Preparation of Chiral Phosphinoferrocene Carboxamide Ligands and Their Application to Palladium-Catalyzed Asymmetric Allylic Alkylation

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A series of phosphinoferrocene carboxamides bearing achiral (benzyl) and chiral [(*R*)- and (*S*)-1-phenylethyl] substituents at the amide nitrogen have been prepared from 1′-(diphenylphosphino)-ferrocenecarboxylic (Hdpf) and (S_p)-2-(diphenylphosphino)ferrocenecarboxylic ((S_p)-**1**) acids and tested as ligands for enantioselective allylic alkylation of 1,3-diphenylallyl acetate with dimethyl malonate. At room temperature, the alkylation reactions proceeded with complete conversions and ee's up to 90%, the most efficient being the planar-only chiral ligand (S_p)-2-(diphenylphosphino)-1-(*N*-benzylcarbamoyl)-ferrocene ((S_p)-**2**). The crystal structures of (S_p)-**2** and the cationic (η^3-allyl)palladium(II) complex [Pd(η^3-1,3-$Ph_2C_3H_3$){(S_p)-**2**-κ^2*O*,*P*}]ClO_4 ((S_p)-**8**) have been determined by single-crystal X-ray diffraction and solution NMR data were obtained to provide an insight into the mechanism of chiral discrimination.

Introduction

Asymmetric allylic alkylation represents one of the most powerful methods available for the construction of new carbon−carbon bonds in a *stereoselective* manner. Many efficient catalytic systems based on combinations of different metals and chiral ligands have been reported to date that allow for performing allylic alkylation with high enantioselectivities and with a wide choice of allylic substrates and nucleophiles.[1] Chiral ferrocene donors have been successfully employed as ligands for this reaction, the most thoroughly studied being bidentate donors of the P,P-, P,N-, and P,S-types.[2] By contrast, ligands of the P,O-type are still rather scarce, although their "organic" analogues, e.g., Trost's diamido diphosphine chiral ligands[1a−c,3] and their donor-unsymmetric analogues,[4] phosphinoamides,[5] and axially [5] chiral biaryl phosphinoethers[6] and phosphino-phosphine oxides,[7] are well established.

The prominent examples of ferrocene P,O-ligands utilized in asymmetric allylic alkylation (Scheme 1) include C_2-symmetric 1,1′-bis(diphenylphosphino)-2,2′-bis(alkoxycarbonyl)ferrocenes and their related bis(*N*-ω-hydroxyalkyl)diamides (**I**, Y = OR and $NH(CH_2)_nOH$),[8] Trost-type ligands **II**,[9] phosphinoferrocene acetals **III** (n = 0, 1 and R^1/R^2 = Me or H; the series includes both (S_p)- and (R_p)-derivatives),[10] and amides derived from Ugi's amine (**IV**).[11]

Recently, we have reported the synthesis of a new phosphinoferrocenecarboxylic ligand[12] combining planar and central chirality, (R,R_p)-2-[1-(diphenylphosphino)ethyl]ferrocenecarboxylic acid (**V**). Testing of acid **V** and amides thereof as ligands for palladium-catalyzed asymmetric allylic alkylation has shown that the degree of asymmetric induction changes greatly with

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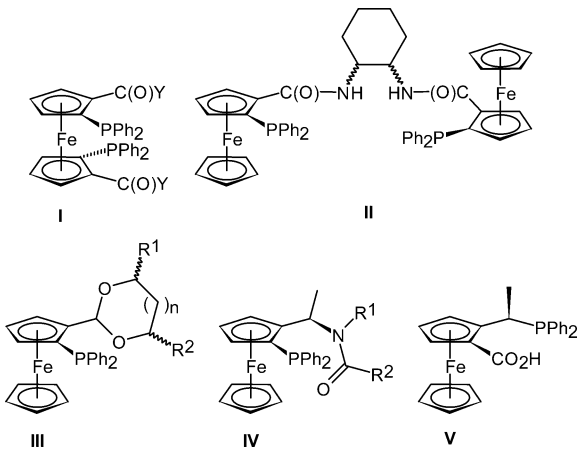
Scheme 1



the ligand structure.[13] This initiated our interest in exploring the catalytic potential of chiral phosphinoferrocene carboxamides. Our interest was stimulated also by our previous work on amides derived from 1′-(diphenylphosphino)ferrocenecarboxylic acid (Hdpf) that have been used as synthetic precursors to C-chiral phosphinoferrocene oxazolines[14] and Fischer-type P-chelated carbenes[15] as well as versatile ligands for palladium complexes and for Suzuki cross-coupling reaction.[16]

