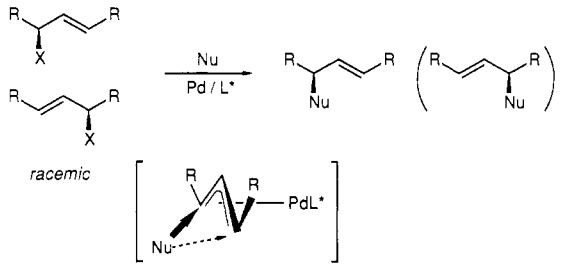


Figure 1. Directed nucleophilic attack by an attractive interaction with a functional group on the pendant side chain.

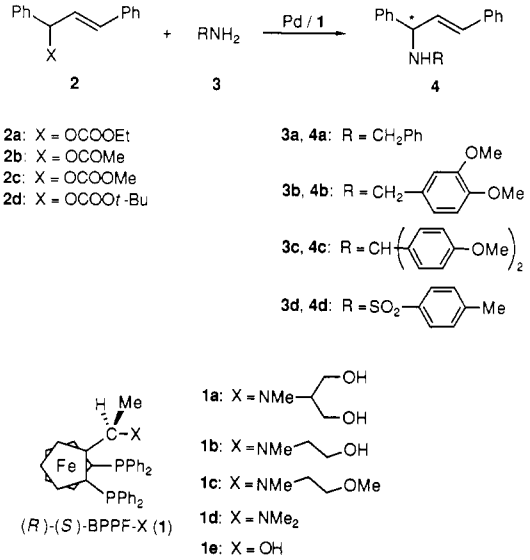
Scheme I



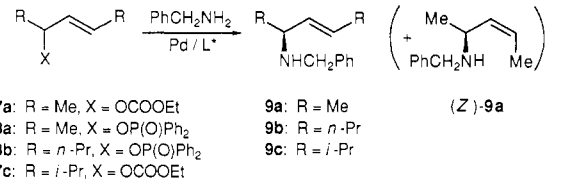
asymmetric reactions that proceed through π-allylpalladium intermediates.[4] The asymmetric allylic substitution reactions are unique in that several types of allylic substrates, either achiral or racemic, can be converted into optically active products via a π-allylpalladium intermediate where the original chirality of the substrate is lost. Bosnich and co-workers have reported[5] a well-designed system where the reaction proceeds via diastereomeric 1,1-diaryl-substituted π-allylpalladium intermediates. In this system, the enantiomeric purity of the product is related to the ratio of the diastereomeric π-allyl intermediates which undergo the epimerization via π-allyl–σ-allyl isomerization. We have studied[6] another type of asymmetric allylic alkylation which proceeds via a π-allylpalladium intermediate containing a meso type π-allyl group[7] (Scheme I). Both enantiomers of racemic 2-propenyl acetate or related substrates bearing the same substituents at 1- and 3-positions form, by oxidative addition to palladium(0), the meso type π-allylpalladium intermediate. The asymmetric induction arises from a preferential attack by the nucleophile on either of the two diastereotopic π-allyl carbon atoms in the π-allylpalladium intermediate. We describe here the asymmetric allylic amination through the meso type π-allylpalladium intermediates, focusing our attention on the design of stereoselective chiral phosphine ligands and the mechanism of the stereocontrol.

Studies on stereochemistry of the palladium-catalyzed allylic amination[8] and stoichiometric amination of π-allylpalladium complexes[9] have revealed that amines as well as soft carbon nucleophiles attack the π-allyl carbon from the side opposite to the palladium. Our strategy for obtaining high stereoselectivity in this type of reaction is to introduce, on a chiral bisphosphine ligand, a pendant side chain bearing a functional group at the terminal position. The terminal functional group, which is located at an appropriate distance from the palladium coordinated with the bisphosphine, is expected to interact with the incoming nucleophile to direct the attack on one of the π-allyl carbon atoms selectively (Figure 1).

Scheme II



Scheme III



Results and Discussion

Asymmetric Allylic Amination. Chiral ferrocenylphosphines that have a 1,1′-bis(diphenylphosphino)ferrocene skeleton are unique ligands where a desired pendant side chain can be introduced according to the demand of the reaction type.[10] For the asymmetric allylic substitution reactions, we have prepared chiral ferrocenylphosphine ligands **1**, some of which have hydroxy group(s) at the terminal of the pendant. They were examined for their stereoselectivity in the asymmetric amination of ethyl (*E*)-1,3-diphenyl-2-propenyl carbonate (**2a**) with benzylamine (**3a**) (Scheme II). A palladium complex generated in situ by mixing a chiral ligand with $Pd_2(dba)_3{\cdot}CHCl_3$ (P/Pd = 2/1) was used as catalyst. The reaction conditions and results are summarized in Table I. Ferrocenylphosphine (*R*)-(*S*)-**1a**[6,11] that contains *N*-methyl-*N*-bis(hydroxymethyl)methylamino group was found to be most selective, giving rise to (*R*)-(−)-*N*-[(*E*)-1,3-diphenyl-2-propenyl]benzylamine (**4a**) of over 97% ee (entries 1–3). The enantiomeric purity was determined by HPLC analysis of benzamide **5** derived from **4a** with a chiral stationary phase column (Sumipax OA-2000), and the absolute configuration (*R*) was assigned by comparison of the optical rotation of methyl *N*-benzoyl-*N*-benzylphenylglycinate (**6**) derived from (−)-**4a** with that of an authentic sample prepared starting with (*R*)-*N*-benzylphenylglycine (see Scheme IV). The stereoselectivity was slightly dependent on the reaction temperature, the highest value (97.6% ee) being obtained at 0 °C (entry 3). Palladium catalyst generated from ligand (*R*)-(*S*)-**1a** and $[(\pi\text{-PhCHCHCHPh})PdCl]_2$ was also catalytically active and stereoselective (entry 4). Similar stereoselectivity (95.3–97.4% ee) was observed in the amination of (*E*)-1,3-diphenyl-2-propenyl acetate (**2b**), methyl carbonate (**2c**), and *tert*-butyl carbonate (**2d**) (entries 5–7), which is reasonable because the leaving group is not likely to affect the

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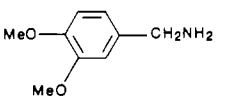
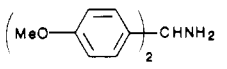
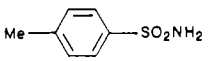
Table I. Asymmetric Allylic Amination of Ethyl 1,3-Diphenyl-2-propenyl Carbonate (**2a**) Catalyzed by Chiral Ferrocenylphosphine–Palladium Complexes[a]

entry	amine **3**	chiral ligand **1**	reaction conditions: temp, °C	reaction conditions: time, h	product (% yield)[b]	% ee[c] (confign)
1	$PhCH_2NH_2$ (**3a**)	**1a**	40	37	**4a** (93)	97.0[d] (*R*)
2	**3a**	**1a**	20	21	**4a** (83)	97.1 (*R*)
3	**3a**	**1a**[e]	0	108	**4a** (30)	97.6 (*R*)
4	**3a**	**1a**[f]	21	3	**4a** (81)	96.4 (*R*)
5[g]	**3a**[h]	**1a**	40	22	**4a** (84)	95.5 (*R*)
6[i]	**3a**	**1a**	40	16	**4a** (98)	95.3 (*R*)
7[j]	**3a**	**1a**	40	14	**4a** (84)	97.4 (*R*)
8	**3a**	**1b**[e]	40	31	**4a** (80)	79.3 (*R*)
9	**3a**	**1c**[e]	40	31	**4a** (75)	26.7 (*R*)
10	**3a**	**1d**	40	24	**4a** (79)	31.4 (*R*)
11	**3a**	**1e**	40	17	**4a** (86)	7.9 (*S*)
12	**3a**	(−)-DIOP[e]	40	21	**4a** (87)	19.1 (*S*)
13	 **3b**	**1a**	40	13	**4b** (87)	95[k]
14	 **3c**	**1a**[e]	40	21	**4c** (86)	85[l]
15	 **3d**	**1a**[e]	40	22	**4d** (67)	88[m]

[a] Reaction of 0.73 mmol of **2** with 0.87 mmol of **3** in 7 mL of THF in the presence of 0.011 mmol of $Pd_2(dba)_3{\cdot}CHCl_3$ and 0.023 mmol of a chiral ligand unless otherwise noted. [b] Isolated yield by preparative TLC on silica gel and based on the 2-propenyl carbonate. [c] The enantiomeric purities of allylamine **4a** were determined by HPLC analysis of benzamide, prepared by benzoylation of **4a** with benzoyl chloride, pyridine, and DMAP in dichloromethane, with a chiral column (Sumitomo Chemical Co., Sumipax OA-2000, hexane/dichloroethane/ethanol = 250/20/1). For the determination of % ee of **4b–d**, see the Experimental Section. [d] $[\alpha]^{20}_D$ −24.8° (*c* 1.4, chloroform). [e] Chiral bisphosphine/$Pd_2(dba)_3{\cdot}CHCl_3$ = 4/1. [f] Reaction in the presence of $[(\pi\text{-PhCHCHCHPh})PdCl]_2$ and **1a** as a catalyst. [g] Reaction of **2b**. [h] **3a**/**2b** = 2.2/1. [i] Reaction of **2c**. [j] Reaction of **2d**. [k] $[\alpha]^{20}_D$ −29.9° (*c* 1.2, chloroform). [l] $[\alpha]^{20}_D$ −48.1° (*c* 0.9, chloroform). [m] $[\alpha]^{20}_D$ −30.5° (*c* 1.1, chloroform).

Table II. Asymmetric Allylic Amination of Allyl Carbonates **7** and Phosphinates **8** with Benzylamine (**3a**) in the Presence of (*R*)-(*S*)-**1a**/Pd Catalyst[a]

entry	allyl substrate	reaction time, h	product (% yield)[b]	ratio[c] *E*/*Z*	% ee[c] (confign): *E*	% ee[c] (confign): *Z*
16[d]	**7a** (R = Me, X = OCOOEt)	38	**9a** (47)	97/3	70 (*S*)	60 (*S*)
17	**8a** (R = Me, X = $OP(O)Ph_2$)	13	**9a** (84)	96/4	73[e] (*S*)	23 (*S*)
18	**8b** (R = *n*-Pr, X = $OP(O)Ph_2$)	20	**9b** (97)	>99/1	82.1[f] (*S*)	
19[d]	**7c** (R = *i*-Pr, X = OCOOEt)	137	**9c** (88)	100/0	97.0[g] (*S*)	

[a] Reaction of 0.50 mmol of **7** or **8** with 1.1 mmol of **3a** in 5 mL of THF in the presence of 0.0025 mmol of $Pd_2(dba)_3{\cdot}CHCl_3$ (1.0 mol%) and 0.010 mmol of (*R*)-(*S*)-**1a** at 40 °C, unless otherwise noted. [b] Isolated yield by preparative TLC. [c] The enantiomeric purities of (*E*)- and (*Z*)-**9a** were determined by HPLC analysis of 3,5-dinitrobenzamide **13a** with a chiral column (Sumipax OA-1100, hexane/dichloroethane/ethanol = 500/20/1). For the determination of % ee of **9b** and **9c** by the HPLC analysis, see the Experimental Section. [d] **7**/**3a**/catalyst = 1/1.2/0.03. [e] Rotation of a mixture of (*E*)- and (*Z*)-**9a**: $[\alpha]^{20}_D$ −18.6° (*c* 1.4, chloroform). [f] $[\alpha]^{20}_D$ −22.3° (*c* 1.2, chloroform). [g] $[\alpha]^{20}_D$ −37.3° (*c* 1.5, chloroform).

amination at the step of stereocontrolling nucleophilic attack. Ferrocenylphosphine **1b**,[10] which has one hydroxy group at the terminal, was somewhat less effective than **1a**, which has two hydroxy groups, but still gave **4a** of high enantiomeric purity (79% ee) (entry 8). Much lower selectivity was observed in the reaction with ferrocenylphosphine **1c**, which has methoxy group instead of hydroxy group on the side chain, and with **1d**,[10] which lacks the pendant side chain (entries 9 and 10). Ferrocenylphosphine **1e**,[10] which has hydroxy group at the ferrocenylmethyl position, gave the amination product with opposite configuration of low % ee (entry 11). Low selectivity was also observed with DIOP, which stands for 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane[12] (entry 12). Thus, the hydroxy group located four atoms away from the ferrocenylmethyl position is essential for the high stereoselectivity. It may be said that the hydroxy group attracts the amino group of benzylamine, probably by hydrogen bonding, to direct the nucleophilic attack on one of the stereogenic π-allyl carbon atoms, as we have expected at the design of chiral phosphine ligand. 3,4-Dimethoxybenzylamine (**3b**), bis(4-methoxyphenyl)methylamine (**3c**), and *p*-toluenesulfonamide (**3d**) were also successfully used for the asymmetric amination to give the corresponding allylamines **4b–d** of over 85% ee in high yields (entries 13–15).

