C_2-Symmetric Diphosphine Ligands with Only the Planar Chirality of Ferrocene for the Palladium-Catalyzed Asymmetric Allylic Alkylation

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Novel C_2-symmetric diphosphine ligands possessing only the planar chirality of ferrocene, 1,1′-bis(diphenylphosphino)-2,2′-disubstituted-ferrocenes, were prepared from 1,1′-bis(diphenylphosphino)-2,2′-bis(oxazolinyl)ferrocene by the transformation of the oxazoline moieties in the molecule. Upon complexation with palladium(II), ligands of this kind were ascertained to form only one of the two possible diastereomeric 1:1 P,P-chelating palladium complexes by ^{1}H NMR spectroscopy using NOE. These ligands afforded excellent enantioselectivity for the palladium-catalyzed allylic alkylation of 1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate. The substituents at the 2,2′-positions of the Cp rings of the ligands had considerable effect on the catalytic activity but minor effect on the enantioselectivity. These ligands also afforded excellent catalytic activity and good enantioselectivity for the allylic alkylation of the less sterically hindered substrate, cyclohex-2-en-1-yl acetate, with dimethyl malonate. It has been shown that the C_2-symmetric ferrocene ligands with only the planar chirality can produce an excellent chiral environment for metal-catalyzed asymmetric reactions.

Introduction

Chiral diphosphines have been proved to be among the most useful and versatile ligands for metal-catalyzed asymmetric reactions, and the design and preparation of such diphosphines remain as active an area of research as ever.[1] Meanwhile, the planar chirality of ferrocene has received intensive attention, and many kinds of planar chiral ferrocene ligands have been developed recently.[2−4] However, most of the ferrocene ligands also possess central chirality besides the planar chirality, and no efficient ferrocene ligands with only the planar chirality have been developed so far. Moreover, C_2-symmetric chiral ferrocene ligands have recently gained some attention,[3,4] but there has been no report on C_2-symmetric ferrocene ligands with only planar chirality until now.[5] As a part of our studies on the development of novel oxazoline ligands with multistereogenic centers,[4,6] we recently reported a simple preparation of novel C_2-symmetric ferrocene diphosphine ligands, 1,1′-bis(diphenylphosphino)-2,2′-bis(oxazolinyl)ferrocenes **1** (Chart 1), via highly diastereoselective *ortho*-lithiation of the corresponding bis(oxazolinyl)ferrocenes.[4a] However, ligands of this kind also possess the central chirality at the oxazoline rings along with the planar chirality of ferrocene and did not form the expected P,P-chelating complex with dichlorobis(acetonitrile)palladium, although

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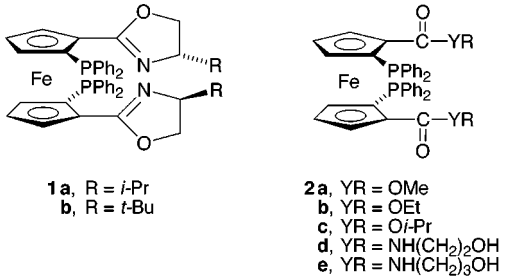
Chart 1



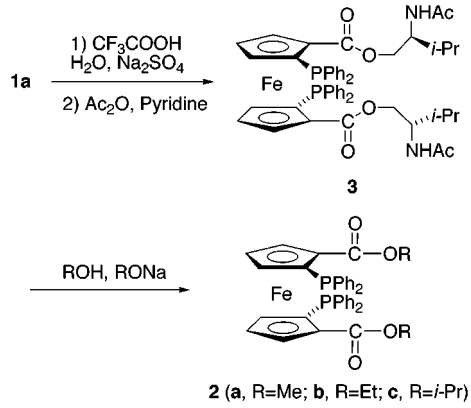
1a, R = *i*-Pr
b, R = *t*-Bu

2a, YR = OMe
b, YR = OEt
c, YR = O*i*-Pr
d, YR = $NH(CH_2)_2OH$
e, YR = $NH(CH_2)_3OH$

they showed excellent enantioselectivity for the palladium-catalyzed allylic alkylation.[4b] In this paper, we report the preparation of C_2-symmetric P,P-chelating ligands with only the planar chirality of ferrocene **2a**−**e** (Chart 1) and their application in asymmetric reactions.[7]

