A Novel Chiral Phosphino−Phosphaferrocene: Its Coordination Behavior and Application to Palladium-Catalyzed Asymmetric Allylic Alkylation

Masamichi Ogasawara, Kazuhiro Yoshida, and Tamio Hayashi*

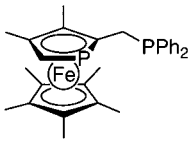
Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan

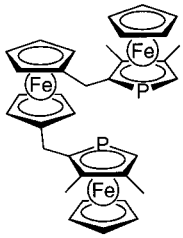
Received May 24, 2001

The synthesis of a novel chiral phosphino−phosphaferrocene ligand is described. The ligand possesses two electronically distinctive donor moieties and behaves either as a monodentate (with a free phosphaferrocene) or a bidentate ligand depending on stoichiometry with a coordinating transition-metal center. In the palladium-catalyzed asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate, a clear correlation was observed between the enantioselectivity of the reaction and a Pd/phosphino−phosphaferrocene molar ratio. With a deficient amount (to the Pd) of the chiral ligand, the highest enantioselectivity (99% ee) was achieved.

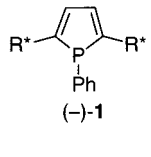
Introduction

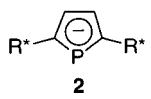
The design of chiral ligands has been a central subject in the development of asymmetric reactions. Recently, Ganter[1] and Fu[2] have reported several chiral phosphaferrocenes. Their chirality is based on the phosphaferrocene planar chirality, and enantiomerically pure samples were obtained by resolution of the corresponding racemates. Some of these new classes of chiral ligands (two representative examples are shown below) have been successfully applied to transition-metal-catalyzed symmetric reactions and have demonstrated their potential usefulness.[1,2]

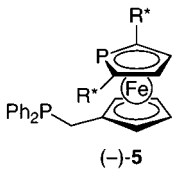


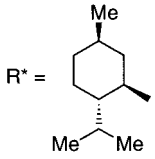


We have recently reported on preparation of the chiral phosphole (−)-**1**.[3] This phosphole is the first example of an enantiomerically pure chiral phosphole in which chiral substituents attach directly to the carbon atoms of the phosphole ring. The phosphole was readily transformed into the corresponding chiral and enantiomerically pure phospholyl anion **2**, from which the novel phosphino−phosphaferrocene (−)-**5** was prepared. The basic framework of our chiral phosphaferrocene (−)-**5** is different from that of the planar chiral phosphaferrocenes of Ganter and Fu, and (−)-**5** is obtained in an enantiomerically pure form without resolution. Phosphaferrocenes are electronically quite different from classical tertiary phosphines in that they have a weak σ-donating and strong π-accepting character.[4] Thus, the phosphino−phosphaferrocene **5** possesses two distinctive ligating moieties, showing two different coordination modes depending on the stoichiometry with a metal.









Here we wish to report on the new chiral phosphino−phosphaferrocene (−)-**5**: its preparation, coordination behavior, and application to the palladium-catalyzed asymmetric allylic alkylation[5] where the enantioselectivity is clearly related to the coordination behavior.

Results

Preparation and Characterization of a Chiral Phosphino−Phosphaferrocene. The chiral phosphi-

(1) (a) Ganter, C.; Brassat, L.; Ganter, B. *Tetrahedron: Asymmetry* **1997**, *8*, 2607. (b) Ganter, C.; Brassat, L.; Ganter, B. *Chem. Ber./Recl.* **1997**, *130*, 1771. (c) Ganter, C.; Brassat, L.; Glinsböckel, C.; Ganter, B. *Organometallics* **1997**, *16*, 2862. (d) Ganter, C.; Glinsböckel, C.; Ganter, B. *Eur. J. Inorg. Chem.* **1998**, 1163. (e) Ganter, C.; Kaulen, C.; Englert, U. *Organometallics* **1999**, *18*, 5444.