The palladium catalyst bearing (*R*)-(*S*)-**1a** was also found to be effective for the allylic amination of 2-propenyl carbonates **7** or phosphinates **8** substituted with alkyl groups (Me, *n*-Pr, and *i*-Pr) at the 1- and 3-positions (Scheme III and Table II). (Diphenylphosphinyl)oxy group was a leaving group of choice for the reaction of allylic substrates with smaller alkyl groups such as methyl and *n*-propyl. Thus, the reaction of (*E*)-1-methyl-2-butenyl carbonate **7a** and phosphinate **8a** with benzylamine gave allylic amination product **9a** in 47% and 84% yield, respectively (entries 16 and 17). The low yield in the amination of carbonate **7a** may be ascribed to the undesired side reaction where **7a** undergoes nucleophilic attack of benzylamine on the carbonyl carbon. The higher enantioselectivity was observed with allylic substrates containing the larger substituents. Reaction of **7c** (R = *i*-Pr) gave a high yield of amination product **9c** in 97% ee (entry 19). Absolute configurations of the allylamines **9a–c** were determined to be all *S* by converting them into L-amino acids, (*S*)-alanine, (*S*)-norvaline, and (*S*)-valine, respectively, and their *N*-benzyl derivatives **12** by a sequence of reactions shown in Scheme IV.

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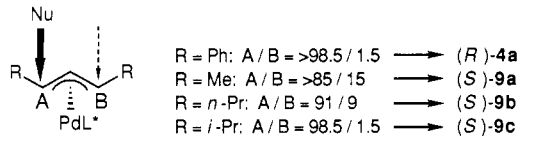
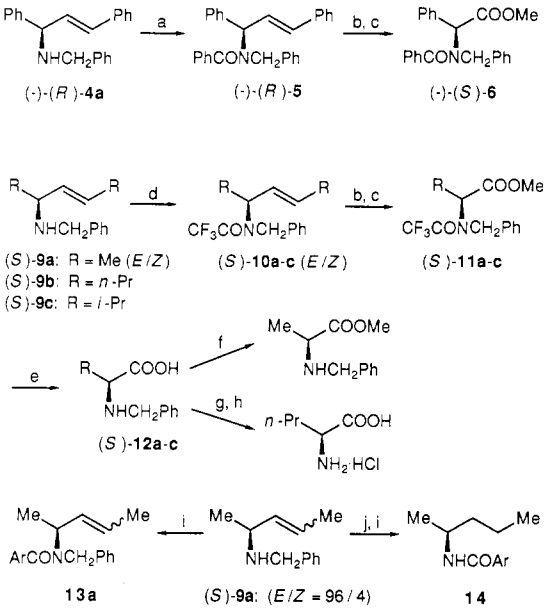


Figure 2. Selective nucleophilic attack on π-allyl carbon A.

Scheme IV[a]



[a] Reagents: (a) PhCOCl, py, DMAP, CH_2Cl_2; (b) $KMnO_4$, $NaIO_4$, K_2CO_3, t-BuOH/H_2O; (c) CH_2N_2, Et_2O; (d) $(CF_3CO)_2O$, Et_3N, DMAP, CH_2Cl_2; (e) 2 N NaOH, MeOH; (f) CH_2N_2, Et_2O/MeOH; (g) 90% HCOOH, 10% Pd–C; (h) concentrated HCl; (i) 3,5-$(NO_2)_2C_6H_3COCl$, Et_3N, CH_2Cl_2; (j) H_2, 10% Pd–C, EtOH.

π-Allylpalladium complexes that contain two alkyl substituents, one at each of the 1- and 3-positions, are known to adopt the conformation where both of the substituents are located in the syn positions with respect to the central hydrogen.[13] The π-allylpalladium intermediates in the present asymmetric reactions are also the case since the amination products of (*E*) geometry were formed with high selectivity for all the reactions (>99/1 for R = Ph, *n*-Pr, *i*-Pr and 96/4–97/3 for R = Me). To summarize the stereochemical results of the allylic amination, all of the substrates **2a–d**, **7a,c**, and **8a,b** underwent the preferential attack of nitrogen nucleophile on π-allyl carbon A over B in π-allylpalladium intermediate where both of the alkyl groups are in the syn position, giving (*R*)-**4** and (*S*)-**9a–c** selectively. The % ee values of the amination products indicate that the ratios of the nucleophilic attack on A over B are 99/1–98/2 for R = Ph and *i*-Pr, 91/9 for R = *n*-Pr, and 87/13–85/15 for R = Me (Figure 2).

Mechanism of Stereocontrol. We have prepared and used chiral ferrocenylphosphine ligands that contain a hydroxy pendant, expecting the effective stereocontrol based on the attractive interactions shown in Figure 1. The stereochemical results obtained above for the asymmetric allylic amination may support the validity of the design of the chiral phosphine–palladium catalysts. In order to obtain an insight into the mechanism of the stereocontrol, we carried out an X-ray crystal-structure analysis of a palladium complex which has both π-allyl group and the chiral ferrocenylphosphine ligand and ^{31}P NMR studies of the π-allylpalladium complexes.

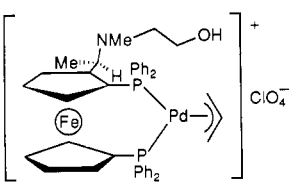
(13) (a) For example, see: Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1983**, *105*, 7767. (b) For a review: Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 6, p 385.

Table III. Fractional Coordinates and Temperature Factors[a]

atom	*x*	*y*	*z*	B_{eq},[b] or *B*
Pd	0.500	0.500	0.500	2.592 (5)
Fe	0.58370 (6)	0.84574 (5)	0.89687 (6)	2.56 (1)
P(1)	0.3988 (1)	0.5905 (1)	0.7167 (1)	2.56 (2)
P(2)	0.5633 (1)	0.6970 (1)	0.5170 (1)	2.59 (2)
O(1)	0.5846 (8)	0.1751 (7)	0.656 (1)	9.5 (2)
N	0.6995 (4)	0.4240 (4)	0.8273 (4)	3.49 (8)
C(1)	0.4971 (4)	0.6891 (4)	0.8785 (4)	2.59 (7)
C(2)	0.6338 (4)	0.6662 (4)	0.9045 (4)	2.80 (8)
C(3)	0.6677 (5)	0.7778 (4)	1.0425 (5)	3.50 (9)
C(4)	0.5607 (6)	0.8669 (5)	1.0999 (5)	3.7 (1)
C(5)	0.4537 (5)	0.8145 (5)	1.0021 (5)	3.30 (9)
C(6)	0.5859 (4)	0.8428 (4)	0.6980 (4)	2.79 (8)
C(7)	0.7072 (5)	0.8715 (5)	0.7777 (5)	3.47 (9)
C(8)	0.6895 (6)	0.9923 (5)	0.9131 (6)	4.4 (1)
C(9)	0.5574 (6)	1.0399 (5)	0.9188 (5)	4.0 (1)
C(10)	0.4922 (5)	0.9465 (4)	0.7850 (5)	3.31 (9)
C(11)	0.7198 (4)	0.5410 (4)	0.8092 (5)	3.15 (8)
C(12)	0.8602 (6)	0.5716 (6)	0.8361 (9)	5.5 (2)
C(13)	0.7704 (6)	0.2971 (5)	0.7235 (7)	4.7 (1)
C(14)	0.7182 (9)	0.1709 (6)	0.7021 (8)	5.8 (2)
C(15)	0.7202 (8)	0.4453 (6)	0.9779 (6)	5.3 (1)
C(16)	0.2550 (4)	0.7067 (4)	0.7284 (5)	2.89 (8)
C(17)	0.2307 (5)	0.7614 (5)	0.6313 (5)	3.6 (1)
C(18)	0.1243 (5)	0.8555 (6)	0.6412 (6)	4.6 (1)
C(19)	0.0400 (5)	0.8891 (6)	0.7482 (7)	4.7 (1)
C(20)	0.0617 (5)	0.8339 (6)	0.8419 (7)	4.5 (1)
C(21)	0.1670 (5)	0.7430 (5)	0.8319 (5)	3.8 (1)
C(22)	0.3365 (4)	0.4661 (5)	0.7525 (5)	3.36 (9)
C(23)	0.3810 (6)	0.4446 (6)	0.8701 (6)	4.7 (1)
C(24)	0.3359 (8)	0.3443 (7)	0.8878 (8)	6.6 (2)
C(25)	0.2449 (9)	0.2682 (7)	0.789 (1)	7.3 (2)
C(26)	0.1923 (7)	0.2955 (7)	0.6780 (9)	6.1 (2)
C(27)	0.2387 (6)	0.3915 (6)	0.6544 (7)	4.7 (1)
C(28)	0.4510 (4)	0.7652 (4)	0.4153 (4)	2.95 (8)
C(29)	0.4332 (6)	0.9035 (5)	0.4540 (5)	3.9 (1)
C(30)	0.3362 (6)	0.9508 (5)	0.3790 (5)	4.5 (1)
C(31)	0.2580 (6)	0.8607 (6)	0.2672 (6)	4.9 (1)
C(32)	0.2763 (6)	0.7258 (6)	0.2288 (6)	4.7 (1)
C(33)	0.3727 (5)	0.6755 (5)	0.3002 (5)	3.8 (1)
C(34)	0.7194 (5)	0.6670 (5)	0.4459 (5)	3.32 (9)
C(35)	0.8042 (5)	0.5644 (6)	0.4502 (6)	4.3 (1)
C(36)	0.9279 (6)	0.5420 (7)	0.4064 (7)	5.1 (1)
C(37)	0.9601 (6)	0.6286 (8)	0.3532 (7)	5.6 (2)
C(38)	0.8763 (6)	0.7282 (6)	0.3473 (6)	4.8 (1)
C(39)	0.7525 (6)	0.7492 (5)	0.3912 (6)	4.2 (1)
C(40)	0.5619 (8)	0.3610 (6)	0.2772 (6)	5.4 (2)
C(41)	0.5631 (8)	0.2871 (6)	0.3545 (7)	5.3 (2)
C(42)	0.4574 (7)	0.2901 (5)	0.4178 (7)	4.8 (1)
Cl	−0.0844 (2)	0.0831 (3)	0.3160 (3)	8.84 (7)
O(2)	−0.0551 (9)	−0.0266 (9)	0.182 (1)	10*
O(3)	−0.2080 (9)	0.0469 (9)	0.338 (1)	10*
O(4)	−0.1174 (9)	0.2106 (9)	0.3385 (9)	10*
O(5)	−0.0180 (9)	0.0646 (9)	0.437 (1)	10*
O(6)	0.2156 (7)	0.3639 (6)	0.2018 (8)	8.1 (2)
C(43)	0.1652 (7)	0.2636 (8)	0.1281 (8)	5.9 (2)
C(44)	0.2269 (9)	0.1255 (9)	0.101 (1)	9.5 (3)
C(45)	0.0343 (9)	0.266 (1)	0.055 (1)	11.0 (3)

[a] Standard deviations of the least significant figures are given in parentheses. [b] $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}a_i\cdot a_j$.