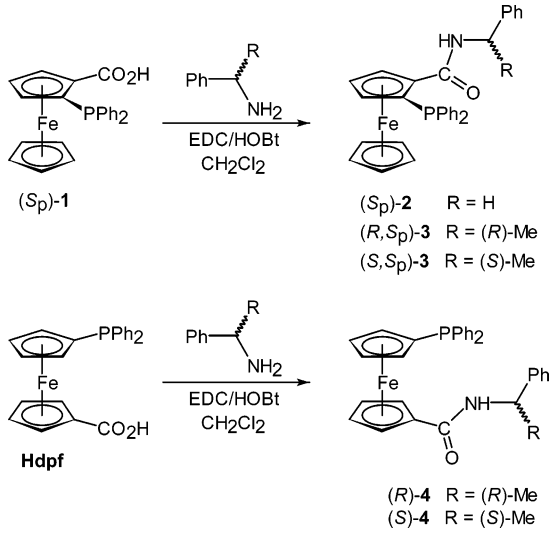
With this contribution we report the preparation and catalytic utilization in asymmetric allylic alkylation of phosphinoferrocene carboxamides derived from the achiral Hdpf and from its planar chiral isomer, (S_p)-2-(diphenylphosphino)ferrocenecarboxylic acid ((S_p)-**1**) and benzylic amines. We also present the X-ray structural and solution NMR study of the best performing ligand, (S_p)-2-(diphenylphosphino)-1-(*N*-benzylcarbamoyl)ferrocene ((S_p)-**2**), and the cationic complex [Pd(η^3-1,3-$Ph_2C_3H_3$){(S_p)-**2**-η^2:κP}]ClO_4 ((S_p)-**8**), which can serve as a model for the reaction intermediate.

Results and Discussion

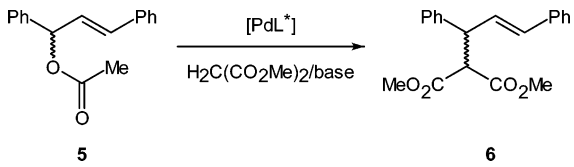
Preparation of the Amido-phosphine Ligands. Compounds **2**−**4** have been obtained by reaction of the respective phosphinocarboxylic acids with the appropriate amines (i.e., benzylamine, (*R*)- and (*S*)-1-phenylethylamine) in the presence of *N*-[3-(dimethylamino)propyl]-*N*′-ethylcarbodiimide and 1-hydroxybenzotriazole (Scheme 2).[15,16c,17] The amides were isolated by column chromatography as air-stable, orange solids and characterized by conventional spectral methods and elemental analysis. In addition, the crystal structure of (S_p)-**2** has been determined by single-crystal X-ray diffraction.

Compounds **2**−**4** show the typical amide bands in IR spectra and molecular ions in their mass spectra. Their NMR spectra display signals attributable to a PPh_2-bearing, 1,2- (for **2** and **3**) or 1,1′-disubstituted (for **4**) ferrocene framework and the amide substituents. Whereas the amide NH protons in (*R*)-**4** and (*S*)-**4** give rise to the expected broad doublets in the ^{1}H NMR

Scheme 2. Preparation of Amidophosphines 2−4 (HOBt = 1-hydroxybenzotriazole, EDC = *N*-[3-(dimethylamino)propyl]-*N*′-ethylcarbodiimide)