(2) (a) Qiao, S.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 4168. (b) Qiao, S.; Hoic, D. A.; Fu, G. C. *Organometallics* **1998**, *17*, 773. (c) Shintani, R.; Lo, M. M.-C.; Fu, G. C. *Org. Lett.* **2000**, *2*, 3695. (d) Tanaka, K.; Qiao, S.; Tobisu, M.; Lo, M. M.-C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 9870.

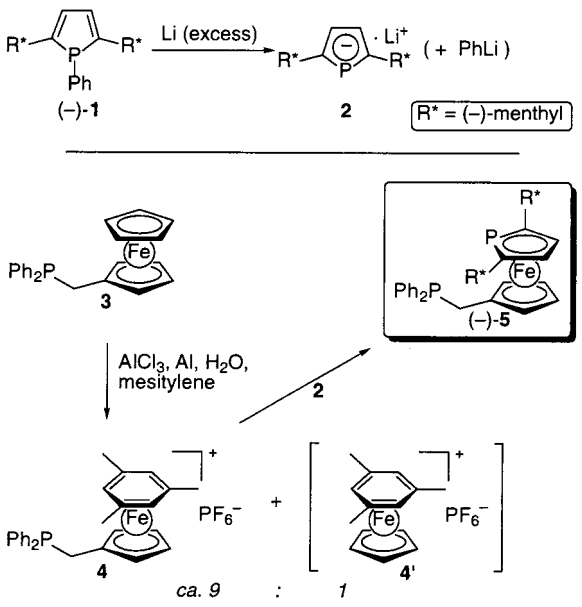
(3) Ogasawara, M.; Yoshida, K.; Hayashi, T. *Organometallics* **2001**, *20*, 1014.

(4) (a) Fischer, J.; Mitschler, A. Ricard, L.; Mathey, F. *J. Chem. Soc., Dalton Trans.* **1980**, 2522. (b) Mathey, F.; Fischer, J.; Nelson, J. H. *Struct. Bonding* **1983**, *55*, 153. (c) Mathey, F. *J. Organomet. Chem.* **1990**, *400*, 149. (d) Mathey, F. *Coord. Chem. Rev.* **1994**, *137*, 1.

(5) (a) Consiglio, G.; Waymouth, R. M. *Chem. Rev.* **1989**, *89*, 257. (b) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089. (c) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (d) Pfaltz, A.; Lautens, M. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; Vol. II, p 833. (e) Trost, B. M.; Lee, C. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: Weinheim, Germany, 2000; p 593.

10.1021/om010440e CCC: $20.00
Publication on Web 08/09/2001

Scheme 1. Synthesis of the Chiral Phosphino−Phosphaferrocene (−)-5



no−phosphaferrocene **5** was prepared by a reaction sequence outlined in Scheme 1. Treatment of (ferrocenylmethyl)diphenylphosphine (**3**)[6] with a mixture of Al/$AlCl_3$/mesitylene in cyclohexane in the presence of a stoichiometric amount of H_2O removed one of the two η^5-cyclopentadienyl ligands to give an 82% yield of a mixture of cationic mesitylene complexes **4** and **4′** in a ratio of 9:1.[7] The preferential formation of the phosphino complex **4** indicates that the unsubstituted η^5-cyclopentadienyl ligand in **3** was more labile than that substituted with the (diphenylphosphino)methyl group. The mixture of **4** and **4′** was used for the next step without separating the two species. The mixture of the cationic complexes was allowed to react with the chiral lithium phospholide **2**, which was generated in situ from (−)-**1** and lithium metal.[8] Subsequent purification by column chromatography over silica gel gave the phosphino−phosphaferrocene (−)-**5** in 31% yield as a highly viscous orange oil.