Palladium-catalyzed asymmetric C−C bond forming reactions with allylic compounds have been investigated with great intensity.[8] Particularly, the palladium-catalyzed allylic alkylation of 1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate has received considerable attention,[8−10] and excellent enantioselectivities have been documented with N,N- and P,N-chelating ligands.[9] However, few P,P-chelating ligands, especially with C_2-symmetry, gave excellent results.[10] Compared to 1,3-diphenylprop-2-en-1-yl acetate, the less sterically hindered substrates, pent-3-en-2-yl acetate[11] and cyclohex-2-en-1-yl acetate,[12] have received little attention, and few chiral ligands gave excellent results for these substrates. With novel C_2-symmetric planar chiral P,P-chelating ligands **2** in hand, we carried out these reactions and examined the effects of the sole planar chirality and the substituents at the 2,2′-positions of the Cp rings on the enantioselectivity and the catalytic activity.

Scheme 1



2 (**a**, R=Me; **b**, R=Et; **c**, R=*i*-Pr)

Results and Discussion

Ligands **2a**−**c** can be easily prepared from **1a**[4a] by the transformation of the oxazoline moieties in the molecule by Meyer's method (Scheme 1).[13] Thus, treatment of **1a** with trifluoroacetic acid in aqueous THF caused ring-opening of the oxazoline moiety to give an unstable ammonium salt. This ammonium salt was acetylated, without isolation, with acetic anhydride in the presence of pyridine to give ester amide **3** in 61% yield. Transesterification of **3** using methanolic sodium methoxide at room temperature for 1 day gave ligand **2a** in 74% yield. Ligands **2b**,**c** were also prepared from **3** by a similar procedure, but in lower yields due to the lower reactivities of sodium ethoxide and sodium isopropoxide than that of sodium methoxide.

It has been reported that the hydroxyl group in several P,P-chelating ligands have some effect on the enantioselectivity.[14] With this idea in mind, we designed diphosphine ligands **2d** and **2e**, each of which possesses two hydroxyl groups in the molecule.

In our previous paper on the preparation of novel bisoxazoline ligands bearing a 1,3-dioxolane backbone, we reported that *N*-(2-hydroxy-1-substituted-ethyl)amide intermediates can be prepared equivalently with ease by heating 4,5-dicarbonyl-1,3-dioxolane dimethyl ester with the corresponding chiral 2-amino alcohol in neat at 100 °C for 1 h.[6a] However, **2d** and **2e** could not be obtained by the same method even by heating methyl ester **2a** with 2-aminoethanol or 3-aminopropanol at 120 °C for 2 days.

However, we found that heating **2a** with 2-aminoethanol or 3-aminopropanol in neat in the presence of a small amount of sodium at 100 °C for 30 min afforded **2d** and **2e**, respectively, in good yields (Scheme 2).

Next, the complexation behavior of ligand **2a** with palladium dichloride was examined. Because of the

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Scheme 2

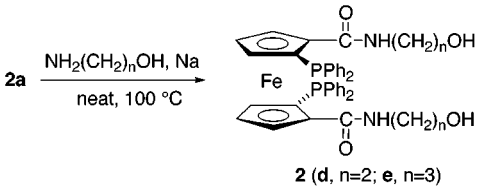
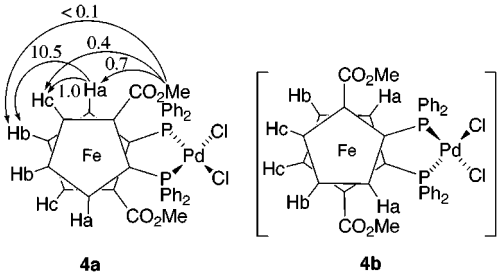


