

Syntheses of Novel Chiral Monophosphines, 2,5-Dialkyl-7-phenyl-7-phosphabicyclo[2.2.1]heptanes, and Their Application in Highly Enantioselective Pd-Catalyzed Allylic Alkylations

Zhaogen Chen, Qiongzong Jiang, Guoxin Zhu, Dengming Xiao, Ping Cao, Cheng Guo, and Xumu Zhang*

Department of Chemistry, 152 Davey Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

Received December 16, 1996[®]

Design and synthesis of chiral phosphines have played a significant role in the development of transition metal catalyzed asymmetric reactions.¹ Many excellent chiral bidentate phosphines such as DIPAMP,² DIOP,³ ChiraPhos,⁴ and BINAP⁵ have been developed for a variety of catalytic reactions. Recent additions to this family of ligands include the Duphos and BPE species of Burk and co-workers.⁶ The most significant characteristics of Duphos and BPE are (1) they contain several alkyl groups attached to the phosphine and thus are more electron rich than many related chiral arylphosphine ligands and (2) the steric environment can be varied by changing the substituents on the chiral carbon centers. Highly enantioselective reactions have been reported with these ligands.⁶ Despite these successes, one potential problem is the conformational flexibility that exists in these ligands which may limit their applicability to other types of reactions. It is well-known that rapid interconversion of the envelope and half-chair conformations can occur in five-membered rings. We now report new chiral phosphines with rigid fused bicyclic rings which do not possess the conformational flexibility associated with the five-membered rings present in the Duphos and BPE ligands (Figure 1).

The rigid fused bicyclic [2.2.1] structure represents a new motif in chiral ligand design. Analogous to Burk's systems, changes in the size of the R group on the ring system can modulate the asymmetric induction and high enantioselectivities can be achieved. Herein, we report the syntheses of chiral monophosphines with this fused bicyclic ring structure (Figure 2)⁷ and their application in Pd-catalyzed asymmetric allylic alkylations.

The ligand synthesis depends on the availability of enantiomerically pure cyclic 1,4-diols. Halterman⁸ and Vollhardt⁹ have previously prepared chiral cyclopentadiene derivatives from the chiral diols.^{8,9} Halterman⁸ has synthesized chiral diols **1** and **2** from the inexpensive starting materials *p*-xylene and *p*-diisopropylbenzene,

respectively. The synthesis employed Birch reduction,¹⁰ followed by asymmetric hydroboration¹¹ and recrystallization to 100% ee. Conversion of the optically pure diols to the corresponding mesylates proceeds cleanly. Nucleophilic substitution by Li₂PPh on the chiral dimesylates **3** and **4** generated the corresponding bicyclic phosphines, which were trapped by BH₃·THF to form the air-stable boron-protected monophosphines **5** and **6**, respectively. Deprotection with a strong acid¹² produces the desired products (**7**, (1*R*,2*S*,4*R*,5*S*)-(+)-2,5-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]heptane; **8**, (1*R*,2*R*,4*R*,5*R*)-(+)-2,5-diisopropyl-7-phenyl-7-phosphabicyclo[2.2.1]heptane) in high yields.

We chose Pd-catalyzed allylic alkylation to test the effectiveness of these new monophosphines as chiral ligands. Although many palladium complexes of multidentate phosphine and nitrogen ligands are excellent catalysts for this reaction,^{13,14} palladium complexes of simple chiral monophosphines are normally not effective.¹⁵ We were delighted to find that Pd-catalyzed allylic

(7) Upon completion of the work reported here, a related chiral fused bicyclic phosphine, 2,6-dimethyl-9-phenyl-9-phosphabicyclo[3.3.1]nonane, was reported for Pd-catalyzed allylic alkylations (Hamada, Y.; Seto, N.; Ohmori, H.; Hatano, K. *Tetrahedron Lett.* **1996**, *37*, 7565). Compared with this ligand, **7** and **8** are more rigid (one less methylene group) and the chiral environment can be varied by changing the R group. We expect that these attributes will be important for fine-tuning activity and selectivity of phosphines like **7** and **8** in various asymmetric catalytic reactions.

