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Pd-Catalyzed asymmetric allylic alkylations using various diphenylphosphino(oxazolinyl)ferrocene ligands

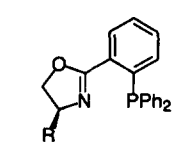
Kyo Han Ahn*,* Chang-Woo Cho, Jaiwook Park* and Sunwoo Lee
Department of Chemistry and Center for Biofunctional Molecules, Pohang University of Science and Technology (POSTECH), San 31 Hyoja-dong, Pohang 790-784, Korea

Abstract: Pd-Catalyzed asymmetric allylic alkylations have been studied using a series of chiral diphenylphosphino(oxazolinyl)ferrocene ligands **4–8**. With these ligands, up to 99% and 63% ee are obtained for *rac*-(*E*)-1,3-diphenylprop-2-enyl-1-acetate and *rac*-(*E*)-1,3-dimethylprop-2-enyl-1-acetate, respectively, with dimethyl malonate as the nucleophile. Some of the ligands **4–6** generate corresponding Pd-catalysts more reactive than those formed from other known ligands. A noticeable influence of the planar chirality on the enantioselectivity is observed. Different coordination modes can be suggested for the distinguishable enantioselectivity and reactivity patterns observed in the reactions with the ligands **4–8**. © 1997 Elsevier Science Ltd

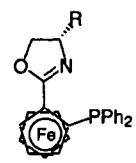
The Pd-catalyzed asymmetric allylic substitution reaction[1] has been demonstrated to be useful in the syntheses of valuable small molecules and complex natural products.[2] A variety of chiral ligands have been studied in the Pd-catalyzed allylic substitutions.[3] Much effort has been made to elucidate crucial factors for the enantioselection of the reaction.[4] With a few exceptions,[2g] one set of chiral ligands that produces high selectivity for acyclic allylic acetates, usually shows greatly decreased selectivity for cyclic substrates, and *vice versa*. Furthermore, for given acetates, the steric bulkiness of the acetate dramatically alters the enantioselectivity.[3p] Therefore, the search for the best ligand for the catalysis may be dependent on the type and steric bulkiness of allylic substrates. A recent introduction of 'hetero-chelates' such as (phosphinoaryl)oxazoline ligands **1** opened up a path to the development of other kinds of hetero-chelates.[3p–r] These *N,P*-chelates, a hybrid of the previously known oxazoline and phosphine ligands, are demonstrated to be efficient in the Pd-catalyzed allylic substitution and other catalytic reactions.[5] Of particular interest is that these ligands generate more reactive Pd-catalysts than most of the known *N,N*- and *P,P*-chelates, seemingly owing to the '*trans effect*'.[6]

Recently we and others have developed a highly diastereoselective lithiation of oxazolinylferrocene compounds,[7] and we have synthesized a variety of diphenylphosphino(oxazolinyl)ferrocene compounds (DPOF **2–8**) which would be potentially useful ligands for organometallic catalysts.[8] A number of ferrocene-based *P,P*-chelates have been successfully utilized in the transition metal-catalyzed asymmetric reactions,[9] and recently the application of ferrocene-based *N,P*-chelates for asymmetric catalysts is attracting interest.[10] Here we report the Pd-catalyzed allylic alkylation with DPOF ligands **4–8**. Since these ligands have different planar chiralities, it is of interest to study their effects on the enantioselectivity. In addition, it is an intriguing question which chelation modes among several possible combinations would operate in the substitution reaction.

* Corresponding author. Email: ahn@vision.postech.ac.kr



1a: R = *i*-Pr
1b: R = *t*-Bu
1c: R = Ph



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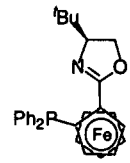

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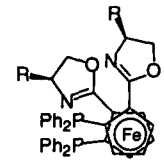
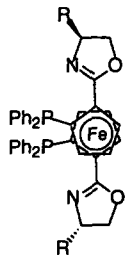
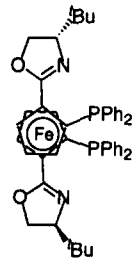


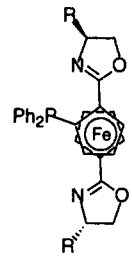
C_1 (*pR*,*pS*)
4a: R = *i*-Pr
4b: R = *t*-Bu