Chart 2. Determination of Complex Structure by NOE (%)



opposite twists of the two Cp rings of the ferrocene backbone, **2a** would give two possible diastereomeric complexes, **4a** and **4b**, upon complexation with palladium dichloride (Chart 2). However, the formation of only one kind of C_2-symmetric 1:1 P,P-chelating complex was found in ^{1}H NMR upon mixing **2a** with 1 equiv of dichlorobis(acetonitrile)palladium(II) in acetonitrile-d_3. Treating **2a** with 1 equiv of dichlorobis(acetonitrile)-palladium(II) in benzene for 1 h followed by filtration gave the complex as a yellow solid in 97% yield. Recrystallization of the complex from dichloromethane−hexane provided orange prismatic crystals, which contain one molecule of dichloromethane per complex as determined by ^{1}H NMR and elemental analysis. We attempted to determine the structure of the complex by the single-crystal X-ray analysis, but failed. Therefore, the complex structure was examined by ^{1}H NMR spectroscopy using the nuclear Overhauser enhancement (NOE). NOEs were observed between H_a and H_b, H_a and H_c, methyl and H_a, and methyl and H_c, respectively (Chart 2). No obvious NOE was observed between methyl and H_b. On the basis of this finding, the complex can be assigned to be **4a**.

The palladium-catalyzed allylic alkylation of 1,3-diphenylprop-2-en-1-yl acetate (**5**) with dimethyl malonate using novel C_2-symmetric planar chiral P,P-chelating ligands **2** and their precursor **3** was carried out and the results are shown in Table 1.

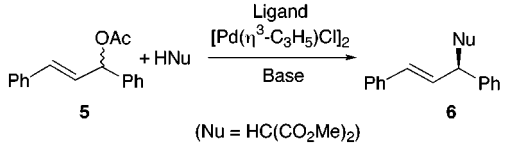
It was seen that all of the ligands show good to excellent enantioselectivity and the ligand structures have some effect on the enantioselectivity and the catalytic activity. From the results with **2a**−**c** it was found that the bulkier the ester group is, the higher the enantioselectivity is, but the lower the catalytic activity becomes (entries 1−3). Compound **3**, which is the precursor of ligands **2** and has the bulkiest ester groups, afforded almost the same ee with **2b** and **2c**, but the lowest catalytic activity (entry 4). Ligands **2d** and **2e** have been expected to exert a positive effect on the enantioselectivity for this allylic alkylation by the interaction between the hydroxyl groups in the ligand and the substrate. In fact, no higher ee than those of **2b**, **2c**, and **3** was obtained (entries 5 and 6).

It was reported that in many cases the base used in this reaction has a significant effect on the enantioselectivity.[8d] In this case, however, there is no great difference between NaH and *N*,*O*-bis(trimethylsilyl)acetamide (BSA) used as the base (entries 1 and 7). The reaction temperature has a considerable influence on the reaction rate. At room temperature, the reaction proceeded fast and completed within 1 h with either BSA or NaH as a base when **2a** was used (entries 1 and 7). Lowering the temperature decreased the reaction rate (entries 8−11). At −25 °C, the reaction was very slow and only 45% yield was obtained after 72 h (entry 9). The reaction temperature also has some influence on the enantioselectivity (entries 8−11), and up to 94% ee was attained at 0 °C with **2c** and **3** (entries 10 and 11). This is one of the best results reported so far for the allylic alkylation of 1,3-diphenylprop-2-en-1-yl acetate using C_2-symmetric P,P-chelating ligands.[10]

It should be interesting to know whether these chiral ligands are effective for other less sterically hindered allylic substrates. So, the palladium-catalyzed allylic alkylation of cyclohex-2-en-1-yl acetate (**7**) with dimethyl malonate was carried out, and the results are shown in Table 2.