(a) Structure of π-Allylpalladium Complex [Pd(1b)(π-C_3H_5)]ClO_4 (15). π-Allylpalladium complex **15**, which contains



15

chiral ferrocenylphosphine **1b**, was prepared by the reaction of bis(μ-chloro)bis(π-allyl)dipalladium with **1b** in methanol, followed by treatment with lithium perchlorate, and recrystallized from

Table IV. Bond Distances (Å) for **15**[a]

Pd-P(1)	2.321 (2)	C(6)-C(7)	1.433 (6)
Pd-P(2)	2.327 (1)	C(6)-C(10)	1.428 (6)
Pd-C(40)	2.201 (6)	C(7)-C(8)	1.416 (5)
Pd-C(41)	2.175 (5)	C(8)-C(9)	1.428 (9)
Pd-C(42)	2.182 (7)	C(9)-C(10)	1.442 (6)
Fe-C(1)	2.026 (5)	C(11)-C(12)	1.549 (8)
Fe-C(2)	2.037 (5)	C(13)-C(14)	1.51 (2)
Fe-C(3)	2.053 (6)	C(16)-C(17)	1.393 (9)
Fe-C(4)	2.053 (5)	C(16)-C(21)	1.392 (7)
Fe-C(5)	2.044 (6)	C(17)-C(18)	1.403 (8)
Fe-C(6)	2.056 (5)	C(18)-C(19)	1.40 (1)
Fe-C(7)	2.065 (6)	C(19)-C(20)	1.36 (1)
Fe-C(8)	2.064 (7)	C(20)-C(21)	1.375 (7)
Fe-C(9)	2.053 (5)	C(22)-C(23)	1.368 (9)
Fe-C(10)	2.050 (5)	C(22)-C(27)	1.412 (8)
Cl-O(2)	1.380 (8)	C(23)-C(24)	1.39 (1)
Cl-O(3)	1.51 (1)	C(24)-C(25)	1.37 (2)
Cl-O(4)	1.33 (2)	C(25)-C(26)	1.37 (1)
Cl-O(5)	1.45 (1)	C(26)-C(27)	1.39 (1)
P(1)-C(1)	1.802 (4)	C(28)-C(29)	1.388 (7)
P(1)-C(16)	1.829 (5)	C(28)-C(33)	1.404 (6)
P(1)-C(22)	1.839 (6)	C(29)-C(30)	1.405 (8)
P(2)-C(6)	1.818 (3)	C(30)-C(31)	1.392 (7)
P(2)-C(28)	1.816 (5)	C(31)-C(32)	1.353 (9)
P(2)-C(34)	1.833 (5)	C(32)-C(33)	1.395 (9)
O(1)-C(14)	1.44 (1)	C(34)-C(35)	1.364 (8)
O(6)-C(43)	1.18 (1)	C(34)-C(39)	1.40 (1)
N-C(11)	1.461 (7)	C(35)-C(36)	1.402 (9)
N-C(13)	1.472 (7)	C(36)-C(37)	1.43 (1)
N-C(15)	1.457 (8)	C(37)-C(38)	1.34 (2)
C(1)-C(2)	1.454 (6)	C(38)-C(39)	1.405 (9)
C(1)-C(5)	1.435 (5)	C(40)-C(41)	1.40 (1)
C(2)-C(3)	1.423 (5)	C(41)-C(42)	1.38 (1)
C(2)-C(11)	1.516 (6)	C(43)-C(44)	1.50 (1)
C(3)-C(4)	1.384 (7)	C(43)-C(45)	1.51 (1)
C(4)-C(5)	1.416 (7)		

[a] Standard deviations of the least significant figures are given in parentheses.

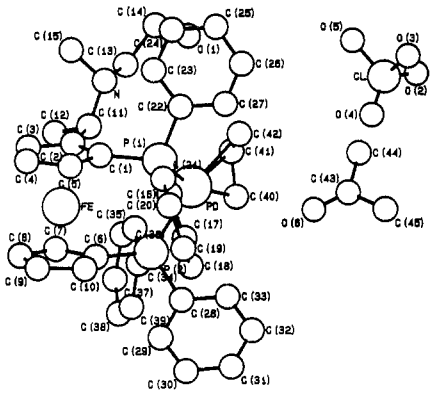


Figure 3. Molecular structure and atom numbering scheme for palladium complex **15**.

acetone and ether. Fractional coordinates, bond lengths, and bond angles are listed in Tables III, IV, and V, respectively. The

Table V. Bond Angles (deg) for **15**[a]

P(1)-Pd-P(2)	100.90 (4)	C(6)-C(10)-C(9)	107.2 (4)
P(1)-Pd-C(40)	162.1 (2)	N-C(11)-C(2)	110.1 (4)
P(1)-Pd-C(41)	128.5 (2)	N-C(11)-C(12)	114.1 (5)
P(1)-Pd-C(42)	95.8 (2)	C(2)-C(11)-C(12)	111.4 (3)
P(2)-Pd-C(40)	96.1 (2)	N-C(13)-C(14)	112.2 (7)
P(2)-Pd-C(41)	128.6 (2)	O(1)-C(14)-C(13)	110.0 (7)
P(2)-Pd-C(42)	163.1 (2)	P(1)-C(16)-C(17)	119.9 (3)
C(40)-Pd-C(41)	37.4 (3)	P(1)-C(16)-C(21)	122.2 (4)
C(40)-Pd-C(42)	67.0 (3)	C(17)-C(16)-C(21)	118.0 (4)
C(41)-Pd-C(42)	36.7 (4)	C(16)-C(17)-C(18)	121.4 (5)
O(2)-Cl-O(3)	100.9 (5)	C(17)-C(18)-C(19)	118.0 (7)
O(2)-Cl-O(4)	124.3 (7)	C(18)-C(19)-C(20)	120.9 (5)
O(2)-Cl-O(5)	111.8 (6)	C(19)-C(20)-C(21)	120.4 (6)
O(3)-Cl-O(4)	101.2 (6)	C(16)-C(21)-C(20)	121.2 (6)
O(3)-Cl-O(5)	92.6 (6)	P(1)-C(22)-C(23)	122.4 (4)
O(4)-Cl-O(5)	117.5 (5)	P(1)-C(22)-C(27)	118.0 (5)
Pd-P(1)-C(1)	113.4 (2)	C(23)-C(22)-C(27)	119.6 (6)
Pd-P(1)-C(16)	115.2 (2)	C(22)-C(23)-C(24)	120.2 (6)
Pd-P(1)-C(22)	115.9 (1)	C(23)-C(24)-C(25)	119.9 (8)
C(1)-P(1)-C(16)	104.3 (2)	C(24)-C(25)-C(26)	120.6 (9)
C(1)-P(1)-C(22)	106.2 (2)	C(25)-C(26)-C(27)	120.5 (7)
C(16)-P(1)-C(22)	100.6 (2)	C(22)-C(27)-C(26)	118.8 (7)
Pd-P(2)-C(6)	118.9 (2)	P(2)-C(28)-C(29)	122.6 (3)
Pd-P(2)-C(28)	111.4 (2)	P(2)-C(28)-C(33)	118.2 (4)
Pd-P(2)-C(34)	112.5 (2)	C(29)-C(28)-C(33)	119.1 (5)
C(6)-P(2)-C(28)	104.5 (2)	C(28)-C(29)-C(30)	119.4 (4)
C(6)-P(2)-C(34)	101.1 (2)	C(29)-C(30)-C(31)	120.7 (5)
C(28)-P(2)-C(34)	107.4 (2)	C(30)-C(31)-C(32)	119.8 (6)
C(11)-N-C(13)	111.5 (5)	C(31)-C(32)-C(33)	120.8 (6)
C(11)-N-C(15)	114.7 (4)	C(28)-C(33)-C(32)	120.2 (5)
C(13)-N-C(15)	112.3 (5)	P(2)-C(34)-C(35)	118.6 (5)
P(1)-C(1)-C(2)	127.9 (2)	P(2)-C(34)-C(39)	121.1 (4)
P(1)-C(1)-C(5)	124.8 (3)	C(35)-C(34)-C(39)	120.4 (5)
C(2)-C(1)-C(5)	107.1 (3)	C(34)-C(35)-C(36)	121.4 (7)
C(1)-C(2)-C(3)	106.4 (3)	C(35)-C(36)-C(37)	117.1 (6)
C(1)-C(2)-C(11)	126.1 (4)	C(36)-C(37)-C(38)	121.5 (6)
C(3)-C(2)-C(11)	127.2 (4)	C(37)-C(38)-C(39)	120.8 (8)
C(2)-C(3)-C(4)	109.8 (4)	C(34)-C(39)-C(38)	118.8 (6)
C(3)-C(4)-C(5)	108.9 (3)	Pd-C(40)-C(41)	70.3 (4)
C(1)-C(5)-C(4)	107.8 (4)	Pd-C(41)-C(40)	72.3 (3)
P(2)-C(6)-C(7)	123.5 (3)	Pd-C(41)-C(42)	71.9 (3)
P(2)-C(6)-C(10)	128.2 (3)	C(40)-C(41)-C(42)	121.5 (7)
C(7)-C(6)-C(10)	108.3 (3)	Pd-C(42)-C(41)	71.4 (4)
C(6)-C(7)-C(8)	108.2 (5)	O(6)-C(43)-C(44)	122.3 (7)
C(7)-C(8)-C(9)	108.1 (4)	O(6)-C(43)-C(45)	122.3 (9)
C(8)-C(9)-C(10)	108.2 (4)	C(44)-C(43)-C(45)	115.3 (8)

[a] Standard deviations of the least significant figures are given in parentheses.

structure of complex **15** was determined by an X-ray diffraction study. A molecular structure of the complex including atom numbering scheme and a stereoscopic view of the complex, where acetone as a crystal solvent and perchlorate are omitted for simplicity, are illustrated in Figures 3 and 4, respectively.

Two phosphorus atoms coordinate with palladium occupying two cis sites in a distorted square-planar coordination geometry. The environment of the palladium and phosphorus atoms is quite similar to that of $PdCl_2(BPPFA)$,[14] where BPPFA stands for

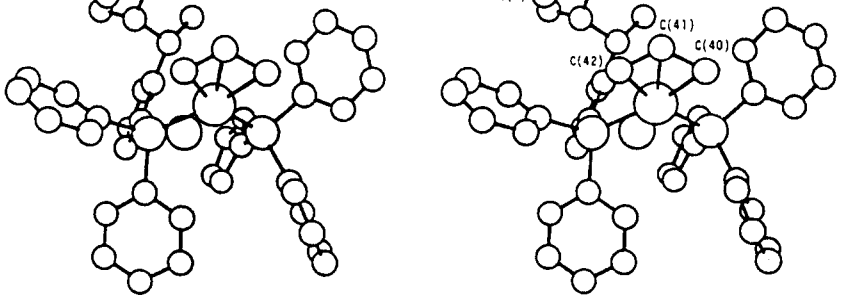


Figure 4. Stereospecific view of palladium complex **15**. Acetone and perchlorate are omitted for clarity.

(*R*)-*N*,*N*-dimethyl-1-[(*S*)-1′,2-bis(diphenylphosphino)-ferrocenyl]ethylamine. Thus, the P–Pd–P angle of 100.90 (4)° is large compared with bisphosphine–palladium complexes $PdCl_2[Ph_2P(CH_2)_nPPh_2]$ (n = 2 and 3),[15] which is characteristic of palladium complexes bearing 1,1′-bis(diphenylphosphino)-ferrocene (dppf) skeleton.[16] The two Pd–P distances 2.321 (2) and 2.327 (1) Å are normal for a phosphine–palladium complex. The two cyclopentadienyl rings, which are nearly parallel (deviation of 3°) to each other, are in a staggered conformation. The dihedral angle between one of the cyclopentadienyl planes and the plane defined by the Pd and two P atoms is 71.5 (1)°. When observed along the plane P–Pd–P, one of the cyclopentadienyl rings that is substituted with the side chain lies above the plane and the other is bisected by the plane. Four phenyl rings are oriented in the face and edge manner, upper left and lower right rings being edge and upper right and lower left rings being face when viewed from the palladium atom (Figure 4).

The allyl group is η^3-bonded to the palladium occupying the opposite sites of palladium to the phosphorus atoms. The distances between Pd and allylic carbons, 2.201 (6), 2.175 (5), and 2.182 (7) Å for C(40), C(41), and C(42), respectively, show that the distances of Pd and two terminal allyl carbons C(40) and C(42) differ slightly from each other and the central allylic carbon atom C(41) is slightly closer to the Pd than the two terminal carbons. The plane defined by the three allylic carbon atoms is at an angle of 62.7 (5)° to the plane P–Pd–P. The dihedral angle between the plane P–Pd–P and the plane defined by the Pd and two terminal allylic carbons is 5.57 ± 1.74°. The central carbon C(41) is above the plane P–Pd–P and the other two carbons C(40) and C(42) are below the plane.

The most significant is the location of oxygen atom O(1) of the terminal hydroxy group on the pendant side chain which is attached to the cyclopentadienyl ring at upper carbon. The side chain reaches out toward the π-allyl group, passing above the palladium (Figure 3). The oxygen atom O(1) of the terminal hydroxy group is located close to the π-allyl. The hydroxy is not coordinating to palladium, as evidenced by the large separation (4.58 (2) Å) of the palladium and oxygen atoms. When viewed from the π-allyl (Figure 4), oxygen atom O(1) is upper left of the π-allyl. The oxygen is much closer to the allylic carbon atom C(42) at the left end than the carbon C(40) at the right end, 3.36 (1) Å compared to 5.24 (1) Å.