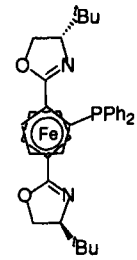
C_2 (*pR*,*pR*)
5a: R = *i*-Pr
5b: R = *t*-Bu



C_2 (*pS*,*pS*)
6



7a: R = *i*-Pr
7b: R = *t*-Bu



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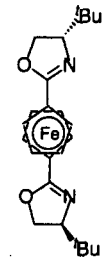

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The Pd-catalyzed allylic alkylation was carried out using racemic (*E*)-1,3-diphenylprop-2-enyl-1-acetate **11a** and (*E*)-1,3-dimethylprop-2-enyl-1-acetate **11b** as standard substrates, and dimethyl malonate as a nucleophile. Bis(π-allylpalladium chloride) was used as the Pd source (eq. 1).[3c,m] Since much increased enantioselectivities were observed with the base system of *N*,*O*-bis(trimethylsilyl)acetamide (BSA-KOAc) compared to those with NaH in THF, the catalytic reactions were carried out under the former reaction conditions. The results are summarized in Tables 1 and 2. The data obtained with DPOF **2–3** are listed for comparison.[11]

The ligands **4–6**, which are '*N*,*N*′,*P*,*P*′-type', exhibited interesting features in the Pd-catalyzed allylic alkylation of the acetate **11a**. When the ligands **4a** and **4b** of (*R*,*S*) planar chirality were used, almost complete enantioselectivities were observed in both cases in spite of the difference in the steric bulkiness of the oxazoline substituents. All the catalysts generated with the ligands **4–6** showed faster reaction rates than those reported so far. In particular those generated with the C_2 symmetric ligands **5** and **6** completed the reaction within 10 min at 25°C. However, the corresponding ee values of the substitution products were noticeably different, which implicated the importance of the planar chirality, although the absolute configuration of the major enantiomer was *S* in all cases. The enantioselectivity obtained with the ligand **6** was 94% ee while those with **5a** and **5b** were less than 40% ee.

As mentioned before, there are various possibilities in the coordination modes of the ligands **4–6** when they act as bidentate ones: *N*,*P*- (or *N*′,*P*′-), *N*,*P*′- (or *N*′,*P*-), *P*,*P*′-, and *N*,*N*′-type (where *N* and *P* indicate the N- and P-atom of the oxazoline and diphenylphosphine groups on one Cp ring, respectively, and *N*′ and *P*′ denote those on the other Cp ring). The *N*,*N*′-mode can be ruled out in all cases because the reaction with the ligand **9** does not give any substitution product. The dominant catalytic species from possible equilibria among several coordination modes could be inferred by comparing the selectivity and reactivity profiles between the *N*,*P*-, *N*,*N*′*P*,*P*′- and *N*,*N*′*P*-type ligands. For the C_2 symmetric ligands **5a** and **5b**, the *N*,*P*- chelated (or *N*′,*P*′-) species may not be the dominant one, because the substitution reactions with these ligands show reactivity and selectivity patterns distinguished from those observed with *N*,*P*-chelates **2** and **3**. The substitution with the *N*,*P*-chelate **2a** proceeded with a much slower rate than that with **2b**, whereas the substitution with **5a** proceeded as fast as with **5b** but much faster than **2a** and **3**. The enantioselectivity observed in the substitution with **5a** was similar to that with **5b** but much lower compared to the cases with **2a** and **3**.

Table 1. Enantioselective Pd-catalyzed allylic substitutions of *rac*-(*E*)-**11a**

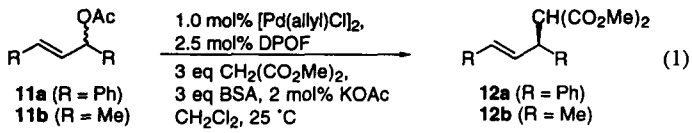
Entry	Ligand	Reaction time[a]	%Ee[b]	**12a** %Yield[c]
1	**2a**	1.5 h	90	95 (*S*)[d]
2	**2b**	30 min	≥99	99 (*S*)
3	**3**	5.0 h	67	73 (*S*)
4	**4a**	30 min	99	99 (*S*)
5	**4b**	30 min	99	99 (*S*)
6	**5a**	10 min	38	99 (*S*)
7	**5b**	10 min	34	99 (*S*)
8	**6**	10 min	94	99 (*S*)
9	**7a**	3.0 h	77	84 (*S*)
10	**7b**	3.0 h	74	53 (*S*)
11	**8**	2.0 h	80	88 (*S*)
12	**9**	48 h	-	0
13	**10**	10 min	-	99

[a] 0.3 M Allylic acetate in CH_2Cl_2. [b] Determined by HPLC (Chiralcel OD®) and ^1H NMR (Eu(hfc)$_3$) analyses. [c] Purified yields by column chromatography on SiO_2. [d] Absolute configuration.