Compared to that of 1,3-diphenylprop-2-en-1-yl acetate (**5**), ligand **2a** showed an excellent catalytic activity for the palladium-catalyzed allylic alkylation of cyclohex-2-en-1-yl acetate (**7**) with BSA as a base, and all the products could be isolated in above 90% yields. At 25 and 0 °C, the reaction was extremely rapid and completed within 10 min (entries 1 and 2). Lowering the reaction temperature decreased the reaction rate (entries 3 and 4), but even at −50 °C, the reaction also proceeded fast and could completed within 1 h (entry 4). Ligand **2a** also afforded good enantioselectivity for the allylic alkylation, and the reaction temperature has some influence on the enantioselectivity. At 25 °C, 75% ee was obtained for product **8** (entry 1), while lowering the reaction temperature to −50 °C afforded up to 83% ee (entry 4). Similarly rapid reaction and good enantioselectivity were observed with NaH as a base instead of BSA (entries 1 and 6). The ligand structure has some influence on the enantioselectivity. Ligand **2b**, which has bulkier ester groups than ligand **2a**, afforded a little lower enantioselectivity than **2a** (entries 2 and 7). This result is different from

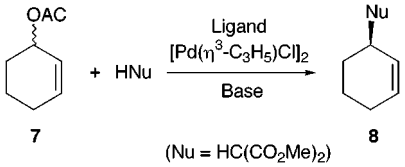
Table 1. Pd-Catalyzed Allylic Alkylation of 5[a]



entry	ligand	base[b]	T (°C)	time (h)	ee (%)[c]
1	**2a**	BSA	25	1	86
2	**2b**	BSA	25	3	91
3	**2c**	BSA	25	8	92
4	**3**	BSA	25	10	91
5	**2d**	BSA	25	5	88
6	**2e**	BSA	25	3	89
7	**2a**	NaH	25	1	84
8	**2a**	BSA	0	7	90
9	**2a**	BSA	−25	72	88
10	**2c**	BSA	0	10	94
11	**3**	BSA	0	68	94

[a] 1 mmol of **5**, 3 mmol of dimethyl malonate, 3 mmol of base, 30 μmol of ligand, and 12.5 μmol of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ in 3 mL of CH_2Cl_2. Product was isolated in above 90% yields except for entries 9 (45%), 10 (63%), and 11 (61%). [b] When BSA was used, 20 μmol of KOAc was added. [c] Determined by HPLC (Chiralcel OD).

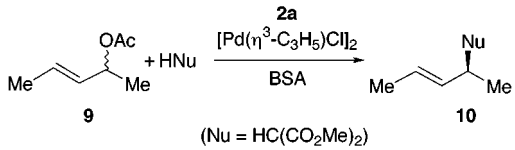
Table 2. Pd-Catalyzed Allylic Alkylation of 7[a]



entry	ligand	base[b]	*T* (°C)	time	ee (%)[c]
1	**2a**	BSA	25	<10 min	75
2	**2a**	BSA	0	<10 min	81
3	**2a**	BSA	−25	20 min	82
4	**2a**	BSA	−50	1 h	83
5[d]	**2a**	BSA	−25	1 h	81
6	**2a**	NaH	25	<10 min	74
7	**2b**	BSA	0	<10 min	77

[a] 1 mmol of **7**, 3 mmol of dimethyl malonate, 3 mmol of base, 30 μmol of ligand, and 12.5 μmol of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ in 3 mL of CH_2Cl_2. Product was isolated in above 90% yields except for entry 5 (80%). [b] When BSA was used, 20 μmol of KOAc was added. [c] Determined by HPLC (Chiralcel OB-H). [d] 12 μmol of ligand and 5.0 μmol of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ were used.

Scheme 3



that of the allylic alkylation of 1,3-diphenylprop-2-en-1-yl acetate (**5**) with ligands **2a** and **2b**.

Ligand **2a** also showed excellent catalytic activity for the palladium-catalyzed allylic alkylation of pent-3-en-2-yl acetate (**9**) with dimethyl malonate (Scheme 3). The reaction proceeded very fast with BSA as a base at 0 °C and was completed within 10 min. Only 12% ee, however, was obtained for product **10**.