(8) (a) Chen, Z.; Halterman, R. L. *Synlett* **1990**, 103. (b) Chen, Z.; Eriks, K.; Halterman, R. L. *Organometallics* **1991**, *10*, 3449. (c) Chen, Z.; Halterman, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 2276. (d) Halterman, R. L.; Chen, Z.; Khan, M. *Organometallics* **1996**, *15*, 3957.

(9) Halterman, R. L.; Vollhardt, K. P. C.; Welker, M. E.; Blaser, D.; Boese, R. *J. Am. Chem. Soc.* **1987**, *109*, 8105.

(10) Kwart, H.; Conley, R. A. *J. Org. Chem.* **1973**, *38*, 2011.

(11) Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *J. Org. Chem.* **1982**, *47*, 5074.

(12) McKinstry, L.; Livinghouse, T. *Tetrahedron* **1995**, *51*, 7655.

(13) Reviews: (a) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (b) Pfaltz, A. *Acc. Chem. Res.* **1993**, *26*, 339. (c) Hayashi, T. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed; VCH Publishers: New York, 1993; p 325. (d) Frost, C. G.; Howarth, J.; Williams, J. M. *J. Tetrahedron: Asymmetry* **1992**, *3*, 1089. (e) Consiglio, G.; Waymouth, R. M. *Chem. Rev.* **1989**, *89*, 257.

(14) For some examples, see: (a) Trost, B. M.; Bunt, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 235. (b) Peña-Cabrera, E.; Norrby, P.-O.; Sjögren, M.; Vitagliano, A.; De Felice, V.; Oslob, J.; Ishii, S.; O'Neil D.; Åkermark, B.; Helquest, P. *J. Am. Chem. Soc.* **1996**, *118*, 4299. (c) Barbaro, P.; Curro, A.; Hermann, J.; Nesper, R.; Pregosin, P. S.; Salzmann, R. *Organometallics* **1996**, *15*, 1879. (d) Knühl, G.; Sennhenn, P.; Helmchen, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1845. (e) Rieck, J.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2687. (f) Andersson, P. G.; Harden, A.; Tanner, D.; Norrby, P. *Chem. Eur. J.* **1995**, *1*, 12. (g) von Matt, P.; Lloyd-Jones, G. L.; Minidis, A. B. E.; Pfaltz, A.; Macko, L.; Neuburger, M.; Zehnder, M.; Rügger, H.; Pregosin, P. S. *Helv. Chim. Acta* **1995**, *78*, 265. (h) Trost, B. M.; Organ, M. G.; O'Doherty, G. A. *J. Am. Chem. Soc.* **1995**, *117*, 9662. (i) Gamez, P.; Dunjic, B.; Fache, F.; Lemaire, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1417. (j) Brown, J. M.; Hulmes, D. I.; Guiry, P. J. *Tetrahedron* **1994**, *50*, 4493. (k) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. A. *J. Am. Chem. Soc.* **1994**, *116*, 4062. (l) Hayashi, T.; Iwamura, H.; Naito, M.; Matsumoto, Y.; Uozumi, Y.; Miki, M.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 775. (m) Trost, B. M.; Bunt, R. C. *J. Am. Chem. Soc.* **1994**, *116*, 4089. (n) Pregosin, P. S.; Rügger, H.; Salzmann, R.; Albinati, A.; Lianza, F.; Kunz, R. W. *Organometallics* **1994**, *13*, 83. (o) Sprinz, J.; Kiefer, *Tetrahedron Lett.* **1994**, *35*, 1523. (p) Allen, J. V.; Coote, S. J.; Dawson, G. J.; Frost, C. G.; Martin, C. J.; Williams, J. M. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2065. (q) von Matt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566. (r) Trost, B. M.; Van Vranken, D. L.; Bingel, C. *J. Am. Chem. Soc.* **1992**, *114*, 9327. (s) Trost, B. M.; Van Vranken, D. L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 328. (t) Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143. (u) Auburn, P. R.; Mackenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033. (v) Trost, B. M.; Strege, P. E. *J. Am. Chem. Soc.* **1977**, *99*, 1649.

