P-CHIRAL 2-{1′-[BUTYL(PHENYL)PHOSPHANYL]FERROCEN-1-YL}-4-ISOPROPYL-4,5-DIHYDROOXAZOLES: A SECOND CHIRALITY CENTER IN CATALYTIC SYSTEM

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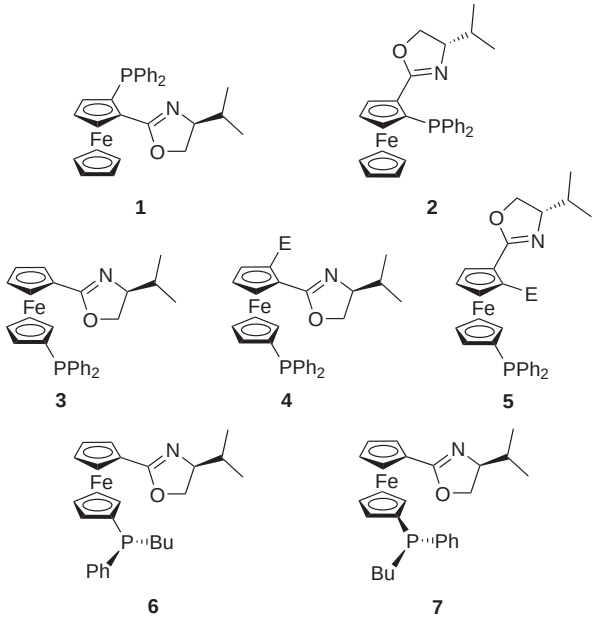
P-Chiral (S,R_P)-2-{1′-[butyl(phenyl)phosphanyl]ferrocen-1-yl}-4-isopropyl-4,5-dihydrooxazole (**6**) and (S,S_P)-2-{1′-[butyl(phenyl)phosphanyl]ferrocen-1-yl}-4-isopropyl-4,5-dihydrooxazole (**7**) were prepared by the procedure developed by Jugé, starting from enantiomerically pure (–)- or (+)-ephedrine and dichloro(phenyl)phosphine. Compounds **6** and **7** were examined for asymmetric induction in the Pd-catalyzed reaction of *rac*-1,3-diphenylallyl acetate with dimethyl malonate. The best results were obtained with **7** (98% ee), while **6** gave 82% ee.
Keywords: Ferrocenes; Oxazolines; P-Chiral ligands; Palladium; Enantioselective catalysis; Allylic substitutions.

Ferrocene-based chiral ligands and their role in asymmetric catalysis have been studied extensively over the past twenty years[1]. An important family of successful ligands involves ferrocenes bearing simultaneously a phosphine and an oxazoline donor groups in either 1,1′- or 1,2-positions of the ferrocene moiety. The 1,2-disubstituted ligands of this type having the two donor groups on the same cyclopentadienyl ring, e.g. **1** and **2** (Chart 1), combine elements of central and planar chirality[2]. Although the central chirality is considered to be the main factor governing asymmetric induction, the planar chirality also plays an important role[1d].

On the other hand, the 1,1′-disubstituted ligands, e.g. **3** in Chart 1, feature only central chirality[3]. However, their coordination to a metal leads to the formation of two conformers **A** and **B** (Scheme 1), differing in the mutual orientation of the cyclopentadienyl rings. This introduces a new source of chirality into the complex formed and, hence, the catalytic system becomes more complicated. All previously published results support the idea



E = e.g. PR_2, SR, $SiMe_3$, Me

CHART 1

that enantioselectivity of the asymmetric reactions catalyzed with these ligands depends on the ratio of these two conformers[4]. As a consequence, ligands of the 1,1′-type generally induce lower asymmetric induction than the 1,2-type ligands.