Scheme 3



spectra, those of (S_p)-**2** and (R,S_p)-**3**/(S,S_p)-**3** are observed as a double triplet and double doublets, respectively. Coupling of the amide proton with ^{31}P in the case of the planar-chiral amides **2** and **3** was clearly established by ^{31}P-decoupled ^{1}H NMR spectra, in which the amide signals collapse into a simple, proton-coupled triplet for (S_p)-**2** or doublets for the 1-phenylethyl amides (R,S_p)-**3** and (S,S_p)-**3**. The associated long-range ^{31}P−^{1}H interaction is unexpectedly large ($^5J_{PH}$ 13−14 Hz) and is likely the consequence of through-bond spin−spin interactions within the extended conjugated π-electron system involving the phosphino-substituted cyclopentadienyl ring and the amide moiety. Such an assumption is supported by the structure determination for (S_p)-**2** (see below), which reveals the P−C−C−C−N atom set to be coplanar within ca. 0.15 Å, while the amide NH group is oriented away from the phosphine group, i.e., in a position unfavorable for a through-space (P···HN) interaction.

Catalytic Tests. Amido-phosphines **2**−**4** were employed as ligands in palladium-catalyzed enantioselective allylic alkylation[1] of racemic (*E*)-1,3-diphenylprop-2-en-1-yl acetate (**5**) with dimethyl malonate to give dimethyl [(*E*)-1,3-diphenylprop-2-en-1-yl]malonate (**6** in Scheme 3). The model substrate **5** has been chosen mainly because of the known reaction mechanism and its symmetric nature and also due to a number of available literature reports concerning this substrate that allow for a comparison of the ligand efficiency. The reactions were carried out in dichloromethane using 5 mol % of palladium catalysts generated *in situ* from the appropriate ligand and di-μ-chloridobis(η^3-allyl)dipalladium(II), with dimethyl malonate-*N*,*O*-bis(trimethylsilyl)acetamide (BSA)/alkali metal acetate as the nucleophile source.[18] The results are summarized in Table 1.

At room temperature, the alkylation reaction in the presence of acid (S_p)-**1** and amides thereof proceeded with complete

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Table 1. Application of the Chiral Amides to Palladium-Catalyzed Enantioselective Allylic Alkylation[a]

entry	ligand	*T* (°C)	time (h)	additive	conversion (%)[b]	ee (%) [config][c]
1	(S_p)-**1**	22	20	KOAc	100 (91)	50 [*R*]
2	(S_p)-**2**	22	20	KOAc	100 (91)	58 [*R*]
3	(R,S_p)-**3**	22	20	KOAc	100 (97)	49 [*R*]
4	(S,S_p)-**3**	22	20	KOAc	100 (95)	21 [*R*]
5	(*R*)-**4**	22	20	KOAc	100 (90)	0
6	(*S*)-**4**	22	20	KOAc	100 (92)	0
7	(S_p)-**2**	22	20	none	85	90 [*R*]
8	(S_p)-**2**	22	20	LiOAc	100	48 [*R*]
9	(S_p)-**2**	22	20	NaOAc	100	84 [*R*]
10	(S_p)-**2**	0	42	NaOAc	41	88 [*R*]
11	(S_p)-**2**	22	20	KOAc	100	58 [*R*]
12	(S_p)-**2**	22	20	RbOAc	100	44 [*R*]
13	(S_p)-**2**	22	20	CsOAc	100	49 [*R*]

[a] The results are an average of two independent runs. For detailed conditions, see Experimental Section. [b] Conversions were determined by ^{1}H NMR spectroscopy. The isolated yield is given in parentheses. [c] Absolute configuration has been assigned via comparison of the sign of the optical rotation with the literature data.[40]

conversions within less than 20 h, yielding predominantly (*R*)-**6**. Amide (S_p)-**2** induced the highest enantioselectivity, followed by the acid (entries 1−6 in Table 1). Introduction of the methyl group onto the aliphatic carbon of the benzyl substituent reduced the degree of asymmetric induction, the decrease being pronounced much more for the *S*-configured phenylethyl group than for its enantiomer. Somewhat unexpectedly, the 1,1′-ferrocene derivatives **4** afforded only racemic **6**. This markedly contrasts with the previous successful applications of the structurally related [1′-(diphenylphosphino)ferrocenyl]oxazolines.[2e,19]