(15) (a) Friad, J. C.; Aribi-Zouieouche, L. *J. Organomet. Chem.* **1985**, *253*, 282. (b) Fiaud, J. C.; Legros, J. Y. *Tetrahedron Lett.* **1991**, *25*, 5089.

* Abstract published in *Advance ACS Abstracts*, June 1, 1997.

(1) (a) Ojima, I., Ed. *Catalytic Asymmetric Synthesis*; VCH: New York, 1993. (b) Sheldon, R. A. *Chirotechnology*; Marcel Dekker: New York, 1993. (c) Noyori, R. *Asymmetric Catalysis In Organic Synthesis*; John Wiley & Sons: New York, 1994.

(2) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106.

(3) Kagan, H. B.; Dang, T.-P. *J. Am. Chem. Soc.* **1972**, *94*, 6429.

(4) Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6262.

(5) (a) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (b) Noyori, R. *Science* **1990**, *248*, 1194.

(6) (a) Burk, M. J.; Feaster, J. E.; Harlow, R. L. *Organometallics* **1990**, *9*, 2653. (b) Burk, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 8518. (c) Burk, M. J.; Feaster, J. E.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 10125. (d) Burk, M. J.; Lee, J. R.; Martinez, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 10847.

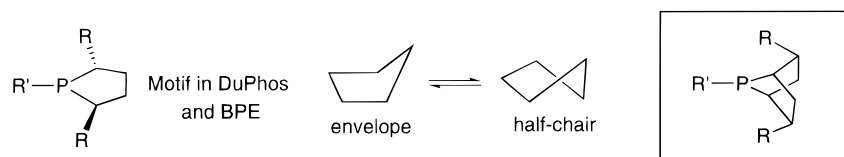


Figure 1.

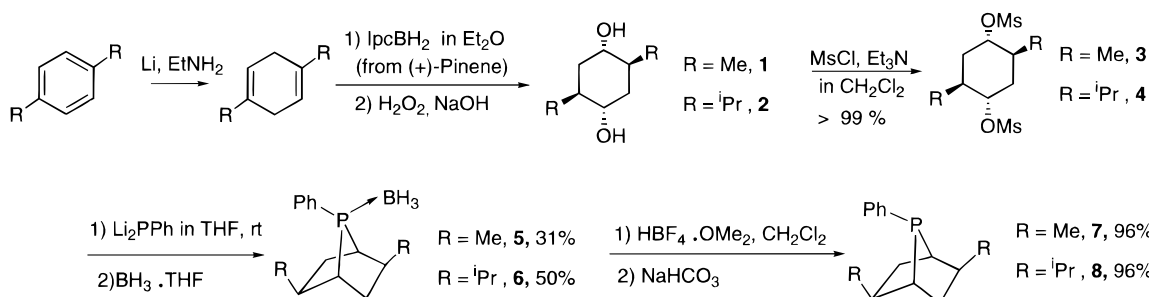
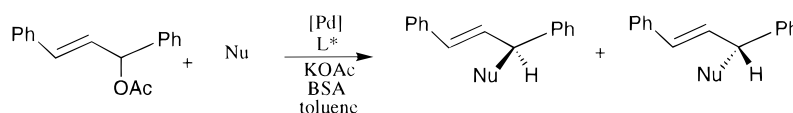


Figure 2.