R = Ph (**3**), R = (R_P)-Bu (**6**), R = (S_P)-Bu (**7**)

SCHEME 1

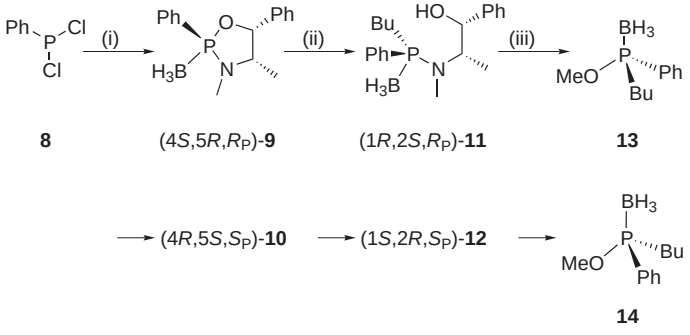
This led us to developing new ligands in which the equilibrium of the conformers is shifted towards the matched chiralities. For example, the introduction of planar chirality to the ligand **3** leading to the diastereoisomeric ligands **4** and **5** (Chart 1)[4] may serve as an example of a successful solution to this problem. Herein we wish to report an alternative approach, which is based on the introduction of the second stereogenic center on the phosphorus atom of the parent ligand **3** via replacement of the diphenyl-

phosphanyl with butyl(phenyl)phosphanyl group. The resulting diastereoisomeric ligands **6** and **7** (Chart 1) were obtained in enantiometrically pure form and tested in the Pd-catalyzed allylic substitution reaction of dimethyl malonate with 1,3-diphenylallyl acetate[1c].

RESULTS AND DISCUSSION

Synthesis of the Oxazoline Ligands

The key intermediates in the synthesis of the P-chiral 2-{1′-[butyl(phenyl)-phosphanyl]ferrocen-1-yl}-4-isopropyl-4,5-dihydrooxazoles (**6** and **7**) were (*S*)-butyl(methoxy)phenylphosphane-borane (**13**) and (*R*)-butyl(methoxy)-phenylphosphane-borane (**14**), respectively. These compounds were prepared by the procedure developed by Jugé et al.[5] (Scheme 2), starting from enantiomerically pure (–)- or (+)-ephedrine and dichloro(phenyl)phosphine (**8**) via oxazaphospholidine-boranes **9** and **10**. This approach offers several

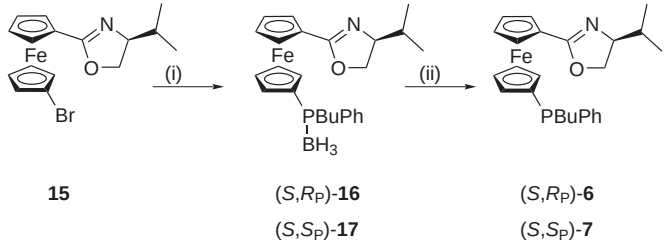


(i) 1. Me_2NH; 2. (-)-ephedrine ((+)-ephedrine gives **10**); 3. $BH_3.SMe_2$;
(ii) 1. BuLi; 2. H_2O, H^+; (iii) MeOH, H_2SO_4

SCHEME 2

advantages in terms of chemical and configurational stability, easy purification and deprotection, and also in possible extension to other substituents. Ligands **6** and **7** were then synthesized from bromo derivative **15** (Scheme 3), which was obtained from ferrocene via 1,1′-dibromoferrocene by Bryce's method[6]. The bromo compound **15** reacted after lithiation with **13** or **14** giving (*S*,R_p)-2-{1′-[butyl(phenyl)phosphanyl]ferrocen-1-yl}-4-isopropyl-4,5-dihydrooxazole-borane adduct (**16**) or (*S*,S_p)-2-{1′-[butyl(phenyl)-phosphanyl]ferrocen-1-yl}-4-isopropyl-4,5-dihydrooxazole-borane adduct (**17**), respectively. Finally, the free phosphines **6** and **7** were obtained by

deboranation of intermediates **16** and **17** with diethylamine at 45 °C in 50–52% overall yields. ^{31}P NMR spectra of the obtained ligands **6** and **7** revealed diastereomerical purity higher 99%.