Conclusion

In summary, we have prepared the first C_2-symmetric diphosphine ligands **2** possessing only the planar chirality of ferrocene from 1,1′-bis(diphenylphosphino)-2,2′-bis(oxazolinyl)ferrocene **1** by the transformation of the oxazoline moieties in the molecule. With this new kind of C_2-symmetric chiral diphosphine ligands and their precursor **3**, the palladium-catalyzed allylic alkylations of 1,3-diphenylprop-2-en-1-yl acetate and cyclohex-2-en-1-yl acetate with dimethyl malonate were carried out, and up to 94% ee and 83% ee were afforded for products **6** and **8**, respectively. These results show that the C_2-symmetric ferrocene ligands with only the planar chirality can produce an excellent asymmetric environment for metal-catalyzed asymmetric reactions.

Experimental Section

General Methods. Complete descriptions of the apparatus have recently been published.[6d] Compound **1** was prepared according to the method reported before.[4a]

Preparation of the Ester Amide 3 in Scheme 1. To a solution of compound **1a** (0.77 g, 0.99 mmol) in THF (20 mL) were added water (1 mL), trifluoroacetic acid (1.9 mL, 24.7 mmol), and Na_2SO_4 (9.40 g), and this suspension was stirred overnight at room temperature. After filtration and removal of the solvent under reduced pressure at below room temperature, an unstable ester ammonium salt was obtained as a brown solid. To a solution of this ester ammonium salt in dichloromethane (20 mL) were added pyridine (3.6 mL, 44.5 mmol) and acetic anhydride (6.0 mL, 38.2 mmol), and the mixture was stirred at room temperature overnight. The mixture was washed with 1 N HCl, water, and then brine and dried over Na_2SO_4. After removal of the solvent, the residue (2.01 g) obtained was purified by silica gel column chromatography with ethyl acetate as an eluent to afford pure ester amide **3** as a yellow solid (0.54 g, 61% overall yield from **1a**). Mp 102−104 °C. $[\alpha]^{25}_{589} = -437.4$ (*c* 0.34, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.02 (6H, d, *J* 6.5 Hz), 1.07 (6H, d, *J* 6.5 Hz), 1.88 (6H, s), 2.08 (2H, m), 3.45 (2H, br s), 3.95 (2H, dd, *J* 7.3, 11.5 Hz), 4.13 (2H, m), 4.41 (2H, dd, *J* 2.6, 11.5 Hz), 5.06 (2H, br s), 4.66 (2H, br s), 6.59 (2H, d, *J* 8.8 Hz), 7.12 (4H, m), 7.22 (8H, m), 7.29 (8H, m). IR (KBr, cm^{-1}): 1714, 1658, 1529. FABMS: *m*/*z* 897 ($[M + 1]^+$).

(−)-(*S*)-(*S*)-1,1′-Bis(diphenylphosphino)-2,2′-bis(methoxycarbonyl)ferrocene (2a). To a solution of ester amide **3** (0.50 g, 0.558 mmol) in THF (10 mL) was added a sodium methoxide solution prepared by the addition of sodium metal (0.513 g, 22.3 mmol) to methanol (35 mL). After being stirred for 24 h, the mixture was neutralized with methanolic acetic acid, and the solvent was removed by evaporation. The residue was dissolved in dichloromethane (60 mL), and the solution was washed with water and then brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified by silica gel column chromatography with ethyl acetate as an eluent to afford **2a** as a yellow solid (0.28 g, 74%). Mp 198 °C dec. $[\alpha]^{25}_{589} = -595.2$ (*c* 0.25, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.48 (2H, br s), 3.74 (6H, s), 4.56 (2H, t, *J* 2.7 Hz), 5.09 (2H, br s), 7.14−7.31 (20H, m). ^{31}P NMR ($CDCl_3$, $P(OCH_3)_3$): δ −160.28. IR (KBr, cm^{-1}): 1707. FABMS: *m*/*z* 670 (M^+). HRMS (EI): calcd for $C_{38}H_{32}O_4P_2Fe$ 670.1127, found 670.1115. Anal. Calcd for $C_{38}H_{32}O_4P_2Fe$: C, 67.91; H, 4.95. Found: C, 68.08; H, 4.81.