Table 1. Palladium-Catalyzed Asymmetric Allylic Alkylation with Chiral Monophosphines^a

entry	L*	[Pd]	[Pd]:L*	Nu	additive	time (h)	yield (%)	% ee ^b
1	7	$\text{Pd}_2(\text{dba})_3$	1:2.2	$\text{CH}_2(\text{CO}_2\text{Me})_2$		1.5	96	74 (R)
2	7	$\text{Pd}(\text{OAc})_2$	1:2.2	$\text{CH}_2(\text{CO}_2\text{Me})_2$		4.0	98	72 (R)
3	7	$[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$	1:1.1	$\text{CH}_2(\text{CO}_2\text{Me})_2$		5.0	97	60 (R)
4	7	$[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$	1:2.2	$\text{CH}_2(\text{CO}_2\text{Me})_2$		2.0	93	95 (R)
5	7	$[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$	1:3.3	$\text{CH}_2(\text{CO}_2\text{Me})_2$		1.5	96	96 (R)
6	7	$[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$	1:2.2	$\text{CH}_2(\text{CO}_2\text{Me})_2$	2.8% AgBF_4	1.0	80	97 (R)
7	7	$[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$	1:2.2	$\text{CH}_2(\text{CO}_2\text{Me})_2$	2.8% LiCl	2.0	95	96 (R)
8	7	$[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$	1:2.2	$\text{CH}_2(\text{CO}_2\text{Me})_2$		2.0	99	>97 ^c (R)
9	7	$[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$	1:2.2	$\text{CH}(\text{NHAc})(\text{CO}_2\text{Et})_2$		2.0	95	>99.5 ^d (S)
10	8	$[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$	1:2.2	$\text{CH}_2(\text{CO}_2\text{Me})_2$		3.5	99	78 (R)

^a The reaction was carried out under N_2 using 1,3-diphenyl-2-propenyl acetate, Nu (nucleophile) (300 mol %), BSA (bis(trimethylsilyl)acetamide) (300 mol %), KOAc (2 mol %), toluene, [Pd] 1.4 mol % and L*. ^b % ee was measured by HPLC using a Chiralcel OD column, and the absolute configuration was determined by comparing the optical rotation with literature values.^{14q} ^c % ee was measured by comparing the optical rotation with literature values.^{14q} ^d % ee was measured by HPLC using a Chiralcel OJ column.

alkylation with the new monophosphine **7** gave excellent enantioselectivities and conversions (Table 1), comparable to the best results (99% ee) reported to date.¹³

In our initial experiments, 1,3-diphenyl-2-propenyl acetate and dimethyl malonate were used as substrates. The enantioselectivity of Pd-catalyzed allylic alkylation strongly depends on the nature of the palladium precursor (entries 1, 2, and 4). The ratio of phosphine to palladium is also important. Our experimental results (entries 3, 4, and 5) showed that 2 equiv of phosphine is required for highly enantioselective allylic alkylation. We have also removed chloride ion using AgBF_4 (entry 6) and have added excess chloride (entry 7), but the enantioselectivity remains about the same under both of these sets of conditions. These observations suggest that chloride does not remain in the coordination sphere of the palladium, perhaps due to the strong coordinating ability of the electron-donating monophosphine **7**. In the catalytic reaction, it is likely that two monophosphines coordinate with one palladium. Changing the nucleophile from dimethyl malonate to 2,4-pentanedione (entry 8) or diethyl acetamidomalonate (entry 9) has some effect on the enantioselectivity. Greater than 99.5% ee was achieved in the alkylation with diethyl acetamidomalonate. When 1,3-diphenyl-2-propenyl acetate was re-

placed with pent-3-en-2-yl acetate ($\text{CH}_3\text{CH}=\text{CHCH}(\text{OAc})\text{CH}_3$), only 34% ee was obtained in the product 2-(1-methylbut-2-enyl)malonic acid dimethyl ester under the same conditions as in entry 4. This is due to the low steric effect of the methyl groups compared to that of the phenyl groups. Finally, altering the size of the substituents on the chiral monophosphine influences the enantioselectivity. Compared to the result with dimethyl ligand **7** (entry 4, 95% ee), lower enantioselectivity was observed with the more sterically demanding diisopropyl ligand **8** (entry 10, 78% ee).

In conclusion, we have developed a family of chiral phosphines with a unique fused bicyclic [2.2.1] ring structure. Pd-catalyzed allylic alkylations with monophosphine **7** gives excellent enantioselectivities. Mechanistic aspects of this reaction are being investigated as are the use of structurally related compounds for other asymmetric catalytic reactions.