Table 2. Enantioselective Pd-catalyzed allylic substitutions of *rac*-(*E*)-**11b**

Entry	Ligand of the Pd-cat	Reaction time (h)	%Ee[a]	**12b** %Yield[b]
14	**2a**	5.0	11	26 (*S*)[c]
15	**2b**	5.0	35	82 (*S*)
16	**2b**	1.0[d]	36	98 (*S*)
17	**4a**	1.0	12	79 (*S*)
18	**4b**	1.0	12	81 (*S*)
19	**5a**	1.0	20	84 (*R*)
20	**5b**	1.0	33	85 (*R*)
21	**6**	1.0	9	88 (*S*)
22	**7a**	5.0	28	17 (*S*)
23	**7b**	5.0	63	56 (*S*)
24	**8**	5.0	32	53 (*S*)

[a] Determined by the comparison of the $[\alpha]_D$ values of distilled samples with literature value.[3p] [b] Purified yields by column chromatography on SiO_2. [c] Absolute configuration. [d] With 10 mol% catalyst.



(1)

A preliminary study using X-ray crystallography and ^{31}P NMR spectroscopy also suggests that (π-allyl)Pd complexes of ligands **5** and **6** exist mainly as *P,P'*-chelated species.[12] The *N,P'*-mode (or *N',P*-) for the ligands **4–6** is also less probable since the reactivity and selectivity profiles observed with the ligands are noticeably different from those obtained with the ligands **7** and **8** that have two possible combinations of the *N,P*- and *N',P*-ligations (*vide infra*). Therefore, for the cases of **5** and **6**, although several ligation modes are possible, it can be suggested that they act mainly as *P,P'*-chelates in the Pd-catalyzed allylic substitution. A simple *P,P'*-chelate, 1,1'-bis(diphenylphosphino)ferrocene **10**[13] produces the corresponding Pd-catalyst similarly reactive as those from **5** and **6**, which also supports our suggestion.

As mentioned before, 99% ee was obtained in the substitution reaction with the ligand **4a** or **4b** but the reactivity of the corresponding catalyst is slightly decreased in comparison to the cases of the C_2 symmetric ligands **5** and **6**. The different reactivity profile observed with the ligand **4** can not be explained by simply *P,P'*-type ligation at present.

When the '*N,P,N'*-type' ligands **7–8** were employed in the Pd-catalyzed reaction, reactivity and selectivity patterns different from the *N,P*- and *N,N',P,P'*-type ligands were observed: Regardless of the oxazoline substituents, they gave enantioselectivities around 74–80% ee (entry 9–11). In addition, the corresponding Pd-catalysts exhibited somewhat decreased reactivity compared to those generated from the *N,P*- (except for **3**) or *N,N',P,P'*-type ligands. An explanation for their ligation modes needs a further study.

The enantioselectivity of the Pd-catalyzed allylic alkylation is known to be greatly dependent on the substrates used. For given allylic acetates, the steric bulkiness as well as electronic effects of the substituents affect the reactivity and enantioselectivity significantly. These phenomena were observed again in this study. We have studied the same catalytic reactions for a simple aliphatic acetate **11b**, which is known to be much less reactive and worse for the enantioselection than the acetate **11a**.[3p] The results are summarized in Table 2.

Using the *N,N',P,P'*-type ligands **4–6**, again very high reactivity was also observed in the catalytic reactions. Also distinguishable reactivity patterns depending on the types of the ligands were observed. Good yields (79–88%) were obtained in all cases after 1 h-reaction period; however, low to moderate enantioselectivities were obtained in all cases. Interestingly, a noticeable enantioselectivity (63% ee) was obtained with the *N,N',P*-type ligand **7b**, albeit in moderate yield. For the acetate **11b**, 71% ee has been reported using the ligand **1b**.[3p,14] The lower enantioselection observed with our DPOF-Pd catalysts for the acetate **11b**, in comparison to the Pd catalyst from the ligand **1b**, may be ascribed to the diminished steric interaction between the substituents of the ligand and the acetate in the enantiodiscriminating stage.[15]