(b) ^{31}P NMR of π-Allylpalladium Complexes. π-Allylpalladium acetate bearing 1,3-diphenyl-π-allyl group, $[(\pi$-PhCHCHCHPh)PdOAc$]_2$ (**16**), was prepared by treatment of $[(\pi$-PhCHCHCHPh)PdCl$]_2$ with silver acetate in methanol and dichloromethane.[5b] To a solution of the π-allylpalladium acetate **16** in $CDCl_3$ was added at −60 °C a solution of ferrocenylphosphine **1a**, which was demonstrated to be most effective for the asymmetric amination, in $CDCl_3$. The solution gave two AB quartets (J_{P-P} = 58.6 and 62.9 Hz) in a ratio of ca. 1/1 for the ^{31}P NMR at −50 °C. The coupling constant, 12.6 Hz between π-allyl protons in ^{1}H NMR, indicated that phenyl groups on the π-allyl are disposed syn with respect to the central hydrogen in both isomers. When warming up the solution gradually, the ratio of the two species started to change at around −40 °C and reached an equilibrium in 1 h at −30 °C (Figure 5). The equilibrium value was 20/1 in the temperature range between −30 and 10 °C (b in Figure 5). These two species are assigned to conformational isomers (rotamers) of π-allylpalladium complex **17** where two unequivalent phosphorus atoms coordinate with palladium, forming a chelate, one being the isomer **17a** that has the π-allyl group of "W" shape and the other being the isomer **17b** that has the π-allyl group of "M" shape when viewed from the same direction as in Figure 4. It seems reasonable to assume that the main isomer in the equilibrium is **17a**, which is analogous to the crystal structure of **15**, though we do not have any direct evidence supporting the structure at the present stage. Amination by addition of an excess of benzylamine to the equilibrated mixture of **17** (**17a**/**17b** = 20/1) was completed in 30 min at −10 °C to give 78% yield of the allylic amination product (*R*)-**4a** of 95.7% ee (determined by the HPLC analysis) (Scheme V). The stereochemistry of **4a** obtained here for the stoichiometric reaction is the same as that for the catalytic amination (entries 1–7 in Table I). During the amination of **17**, the ratio of the isomers was observed to be almost constant, indicating that both isomers undergo the amination with comparable reaction rates or the equilibration between the isomers is fast compared with the amination.

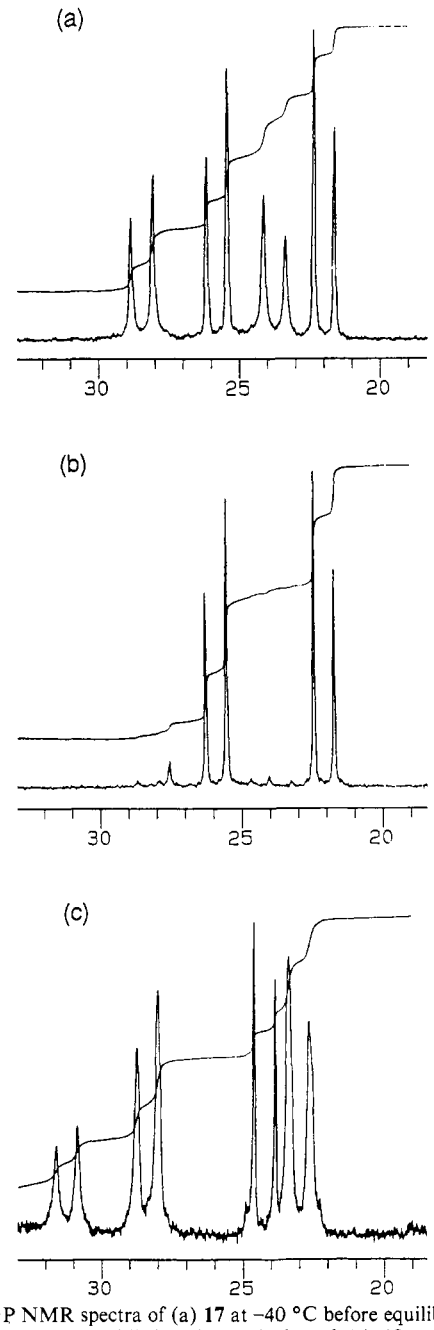


Figure 5. ^{31}P NMR spectra of (a) **17** at −40 °C before equilibration, (b) **17** at −30 °C after equilibrium is reached, and (c) **18** at −10 °C in equilibrium.

Palladium complex **18** prepared in $CDCl_3$ from π-allylpalladium acetate **16** and BPPFA (**1d**), which lacks the hydroxy pendant, also gave two AB quartets (J_{P-P} = 59.9 and 60.3 Hz) for the ^{31}P NMR. The equilibrium value for **18** was not as large as that observed for **17**, the ratio of the two isomers being 2/1 at the temperature between −30 and 10 °C (c in Figure 5). Upon treatment of the equilibrated **18** with benzylamine was obtained (*R*)-**4a** of lower enantiomeric purity (62.3% ee), which is consistent

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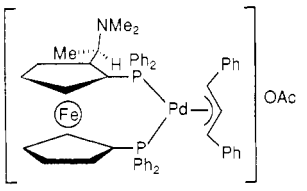
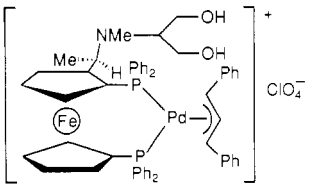


18



19

with the low selectivity of **1d** for the catalytic amination (entry 10 in Table I).

Interestingly, the equilibrated ratio of the isomers of π-allylpalladium **17** was strongly dependent on the solvent and anionic part of the palladium complex. Thus, the ratio of **17a** to **17b** in CD_3OD was 3.5/1 at −20 °C, and the ratio of isomers of perchlorate analogue [(π-PhCHCHCHPh)Pd(**1a**)]ClO_4 (**19**) in $CDCl_3$ was about 2.5/1 in the range between −30 and 20 °C. Amination of perchlorate complex **19** upon addition of benzylamine in $CDCl_3$ at −10 °C gave (*R*)-**4a** of 59.4% ee. Catalytic allylic amination of **2a** carried out in the presence of **19** as a catalyst under standard conditions (3 mol % of **19**, in THF at 40 °C for 1 h) gave 80% yield of (*R*)-**4a** of 22.1% ee. The lower stereoselectivity observed in both stoichiometric and catalytic amination reactions is in good agreement with the lower ratio of the isomers of perchlorate **19**. The marked effect of the solvent and anion of the palladium complexes on the equilibrated ratio of isomers may suggest that the acetate anion in **17** coordinates (or interacts weakly) with palladium in less polar solvents such as chloroform or THF, where the catalytic asymmetric amination was carried out, and that the interaction plays an important role for the high selectivity.

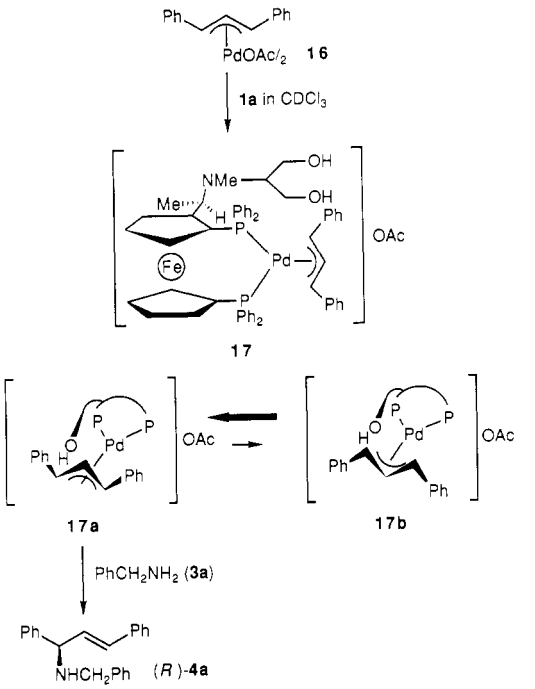
The results obtained in the X-ray structure analysis and ^{31}P NMR studies are summarized as follows. It was shown that the pendant side chain on the ferrocenylphosphine ligand is directed toward the reaction site on palladium and that the terminal hydroxy group is located at the position close to one of the π-allyl carbon atoms, which corresponds to carbon A in Figure 2. The 1,3-diphenyl-π-allyl group on the palladium acetate complex **17** containing ferrocenylphosphine ligand **1a**, which is considered to be a key intermediate for the stereoselective catalytic amination, was shown to adopt one of the two possible conformations with high selectivity (20/1) in an equilibrium state. In conclusion, the high stereoselectivity of the ferrocenylphosphine ligand bearing the hydroxy pendant for the present allylic amination can be ascribed to the selective formation of one conformational isomer of π-allylpalladium intermediates, probably "W" shape **17a** in Scheme V, and the selective nucleophilic attack of amine on one of the stereogenic π-allyl carbon atoms (carbon A in Figure 2), which is directed by the hydroxy group at the terminal of the pendant.

Experimental Section

General Procedures. Optical rotations were measured with a Perkin-Elmer 243 polarimeter. ^1H NMR spectra were measured with a JEOL JNM-MH-100 (100 MHz), Varian VXR-200 (200 MHz), or JEOL JNM-GX-400 (400 MHz) spectrometer. ^{31}P $\{^1H\}$ NMR spectra (81 MHz) were measured with Varian VXR-200 spectrometer. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-DX-300 mass spectrometer. Analytical HPLC was carried out with a Shimadzu HPLC system equipped with a chiral stationary phase column, Sumitomo Chemical Co., Sumipax OA series, and hexane/dichloroethane/ethanol as eluting solvent. Preparative medium-pressure liquid chromatography (MPLC) was performed with a silica gel prepacked C.I.G. (Kusano) column.

Materials. The preparation of optically active ferrocenylphosphines (*R*)-(*S*)-**1a,b,d,e** has been reported.[10a,11] Allylic acetate **2b** was prepared by acetylation of the corresponding allylic alcohol with acetic anhydride. Allylic carbonate **7a** was prepared from pent-3-en-2-ol and ethyl chloroformate.[17] Benzylamine was distilled before use. Veratrylamine and *p*-toluenesulfonamide were purchased and used without further purification. 4,4′-Dimethoxybenzhydrylamine was prepared by the reported procedure.[8a]

Scheme V



Preparation of Chiral Ferrocenylphosphine 1c. In a similar manner to the procedure reported for the preparation of **1b**,[11] the ferrocenylphosphine (*R*)-(*S*)-**1c** was prepared by the reaction of (*R*)-1-[(*S*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethyl acetate with 2-(*N*-methylamino)ethyl methyl ether in refluxing methanol (89%): $[\alpha]^{25}_D$ −323° (*c* 0.75, chloroform); ^1H NMR ($CDCl_3$) δ 1.18 (d, J = 7 Hz, 3 H), 1.76 (S, 3 H), 2.16–3.01 (m, 4 H), 3.09 (s, 3 H), 3.54, 3.70, 3.94–4.48 (m, 1 H, 1 H, 6 H), 6.98–7.74 (m, 20 H). Anal. Calcd for $C_{40}H_{41}NOP_2Fe$: C, 71.75; H, 6.17; N, 2.09. Found: C, 71.46; H, 6.04; N, 2.04.

Allylic Alcohols. (*E*)-1,3-Diphenylprop-2-en-1-ol was prepared by the reaction of phenylmagnesium bromide with cinnamaldehyde.[5a] (*E*)-Pent-3-en-2-ol was prepared from methylmagnesium bromide and crotonaldehyde.

(*E*)-2,6-Dimethylhept-4-en-3-ol. To a stirred solution of 38 mL (67 mmol) of 1.75 M isopropylmagnesium chloride in ether at 0 °C was added dropwise a solution of 4.9 g (50 mmol) of (*E*)-4-methyl-2-pentenal, prepared according to the reported procedure,[18] in 25 mL of ether over 30 min. The mixture was allowed to reflux for 2 h and then was quenched with saturated ammonium chloride solution. The aqueous layer was extracted three times with ether, and the combined ether extracts were washed with saturated sodium hydrogen carbonate solution and then water and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by preparative MPLC (hexane/ethyl acetate = 4/1) gave 3.5 g (50%) of the alcohol: ^1H NMR ($CDCl_3$) δ 0.87 (d, J = 6.8 Hz, 3 H), 0.93 (d, J = 6.8 Hz, 3 H), 1.01 (d, J = 6.8 Hz, 6 H), 1.52 (s, 1 H), 1.70 (octet, J = 6.8 Hz, 1 H), 2.31 (octet, J = 6.8 Hz, 1 H), 3.77 (t, J = 6.8 Hz, 1 H), 5.40 (ddd, J = 6.8, 15.6, and 1.0 Hz, 1 H), 5.62 (dd, J = 6.8 and 15.6 Hz, 1 H). Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.76. Found: C, 75.70; H, 13.02.

(*E*)-Non-5-en-4-ol. This compound was prepared by the reaction of trans-2-hexenal with propylmagnesium bromide, following the procedure described above. The product (90%) was isolated by distillation (89–92 °C/21 mm): ^1H NMR ($CDCl_3$) δ 0.90 (t, J = 7.4 Hz, 3 H), 0.92 (t, J = 7.1 Hz, 3 H), 1.20–1.64 (m, 7 H), 2.01 (q, J = 6.4 Hz, 2 H), 4.06 (q, J = 6.6 Hz, 1 H), 5.45 (ddt, J = 6.6, 15.4, and 1.4 Hz, 1 H), 5.64 (dt, J = 15.4 and 6.4 Hz, 1 H); HRMS calcd for $C_9H_{18}O$ m/e 142.1358, found m/e 142.1335.