Experimental Section

General Procedure. THF and toluene were distilled under nitrogen from a sodium/benzophenone ketyl. Methylene chloride was distilled under nitrogen from CaH_2 . Compounds **1–4** were prepared according to the literature procedure.⁸

(1R,2S,4R,5S)-(+)-2,5-Dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]heptane-Borane (5). To phenylphosphine (3.0

mL, 27.3 mmol) in THF (200 mL) was added *n*-BuLi (34.5 mL of a 1.6 M solution in hexane, 55 mmol) via syringe at -78°C over 20 min. Then the orange solution was warmed up to rt and stirred for 1 h at rt. To the resulting orange-yellow suspension was added a solution of (1*S*,2*S*,4*S*,5*S*)-2,5-dimethylcyclohexane-1,4-diol bis(methanesulfonate) (**3**, 8.25 g, 27.5 mmol) in THF (100 mL) over 15 min. After the mixture was stirred overnight at rt, the pale-yellow suspension was hydrolyzed with a saturated NH_4Cl solution. The mixture was extracted with ether (2×50 mL), and the combined organic solution was dried over anhydrous sodium sulfate. After filtration, the solvents were removed under reduced pressure. The residue was dissolved in methylene chloride (100 mL) and treated with $\text{BH}_3 \cdot \text{THF}$ (40 mL of a 1.0 M solution in THF, 40 mmol), and the mixture was stirred overnight. It was then poured into a saturated NH_4Cl solution and extracted with CH_2Cl_2 (3×50 mL). The combined organic solution was dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The residue was subjected to chromatography on a silica gel column and eluted with hexanes/ CH_2Cl_2 (4:1), affording the product as a white solid. Yield: 1.95 g (31%). $[\alpha]_D^{25} = +59.5^{\circ}$ (*c* 1.07, CHCl_3). $^1\text{H NMR}$ (CDCl_3) δ 7.60–7.30 (m, 5 H), 2.60–2.40 (m, 2 H), 2.15–2.05 (m, 1 H), 2.04–1.80 (m, 4 H), 1.65–1.50 (m, 1 H), 1.32 (d, $^3J(\text{HH}) = 6.5$ Hz, 3 H), 0.59 (d, $^3J(\text{HH}) = 6.7$ Hz, 3 H), 1.6–0.2 (br); $^{13}\text{C NMR}$ (CDCl_3) δ 131.7 (d, $^2J(\text{PC}) = 7.3$ Hz), 130.6 (d, $^1J(\text{PC}) = 43.9$ Hz), 129.9 (d, $^4J(\text{PC}) = 2.0$ Hz), 128.4 (d, $^3J(\text{PC}) = 8.6$ Hz), 43.07 (d, $^1J(\text{PC}) = 30.5$ Hz), 40.9 (d, $^1J(\text{PC}) = 31.6$ Hz), 36.3, 36.7 (d, $^3J(\text{PC}) = 13.5$ Hz), 35.9 (d, $^2J(\text{PC}) = 3.5$ Hz), 34.7 (d, $^2J(\text{PC}) = 9.8$ Hz), 20.8, 20.5; $^{31}\text{P NMR}$ (CDCl_3): δ 36.3 (d, broad, $^1J(\text{PB}) = 58.8$ Hz); MS: *m/z* 232 (M^+ , 0.42), 218 ($\text{M}^+ - \text{BH}_3$, 100), 203 (7.41), 176 (14.60), 136 (9.81), 109 (16.67), 91 (6.59), 77 (5.51), 65 (3.71); HRMS: calcd for $\text{C}_{14}\text{H}_{22}\text{BP}$ 232.1552 (M^+), found 232.1578; calcd for $\text{C}_{14}\text{H}_{19}\text{P}$ 218.1224 ($\text{M}^+ - \text{BH}_3$), found 218.1233.