(−)-(*S*)-(*S*)-1,1′-Bis(diphenylphosphino)-2,2′-bis(ethoxycarbonyl)ferrocene (2b). Following a procedure identical to that described for the preparation of **2a**, the reaction of **3** (0.16 g, 0.185 mmol) in THF (6 mL) with a sodium ethoxide solution prepared by the addition of sodium metal (0.30 g, 13.04 mmol) to ethanol (20 mL) for 48 h afforded **2b** as a yellow solid (0.055 g, 43%). Mp 207 °C dec. $[\alpha]^{25}_{589} = -454.0$ (*c* 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (6H, t, *J* 7.1 Hz), 3.46 (2H, br s), 4.11−4.20 (2H, m), 4.25−4.33 (2H, m), 4.66 (2H, t, *J* 2.4 Hz), 5.08 (2H, br s), 7.12−7.31 (20H, m). ^{31}P NMR ($CDCl_3$, $P(OCH_3)_3$): δ −160.28. IR (KBr, cm^{-1}): 1712. FABMS: *m*/*z* 698 (M^+). HRMS (EI): calcd for $C_{40}H_{36}O_4P_2Fe$ 698.1440, found 698.1425. Anal. Calcd for $C_{40}H_{36}O_4P_2Fe\cdot 0.25H_2O$: C, 68.34; H, 5.23. Found: C, 68.28; H, 5.40.

(−)-(*S*)-(*S*)-1,1′-Bis(diphenylphosphino)-2,2′-bis(isopropoxycarbonyl)ferrocene (2c). Following a procedure identical to that described for the preparation of **2a**, the reaction of **3** (0.19 g, 0.223 mmol) in THF (6 mL) with a sodium isopropoxide solution prepared by the addition of solid sodium (0.36 g, 15.7 mmol) to 2-propanol (30 mL) for 20 h afforded **2c** as a yellow solid (0.028 g, 17%). Mp 200 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (6H, d, *J* 6.2 Hz), 1.30 (6H, d, *J* 6.2 Hz), 3.45 (2H, br s), 4.72 (2H, t, *J* 2.6 Hz), 5.05 (2H, br s), 5.10 (2H, m), 7.12−7.30 (20H, m). ^{31}P NMR ($CDCl_3$, $P(OCH_3)_3$): δ −160.28. IR (KBr, cm^{-1}): 1712. FABMS: *m*/*z* 727 ($[M + 1]^+$). HRMS (EI): calcd for $C_{42}H_{40}O_4P_2Fe$ 726.1753, found 726.1769.

(−)-(*S*)-(*S*)-1,1′-Bis(diphenylphosphino)-2,2′-bis[*N*-(2-hydroxyethyl)amido]ferrocene (2d). A mixture of **2a** (0.090 g, 0.134 mmol), 2-aminoethanol (1 mL, 16.6 mmol), and a small amount of sodium was heated at 100 °C for 30 min. The mixture was diluted with dichloromethane (20 mL) and neutralized with acetic acid. The neutralized solution was washed with water and then with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography with acetone as an eluent to afford **2d** as a yellow solid (0.066 g, 68%). Mp 116−117 °C. $[\alpha]^{25}_{589} = -336.9$ (*c* 0.49, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.48−3.57 (8H, m), 3.80 (4H, q), 4.39 (2H, t, *J* 2.9 Hz), 5.00 (2H, br s), 7.00−7.53 (22H, m). ^{31}P NMR ($CDCl_3$, $P(OCH_3)_3$): δ −162.58. IR (KBr, cm^{-1}): 3400, 1633, 1538. FABMS: *m*/*z*

729 ([M + 1]$^+$). Anal. Calcd for $C_{40}H_{38}N_2O_4P_2Fe{\cdot}H_2O$: C, 64.35; H, 5.40; N, 3.75. Found: C, 64.43; H, 5.41; N, 3.79.