Allylic Substrates. Ethyl (*E*)-1,3-Diphenyl-2-propenyl Carbonate (2a). To a solution of 3.0 g (14 mmol) of (*E*)-1,3-diphenylprop-2-en-1-ol and 4.4 mL (54 mmol) of pyridine and a catalytic amount of 4-(dimethylamino)pyridine in 14 mL of THF was added 3.6 mL (47 mmol) of ethyl chloroformate at 0 °C under nitrogen. The mixture was stirred at room temperature for 8 h, quenched with water, and extracted three times with ether. The ether extracts were washed three times with 10% hydrochloric acid, once with saturated sodium bicarbonate solution, and once with

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water, and dried over anhydrous magnesium sulfate. Evaporation of the solvent in vacuo followed by preparative MPLC (hexane/ethyl acetate = 3/1) of the residue gave 3.3 g (82%) of the carbonate **2a**: ^{1}H NMR ($CDCl_3$) δ 1.30 (t, J = 7.0 Hz, 3 H), 4.20 (q, J = 7.0 Hz, 2 H), 6.26 (d, J = 7.0 Hz, 1 H), 6.37 (dd, J = 7.0 and 15.4 Hz, 2 H), 6.69 (d, J = 15.4 Hz, 1 H), 7.18–7.49 (m, 10 H). Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.31; H, 6.41.

The allylic carbonates **2c** and **7c** were prepared in a similar manner. *tert*-Butyl carbonate **2d** was prepared by the reaction of (*E*)-1,3-diphenylprop-2-en-1-ol with di-*tert*-butyl dicarbonate in essentially the same manner as the preparation of **2a**.

2c: 59% yield; ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 3 H), 6.27 (d, J = 6.8 Hz, 1 H), 6.37 (dd, J = 6.8 and 15.2 Hz, 1 H), 6.70 (d, J = 15.2 Hz, 1 H), 7.19–7.54 (m, 10 H). Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.31; H, 5.93.

7c: 81% yield; ^{1}H NMR ($CDCl_3$) δ 0.90 (d, J = 6.6 Hz, 3 H), 0.93 (d, J = 6.6 Hz, 3 H), 0.99 (d, J = 6.8 Hz, 6 H), 1.30 (t, J = 7.0 Hz, 3 H), 1.89 (octet, J = 6.6 Hz, 1 H), 2.31 (d octet, J = 1.4 and 6.8 Hz, 1 H), 4.18 (q, J = 7.0 Hz, 2 H), 4.80 (dd, J = 6.6 and 7.6 Hz, 1 H), 5.34 (ddd, J = 15.6, 7.6, and 1.4 Hz, 1 H), 5.72 (dd, J = 15.6 and 6.8 Hz, 1 H). Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.26; H, 10.35. Found: C, 67.08; H, 10.53.

2d: 67% yield; ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 9 H), 6.20 (d, J = 6.8 Hz, 1 H), 6.37 (dd, J = 6.8 and 15.6 Hz, 1 H), 6.66 (d, J = 15.6 Hz, 1 H), 7.17–7.47 (m, 10 H). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.56; H, 7.28.

(*E*)-1-Methyl-2-butenyl Diphenylphosphinate (8a). To a solution of 3.0 mL (29 mmol) of (*E*)-pent-3-en-2-ol and 4.9 mL (35 mmol) of triethylamine and a catalytic amount of 4-(dimethylamino)pyridine in 25 mL of dry THF was added dropwise at room temperature a solution of 4.7 mL (25 mmol) of diphenylphosphinyl chloride in 9 mL of dry THF over 15 min under nitrogen. The mixture was refluxed for 1 h and then the solvent was removed in vacuo. To the residue was added benzene, and the white precipitates formed were removed by filtration. After evaporation of the solvent, the residue was chromatographed on alumina (hexane/ethyl acetate = 1/1) to give 4.2 g (59%) of **8a**: ^{1}H NMR ($CDCl_3$) δ 1.42 (d, J = 6.4 Hz, 3 H), 1.59 (d, J = 4.0 Hz, 3 H), 4.85–5.05 (m, 1 H), 5.42–5.67 (m, 2 H), 7.34–7.58 (m, 6 H), 7.73–8.00 (m, 4 H); HRMS calcd for $C_{17}H_{19}O_2P$ m/e 286.1124, found m/e 286.1113.

(*E*)-1-Propyl-2-hexenyl Diphenylphosphinate (8b). This compound was prepared from (*E*)-non-5-en-4-ol and diphenylphosphinyl chloride by a procedure similar to that given for **8a** in 61% yield: ^{1}H NMR ($CDCl_3$) δ 0.81 (t, J = 7.2 Hz, 3 H), 0.88 (t, J = 7.2 Hz, 3 H), 1.23 (sextet, J = 7.2 Hz, 2 H), 1.37 (sextet, J = 7.2 Hz, 2 H), 1.55–1.80 (m, 2 H), 1.85 (q, J = 7.2 Hz, 2 H), 4.81 (quintet, J = 7.1 Hz, 1 H), 5.32–5.54 (m, 2 H), 7.30–7.57 (m, 6 H), 7.72–7.87 (m, 4 H). Anal. Calcd for $C_{21}H_{27}O_2P$: C, 73.66; H, 7.95; P, 9.05. Found: C, 73.42; H, 8.08; P, 8.77.

Asymmetric Allylic Amination of Ethyl (*E*)-1,3-Diphenyl-2-propenyl Carbonate (2a) with Benzylamine. General Procedure. A chiral ligand (0.023 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (11 mg, 0.011 mmol) were placed in a two-necked flask equipped with a magnetic stirring bar, a serum cap, and a three-way stopcock. The flask was filled with argon after evacuation and to it was added 7 mL of dry THF. The mixture was stirred for 20 min at room temperature, and then 205 mg (0.726 mmol) of ethyl (*E*)-1,3-diphenyl-2-propenyl carbonate (**2a**) and 93.4 mg (0.871 mmol) of benzylamine (**3a**) were added. The mixture was kept stirring at a given temperature for 14–108 h. The solvent was removed in vacuo, and the product *N*-((*E*)-1,3-diphenyl-2-propenyl)benzylamine (**4a**) was isolated by preparative TLC on silica gel (hexane/ethyl acetate = 3/1). Experimental results are summarized in Table I. **4a**: ^{1}H NMR ($CDCl_3$) δ 1.76 (s, 1 H), 3.77 (s, 2 H), 4.39 (d, J = 7.4 Hz, 1 H), 6.31 (dd, J = 7.4 and 15.6 Hz, 1 H), 6.58 (d, J = 15.6 Hz, 1 H), 7.10–7.53 (m, 15 H). Anal. Calcd for $C_{22}H_{21}N$: C, 88.25; H, 7.07; N, 4.68. Found: C, 88.25; H, 7.09; N, 4.58. The maximum rotation is calculated to be $[\alpha]^{20}_D$ 25.6° (chloroform). The enantiomeric purity was determined by HPLC equipped with a chiral stationary column after converting **4a** into benzamide **5**.

Conversion of 4a into Methyl *N*-Benzoyl-*N*-benzylphenylglycinate (6). To a solution of 176 mg (0.588 mmol) of **4a** ($[\alpha]^{20}_D$ −24.8° (*c* 1.4, chloroform)) and 112 mg (1.42 mmol) of pyridine and a catalytic amount of 4-(dimethylamino)pyridine in 5.9 mL of dichloromethane was added 166 mg (1.18 mmol) of benzoyl chloride. The mixture was stirred at room temperature for 17 h and then the solvent was evaporated. Preparative TLC on silica gel (hexane/ethyl acetate = 3/1) of the residue gave 203 mg (86%) of benzamide **5**: $[\alpha]^{20}_D$ −36.7° (*c* 1.2, chloroform); ^{1}H NMR ($CDCl_3$) δ 4.32 (br d, J = 16 Hz, 1 H), 4.76–5.23 (br, 1 H), 5.65–6.61 (br m, 3 H), 7.00–7.77 (m, 20 H); HRMS calcd for $C_{29}H_{25}NO$ m/e 403.1938, found m/e 403.1908.

The enantiomeric purity of **5** was determined to be 97.0% by HPLC analysis with a chiral stationary phase column (Sumipax OA-2000, hexane/dichloroethane/ethanol = 250/20/1).

To a solution of 187 mg (0.464 mmol) of **5** ($[\alpha]^{20}_D$ −36.7° (*c* 1.2, chloroform), 97.0% ee) in 14 mL of *tert*-butyl alcohol was added 196 mg (1.42 mmol) of potassium carbonate in 12 mL of water. A solution of 792 mg (3.71 mmol) of sodium periodate and 100 mg (0.633 mmol) of potassium permanganate in 12 mL of water was added and the solution was adjusted to pH 8.5 with 2 N sodium hydroxide solution. After stirring at room temperature for 1 h, *tert*-butyl alcohol was evaporated. The residue was acidified with concentrated hydrochloric acid to pH 2.5, sodium hydrogen sulfite was added to destroy the MnO_2, and the solution was made basic with 2 N sodium hydroxide solution. The resulting solution was washed twice with ether, acidified with concentrated hydrochloric acid, and extracted three times with ether. The extracts were dried over anhydrous sodium sulfate and stripped of solvent. To a solution of the residue in ether at 0 °C was added excess ethereal diazomethane, and the solution was stirred at room temperature for 1 h. Excess acetic acid was added and the solution was washed successively twice with saturated sodium bicarbonate solution and water and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by preparative TLC on silica gel (hexane/ethyl acetate = 2/1) of the residue gave 100 mg (60%) of the ester **6**: $[\alpha]^{20}_D$ −39.8° (*c* 0.91, chloroform); ^{1}H NMR ($CDCl_3$) δ 3.74 (br s, 3 H), 4.34 and 4.77 (AB q, J = 16.6 Hz, 2 H), 5.55 (br s, 1 H), 6.93–7.55 (m, 15 H); HRMS calcd for $C_{23}H_{21}NO_3$ m/e 359.1522, found m/e 359.1518.

(*R*)-Methyl *N*-Benzoyl-*N*-benzylphenylglycinate (6) from (*R*)-*N*-Benzylphenylglycine. Thionyl chloride (1.41 mL, 19.4 mmol) was added dropwise at −10 °C to 4.9 mL of methanol over 5 min under nitrogen. The solution was stirred at −10 °C for 30 min, and 1.17 g (4.85 mmol) of (*R*)-*N*-benzylphenylglycine[19] was added. The mixture was warmed to room temperature and stirred for 30 min and then refluxed for 4 h. The solvent was evaporated, and dichloromethane was added to the residue. The mixture was washed successively with saturated sodium bicarbonate solution and water, dried over anhydrous magnesium sulfate, and stripped of solvent in vacuo. The residue was passed through a short silica gel column to give 1.10 g (89%) of (*R*)-methyl *N*-benzylphenylglycinate: $[\alpha]^{20}_D$ −107° (*c* 1.4, chloroform); ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 1 H), 3.67 (s, 3 H), 3.73 (s, 2 H), 4.40 (s, 1 H), 7.16–7.48 (m, 10 H). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.57; H, 6.59; N, 5.49.

Conversion of (*R*)-methyl *N*-benzylphenylglycinate thus obtained into (*R*)-**6** was carried out in the same manner as that of **4a** (92%). (*R*)-**6**: $[\alpha]^{20}_D$ +41.0° (*c* 1.3, chloroform).

Asymmetric Allylic Amination of Ethyl (*E*)-1,3-Diphenyl-2-propenyl Carbonate (2a) with Other Nucleophiles. Veratrylamine (**3b**), 4,4′-dimethoxybenzhydrylamine (**3c**), and *p*-toluenesulfonamide (**3d**) were used as nucleophiles. All the reactions were carried out in essentially the same manner as that of benzylamine (**3a**). The reaction conditions and results containing optical rotation data and enantiomeric purities of the reaction products **4b–d** are summarized in Table I. The enantiomeric purity of the *p*-toluenesulfonamide **4d** was determined by HPLC (OA-1100, hexane/dichloroethane/ethanol = 250/20/1). The enantiomeric purity of the veratrylamine **4b** was determined after converting it into the *N*-3,5-dinitrobenzoyl derivative by the reaction of **4b** with 3,5-dinitrobenzoyl chloride (OA-1100, hexane/dichloroethane/ethanol = 250/20/1). The enantiomeric purity of 4,4′-dimethoxybenzhydrylamine **4c** was determined by the HPLC analysis (OA-1100, hexane/dichloroethane/ethanol = 100/20/1) of *N*-(1,3-diphenyl-2-propenyl)-3,5-dinitrobenzamide, which was obtained by removal of the 4,4′-dimethoxybenzhydryl group of **4c** by formolysis[8a] followed by the N-3,5-dinitrobenzoylation.