(1*R*,2*R*,4*R*,5*R*)-(+)-2,5-Diisopropyl-7-phenyl-7-phosphabicyclo[2.2.1]heptane-borane (6). The same procedure as in the preparation of **5** was used. Yield: 0.33 g (50%). $[\alpha]_D^{25} = +25.5^{\circ}$ (*c* 1.02, CHCl_3). $^1\text{H NMR}$ (CDCl_3): δ 7.55–7.30 (m, 5 H), 2.85–2.70 (m, 2 H), 2.30–2.20 (m, 1 H), 2.18–2.00 (m, 1 H), 1.95–1.65 (m, 4 H), 1.40–1.20 (m, 2 H), 1.03 (d, $^3J(\text{PH}) = 6.5$, 3H), 0.87 (d, $^3J(\text{PH}) = 6.7$, 3H), 0.85 (d, $^3J(\text{PH}) = 7.4$, 3H), 0.53 (s, broad, 3 H), 1.5–0.2 (br). $^{13}\text{C NMR}$ (CDCl_3): δ 131.2 (d, $^2J(\text{PC}) = 8.3$ Hz), 130.7 (d, $^1J(\text{PC}) = 45.2$ Hz), 130.0 (d, $^4J(\text{PC}) = 2.5$ Hz), 128.5 (d, $^3J(\text{PC}) = 9.5$ Hz), 50.3 (d, $^2J(\text{PC}) = 2.1$ Hz), 48.8 (d, $^2J(\text{PC}) = 9.7$ Hz), 38.3 (d, $^1J(\text{PC}) = 30.5$ Hz), 36.8 (CH_2), 36.7 (d, $^1J(\text{PC}) = 31.5$ Hz), 34.7 (d, $^3J(\text{PC}) = 13.7$ Hz), 31.9, 31.1, 22.4, 21.6, 20.7, 20.1. $^{31}\text{P NMR}$ (CDCl_3): δ 36.8 (d, broad, $^1J(\text{PB}) = 51.4$ Hz). MS: *m/z* 288 (M^+ , 0.49), 274 ($\text{M}^+ - \text{BH}_3$, 100), 259 (9.96), 231 (34.54), 190 (8.15), 163 (9.80), 136 (12.91), 109 (16.19), 77 (6.33), 65 (3.89), 43 (22.82). HRMS: calcd for $\text{C}_{18}\text{H}_{27}\text{P}$ 274.1850, ($\text{M}^+ - \text{BH}_3$), found 274.1855.

(1*R*,2*S*,4*R*,5*S*)-(+)-2,5-Dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]heptane (7). To a solution of the corresponding borane complex of the phosphine (**5**, 1.0 g, 4.31 mmol) in CH_2Cl_2 (22 mL) was added tetrafluoroboric acid-dimethyl ether complex (2.63 mL, 21.6 mmol) dropwise via a syringe at -5°C . After the addition, the reaction mixture was allowed to warm up slowly and stirred at rt. After 20 h, $^{31}\text{P NMR}$ showed the reaction was over, and it was diluted by CH_2Cl_2 and neutralized by a saturated NaHCO_3 aqueous solution. The aqueous layer was extracted with CH_2Cl_2 . The combined organic solution was

washed with brine, followed by water, and then dried over Na_2SO_4 . Evaporation of the solvent gave a pure phosphine product, which was confirmed by NMR. Yield: 0.9 g (96%). $[\alpha]_D^{25} = +92.5^{\circ}$ (*c* 2.3, toluene). $^1\text{H NMR}$ (CDCl_3 , 360 MHz): δ 7.38–7.34 (m, 2H), 7.26–7.21 (m, 2H), 7.19–7.16 (m, 1H), 2.60–2.54 (m, 2H), 1.89–1.62 (m, 5H), 1.44–1.42 (m, 1H), 1.16 (d, $J = 6.12$ Hz, 3H), 0.55 (d, $J = 6.95$ Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3): δ 138.7 (d, $J = 29.3$ Hz), 131.4 (d, $J = 13.0$ Hz), 127.9 (d, $J = 2.35$ Hz), 126.6 (s), 47.3 (d, $J = 13.5$ Hz), 45.3 (d, $J = 10.2$ Hz), 39.2 (d, $J = 6.7$ Hz), 39.2 (d, $J = 5.3$ Hz), 38.7 (d, $J = 6.7$ Hz), 34.7 (d, $J = 17.2$ Hz), 22.4 (d, $J = 7.8$ Hz), 21.5 (s). $^{31}\text{P NMR}$ (CDCl_3): δ -7.29.