In summary, we have studied Pd-catalyzed allylic alkylations using a variety of ferrocene-based DPOF ligands. A dramatic influence of planar chirality on the enantioselection is observed. Some of the ligands produce very reactive and highly enantioselective Pd-catalysts for the allylic substitution. Among several competing ligation modes for the Pd-catalysts, the *P,P'*-chelation seems to operate for the *N,N',P,P'*-type ligands **5–6** dominantly during the catalytic reaction. A further study on the exact chelation modes for the ligands **4** and *N,N',P*-type ligands (**7** and **8**) including a possibility of third ligation by spectroscopic methods and crystallography is under way.

Experimental

All reactions were carried out under an argon atmosphere. CH_2Cl_2 was distilled from CaH. Column chromatography was carried out on SiO_2 (mesh size 230–400). All the commercially available reagents

were used without further purification. All the chiral DPOF ligands and allylic acetates used were synthesized.[8]

General procedures for the Pd-catalyzed allylic substitution

A mixture of (π-allyl)palladium chloride dimer (3.7 mg, 0.01 mmol) and a DPOF ligand (0.025 mmol) in CH_2Cl_2 (1.7 mL) was stirred at 25°C for 1 h. To this Pd catalyst was added the acetate **11a** or **11b** (1.0 mmol) in CH_2Cl_2 (1.7 mL), followed by dimethyl malonate (0.34 mL, 3.0 mmol), BSA [*N*,*O*-bis(trimethylsilyl)acetamide), 0.74 mL, 3.0 mmol] and KOAc (2.0 mg, 0.02 mmol) sequentially. After the reaction was complete (judging from TLC analysis) or after a certain time was elapsed, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and poured into a cold saturated aqueous NH_4Cl solution (15 mL). The organic layer was separated and dried over anhydrous $MgSO_4$. After evaporation of solvent *in vacuo*, the residue was purified by column chromatography (eluant: 20% ethyl acetate in hexanes).

Determination of % ee values of products

For the acetate **12a**, enantioselectivity was determined by HPLC analysis with a chiral column [Chiralcel OD; 25 cm×0.46 cm; hexanes: *i*-PrOH=99:1; flow rate=0.9 mL/min; t_R=14.10 (*R*-**12a**), 15.44 (*S*-**12a**) min] and ^1H NMR analysis with chiral shift reagent Eu(hfc)$_3$ (one of the two methyl ester groups that appears at 3.70 was splitted into two peaks, for example, at 3.97 (*R*-**12a**) and 3.93 (*S*-**12a**) when 0.8 equiv of the shift reagent was added). For the acetate **12b**, enantioselectivity was estimated by comparison of its specific rotation value with a literature value[3p] $[\alpha]_D^{23}=-19.8$ (*c*=1.1, $CHCl_3$): 71% ee. The absolute stereochemistry of the products was assigned by comparing the sign of its optical rotation with literature data.

Acknowledgements

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References

1. Reviews: (a) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089; (b) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395.
2. Some recent examples: (a) Trost, B. M.; Van Vranken, D. L. *J. Am. Chem. Soc.* **1993**, *115*, 444; (b) Trost, B. M.; Bunt, R. C. *J. Am. Chem. Soc.* **1994**, *116*, 4089; (c) Trost, B. M.; Organ, M. G. *J. Am. Chem. Soc.* **1994**, *116*, 10320; (d) von Matt, P.; Loiseleur, O.; Koch, G.; Pfaltz, A.; Lefeber, C.; Feucht. T.; Helmchen, G. *Tetrahedron: Asymmetry* **1994**, *5*, 573; (e) Rieck, H.; Helmchen, G. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2687; (f) Trost, B. M.; Stenkamp, D.; Pulley, S. R. *Chem. Eur. J.* **1995**, *1*, 568; (g) Trost, B. M.; Bunt, R. C. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 99.
3. Selected papers: *P*,*P*-chelates: (a) Trost, B. M.; Dietsche, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 8200; (b) Auburn, P. R.; Mackenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033; (c) Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143; (d) Hayashi, T.; Yamamoto, A.; Hagihara, T.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 191; (e) Yamaguchi, M.; Shima, T.; Yamagishi, T.; Hida, M. *Tetrahedron Lett.* **1990**, *31*, 5049; (f) Trost, B. M.; Van Vranken, D. L. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 228; (g) Yamazaki, A.; Morimoto, T.; Achiwa, K. *Tetrahedron: Asymmetry* **1993**, *4*, 2287; (h) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062; (i) Hayashi, T.; Ohno, A.; Lu, S.; Matsumoto, Fukuyo. E.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 4221; (j) Seebach, D.; Devaquet, E.; Ernst, A.; Hayakawa, M.; Khnle, F. N. M.; Schweizer, W. B.; Weber, B. *Helv. Chim. Acta* **1995**, *78*, 1636; (k) Yamazaki, A.; Achiwa, K. *Tetrahedron: Asymmetry* **1995**, *6*, 51; *N*,*N*-chelates: (l) Togni, A. *Tetrahedron: Asymmetry* **1991**, *2*, 683; (m) Leutenegger, U.; Umbricht, G.; Fahrni, C.; von Matt, P.; Pfaltz, A. *Tetrahedron* **1992**, *48*, 2143; (n) Kubota, H.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* **1993**, *34*,