Because the C_2 symmetry of **2** is lost when it is incorporated into the phosphaferrocene (−)-**5**, the ligand has no symmetry elements. The four H−C_5 hydrogens in η^5-$C_5H_4CH_2PPh_2$ are inequivalent to one another and give four resonances in the ^{1}H NMR spectrum. Analogously, the two β-hydrogens in the phosphacyclopentadienyl ligand in (−)-**5** are diastereotopic and are detected as two clearly separated ^{1}H NMR resonances. The ^{31}P NMR spectrum of (−)-**5** shows two signals at δ −11.1 and −63.4, which are assigned to the $-PPh_2$ and the phospholyl, respectively (Figure 1). No coupling is detected between the two ^{31}P signals.

Coordination Behavior of the Phosphino−Phosphaferrocene. Reactions of (−)-**5** with $PdCl_2$(cod) (**6**) in CD_2Cl_2 were examined in various (−)-**5**:**6** molar ratios. The coordination behavior of (−)-**5** was monitored by ^{31}P{^{1}H} NMR (Figure 1). Treatment of (−)-**5** with an equimolar or a slight excess of **6** completely consumed the phosphino−phosphaferrocene to give the new

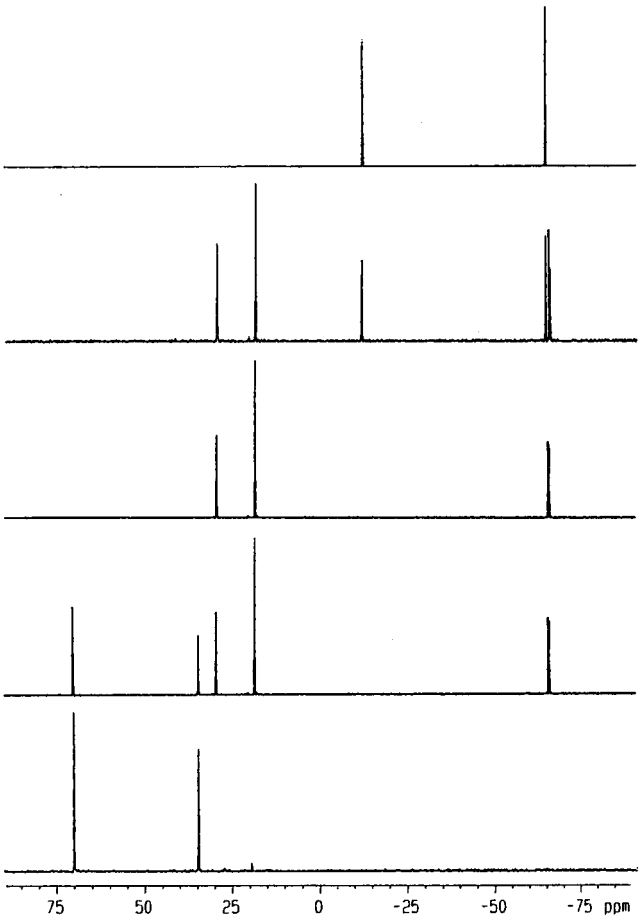
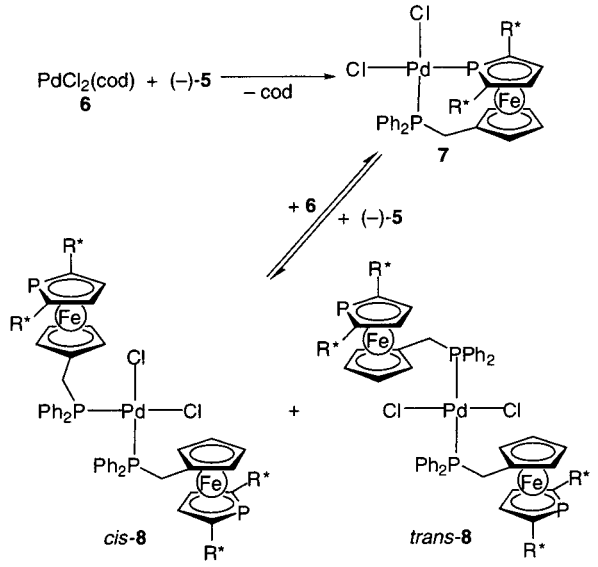


Figure 1. ^{31}P NMR spectra of reaction mixtures of (−)-**5** and **6** with varied molar ratios (from top to bottom, (−)-**5**/**6** = 1/0, 3/1, 2/1, 1.5/1, and 1/1) recorded at 202 MHz in CD_2Cl_2.