(−)-(*S*)-(*S*)-1,1′-Bis(diphenylphosphino)-2,2′-bis[*N*-(3-hydroxylpropyl)amido]ferrocene (2e). Following a procedure identical to that described for the preparation of **2d**, the reaction of **2a** (0.050 g, 0.075 mmol), 3-aminopropanol (0.77 mL, 10.1 mmol), and a small amount of sodium at 80 °C for 30 min afforded **2e** as a yellow solid (0.046 g, 82%). Mp 85−86 °C. $[\alpha]^{25}_{589} = -371.1$ (*c* 1.44, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.40 (2H, br s), 3.52 (4H, q, *J* 5.9 Hz), 3.64−3.77 (8H, m), 4.38 (2H, t, *J* 2.6 Hz), 4.96 (2H, br s), 7.10−7.54 (22H, m). ^{31}P NMR($CDCl_3$, $P(OCH_3)_3$): δ −162.58. IR (KBr, cm^{-1}): 3330, 1629, 1540. FABMS: *m*/*z* 757 ([M + 1]$^+$). Anal. Calcd for $C_{42}H_{42}N_2O_4P_2Fe{\cdot}1.25H_2O$: C, 64.75; H, 5.76; N, 3.60. Found: C, 64.57; H, 5.69; N, 3.49.

Complexation Behavior of 2a with Dichlorobis(acetonitrile)palladium. Compound **2a** (6.9 mg, 0.01 mmol) was dissolved in acetonitrile-d_3 (0.40 mL) to give solution A, and dichlorobis(acetonitrile)palladium (8.0 mg, 0.03 mmol) was dissolved in acetonitrile-d_3 (1.50 mL) to give solution B. Addition of 0.25 mL of solution B (0.005 mmol) to solution A gave a solution containing **2a** and a C_2-symmetric 1:1 complex, **4** ([**2a**]$PdCl_2$), judging from the ^{1}H NMR analysis. When 0.50 mL of solution B (0.01 mmol) was added, compound **2a** disappeared, and only complex **4** was formed as determined by ^{1}H NMR analysis. The addition of more than 0.5 mL of solution B gave the same result as above and did not produce a new complex. ^{1}H NMR (400 MHz, CD_3CN): δ 3.35 (6H, s), 4.30 (2H, br s), 4.63 (2H, br s), 4.86 (2H, br s), 7.25−7.39 (12H, m), 8.01 (4H, dd, *J* 7.0, 11.2 Hz), 8.25 (4H, dd, *J* 7.3, 11.5 Hz). For comparison with **4**, the ^{1}H NMR data of ligand **2a** in CD_3CN were determined. ^{1}H NMR (400 MHz, CD_3CN): δ 3.47 (2H, br s), 3.69 (6H, s), 4.55 (2H, t, *J* 2.6 Hz), 5.06 (2H, br s), 7.11 (4H, m), 7.28 (14H, m), 7.35 (2H, m).

Preparation of Complex 4. A suspension of **2a** (33.5 mg, 0.05 mmol) and dichlorobis(acetonitrile)palladium (13.0 mg, 0.05 mmol) in dry benzene (2 mL) was stirred under argon for 1 h to produce a precipitate. After filtration, **4** (41.2 mg, 97%) was obtained as a yellow solid. Recrystallization of **4** from dichloromethane−hexane provided orange prismatic crystals, which contain one molecule of dichloromethane per complex as determined by ^{1}H NMR and elemental analysis. Mp 236 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.35 (6H, s), 4.29 (2H, br s), 4.49 (2H, t, *J* 2.7 Hz), 4.81 (2H, br s), 5.30 (2H, s), 7.40 (12H, m), 8.11 (4H, m), 8.25 (4H, m). ^{31}P NMR($CDCl_3$, $P(OCH_3)_3$): δ −95.69. IR (KBr, cm^{-1}): 1720. FABMS: *m*/*z* 848 ([M + 1]$^+$). Anal. Calcd for $C_{38}H_{32}O_4P_2FePdCl_2{\cdot}CH_2Cl_2$: C, 50.22; H,3.67. Found: C, 50.08; H, 3.63.