15 (*S*,*R*$_P$)-**16** (*S*,*R*$_P$)-**6**

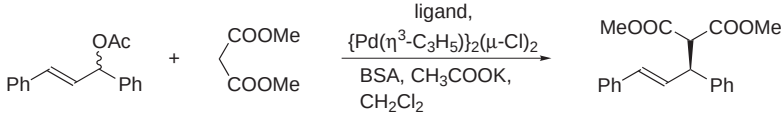
(*S*,*S*$_P$)-**17** (*S*,*S*$_P$)-**7**

(i) 1. *sec*-BuLi; 2. **13** or **14**; (ii) Et_2NH

SCHEME 3

The Ligands in Catalysis

Ligands **6** and **7** were examined for asymmetric induction in the reaction of *rac*-1,3-diphenylallyl acetate (**18**) with dimethyl malonate in the presence of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) as a base and [{Pd(η^3-C_3H_5)}$_2$-(μ-Cl)$_2$] (1 mole % Pd) as the metal source to give the substitution products **19** (Scheme 4). This reaction allowed for a direct comparison with the previously reported ligands **1**–**5**, which were tested similarly.



18 **19**

SCHEME 4

The reaction conditions were chosen on considering the optimized reaction parameters reported for ligand[3] **3** (see Experimental for details). We tested not only pure ligands **6** and **7**, but also their mixtures (Table I) to see the influence of the central chirality element at phosphorus atom.

The results summarized in Table I show, that the catalytic system based on ligand (*S*,*S*$_P$)-**7** give the highest enantioselectivity up to 98% ee (Table I, entry 5). Notably, the parent structure **3** gave under very similar conditions enantioselectivity only up to 91% ee [3a], which corresponds to the result obtained for a mixture of (*S*,*S*$_P$)-**7** and (*S*,*R*$_P$)-**6** in molar 1:1 ratio (Table I, entry 3). On the other hand, pure ligand (*S*,*R*$_P$)-**6** showed the lowest level of

enantiomeric excess (82% ee) of all tested structures (Table I, entry 1). Thus, ligand (S,S_P)-**7** very likely represents a structure with the matched chirality-conformation, whereas (S,R_P)-**6** gives mismatched intermediate.

TABLE I
Pd-catalyzed reaction of 1,3-diphenylallyl acetate (**18**) with dimethyl malonate

Entry	Ligand	$[\alpha]_D$ ligand	Yield, %	ee[a], %	Product configuration[b]
1	(S,R_P)-**6**	+7.7	98	82	(–)-(*S*)
2	80% (S,R_P)-**6** + 20% (S,S_P)-**7**	0	98	83	(–)-(*S*)
3	50% (S,R_P)-**6** + 50% (S,S_P)-**7**	–49.5	99	90	(–)-(*S*)
4	25% (S,R_P)-**6** + 75% (S,S_P)-**7**	–94.2	98	94	(–)-(*S*)
5	(S,S_P)-**7**	–127.7	99	98	(–)-(*S*)

[a] Determined by ^{1}H NMR using Eu(hfc)$_3$ in C_6D_6. [b] The absolute configuration was assigned by comparing the sign of its optical rotation with literature data[11].

CD Spectroscopy

Ligands **6** and **7** were further studied by UV-VIS and CD spectra. The former showed a broad band with absorption at about 450 nm and at least two much less intense bands at lower wavelengths (340 and 260 nm) (Fig. 1, bottom part). There is practically no difference between ligands **6** and **7**, and the position of the band maxima correspond well with the data re-