4b: ^{1}H NMR ($CDCl_3$) δ 1.80 (s, 1 H), 3.73 (s, 2 H), 3.86 (s, 3 H), 3.87 (s, 3 H), 4.39 (d, J = 7.2 Hz, 1 H), 6.32 (dd, J = 7.2 and 15.8 Hz, 1 H), 6.58 (d, J = 15.8 Hz, 1 H), 6.78–6.92 (m, 3 H), 7.14–7.50 (m, 10 H); HRMS calcd for $C_{24}H_{25}NO_2$ m/e 359.1887, found m/e 359.1902.

***N*-3,5-Dinitrobenzoyl-4b**: ^{1}H NMR ($CDCl_3$) δ 3.64 (s, 3 H), 3.80 (s, 3 H), 4.39 and 4.82 (AB q, J = 16 Hz, 2 H), 5.74–6.22 (br, 1 H), 6.27–6.84 (br m, 5 H), 7.06–7.60 (m, 10 H), 8.49 (d, J = 2 Hz, 2 H), 8.95 (t, J = 2 Hz, 1 H).

4c: ^{1}H NMR ($CDCl_3$) δ 1.82 (s, 1 H), 3.77 (s, 6 H), 4.27 (d, J = 7.0 Hz, 1 H), 4.78 (s, 1 H), 6.29 (dd, J = 7.0 and 15.8 Hz, 1 H), 6.50 (d, J = 15.8 Hz, 1 H), 6.78–6.88 (m, 4 H), 7.13–7.48 (m, 14 H).

***N*-(1,3-Diphenyl-2-propenyl)-3,5-dinitrobenzamide**: ^{1}H NMR ($CDCl_3$) δ 5.99 and 6.03 (a pair of d, J = 6.4 and 6.4 Hz, 2 H), 6.46 (dd, J = 6.4 and 15.6 Hz, 1 H), 6.64 (d, J = 15.6 Hz, 1 H), 6.91 and 6.95 (a pair of s, 1 H), 7.19–7.49 (m, 10 H), 8.99 (d, J = 2.0 H, 2 H), 9.15 (t, J = 2.0 Hz, 1 H).

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4d: ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3 H), 5.08 and 5.12 (a pair of d, J = 6.6 and 6.6 Hz, 1 H), 5.21 and 5.25 (a pair of s, 1 H), 6.06 (dd, J = 6.6 and 15.8 Hz, 1 H), 6.34 (d, J = 15.8 Hz, 1 H), 7.12 and 7.65 (AB q, J = 8.1 Hz, 4 H), 7.16–7.35 (m, 10 H). Anal. Calcd for $C_{22}H_{21}NO_2S$: C, 72.70; H, 5.82; N, 3.85; S, 8.82. Found: C, 72.72; H, 5.76; N, 3.72; S, 8.72.

Asymmetric Allylic Amination of 7a,c and 8a,b with Benzylamine. All the reactions were carried out in essentially the same manner as that of **2a**, except that 2.2 equiv of benzylamine was used relative to the phosphinates in the reaction of phosphinates **8**. In the reaction of **8**, the products were isolated after filtering off the white precipitates (probably benzylammonium phosphinate salts) formed during the amination. The trans/cis ratio of **9a** and the enantiomeric purities of **9a** and **9b** were determined by HPLC analysis of their *N*-3,5-dinitrobenzoyl derivatives (OA-1100, hexane/dichloroethane/ethanol = 500/20/1). The enantiomeric purity of **9c** was determined after converting it into a *N*-benzyloxycarbonyl derivative by the reaction of **9c** with benzyl chloroformate (OA-2500 and OA-2000I cascade, hexane/dichloroethane/ethanol = 1250/20/1). The reaction conditions and results are summarized in Table II.

9a (a mixture of trans and cis isomers): ^{1}H NMR ($CDCl_3$) for *trans*-**9a** δ 1.15 (d, J = 6.4 Hz, 3 H), 1.54 (br s, 1 H), 1.70 (dd, J = 6.2 and 1.4 Hz, 3 H), 3.18 (quintet, J = 6.4 Hz, 1 H), 3.66 and 3.79 (AB q, J = 13.1 Hz, 2 H), 5.34 (ddq, J = 15.2, 6.4, and 1.4 Hz, 1 H), 5.56 (dq, J = 15.2 and 6.2 Hz, 1 H), 7.17–7.37 (m, 5 H). ^{1}H NMR ($CDCl_3$) for *cis*-**9a** δ 1.13 (d, J = 6.4 Hz, 3 H), 1.60 (dd, J = 6.8 and 1.8 Hz, 3 H). Anal. Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.50; H, 9.99; N, 8.00.

***N*-3,5-Dinitrobenzoyl-9a (13a)**: ^{1}H NMR ($CDCl_3$) δ 1.31 (br, 3 H), 1.72 (d, J = 6.0 Hz, 3 H), 4.21–4.97 (br, 2 H), 4.43 (br d, J = 14.6 Hz, 1 H), 5.55 (br, 2 H), 6.95–7.57 (br m, 5 H), 8.50 (br, 2 H), 9.01 (br, 1 H).

9b: ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 7.2 Hz, 3 H), 0.92 (t, J = 7.2 Hz, 3 H), 1.20–1.70 (m, 7 H), 2.04 (dq, J = 1.4 and 6.6 Hz, 2 H), 2.98 (dt, J = 5.4 and 8.2 Hz, 1 H), 3.63 and 3.83 (AB q, J = 13.1 Hz, 2 H), 5.21 (ddt, J = 15.3, 8.3, and 1.4 Hz, 1 H), 5.50 (dt, J = 15.3 and 6.6 Hz, 1 H), 7.20–7.37 (m, 5 H). Anal. Calcd for $C_{16}H_{25}N$: C, 83.06; H, 10.89; N, 6.05. Found: C, 83.16; H, 11.18; N, 5.82.

***N*-3,5-Dinitrobenzoyl-9b**: ^{1}H NMR ($CDCl_3$) δ 0.54–1.90 (br m, 7 H), 0.89 (t, J = 7.2 Hz, 3 H), 1.39 (sextet, J = 7.2 Hz, 2 H), 2.02 (q, J = 7.2 Hz, 2 H), 4.05 (br, 1 H), 4.63 (br, 2 H), 5.46 (br, 2 H), 6.82–7.54 (br m, 5 H), 8.22–8.73 (br m, 2 H), 9.05 (br, 1 H).

9c: ^{1}H NMR ($CDCl_3$) δ 0.86 (d, J = 6.8 Hz, 3 H), 0.89 (d, J = 6.8 Hz, 3 H), 1.01 (d, J = 6.8 Hz, 3 H), 1.02 (d, J = 6.8 Hz, 3 H), 1.52 (br s, 1 H), 1.67 (octet, J = 6.8 Hz, 1 H), 2.33 (d octet, J = 1.2 and 6.8 Hz, 1 H), 2.70 (dd, J = 6.8 and 8.6 Hz, 1 H), 3.61 and 3.83 (AB q, J = 13.2 Hz, 2 H), 5.17 (ddd, J = 8.6, 15.6, and 1.2 Hz, 1 H), 5.46 (dd, J = 6.8 and 15.6 Hz, 1 H), 7.17–7.37 (m, 5 H). Anal. Calcd for $C_{16}H_{25}N$: C, 83.06; H, 10.89; N, 6.05. Found: C, 83.09; H, 11.08; N, 6.14.

***N*-Benzyloxycarbonyl-9c**: ^{1}H NMR ($CDCl_3$) δ 0.83 (d, J = 6.6 Hz, 6 H), 0.85 (d, J = 6.6 Hz, 6 H), 1.85–2.26 (m, 2 H), 3.64–4.10 (br m, 1 H), 4.33 and 4.55 (AB q, J = 15.8 Hz, 2 H) 4.98–5.62 (br m, 4 H), 6.99–7.48 (br m, 10 H).

Conversion of 9a into Methyl *N*-(Trifluoroacetyl)-*N*-benzylalaninate (11a). To a solution of 1.00 g (5.71 mmol) of **9a** [$[\alpha]^{20}_D$ −18.6° (c 1.4, chloroform), trans (73% ee)/cis (23% ee) = 96/4] and 1.15 mL (8.22 mmol) of triethylamine and a catalytic amount of 4-(dimethylamino)-pyridine in 28 mL of dichloromethane was added 0.97 mL (6.9 mmol) of trifluoroacetic anhydride at 0 °C. The solution was kept stirring at room temperature for 17 h and the solvent was removed in vacuo. The residue was passed through a short silica gel column (hexane/ethyl acetate = 1/2) and distillation [110–130 °C (0.95 mm), Kugelrohr] gave 1.55 g (100%) of trifluoroacetamide **10a**: $[\alpha]^{20}_D$ −41.1° (c 1.13, chloroform). ^{1}H NMR ($CDCl_3$) indicated that **10a** consisted of two conformational isomers in a ratio of 2/1: ^{1}H NMR ($CDCl_3$) for major isomer δ 1.26 (d, J = 6.8 Hz, 3 H), 1.69 (d, J = 6.4 Hz, 3 H), 4.39 and 4.67 (AB q, J = 15.4 Hz, 2 H), 4.46–4.79 (m, 1 H), 5.36–5.78 (m, 2 H), 7.16–7.34 (m, 5 H). ^{1}H NMR ($CDCl_3$) for minor isomer δ 1.22 (d, J = 7.0 Hz, 3 H), 1.61 (d, J = 6.4 Hz, 3 H), 4.46–4.79 (m, 1 H), 4.58 (s, 2 H), 5.36–5.78 (m, 2 H), 7.16–7.34 (m, 5 H). Anal. Calcd for $C_{14}H_{16}NOF_3$: C, 61.99; H, 5.94; N, 5.16. Found: C, 61.75; H, 6.02; N, 5.01.

Trifluoroacetamide **10a** was converted to **11a** by oxidative cleavage of the carbon–carbon double bond with $KMnO_4$ and $NaIO_4$ followed by esterification with diazomethane in essentially the same manner as that of **5** (78% yield). **11a** (conformational isomers in a ratio of 3/1): $[\alpha]^{20}_D$ −32.5° (c 1.5, chloroform); ^{1}H NMR ($CDCl_3$) for major isomer δ 1.38 (d, J = 7.2 Hz, 3 H), 3.69 (s, 3 H), 4.00 (q, J = 7.2 Hz, 1 H), 4.65 and 4.76 (AB q, J = 16.2 Hz, 2 H), 7.17–7.50 (m, 5 H). ^{1}H NMR ($CDCl_3$) for minor isomer δ 1.47 (d, J = 7.0 Hz, 3 H), 3.60 (s, 3 H), 4.38 and 4.92 (AB q, J = 15.8 Hz, 2 H), 4.78 (q, J = 7.0 Hz, 1 H), 7.17–7.50 (m, 5 H). Anal. Calcd for $C_{13}H_{14}NO_3F_3$: C, 53.98; H, 4.88; N, 4.84; F, 19.70. Found: C, 54.26; H, 4.87; N, 4.81; F, 19.73.

Conversion of 9b,c into 11b,c. Benzylamines **9b** [$[\alpha]^{20}_D$ −22.3° (c 1.2, chloroform), 82.1% ee] and **9c** [$[\alpha]^{20}_D$ −37.3° (c 1.5, chloroform), 97.0% ee] were converted into **11b** and **11c**, respectively, via trifluoroacetamides **10** in essentially the same manner as the conversion of **9a** into **11a**.

10b (100% yield, conformational isomers in a ratio of 1.5/1): $[\alpha]^{20}_D$ −23.2° (c 1.2, chloroform); ^{1}H NMR ($CDCl_3$) for major isomer δ 0.77 (t, J = 7.2 Hz, 3 H), 0.86 (t, J = 7.2 Hz, 3 H), 0.98–1.74 (m, 6 H), 1.97 (q, J = 7.2 Hz, 2 H), 4.46 (q, J = 7.8 Hz, 1 H), 4.45 and 4.65 (AB q, J = 15.5 Hz, 2 H), 5.30–5.74 (m, 2 H), 7.15–7.40 (m, 5 H). ^{1}H NMR ($CDCl_3$) for minor isomer δ 0.80 (t, J = 7.0 Hz, 3 H), 0.83 (t, J = 7.2 Hz, 3 H), 0.98–1.74 (m, 6 H), 1.89 (q, J = 7.2 Hz, 2 H), 4.16 (q, J = 7.6 Hz, 1 H), 4.58 (s, 2 H), 5.30–5.74 (m, 2 H), 7.15–7.40 (m, 5 H). Anal. Calcd for $C_{18}H_{24}NOF_3$: C, 66.04; H, 7.39; N, 4.28; F, 17.41. Found: C, 65.87; H, 7.64; N, 4.29; F, 17.26.