General Procedure for Palladium-Catalyzed Allylic Alkylation. The reaction of 1,3-diphenylprop-2-en-1-yl acetate (**5**) is illustrative of the general method for all catalytic reactions described in this study. A mixture of ligand **2a** (20.1 mg, 30 μmol) and [Pd(η^3-C_3H_5)Cl]$_2$ (4.6 mg, 12.5 μmol) in dry dichloromethane (1 mL) was stirred at room temperature under argon for 1 h, and the resulting yellow solution was added to a mixture of **5** (0.252 g, 1.00 mmol) and potassium acetate (0.002 g, 20 μmol) in dry dichloromethane (2 mL) via a cannula, followed by the addition of dimethyl malonate (0.396 g, 3.00 mmol) and BSA (0.613 g, 3.00 mmol). When NaH was used as a base instead of BSA, the catalyst solution was added to a mixture of acetate **5** (0.252 g, 1.00 mmol) and dimethyl sodiummalonate prepared from dimethyl malonate (0.396 g, 3.00 mmol) and NaH (72% in Nujol, 0.100 g, 3.00 mmol). The reactions were carried out at room temperature and monitored by TLC for the disappearance of **5** (**5**, $R_f = 0.42$; **6**, $R_f = 0.30$; solvent, hexane−ethyl acetate, 3:1). When **5** disappeared, the solvent was evaporated and the resulting mixture was extracted with ether (50 mL). The extract was washed twice with ice-cold saturated NH_4Cl aqueous solution (50 mL) and then dried over Na_2SO_4. After removal of the ether, the residue was purified on silica gel column chromatography with hexane−ethyl acetate (3:1) to afford pure product **6**.

(−)-(*S*)-Dimethyl (1,3-Diphenylprop-2-en-1-yl)malonate (6). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.52 (3H, s), 3.70 (3H, s), 3.93 (1H, d, *J* 10.7 Hz), 4.27 (1H, dd, *J* 8.8, 10.7 Hz), 6.30 (1H, dd, *J* 15.8, 8.8 Hz), 6.44 (1H, d, *J* 15.8 Hz), 7.19−7.32 (10H, m). The enantiomeric excess was determined by HPLC analysis at 25 °C [Chiralcel OD, 25 cm × 0.46 cm; hexane:2-propanol = 99.5:0.5; flow rate 0.9 mL/min; t_R = 19.8 min ((*R*)-**6**), t_R = 21.1 min ((*S*))-**6**)].

(+)-(*R*)-Dimethyl (Cyclohex-2-en-1-yl)malonate (8). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (1H, m), 1.58 (1H, m), 1.68−1.83 (2H, m), 1.96−2.03 (2H, m), 2.92 (1H, m), 3.30 (1H, d, *J* 9.6 Hz), 3.74 (3H, s), 3.75 (3H, s), 5.53 (1H, m), 5.79 (1H, m). The enantiomeric excess was determined by HPLC analysis at 40 °C [Chiralcel OB-H, 25 cm × 0.46 cm; hexane:2-propanol = 90:10; flow rate 0.5 mL/min; t_R = 13.2 min ((*R*)-**8**), t_R = 17.1 min ((*S*)-**8**)].

(−)-(*S*)-Dimethyl (Pent-3-en-2-yl)malonate (10). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (3H, d, *J* 7.0 Hz), 1.64 (3H, dd, *J* 6.2, 1.5 Hz), 2.91 (1H, m), 3.27 (1H, d, *J* 9.2 Hz), 3.70 (3H, s), 3.74 (3H, s), 5.35 (1H, m), 5.53 (1H, m). The enantiomeric excess was determined by comparison of its specific rotation value with a literature value[9g] [$[\alpha]^{23}_{589} = -3.3$ (c 1.1, $CHCl_3$); 12% ee].

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