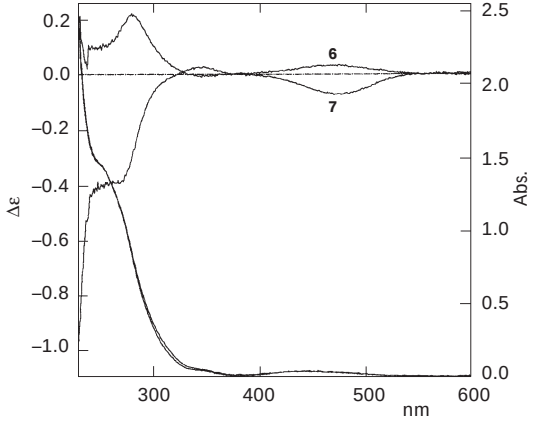


FIG. 1
CD spectra of P-chiral ligands **6** and **7**

ported for ferrocene itself (cf. 440 and 325 nm in ethanol[7a] and 441, 325, 265 nm[7b]).

The CD spectra of the ligands are also shown in Fig. 1 (upper part). The general pattern of the spectra is analogous to the related systems published previously[2b,3b]. The different configurations at the phosphorus atoms in ligands **6** and **7** are clearly reflected by the opposite signs of Cotton effects for three major bands at ca. 480, 350 and 280 nm. The rather large differences in the CD spectra of compounds **6** and **7** may arise due to different conformational preferences of the two diastereoisomers.

CONCLUSIONS

In summary, we have shown that the introduction of chirality at the phosphorus atom in ferrocene-based phosphine-oxazoline ligands of the 1,1′-type (parent structure **3**) improves enantioselectivity of Pd-catalyzed allylic substitution reaction. In the series studied, the ligand (*S*,S_P)-**7** represents the structure with two central chiralities that match each other, while the ligand with opposite configuration at phosphorus, (*S*,R_P)-**6**, is the case with mismatched chiralities. The overall span of ee between the ligand (*S*,R_P)-**6** and the ligand (*S*,S_P)-**7** is 16% ee.

EXPERIMENTAL

All syntheses were carried under argon. The solvents were dried and degassed by standard procedures. Radial-layer chromatography on silica gel (Chromatotron Model 8924, 2 mm thick plate) was used for purification of crude products. Column chromatography was performed on silica gel (Merck, 70–230 mesh). NMR spectra were recorded on a Varian Gemini 300 (^{1}H, 300.07 MHz; ^{13}C, 75.46 MHz), a Bruker AMX3 400 (^{1}H, 400.13 MHz; ^{13}C, 100.62 MHz; ^{31}P, 161.98 MHz) or a Bruker DRX 500 Avance (^{1}H, 500.13 MHz; ^{13}C, 125.77 MHz; ^{31}P, 202.46 MHz) spectrometer at 298 K. Chemical shifts (δ, ppm) are given relative to internal Me_4Si (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P) standards; coupling constants (*J*) are given in Hz. Unambiguous assignment of NMR signals is based on ^{13}C{^{1}H}, ^{13}C{^{1}H, ^{31}P}, ^{13}C APT, COSY and ^{13}C HMQC spectra. IR spectra (in cm^{-1}) in Nujol mulls were recorded on a Nicolet 750 FT-IR spectrometer. Optical rotations were determined on an automatic polarimeter Autopol III (Rudolph Research, New Jersey) and are given in 10^{-1} deg cm^2 g^{-1}. UV-VIS and CD spectra were recorded at room temperature on a Jobin Yvon Mark VI dichrograph for methanol solutions (ca. 1×10^{-3} mol l^{-1}) in a quartz cell with the optical path 1.0 mm. The spectra recorded were averages of two subsequent scans (no time dependence was observed) and further replotted using Spetracalc and Gramms (Galactic Industries) software for spectral analysis. Compounds [{Pd(η^3-C_3H_5)}$_2$(μ-Cl)$_2$] [8], *rac*-1,3-diphenylallyl acetate[9] (**18**), 2-(1′-bromoferrocen-1-yl)-4-isopropyl-4,5-dihydrooxazole[6] (**15**), oxazaphospholidine-boranes[5] (**9**, **10**) and aminophosphane-borane complexes[10] (**11**, **12**) were synthesized by literature procedures.