11b (73% yield, conformational isomers in a ratio of 2/1): $[\alpha]^{20}_D$ −44.0° (c 1.6, chloroform); ^{1}H NMR ($CDCl_3$) for major isomer δ 0.78 (t, J = 7.2 Hz, 3 H), 1.19 (sextet, J = 7.2 Hz, 2 H), 1.93–2.15 (m, 2 H), 3.61 (s, 3 H), 3.98 (t, J = 7.1 Hz, 1 H), 4.67 (s, 2 H), 7.21–7.48 (m, 5 H). ^{1}H NMR ($CDCl_3$) for minor isomer δ 0.75 (t, J = 7.2 Hz, 3 H), 1.19 (sextet, J = 7.2 Hz, 2 H), 1.64–1.87 (m, 2 H), 3.56 (s, 3 H), 4.45 and 4.86 (AB q, J = 15.4 Hz, 2 H), 5.55 (dd, J = 5.6 and 8.4 Hz, 1 H), 7.21–7.48 (m, 5 H). Anal. Calcd for $C_{15}H_{18}NO_3F_3$: C, 56.78; H, 5.72; N, 4.41; F, 17.96. Found: C, 56.98; H, 5.87; N, 4.49; F, 17.98.

10c (92% yield, conformational isomers in a ratio of 1.2/1): $[\alpha]^{20}_D$ +45.2° (c 1.1, chloroform); ^{1}H NMR ($CDCl_3$) for major isomer δ 0.73–0.96 (m, 12 H), 1.84–2.42 (m, 2 H), 3.97 (t, J = 8.8 Hz, 1 H), 4.31 and 4.86 (AB q, J = 15.4 Hz, 2 H), 5.12–5.24 (m, 1 H), 5.64 (dd, J = 6.4 and 15.4 Hz, 1 H), 7.15–7.39 (m, 5 H). ^{1}H NMR ($CDCl_3$) for minor isomer δ 0.73–0.96 (m, 12 H), 1.84–2.42 (m, 2 H), 3.64 (t, J = 9.8 Hz, 1 H), 4.52 and 4.66 (AB q, J = 16.0 Hz, 2 H), 5.12–5.24 (m, 1 H), 5.43 (dd, J = 9.2 and 16.6 Hz, 1 H), 7.15–7.39 (m, 5 H). Anal. Calcd for $C_{18}H_{24}NOF_3$: C, 66.04; H, 7.39; N, 4.28; F, 17.41. Found: C, 66.17; H, 7.38; N, 4.24; F, 17.62.

11c (19% yield, conformational isomers in a ratio of 1/1): $[\alpha]^{20}_D$ −60.9° (c 1.1, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.82 (d, J = 6.8 Hz, 3 H), 0.85 (d, J = 6.8 Hz, 3 H), 0.99 (d, J = 6.4 Hz, 6 H), 2.34–2.62 (m, 1 H + 1 H), 3.40 (s, 3 H), 3.42 (s, 3 H), 4.12 (d, J = 10.0 Hz, 1 H + 1 H), 4.46 and 4.96 (AB q, J = 15.4 Hz, 2 H), 4.62 and 4.75 (AB q, J = 16.6 Hz, 2 H), 7.15–7.45 (m, 5 H + 5 H). Anal. Calcd for $C_{15}H_{18}NO_3F_3$: C, 56.78; H, 5.72; N, 4.41; F, 17.96. Found: C, 56.99; H, 5.68; N, 4.40; F, 17.91.

Methyl *N*-Benzylalaninate. To a solution of 1.24 g (4.29 mmol) of **11a** ($[\alpha]^{20}_D$ −32.5° (c 1.5, chloroform)) in 17 mL of methanol was added 11 mL of 2 N sodium hydroxide solution. After the solution was stirred at room temperature for 12 h, the methanol was evaporated. The solution was adjusted to pH 7 with 6 N hydrochloric acid. Free amino acid *N*-benzylalanine **12a** (0.62 g, 80%) was obtained by passing the residue through a column of Amberlite IR-120B (H^+ form). **12a**: ^{1}H NMR (D_2O) for **12a·HCl** δ 1.59 (d, J = 7 Hz, 3 H), 3.97 (q, J = 7 Hz, 1 H), 4.27 (s, 2 H), 7.48 (s, 5 H).

N-Benzylalanine (**12a**) (174 mg, 0.971 mmol) was suspended in 2 mL of methanol and stirred with ethereal diazomethane in excess until a homogeneous solution was obtained. Removal of the solvent followed by preparative TLC on silica gel (hexane/ethyl acetate = 2/1) gave 25 mg (13%) of methyl *N*-benzylalaninate: $[\alpha]^{21}_D$ −26.3° (c 1.2, methanol) [lit.[20] for *S* isomer $[\alpha]^{21}_D$ −41.0° (c 1.8, methanol)]; ^{1}H NMR ($CDCl_3$) δ 1.30 (d, J = 7 Hz, 3 H), 1.86 (s, 1 H), 3.36 (q, J = 7 Hz, 1 H), 3.62 and 3.70 (AB q, J = 13 Hz, 2 H), 3.69 (s, 3 H), 7.22 (m, 5 H).

***N*-(2-Pentyl)-3,5-dinitrobenzamide (14).** A solution of 81.6 mg (0.466 mmol) of **9a** [$[\alpha]^{20}_D$ −18.6° (c 1.4, chloroform), trans (73% ee)/cis (23% ee) = 96/4, the configuration of trans isomer was determined to be *S* as described above] and 20 mg of 10% Pd–C in 1.5 mL of ethanol was placed in a stainless micro autoclave and magnetically stirred at 80 °C with hydrogen at 135 atm for 17 h. Pd–C was filtered off and washed with 3 mL of THF. To the solution were added at 0 °C 215 mg (0.932 mmol) of 3,5-dinitrobenzoyl chloride and 0.16 mL (1.1 mmol) of triethylamine. The resulting mixture was stirred at 0 °C for 2 h. Preparative TLC on silica gel (hexane/ethyl acetate = 3/1) gave 77 mg (59%) of **14**: ^{1}H NMR ($CDCl_3$) δ 0.96 (t, J = 7.0 Hz, 3 H), 1.31 (d, J = 6.6 Hz, 3 H), 1.34–1.67 (m, 4 H), 4.26 and 4.27 (a pair of sextets, J = 7.0 and 7.0 Hz, 1 H), 6.37 and 6.41 (a pair of br s, 1 H), 8.96 (d, J = 2.0 Hz, 2 H), 9.15 (t, J = 2.0 Hz, 1 H). The enantiomeric purity of **14** was determined to be 70.7% by HPLC (OA-4500, hexane/dichloroethane/ethanol = 50/15/1). The configuration of *cis*-**9a** is determined to be *S*

(20) Szilagyi, L.; Gyorgydeak, Z. *J. Am. Chem. Soc.* **1979**, *101*, 427.

since the enantiomeric purity of **14** is in good agreement with the calculated value (71% ee) in case that both *trans*- and *cis*-**9a** have the same configuration *S*.

Norvaline Hydrochloride. To a solution of 0.70 g (2.2 mmol) of **11b** ($[\alpha]^{20}_D$ −44.0° (*c* 1.6, chloroform)) in 8.8 mL of methanol was added 5.5 mL of 2 N sodium hydroxide solution. After the solution was stirred at room temperature for 12 h, methanol was evaporated. Neutralization of the solution with 6 N hydrochloric acid gave 227 mg (50%) of *N*-benzylnorvaline (**12b**): ^{1}H NMR (D_2O) for **12b**·HCl δ 0.89 (t, *J* = 7 Hz, 3 H), 1.12–2.08 (m, 4 H), 3.74 (t, *J* = 6 Hz, 1 H), 4.26 (s, 2 H), 7.50 (s, 5 H).

Removal of benzyl group was performed according to the reported procedure.[21] To a solution of 206 mg (0.994 mmol) of *N*-benzylnorvaline (**12b**) in 2 mL of 90% formic acid was added 206 mg of 10% Pd–C. The mixture was stirred at room temperature for 63 h, the Pd–C was filtered off, and the solvent was evaporated. To the residue was added concentrated hydrochloric acid. Removal of solvent gave norvaline hydrochloride quantitatively: $[\alpha]^{20}_D$ +13.2° (*c* 0.91, 6 N HCl) [lit.[22] for *S* isomer $[\alpha]^{20}_D$ +23° (*c* 10, 6 N HCl)].

***N*-Benzylvaline (12c).** A solution of 123 mg (0.406 mmol) of **11c** ($[\alpha]^{20}_D$ −60.9° (*c* 1.1, chloroform)) in 1.0 mL of 2 N sodium hydroxide was heated to 60 °C for 22 h. Neutralization of the solution with 6 N hydrochloric acid gave 69 mg (82%) of free amino acid **12c**: $[\alpha]^{21}_D$ +15.0° (*c* 1.0, 6 N HCl) [lit.[23] for (*S*)-**12c** $[\alpha]^{21}_D$ +20.2° (*c* 1, 6 N HCl)]; ^{1}H NMR (D_2O) for **12c**·HCl δ 1.03 (t, *J* = 7 Hz, 6 H), 2.07–2.52 (m, 1 H), 3.75 (d, *J* = 4 Hz, 1 H), 4.28 (s, 2 H), 7.46 (s, 5 H).

Preparation of [Pd(1b)(π-allyl)]ClO_4·CH_3COCH_3 (15). A mixture of 27.9 mg (0.0763 mmol) of bis(μ-chloro)bis(π-allyl)dipalladium and 100 mg (0.153 mmol) of (*R*)-*N*-methyl-*N*-(2-hydroxyethyl)-1-[(*S*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine (**1b**) in 2.0 mL of methanol was stirred at room temperature. The solids almost dissolved after 30 min and gave an orange solution. After small amount of insoluble solids were filtered off, $LiClO_4$·$3H_2O$ (123 mg, 0.765 mmol) in 1.5 mL of methanol was added and the mixture was kept stirring at room temperature for 2 h. Water was added until no more yellow precipitates were formed. [Pd(**1b**)(π-allyl)]ClO_4 (132 mg, 96%) was obtained by filtration, washed with water, and dried in vacuo. For a single-crystal X-ray analysis, the product was recrystallized from acetone/ether giving **15** as orange crystals: ^{1}H NMR ($CDCl_3$) δ 1.194 and 1.437 (a pair of d, *J* = 6.6 and 6.3 Hz, 3 H), 1.873 and 1.960 (a pair of s, 3 H), 2.18 (s, 6 H), 2.52–2.67 (m, 2 H), 3.24–3.41 (m, 2 H), 3.710 (dd, *J* = 13.3 and 9.6 Hz, 1 H), 3.928 (dd, *J* = 13.3 and 10.3 Hz, 1 H), 3.606, 4.018, 4.320, 4.347, 4.398, 4.469, 4.700 (m, 7 H), 4.55 (m, 1 H), 4.62 (m, 1 H), 6.104 (tt, *J* = 13.3 and 7.1 Hz, 1 H), 7.07–7.77 (m, 20 H). Anal. Calcd for $C_{45}H_{50}NO_6ClP_2FePd$: C, 56.27; H, 5.25; N, 1.46; Cl, 3.69. Found: C, 56.25; H, 5.23; N, 1.47; Cl, 3.62.

X-ray Structure of Palladium Complex 15. An orange crystal (0.43 × 0.35 × 0.20 mm) grown from acetone and ether by a diffusion method was used for data collection. **Crystal data**: $C_{42}H_{44}NOP_2FePd$·ClO_4·C_3H_6O, M_r = 962.72, triclinic, space group *P*1, *a* = 10.683 (2) Å, *b* = 11.206 (2) Å, *c* = 10.401 (2) Å, α = 118.83 (1)°, β = 97.74 (1)°, γ = 81.07 (1)°, *V* = 1075.0 Å^3, d_{calcd} = 1.394 g cm^{-3}, and (Mo Kα) = 9.26 cm^{-1}.

A total of 4936 reflections with 2θ < 55° were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structure was solved by a heavy-atom method using SHELXS-86 and refined by full-matrix least squares. The thermal factors of oxygen atoms in ClO_4 group were fixed at 10 Å^2. Remaining non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were not included in the calculation. The final *R* and R_w factors were 0.035 and 0.049, respectively, for 4705 observed reflections ($I > 3\sigma(I)$). All crystallographic calculations were performed on a microVAX II using Enraf-Nonius SDP program system. A molecular structure is shown in Figure 3, together with the numbering scheme for the complex. Stereoscopic view of the complex is shown in Figure 4. Fractional coordinates, bond distances, and bond angles are given in Tables III, IV, and V, respectively. Additional crystallographic details can be found in the supplementary material.