Scheme 2. Coordination Behavior of (−)-5 toward Pd(II)

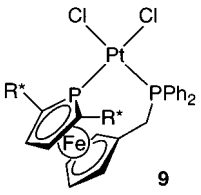


Pd complex $PdCl_2$[(−)-**5**] (**7**) cleanly (Scheme 2). The two ^{31}P NMR resonances of **7**, detected at δ 35.0 ($-PPh_2$) and δ 70.0 (phosphaferrocene), were coupled with each other with a small coupling constant ($^2J_{PP}$ = 9.1 Hz). This indicates the coordination of (−)-**5** in a cis fashion. When a slight excess of (−)-**5** (1.5 equiv with respect to **6**) was used, no free ligand was detected and two new

(6) Marr, G.; White, T. M. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1995.
(7) Astruc, D. *Tetrahedron* **1983**, *39*, 4027.
(8) Robert, R. M. G.; Wells, A. S. *Inorg. Chim. Acta* **1986**, *112*, 171.

palladium species emerged in addition to **7**. The two new species were generated in a ca. 55:45 molar ratio at 20 °C, and each of them showed a pair of singlet resonances in the ^{31}P NMR spectrum (δ −64.1 and 19.0 for the major isomer; δ −64.6 and 29.9 for the minor isomer). The NMR analyses revealed that the two new species are *cis*- and *trans*-$PdCl_2$[(−)-**5**]$_2$ (*cis*- and *trans*-**8**), in which (−)-**5** coordinates with the PPh_2 moiety as a monodentate ligand. The major and minor isomers were assigned to *trans*-**8** and *cis*-**8**, respectively, by comparison of the ^{31}P NMR chemical shifts of the coordinating PPh_2 moieties.[9] As expected, the two new species were generated cleanly from the reaction of (−)-**5** with **6** in a 2:1 molar ratio. With a large excess of (−)-**5** (>2 equiv with respect to **6**), unreacted (−)-**5** was observed in addition to *cis*- and *trans*-**8**, and no **7** was detected. All these processes are reversible, and addition of **6** to the mixture of *cis*- and *trans*-**8** regenerates **7** quantitatively.

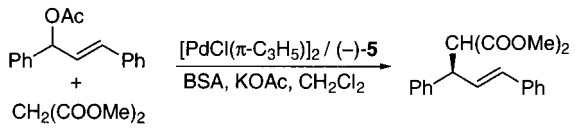
The coordination behavior of (−)-**5** toward palladium(II), a tendency to be a monodentate ligand rather than a chelating ligand in the presence of an extra amount of the ligand, indicates that coordination of the phosphaferrocene moiety is weaker than that of the PPh_2 moiety. The ^{31}P NMR measurement of the closely related platinum(II) complex $PtCl_2$[(−)-**5**] (**9**), which was prepared from $PtCl_2$(cod) and (−)-**5** in dichloromethane, confirmed the difference in their coordination abilities. In the ^{31}P NMR spectrum of **9**, two resonances were detected at δ 10.1 and 49.4 with a small $^2J_{PP}$ coupling of 15.5 Hz, and they were assigned to the $-PPh_2$ and the phospholyl, respectively. The two signals were accompanied by ^{195}Pt−^{31}P satellite signals, and the $^1J_{PtP}$ coupling constants were 4183 Hz for the $-PPh_2$ signal and 3586 Hz for the phospholyl signal. The observation demonstrates that the Pt−PPh_2 bond is shorter than the Pt−phospholyl bond: i.e., the former is stronger than the latter.[10] Because both PPh_2 and the phospholyl moieties have identical ligands (chlorides) at their trans positions in the complex **9**, the relative Pt−P bond length (bond strength) between the two in **9** should directly correlate with the relative coordination abilityies of the two phosphorus moieties in (−)-**5**.