(*S*)-Butyl(methoxy)phenylphosphane-borane (**13**)

Concentrated H_2SO_4 (3.2 ml) was added dropwise to a solution of aminophosphane-borane **11** (18 g, 58 mmol) in methanol (200 ml) at 0 °C under stirring. The reaction mixture was stirred under argon at room temperature for 3 days. Filtration of the resulting mixture through silica, and evaporation of methanol from the filtrate gave an oil, which was purified by chromatography on silica gel column (ethyl acetate–petroleum ether 95:5) to give a colorless and not malodorous oily substance **13** (7 g) in 60% yield. ^{1}H NMR (300.07 MHz, $CDCl_3$, 293 K): 0.30–1.70 (br m, 3 H, B**H**$_3$); 0.88 (t, J_{HH} = 7.14, 3 H, C**H**$_3$); 1.25–1.60 (br m, 4 H, CH_2-C**H**$_2$-C**H**$_2$-CH_3); 1.90 (m, 2 H, P-C**H**$_2$); 3.60 (d, J_{PH} = 11.54, 3 H, OC**H**$_3$); 7.50 (m, 3 H, Ph); 7.72 (m, 2 H, Ph). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$, 293 K): 13.31 (s, **C**H_3); 23.75 (m, CH_2-**C**H_2-CH_3); 30.00 (d, J_{PC} = 45.00, P-**C**H_2); 53.53 (d, J_{PC} = 2.90, O**C**H_3); 128.48 (d, J_{PC} = 9.90, Ph, **C**H); 130.67 (d, J_{PC} = 10.70, Ph, **C**H); 131.75 (d, J_{PC} = 1.80, Ph, **C**H). ^{31}P{^{1}H} NMR (202.46 MHz, $CDCl_3$, 293 K): 117.82 (br, q, J_{PB} = 62.00). IR (neat): 1088 (s), 1118 (m), 1437 (m), 2341 (m) (B–H), 2369 (s) (B–H), 2872 (m), 2949 (s), 2959 (s), 3058 (w). $[\alpha]_D^{23}$ –91.10 (*c* 2.59, $CHCl_3$). For $C_{11}H_{20}BOP$ (210.1) calculated: 62.86% C, 9.60% H; found: 62.71% C, 9.94% H.

(*R*)-Butyl(methoxy)phenylphosphane-borane (**14**)

Starting with aminophosphane-borane **12**, using the same procedure as for compounds **13** and **14** was obtained as a colorless, and not malodorous oily substance in 66% yield. $[\alpha]_D^{22}$ +91.21 (*c* 2.05, $CHCl_3$). For $C_{11}H_{20}BOP$ (210.1) calculated: 62.86% C, 9.60% H; found: 62.80% C, 9.83% H.

(*S*,*R*$_P$)-2-{1′-[Butyl(phenyl)phosphanyl]ferrocen-1-yl}-4-isopropyl-4,5-dihydrooxazole (**6**)

To a solution of 2-(1′-bromoferrocen-1-yl)-4-isopropyl-4,5-dihydrooxazole (**15**; 1.38 g, 3.66 mmol) in dry diethyl ether (20 ml), *sec*-BuLi (3.1 ml, 1.3 M in hexanes) was added under stirring at –78 °C, and the mixture was kept at this temperature for 2 h. Then, a solution of phosphane-borane **13** (1 g, 4.76 mmol) in diethyl ether (10 ml) was added, and the resulting mixture was allowed to warm up to room temperature and stirred for another 2 h. Filtration of the mixture through silica and evaporating of the solvent to dryness gave crude **16**, which was used without further purification.