Preparation of [Pd(1,3-diphenyl-π-allyl)OAc]$_2$ (16). To a solution of 4.0 g (19 mmol) of (*E*)-1,3-diphenylprop-2-en-1-ol in 6.0 mL of THF at 0 °C was added 6.0 mL of concentrated hydrochloric acid. The mixture was stirred at 0 °C for 30 min and then was extracted twice with ether. The ether extracts were washed successively twice with water, once with saturated sodium hydrogen carbonate solution, and once with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by distillation [160–180 °C (0.80 mm), Kugelrohr] gave 3.3 g (76%) of (*E*)-1,3-diphenyl-3-chloroprop-1-ene: ^{1}H NMR ($CDCl_3$) δ 5.64 (d, *J* = 6 Hz, 1 H), 6.44 (dd, *J* = 6 and 15 Hz, 1 H), 6.66 (d, *J* = 15 Hz, 1 H), 7.00–7.68 (m, 10 H).

According to Bosnich's procedure,[5] [Pd(1,3-diphenyl-π-allyl)Cl]$_2$ was prepared as follows. Palladium chloride (638 mg, 3.60 mmol) and lithium chloride (638 mg, 15.1 mmol) were dissolved in hot water (0.9 mL). Ethanol (7.2 mL) and (*E*)-1,3-diphenyl-3-chloroprop-1-ene (3.30 g, 14.4 mmol) were added, and the resulting solution was warmed to 45 °C. At this temperature, carbon monoxide was kept passing through the solution for 3 h and then the mixture was stirred for 20 h at room temperature under a carbon monoxide atmosphere. The yellow powder was filtered and washed with water, methanol, and ether and dried in vacuo to give 1.21 g (100%) of [Pd(1,3-diphenyl-π-allyl)Cl]$_2$: ^{1}H NMR (DMSO-d_6) δ 5.25 (d, *J* = 12.2 Hz, 2 H), 6.98 (t, *J* = 12.2 Hz, 1 H), 7.32–7.48 (m, 6 H), 7.73–7.85 (m, 4 H).

To a mixture of 14.7 mg (0.0439 mmol) of [Pd(1,3-diphenyl-π-allyl)Cl]$_2$ in 2 mL of methanol and 2 mL of dichloromethane at room temperature was added 36.6 mg (0.219 mmol) of silver acetate. The mixture was stirred for 30 min and then was filtered. Evaporation of the filtrate gave the yellow powder **16** quantitatively. Variable-temperature ^{1}H NMR studies showed that the acetate dimer **16** consisted of two isomers in 1/1 ratio at −50 °C and they interconvert at room temperature: ^{1}H NMR ($CDCl_3$ at −50 °C) δ 1.27 (s, 3 H), 3.95 and 5.02 (a pair of d, *J* = 10.8 Hz, 2 H), 6.10 and 6.44 (a pair of t, *J* = 10.8 Hz, 1 H), 7.17–7.78 (m, 10 H).

Preparation and Reaction of [Pd(1a)(1,3-diphenyl-π-allyl)]OAc (17). A $CDCl_3$ solution of 1,3-diphenyl-π-allylpalladium complex **17** containing ferrocenylphosphine **1a** was prepared as follows. A solution of the acetate dimer **16** (0.0721 mmol) in $CDCl_3$ (0.30 mL) was placed in a NMR tube. The NMR tube was filled with nitrogen and then was cooled to −60 °C. To the solution was added a cooled solution (−60 °C) of the ferrocenylphosphine **1a** (49.4 mg, 0.0721 mmol) in $CDCl_3$ (0.4 mL). ^{31}P NMR and ^{1}H NMR spectra at −50 and −40 °C indicated that **17** was formed quantitatively as a 1/1 mixture of isomers **17a** and **17b**. The ratio of the isomers changed to 20/1 by equilibration at higher temperature. ^{31}P NMR (−40, −20, and −10 °C) and ^{1}H NMR (−10 °C) spectra of **17** are as follows. **17a** (major isomer after equilibration): ^{31}P NMR ($CDCl_3$ at −40 °C) δ 22.00 and 25.81 (AB q, *J* = 58.8 Hz); (at −20 °C) δ 22.35 and 26.18 (AB q, *J* = 59.0 Hz); (at −10 °C) δ 22.51 and 26.35 (AB q, *J* = 59.0 Hz). ^{1}H NMR ($CDCl_3$ at −10 °C) δ 1.47 (d, *J* = 5.8 Hz, $CHCH_3$), 1.90 (s, NCH_3), 2.06 (s, 3 H), 3.03, 3.28, 3.44, 3.73–4.12, 4.50 (m, 1 H, 1 H, 1 H, 8 H, 1 H), 5.28–5.40 (m, 1 H), 5.34 (br t, *J* = 12.6 Hz, 1 H), 5.88 (br t, *J* = 12.6 Hz, 1 H), 6.46 (t, *J* = 12.6 Hz, 1 H), 6.62–7.76 (m, 30 H). **17b** (minor isomer after equilibration): ^{31}P NMR (at −40 °C) δ 23.74 and 28.45 (AB q, *J* = 63.2 Hz); (at −20 °C) δ 23.87 and 28.39 (AB q, *J* = 63.3 Hz); (at −10 °C) δ 23.99 and 28.32 (AB q, *J* = 63.3 Hz). ^{1}H NMR ($CDCl_3$ at −10 °C) δ 0.60 (d, *J* = 5.4 Hz, $CHCH_3$), 1.58 (s, NCH_3). The ^{31}P NMR ($CDCl_3$) spectrum at −40 °C before equilibration and that at −30 °C after equilibration are shown in Figure 5.

Benzylamine (77.3 mg, 0.721 mmol) was added at −10 °C to a solution of palladium complex **17** (**17a**/**17b** = 20/1) formed above in $CDCl_3$ in the NMR tube. The reaction was monitored by ^{31}P NMR. Both AB quartets in **17a** and **17b** disappeared in 30 min. The product **4a** was isolated by preparative TLC on silica gel (hexane/ethyl acetate = 3/1) (16.8 mg, 78%). The enantiomeric purity of **4a** was determined to be 95.7% by the HPLC analysis (vide supra).

π-Allylpalladium complex **17** prepared in CD_3OD gave 3.5/1 mixture of isomers **17a** and **17b**: ^{31}P NMR (CD_3OD at −20 °C) δ 23.19 and 27.20 (AB q, *J* = 59.0 Hz) for **17a** and 26.46 and 30.21 (AB q, *J* = 60.3 Hz) for **17b**.

Preparation and Reaction of [Pd(1d)(1,3-diphenyl-π-allyl)]OAc (18). Preparation (at −60 °C) and ^{31}P NMR analysis of **18** were carried out in a similar manner to those of **17**. Complex **18** consisted of two isomers in a ratio of 2/1 after equilibration. **18** (major isomer): ^{31}P NMR ($CDCl_3$ at −10 °C) δ 23.03 and 28.37 (AB q, *J* = 59.9 Hz). ^{1}H NMR ($CDCl_3$ at −10 °C) δ 1.44 (d, *J* = 6 Hz, $CHCH_3$). **18** (minor isomer): ^{31}P NMR ($CDCl_3$ at −10 °C) δ 24.25 and 31.24 (AB q, *J* = 60.3 Hz). ^{1}H NMR ($CDCl_3$ at −10 °C) δ 0.63 (d, *J* = 6 Hz, $CHCH_3$). The ^{31}P NMR spectrum at −10 °C is shown in Figure 5.

The enantiomeric purity of the product **4a** obtained in 71% yield by the reaction with benzylamine at −10 °C in the NMR tube was determined to be 62.3% by the HPLC analysis.

Preparation and Reaction of [Pd(1a)(1,3-diphenyl-π-allyl)]ClO_4 (19). Preparation of **19** was carried out in a similar manner to that of **15** starting with [Pd(1,3-diphenyl-π-allyl)Cl]$_2$ and **1a** (94% yield). **19** (major isomer): ^{31}P NMR ($CDCl_3$ at −10 °C) δ 23.19 and 26.16 (AB q, *J* = 58.9 Hz). ^{1}H NMR ($CDCl_3$ at room temperature) δ 1.54 (br d, *J* = 4.0 Hz, 3 H), 1.97 (s, 3 H), 3.05 (br m, 1 H), 3.45–3.87 (m, 4 H),

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3.96, 4.04, 4.14, 4.19, 4.24, 4.33, 4.41, 4.58 (m, 7 H), 4.48 (br m, 1 H), 5.23-5.33 (m, 1 H), 5.66 (br t, J = 12.6 Hz, 1 H), 6.49 (t, J = 12.6 Hz, 1 H), 6.66-7.73 (m, 30 H). **19** (minor isomer): ^{31}P NMR ($CDCl_3$ at -10 °C) δ 25.19 and 28.93 (AB q, J = 61.3 Hz). ^{1}H NMR ($CDCl_3$ at room temperature) δ 0.72 (br d, J = 5.8 Hz, 3 H), 1.47 (s, 3 H), 2.39-2.48 (br m, 1 H), 2.94-3.34 (m, 5 H), 3.96, 4.04, 4.14, 4.19, 4.24, 4.33, 4.41, 4.58 (m, 7 H), 4.89-4.98 (br m, 1 H), 5.23-5.33 (m, 1 H), 6.59 (t, J = 12.5 Hz, 1 H), 6.66-7.73 (m, 30 H).

The reaction of **19** with benzylamine at -10 °C was carried out in a similar manner to that of **17**. The enantiomeric purity of the product **4a** (72% yield) was determined to be 59.4%.

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Supplementary Material Available: Crystallographic data for palladium complex **15** and a table of anisotropic thermal parameters (2 pages); observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

The Effect of Phenyl Ring Torsional Rigidity on the Photophysical Behavior of Tetraphenylethylenes

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Abstract: The synthesis and photochemical behavior of several members of the bis[n.1]metacyclophanylidene series are presented. The properties of these compounds are compared to a model compound, tetra-3-tolylethylene. The photophysical properties of the tethered tetraphenylethylenes change dramatically with the length of hydrocarbon tethers connecting the *gem*-phenyl rings. From these changes in photophysical properties and analysis of ground-state structures and properties, we propose that phenyl ring torsional motion plays a significant, if not primary, role in the photochemistry of tetraphenylethylenes.

Since photoexcitation involves the same orbitals as redox transformations, redox-induced geometric changes may be predicted by observing a molecule's photophysical properties. Electrochemical precedent[1] exists for geometrically linked multiple-electron transfers; therefore, one might expect that geometric changes induced by electronic excitation might control their redox properties as well. Tetraphenylethylenes are excellent models for testing this relationship because they are known to participate in multiple-electron redox reactions.[2,3]

To better understand the geometry changes that accompany deactivation of the singlet excited state of tetraphenylethylenes, we have synthesized and studied a class of torsionally restricted tetraphenylethylenes: the bis[n.1]metacyclophanylidenes ([n.1]MCs), Figure 1. Previously, we gave a brief account of the fluorescence properties of the [n.1]MCs (n = 4-6).[4] In this paper we describe in detail the synthesis, spectroscopic properties, and photophysical behavior of four torsionally restricted tetraphenylethylenes ([n.1]MCs: n = 4-7). The spectral properties are compared with those of tetraphenylethylene and/or tetra-*m*-tolylethylene (TTE).

Much of the discussion of the photophysical properties of the [n.1]MCs is related to the studies of the photochemical cis-trans isomerization of stilbenes,[5] a thoroughly investigated photochemical reaction. Indeed, details concering its mechanism continue to fascinate chemists.[6] Similarities between tetraphenylethylene and stilbene photochemistry exist primarily because of similarities in the nodal properties of their HOMOs and LUMOs. Both molecules are arylethylenes that exhibit olefinic bonding and essential single bond antibonding interactions in the HOMO, and olefinic antibonding and essential single bond bonding interactions in the LUMO. Therefore, changes in the geometry of these molecules, with respect to these bonds, will affect their energies in similar ways. Tetraphenylethylene is more akin to *cis*-stilbene than to the trans isomer, owing to phenyl ring torsion and steric repulsion of the *cis*-phenyl rings. This geometric likeness results in similar photophysics. Tetraphenylethylene, like *cis*-stilbene, has an exceedingly short singlet excited-state lifetime, a negligible fluorescence quantum yield (at room temperature in fluid solution), and a slow rate of intersystem crossing.

Our data indicate that the photophysical properties of tetraphenylethylenes change dramatically when hydrocarbon tethers connect *gem*-phenyl rings. In addition, the length of the chain determines the relative partitioning among deactivation pathways available to the singlet excited state. From these changes in photophysical properties and analysis of ground state structures and properties, we postulate that phenyl ring torsional motion plays a significant, if not primary, role in the photochemistry of tet-

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