9

Application of (−)-5 to Palladium-Catalyzed Allylic Alkylation. The potential of (−)-**5** as a chiral ligand in asymmetric synthesis was explored for the palladium-catalyzed enantioselective allylic alkylation.[5] It was found that a palladium complex generated in situ from [PdCl(π-C_3H_5)]$_2$ and (−)-**5** is an effective catalyst for asymmetric allylic alkylation of racemic 1,3-diphenyl-2-propenyl acetate with dimethyl malonate in the presence of BSA (Table 1).[11] The reaction at 20 °C was completed in 24 h to give a quantitative yield of the alkylation product. The enantioselectivity of the reaction was sensitive to stoichiometry between palladium and the chiral ligand (−)-**5**. The product with 97% ee was obtained from 1.5 equiv (with respect to Pd monomer) of (−)-**5** (entry 1). The absolute configuration of the product was determined to be *R* on the basis of the sign of the specific rotation.[12] The enantioselectivity decreased as the (−)-**5**/Pd ratio increased. The ee value in the product was diminished to 91% with 3 equiv of the ligand (entry 3) and to 77% with a large excess (8 equiv) of (−)-**5** (entry 5). On the other hand, a deficient amount of (−)-**5** ((−)-**5**/Pd = 0.75) enhanced the selectivity to 98% ee (entry 6). Although lowering the temperature to −20 °C slowed the reaction, the enantioselectivity was further improved to 99% ee and the product was obtained in 99% yield in 96 h (entry 7). This enantioselectivity is one of the highest values reported to date for the reaction.

Table 1. Asymmetric Allylic Alkylation of *rac*-1,3-Diphenyl-2-propenyl Acetate Catalyzed by a Palladium/(−)-5 Complex



entry	(−)-**5**/Pd[a] (mol/mol)	temp (°C)	time (h)	yield[b] (%)	% ee[c] (config[d])
1	1.5/1	20	24	97	97 (*R*)
2	2/1	20	24	99	97 (*R*)
3	3/1	20	24	99	91 (*R*)
4	4/1	20	24	97	87 (*R*)
5	8/1	20	24	99	77 (*R*)
6	0.75/1	20	24	97	98 (*R*)
7	0.75/1	−20	96	99	99 (*R*)

[a] A relative molar ratio between (−)-**5** and palladium (as a monomer). [b] Isolated yield by silica gel chromatography. [c] Determined by HPLC analyses with a chiral stationary phase column (Daicel Chiralcel OD-H, 98/2 hexane/2-propanol). [d] Determined on the basis of the sign of the specific rotation of the product.[15]

Discussion

When the phosphino−phosphaferrocene (−)-**5** is applied to the palladium-catalyzed allylic alkylation as a chiral ligand, the phosphaferrocene part in (−)-**5** is responsible for constructing an effective chiral environment at the palladium center of the catalyst. At the monodentate coordination of (−)-**5**, the phosphaferrocene moiety is apart from the metal center, and thus high enantioselectivity is not expected for the catalyst with the monodentate (−)-**5** (Figure 2). The correlation between the (−)-**5**/Pd molar ratio and the enantioselectivity in the Pd-catalyzed allylic alkylation can be explained by competitive catalysis of several palladium species with the different coordination modes of (−)-**5**. With the deficient amount of the ligand, the monodentate coordination of (−)-**5** could be effectively eliminated, and all of the ligand coordinates to the palladium in a bidentate manner. Since the remaining palladium precursor [PdCl(π-C_3H_5)]$_2$ is not an effective catalyst of the

(9) Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1975**, *14*, 50.
(10) Mather, G. G.; Pidcock, A.; Rapsey, G. J. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2095.
(11) Trost, B. M.; Brickner, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 568.
(12) (a) Hayashi, T.; Yamamoto, A.; Hagihara, T.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 191. (b) Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301.