The crude product **16** was suspended in freshly distilled diethylamine (50 ml) and the mixture stirred at 45 °C for 4 h. Diethylamine was evaporated under vacuum, and the crude compound **6** was purified by radial-layer chromatography on Chromatotron (silica gel, 2 mm plate, petroleum ether–dichloromethane 3:1). Subsequent crystallization from pentane gave **6** as orange crystals. Yield: 800 mg, 50%. M.p. 46–48 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, 293 K): 0.90 (t, J_{HH} = 7.00, 3 H, CH_2-CH_2-CH_2-C**H**$_3$); 0.92 (d, J_{HH} = 6.50, 3 H, CH-C**H**$_3$); 1.00 (d, J_{HH} = 6.50, 3 H, CH-C**H**$_3$); 1.30–1.50 (br m, 4 H, CH_2-C**H**$_2$-C**H**$_2$-CH_3); 1.83 (m, 1 H, C**H**$(CH_3)_2$); 1.90–2.00 (br m, 2 H, P-C**H**$_2$); 3.94–3.99 (m, 2 H, C**H** oxazoline + C**H** Fc, Cp bearing oxazoline); 4.04 (dd, J_{HH} = 7.50, 2 H, C**H**$_2$ oxazoline); 4.15 (bs, 1 H, C**H** Fc, Cp bearing phosphine); 4.26–4.35 (m, 4 H, C**H** Fc, Cp bearing phosphine + Cp bearing oxazoline); 4.70 (m, 1 H, C**H** Fc, Cp bearing oxazoline); 4.76 (m, 1 H, C**H** Fc, Cp bearing oxazoline); 7.27–7.47 (m, 5 H, Ph). ^{13}C{^{1}H} NMR, ^{13}C{^{1}H,^{31}P} NMR, ^{13}C APT NMR, HMQC (125.77 MHz, $CDCl_3$, 293 K): 13.82 (s, CH_2-CH_2-CH_2-**C**H_3); 17.85 (s, CH-**C**H_3); 18.99 (s, CH-**C**H_3); 24.25 (d, J_{PC} = 13.20, **C**H_2); 28.21 (d, J_{PC} = 8.60, **C**H_2); 28.48 (d, J_{PC} = 17.00, **C**H_2); 32.31

(s, C**H**$(CH_3)_2$); 69.36 (C**H**$_2$ oxazoline); 69.60, 69.88 (Cp bearing oxazoline); 71.20 (C$_{ipso}$, Cp bearing oxazoline); 71.35 (Cp bearing oxazoline); 71.42, 71.47 (Cp bearing phosphine); 71.87 (Fc, Cp bearing oxazoline); 72.32 (C**H** oxazoline, Cp bearing phosphine); 73.99 (Cp bearing phosphine); 79.47 (C$_{ipso}$, Cp bearing phosphine); 128.09 (d, J_{PC} = 6.80, C**H**, Ph); 128.61 (s, C**H**, Ph); 132.74 (d, J_{PC} = 19.90, C**H**, Ph); 139.57 (d, J_{PC} = 14.00, C$_{ipso}$, Ph); 165.27 (C=N). $^{31}P\{^1H\}$ NMR (202.45 MHz, $CDCl_3$, 293 K): –28.17 (s). IR ($CHCl_3$): 1659 (s), 2874 (w), 2933 (m), 2961 (s), 3008 (w). $[\alpha]_D^{23}$ +7.7 (*c* 0.87, $CHCl_3$). For $C_{26}H_{32}FeNOP$ (461.4) calculated: 67.68% C, 6.99% H, 3.04% N; found: 67.89% C, 6.97% H, 2.99% N.

(*S*,*S*$_P$)-2-{1′-[Butyl(phenyl)phosphanyl]ferrocen-1-yl}-4-isopropyl-4,5-dihydrooxazole (**7**)