8135; (o) Tanner, D.; Andersson, P. G.; Harden, A.; Somfai, P. *Tetrahedron Lett.* **1994**, *35*, 4631; *N,P*-chelates: (p) von Matt, P.; Pfaltz, A. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 566; (q) Sprinz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769; (r) Dawson, G. J.; Frost, C. G.; Williams, J. M. J. *Tetrahedron Lett.* **1993**, *34*, 3149; (s) Kubota, H.; Koga, K. *Tetrahedron Lett.* **1994**, *35*, 6689; others: (t) Okada, Y.; Minami, T.; Umezu, Y.; Nishikawa, S.; Mori, R.; Nakayama, Y. *Tetrahedron: Asymmetry* **1991**, *2*, 667; (u) Knhl, G.; Sennhenn, P.; Helmchen, G. *J. Chem. Soc. Chem. Soc.* **1995**, 1845; (v) Chelucci, G.; Cabras, M. A. *Tetrahedron: Asymmetry* **1996**, *7*, 965; (w) Brenchley, G.; Fedouloff, M.; Merifield, E.; Wills, M. *Tetrahedron: Asymmetry* **1996**, *7*, 2809.

4. Selected papers: (a) Mackenzie, P. B.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2046; (b) Hansson, S.; Norrby, P.-O.; Sjgren, M. P. T.; Åkermark, B.; Cucciolito, M. E.; Giordano, F.; Vitagliano, A. *Organometallics* **1993**, *12*, 4940; (c) Gogoll, A.; Örnebro, J.; Grennberg, H.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1994**, *116*, 3631; (d) Breutel, C.; Pregosin, P. S.; Salzmann, R.; Togni, A. *J. Am. Chem. Soc.* **1994**, *116*, 4067; (e) Sprinz, J.; Kiefer, M.; Helmchen, G.; Reggelin, M.; Huttner, G.; Walter, O.; Zsolnai, L. *Tetrahedron Lett.* **1994**, *35*, 1523; (f) Brown, J. M.; Hulmes, D. I.; Guiry, P. J. *Tetrahedron* **1994**, *50*, 4493; (g) Sjgren, M. P.; Hansson, S.; Åkermark, B.; Vitagliano, A. *Organometallics* **1994**, *13*, 1963; (h) von Matt, P.; Lloyd-Jones, G. C.; Minidis, A. B. E.; Pfaltz, A.; Macko, L.; Neuburger, M.; Zehnder, M.; Regger, H.; Pregosin, P. S. *Helv. Chim. Acta* **1995**, *78*, 265; (i) Andersson, P. G.; Harden, A.; Tanner, D.; Norrby, P.-O. *Chem. Eur. J.* **1995**, *1*, 12; (j) Trost, B. M.; Bunt, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 235; (k) Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P. S.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031; (l) Burckhardt, U.; Gramlich, V.; Hofmann, P.; Nesper, R.; Pregosin, P.; Salzmann, R.; Togni, A. *Organometallics* **1996**, *15*, 3496.
5. (a) Lloyd-Jones, G. C.; Pfaltz, A. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 462; (b) Loiseleur, O.; Meier, M.; Pfaltz, A. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 200; (c) Newman, L. M.; Williams, J. M. J.; McCague, R.; Potter, G. A. *Tetrahedron: Asymmetry* **1996**, *7*, 1597; (d) Langer, T.; Jassen, J.; Helmchen, G. *Tetrahedron: Asymmetry* **1996**, *7*, 1599.
6. For a review, see: Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.
7. (a) Samakia, T.; Latham, H. A.; Schaad, D. R. *J. Org. Chem.* **1995**, *60*, 10; (b) Richards, C.; Damalidis, T.; Hibbs, D. E.; Hursthose, M. B. *Synlett* **1995**, 74; (c) Nishibashi, Y.; Uemura, S. *Synlett* **1995**, 79; (d) Park, J.; Lee, S.; Ahn, K. H.; Cho, C.-W. *Tetrahedron Lett.* **1995**, *36*, 7263; (e) Ahn, K. H.; Cho. C.-W.; Baek, H.-H.; Park, J.; Lee, S. *J. Org. Chem.* **1996**, *61*, 4937.