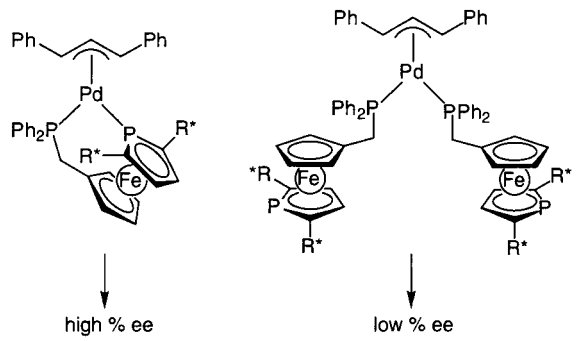


Figure 2. Two catalytically active species.

allylic alkylation, the highest ee value was obtained with an excellent chemical yield.

Concluding Remarks

The novel chiral phosphino−phosphaferrocene (−)-**5** was prepared from the chiral phosphole (−)-**1**. Because of the different electronic characteristics between the two donor moieties in (−)-**5**, it behaves either as a monodentate or a bidentate ligand. The two coordination modes of (−)-**5** can be controlled by adjusting a (−)-**5**/transition-metal molar ratio. The new chiral ligand was applied to the enantioselective palladium-catalyzed allylic alkylation, and the very high enantioselectivity (99% ee) was achieved under the conditions where the bidentate coordination of (−)-**5** was dominant.

Experimental Section

General Considerations. All anaerobic and/or moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. Tetrahydrofuran, Et_2O, and 1,4-dioxane were distilled from benzophenone−ketyl under nitrogen prior to use. Dichloromethane was distilled from CaH_2 under nitrogen prior to use. EtOH was dried over magnesium ethoxide, distilled, and stored in a glass flask with a Teflon stopcock under nitrogen. CD_2Cl_2 and $CDCl_3$ were dried over P_2O_5, vacuum-distilled, and stored in the glovebox. Ferrocenylmethanol was prepared from formylferrocene and $LiAlH_4$. Racemic 1,3-diphenyl-2-propenyl acetate was obtained from the corresponding alcohol and acetic anhydride. The chiral phosphole **1**,[3] Ph_2PH,[13] $PdCl_2$(cod),[14] $PtCl_2$(cod),[15] and [PdCl(π-C_3H_5)]$_2$[16] were prepared as reported. Aluminum powder, NH_4PF_6, KOAc, *N*,*O*-bis(trimethylsilyl)acetamide, and dimethyl malonate were purchased from Wako Pure Chemical Industries and used as received. Oxalyl chloride and lithium metal were purchased from Aldrich Chemical Co. and used as received. DMF, aluminum chloride, mesitylene, and cyclohexane were purchased from Nacalai Tesque and used as received. The reaction progress was monitored by analytical thin-layer chromatography (TLC) using 0.25 mm Merck F-254 silica gel glass plates. Visualization of the TLC plates was achieved by UV illumination. NMR spectra were recorded on a JEOL JNM LA500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{31}P, 202 MHz). ^{1}H and ^{13}C chemical shifts are reported in ppm downfield of internal tetramethylsilane. ^{31}P NMR chemical shifts are externally referenced to 85% H_3PO_4. Optical rotations were measured on a JASCO DIP-370 polarimeter.

((Diphenylphosphino)methyl)ferrocene (3). Oxalyl chloride (56.7 mL, 650 mmol) was added dropwise to a solution of ferrocenylmethanol (8.85 g, 41.0 mmol) in THF (320 mL) containing a catalytic amount of DMF (0.56 mL) at −20 °C. After gas evolution had ceased, the reaction mixture was concentrated under reduced pressure. The residual solid was dissolved in THF and filtered through a pad of Celite. The filtrate was cooled to −78 °C, and to this was added dropwise $KPPh_2$ solution, which was prepared from diphenylphosphine (17.1 mL, 98.4 mmol) and potassium hydride (3.98 g, 98.4 mmol) in THF (200 mL) at 0 °C. After the addition, the solution was warmed to room temperature and stirred overnight. The mixture was quenched with water and evaporated to dryness under reduced pressure. The residue was extracted with CH_2Cl_2 under nitrogen. The crude material was prepurified by silica gel column chromatography (benzene as an eluent) under nitrogen. The pure product was obtained by a second silica gel column chromatography (elution with 3/1 hexane/benzene) under nitrogen. Yield: 11.2 g (29.2 mmol, 71%). This product is characterized by comparison of the spectroscopic data with those reported previously.[6]