The procedure as above but with phosphane-borane **14** gave pure compound **7** as orange crystals in 52% yield. M.p. 67–70 °C. ^1H NMR (500.13 MHz, $CDCl_3$, 293 K): 0.90 (t, J_{HH} = 7.08, 3 H, CH_2-CH_2-CH_2-C**H**$_3$); 0.93 (d, J_{HH} = 6.93, 3 H, CH-C**H**$_3$); 1.01 (d, J_{HH} = 6.76, 3 H, CH-C**H**$_3$); 1.30–1.55 (br m, 4 H, CH_2-C**H**$_2$-C**H**$_2$-CH_3); 1.86 (m, 1 H, C**H**$(CH_3)_2$); 1.89–2.01 (br m, 2 H, P-C**H**$_2$); 3.97–4.01 (m, 2 H, C**H** oxazoline + C**H** Fc, Cp bearing oxazoline); 4.06 (dd, J_{HH} = 7.55, 2 H, C**H**$_2$ oxazoline); 4.15 (bs, 1 H, C**H** Fc, Cp bearing phosphine); 4.27–4.39 (m, 4 H, C**H** Fc, Cp bearing phosphine + Cp bearing oxazoline); 4.72 (m, 1 H, C**H** Fc, Cp bearing oxazoline); 4.76 (m, 1 H, C**H** Fc, Cp bearing oxazoline); 7.30–7.45 (m, 5 H, Ph). $^{13}C\{^1H\}$ NMR, $^{13}C\{^1H,^{31}P\}$ NMR, ^{13}C APT NMR, HMQC (125.77 MHz, $CDCl_3$, 293 K): 13.78 (s, CH_2-CH_2-CH_2-C**H**$_3$); 17.84 (s, CH-C**H**$_3$); 18.93 (s, CH-C**H**$_3$); 24.28 (d, J_{PC} = 13.01, C**H**$_2$); 28.22 (d, J_{PC} = 8.40, C**H**$_2$); 28.51 (d, J_{PC} = 16.70, C**H**$_2$); 32.29 (s, C**H**$(CH_3)_2$); 69.47 (C**H**$_2$ oxazoline); 69.68, 70.01 (Cp bearing oxazoline); 71.10 (C$_{ipso}$, Cp bearing oxazoline); 71.48 (Cp bearing oxazoline); 71.56 (Cp bearing phosphine); 71.90 (Cp bearing oxazoline); 72.38 (C**H** oxazoline + Cp bearing phosphine); 74.09 (Cp bearing phosphine); 79.58 (C$_{ipso}$, Cp bearing phosphine); 128.12 (C**H**, Ph); 128.63 (C**H**, Ph); 132.74 (d, J_{PC} = 19.32, C**H**, Ph); 139.63 (d, J_{PC} = 12.98, C$_{ipso}$, Ph); 165.30 (C=N). $^{31}P\{^1H\}$ NMR (202.45 MHz, $CDCl_3$, 293 K): –28.18 (s). IR ($CHCl_3$): 1659 (s), 2874 (w), 2933 (m), 2961 (s), 3011 (w). $[\alpha]_D^{22}$ –127.7 (*c* 1.01, $CHCl_3$). For $C_{26}H_{32}FeNOP$ (461.4) calculated: 67.68% C, 6.99% H, 3.04% N; found: 67.79% C, 6.98% H, 3.01% N.

Allylic Substitution. General Procedure

Compound **6** or **7** (4 μmol) and $[\{Pd(\eta^3\text{-}C_3H_5)\}_2(\mu\text{-}Cl)_2]$ (2 μmol) were dissolved in dry degassed dichloromethane (3 ml). The solution was stirred at room temperature for 1 h and then transferred to a mixture of *rac*-1,3-diphenylallyl acetate (**18**; 0.1 g, 0.4 mmol), dimethyl malonate (0.14 ml, 1.2 mmol), BSA (0.3 ml, 1.2 mmol) and potassium acetate (0.8 mg, 8 μmol) in dichloromethane (3 ml). After stirring at room temperature for 2 h, the reaction mixture was partitioned between water and diethyl ether, organic layer was dried over anhydrous $MgSO_4$, the solvents were evaporated and product **19** was purified by chromatography (silica gel, hexane–dichloromethane 1:1). Enantiomeric excesses were determined by ^1H NMR in C_6D_6 solutions using chiral lanthanide shift reagent Eu(hfc)$_3$. The yields and ee are reported in Table I.

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