8. The synthesis and characterization for the ligands **2–9**: (a) Compounds **2** and **3**: ref 7e; for the synthesis of **2**, see also ref 7c; for the synthesis of **2a**, see also ref 7b; (b) Compounds **4–6**, and **9**: ref 7d; for the synthesis of **4a** and **6**, see also: Zhang, W.; Adachi, Y.; Hirao, T.; Ikeda, I. *Tetrahedron: Asymmetry* **1996**, *7*, 451; (c) Compounds **7** and **8** with the reassignment of the stereochemistry for **7** including the X-ray structure of **7b**: Park, J.; Lee, S.; Ahn, K. H.; Cho, C.-W. *Tetrahedron Lett.* **1996**, *37*, 6137.
9. (a) Hayashi, T. *Pure and Appl. Chem.* **1988**, *60*, 7; (b) Sawamura, M.; Ito, Y. *Chem. Rev.* **1992**, *92*, 857; (c) Hayashi, T. in Ferrocenes, Togni, A.; Hayashi, T. Eds., VCH Publisher, Weinheim, 1995, pp 105–142.
10. (a) Jedlicka, B.; Kratky, C.; Weissensteiner, W.; Widhalm, M. *J. Chem. Soc. Chem. Commun.* 1993, 1329; (b) Nishibayashi, Y.; Segawa, K.; Ohe, K.; Uemura, S. *Organometallics* **1995**, *14*, 5486; (c) Richards, C. J.; Hibbs, D. E.; Hursthouse, M. B. *Tetrahedron Lett.* **1995**, *36*, 3745; (d) Nishibayashi, Y.; Segawa, K.; Takada, H.; Ohe, K.; Uemura, S. *J. Chem. Soc. Chem. Commun.* **1996**, 847; (e) Zhang, W.; Kida, T.; Nakatsuji, Y.; Ikeda, I. *Tetrahedron Lett.* **1996**, *37*, 7795.
11. The Pd-catalyzed allylic substitution using the ligands **2** and **3** including a steric strain-reactivity relationship argument is submitted for publication.
12. After completion of our work, Ikeda and co-workers reported Pd-catalyzed allylic substitution with the ligands **2a**, **4a**, and **6**, and implied *N,P*-chelated Pd-catalysis for **6** based on its $PdCl_2$ complex: Zhang, W.; Hirao, T.; Ikeda, I. *Tetrahedron Lett.* **1996**, *37*, 4545. We also obtained a

N,P-chelated $PdCl_2$ complex for **6** and also for **5**. However, we have found that the chelation mode was dependent on the Pd source used. Thus, with $[(\pi\text{-allyl})PdCl]_2$ which would generate a (π-allyl)Pd complex close to a real intermediate, a *P,P*-chelated Pd-complex was obtained for **6**, which was identified by X-ray crystallography and ^{31}P NMR spectroscopy. Details of the X-ray crystallography and NMR analysis for ligands **4–8** will be reported in due course.

13. On the efficiency and superiority of the DPPF ligand in Pd-catalyzed coupling reactions, see: Gan, K.-S.; Andy Hor, T. S. in Ferrocenes, Togni, A.; Hayashi, T. Eds., VCH Publisher, Weinheim, 1995, pp 3–104.
14. Recently 92% ee is achieved: Trost, B. M.; Krueger, A. C.; Bunt, R. C.; Zambrano, J. *J. Am. Chem. Soc.* **1996**, *118*, 6520.
15. (a) Trost, B. M.; Van Vranken, D. L. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 228; (b) Dawson, G. J.; Frost, C. G.; Martin, C. J.; Williams, J. M. J. *Tetrahedron Lett.* **1993**, *34*, 7793.

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