(η^6-Mesitylene)[η^5-((diphenylphosphino)methyl)cyclopentadienyl]iron(II) Hexafluorophosphate (4). Aluminum chloride (5.87 g, 44.0 mmol), aluminum powder (0.30 g, 11.0 mmol), **3** (4.23 g, 11.0 mmol), 1,3,5-mesitylene (5.78 mL, 41.5 mmol), and water (0.20 mL, 11.0 mmol) were refluxed in cyclohexane (30 mL) for 5 h. The mixture was cooled to 0 °C and quenched with cold water (40 mL). The aqueous layer was separated, filtered, and washed with ether. Excess NH_4PF_6 solution was added, and the resulting yellow solid was collected on a filter and washed with cold water. The solid was dried, washed with ether, and recrystallized from CH_2Cl_2/ether to give the title compound with ca. 10% of inseparable byproduct, which was (η^6-mesitylene)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate (**4′**).[17] Yield: 5.09 g (ca. 74% of **4** and 8% of **4′**). ^{1}H NMR (acetone-d_6): δ 2.46 (s, 9H), 3.35 (s, 2H), 4.56 (t, J = 2.0 Hz, 2H), 4.83 (t, J = 2.0 Hz, 2H), 6.15 (s, 3H), 7.30−7.39 (m, 10H). ^{31}P{^{1}H} NMR (acetone-d_6): δ −7.40 (s), 69.7 (m).

1′-((Diphenylphosphino)methyl)-2,5-bis[(−)-menthyl]-1-phosphaferrocene (5). Lithium metal (125 mg, 18.0 mmol) was added to a solution of **1** (786 mg, 1.80 mmol) in THF (30 mL) at room temperature. The mixture was stirred until disappearance of **1** (checked by TLC). The solvent was removed in vacuo, and the residue was dissolved in 1,4-dioxane (30 mL). The mixture was added to a solution of **4** (2.24 g, ca. 90% purity, ca. 3.60 mmol) in 1,4-dioxane (60 mL) at 100 °C. The resulting mixture was stirred for 2 h at this temperature. After this mixture was cooled, ca. 60 mL of benzene was added and the solution was filtered through a pad of Celite. The mixture was evaporated to dryness under reduced pressure, and the crude product was chromatographed on silica gel (elution with 4/1 hexane/benzene) under nitrogen. Yield: 376 mg (0.554 mmol, 31%). ^{1}H NMR ($CDCl_3$): δ 0.68−1.09 (m, 26H), 1.32−1.39 (m, 2H), 1.58−1.62 (m, 2H), 1.70−1.75 (m, 3H), 1.78−1.91 (m, 4H), 2.01 (dq, J = 12.8 and 2.2 Hz, 1H), 3.23 (unresolved q, 2H), 3.77 (m, 1H), 3.87 (m, 1H), 4.10−4.11 (m, 1H), 4.31−4.32 (m, 1H), 4.78 (dd, J_{PH} = 4.9 Hz and J_{HH} = 2.9 Hz, 1H), 4.81 (dd, J_{PH} = 5.6 Hz and J_{HH} = 2.9 Hz, 1H), 7.31−7.34 (m, 6H), 7.36−7.42 (m, 4H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −63.4 (s), −11.1 (s). $[\alpha]^{20}_D$ = −142 (*c* 1.00, $CHCl_3$). Anal. Calcd for $C_{42}H_{56}FeP_2$: C, 74.33; H, 8.32. Found: C, 74.21; H, 8.41.