(1*R*,2*R*,4*R*,5*R*)-(+)-2,5-Diisopropyl-7-phenyl-7-phosphabicyclo[2.2.1]heptane (8). The same procedure as in the preparation of **7** was used. Yield: 1.0 g (95.5%). $[\alpha]_D^{25} = +43.9^{\circ}$ (*c* 1.2, toluene). $^1\text{H NMR}$ (CDCl_3 , 360 MHz): δ 7.35–7.30 (m, 2H), 7.24–7.14 (m, 3H), 2.94–2.85 (m, 2H), 1.76–1.53 (m, 5H), 1.25–1.14 (m, 2H), 1.06 (d, $J = 7.77$ Hz, 3H), 0.95–0.80 (m, 1H), 0.87 (dd, $J = 3.77$ Hz, 7.89 Hz, 6 H), 0.49 (d, $J = 9.30$ Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3): δ 138.8 (d, $J = 30.49$ Hz), 130.7 (d, $J = 12.2$ Hz), 127.7 (d, $J = 2.87$ Hz), 126.5 (s), 53.4 (d, $J = 6.34$ Hz), 48.6 (d, $J = 17.06$ Hz), 42.0 (d, $J = 13.43$ Hz), 40.5 (d, $J = 9.96$ Hz), 37.6 (d, $J = 11.09$ Hz), 37.4 (d, $J = 9.74$ Hz), 33.0 (d, $J = 6.11$ Hz), 31.9 (s), 21.9 (s), 21.8 (s), 21.2 (s), 20.4 (s). $^{31}\text{P NMR}$ (CDCl_3): δ -7.49.

Enantioselective Allylic Alkylation. The procedures are exemplified by the experiments carried out with ligand **7** in toluene. To a stirring solution of $[\text{Pd}_2(\eta^3\text{-C}_3\text{H}_5)_2\text{Cl}_2]$ (3.0 mg, 0.008 mmol) in toluene (1.5 mL) was added ligand **7** (0.36 mL of 0.1 M solution in toluene, 0.036 mmol) under a nitrogen atmosphere. After 30 min, racemic 1,3-diphenyl-1-acetoxypropene (150 mg, 0.60 mmol) was added. Then the solution was allowed to be stirred for 30 min. *N,O*-Bis(trimethylsilyl)acetamide (0.44 mL, 1.8 mmol), dimethyl malonate (0.21 mL, 1.8 mmol), and potassium acetate (3 mg, 0.03 mmol) were added in this order. The reaction was monitored by TLC (eluent: hexane/ethyl acetate = 10/1). After 1.5 h, TLC showed the reaction was over. After the solvent was evaporated in vacuo, column chromatography on silica gel (eluent: hexane/ethyl acetate = 10/1) of the residue yielded the pure product: yield 190 mg, 97.7%. The optical purity was determined to be 95.5% ee by HPLC (Daicel Chiralcel OD column, 1 mL/min, hexane/2-propanol = 99/1).

Acknowledgment. This work was supported by a Camille and Henry Dreyfus New Faculty Award, an ONR young investigator award, a DuPont Young Faculty Award, and Hoechst Celanese Corporation. We acknowledge a generous loan of precious metals from Johnson Matthey Inc. We thank Supelco for the gift of a β -DEX GC column.

Supporting Information Available: $^1\text{H NMR}$, $^{13}\text{C NMR}$, and $^{31}\text{P NMR}$ spectra for compounds **5–8** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS; see any current masthead page for ordering information.

JO9623548