Dichloro[1′-((diphenylphosphino)methyl)-2,5-bis[(−)-menthyl]-1-phosphaferrocene]platinum (9). An equimolar mixture of $PtCl_2$(cod) and (−)-**5** in dichloromethane was stirred for 1 h at room temperature, and then all the volatiles were

(13) Bourumeau, K.; Gaumont, A. C.; Denis, J. M. *J. Organomet. Chem.* **1997**, *529*, 205.
(14) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1972**, *13*, 52.
(15) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.
(16) Tatsuno, A.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 220.
(17) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1968**, 2257.

removed under reduced pressure. The yellow residue was dissolved in a minimum amount of CH_2Cl_2. Recrystallization by slow diffusion of acetone into the CH_2Cl_2 solution at room temperature gave the title complex quantitatively as a yellow solid. ^{1}H NMR ($CDCl_3$): δ 0.56 (q, J = 12.2 Hz, 1H), 0.64 (d, J = 6.5 Hz, 3H), 0.71−0.75 (m, 8H), 0.85−0.99 (m, 10H), 1.12−1.22 (m, 4H), 1.43 (br, 1H), 1.62−1.75 (m, 7H), 1.82−1.97 (m, 3H), 2.22 (q, J = 11.8 Hz, 1H), 2.65−2.72 (m, 1H), 2.99 (dd, J = 16.1 and 10.3 Hz, 1H), 3.25 (s, 1H), 3.89 (s, 1H), 4.10 (s, 1H), 4.49 (s, 1H), 4,84 (br, 1H), 4.88 (br, 1H), 7.41 (br, 3H), 7.47−7.51 (m, 2H), 7.60−7.66 (m, 3H), 8.22−8.25 (m, 2H). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 10.1 ($^1J_{Pt-PPh_2}$ = 4183 Hz, $^2J_{PP}$ = 15.5 Hz), 49.4 ($^1J_{Pt-phospholyl}$ = 3583 Hz, $^2J_{PP}$ = 15.5 Hz). $[\alpha]^{20}_D$ = −43.6 (*c* 0.570, $CHCl_3$). Mp: >300 °C. Anal. Calcd for $C_{42}H_{56}Cl_2FeP_2Pt$: C, 53.40; H, 5.98. Found: C, 52.95; H, 5.98.

Pd-Catalyzed Allylic Alkylations. A typical procedure is given for the reaction of entry 7 in Table 1. To a mixture of [PdCl(π-C_3H_5)]$_2$ (4.3 mg, 11.7 μmol), (−)-**5** (11.9 mg, 17.5 μmol), KOAc (2.0 mg, 20 μmol), and *rac*-1,3-diphenyl-2-propenyl acetate (82.2 mg, 326 μmol) in CH_2Cl_2 (2.0 mL) was added a solution of *N*,*O*-bis(trimethylsilyl)acetamide (260 μL, 1.05 mmol), and dimethyl malonate (120 μL, 1.05 mmol) in CH_2Cl_2 (1.7 mL) at −78 °C under nitrogen. The flask was immersed in a bath maintained at −20 °C, and the solution was stirred for 96 h. The reaction mixture was quenched with a small amount of saturated NH_4Cl aqueous solution. The mixture was extracted with CH_2Cl_2 three times, and the combined organic layer was dried over $MgSO_4$. After evaporation, the crude product was purified by preparative TLC on silica gel (eluent 3/1 hexane/EtOAc) to give the alkylated product in pure form. Yield: 128 mg (325 μmol, 99%). The enantiomeric purity was determined to be 99% ee by HPLC analysis with a chiral stationary phase column, Chiralcel OD-H (98/2 hexane/2-propanol).

Acknowledgment. This work was supported by the "Research for the Future" Program (the Japan Society for the Promotion of Science), a Grant-in-Aid for Scientific Research (the Ministry of Education of Japan), and the Mitsubishi Chemical Corporation Fund (to M.O.). K.Y. thanks the Japan Society for the Promotion of Science for the award of a fellowship for graduate students.

OM010440E