The reaction conditions were subsequently optimized for ligand (S_p)-**2** by changing the base additive and the reaction temperature (entries 2 and 7−13). Reaction performed without a base proceeded with a slower rate but with the highest ee (entry 7). Among the reactions performed in the presence of alkali metal acetates (entries 2 and 8−13), the one with NaOAc proceeded with the highest enantioselectivity. The enantioselectivity further increased upon cooling to 0 °C, though on account of the reaction rate (entries 9 and 10). The influence of the acetate additive is difficult to rationalize since its solubility, basicity, size of the counterion, and its ability to form ion pairs with the formed carbanion may all influence the enantioselectivity.[20] Generally, the trends differ for individual catalytic systems, even among the ferrocene donors. For instance, a continuous rise in ee values with increasing size of the alkali metal cation has been observed in alkylation of **5** in the presence of Trost-type ligand **II**[9a] as well as in the alkylation of cyclohex-2-enyl acetate in the presence of C_2-symmetric ferrocene diphosphine-disulfone.[21] By contrast, catalysts based on [2-(thioalkyl)ferrocenyl]oxazolines showed only marginal variation in ee's upon changing the alkali metal cation.[22]

Preparation of Complex (S_p)-8 and Structural Study. Cationic (η^3-allyl)palladium complex (S_p)-**8** was obtained by bridge cleavage of di-μ-chloridobis(η^3-1,3-diphenylallyl)dipalladium(II) (**7**) with the stoichiometric amount of (S_p)-**2** in dichloromethane followed by halide abstraction with silver(I) perchlorate (Scheme 4). The complex was isolated by crystal-

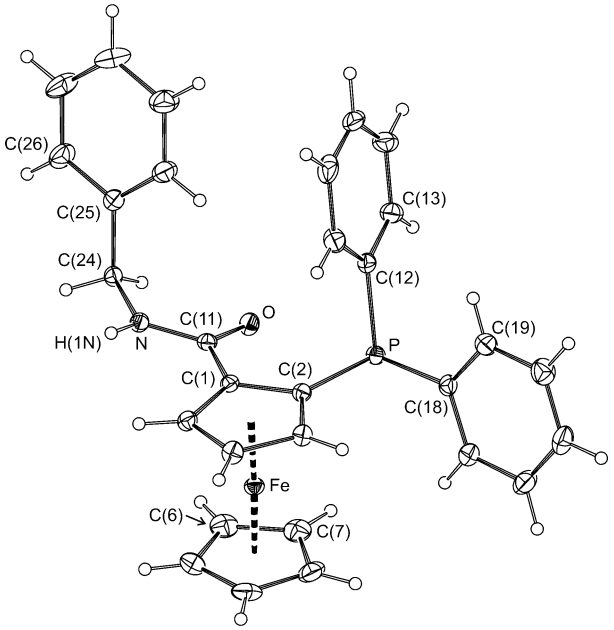
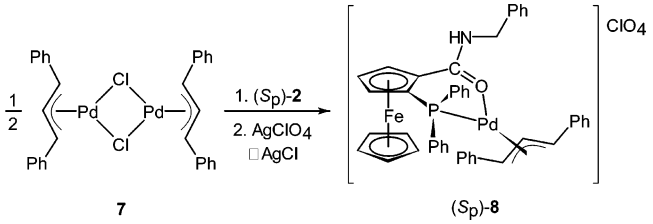


Figure 1. PLATON plot of the molecular structure of (S_p)-**2**. Displacement ellipsoids are shown at the 30% probability level. Only labels for the pivotal and their adjacent carbon atoms with the consecutively numbered rings are shown.

Scheme 4



lization from a dichloromethane−diethyl ether mixture and characterized by NMR, IR, and ESI-MS spectra and by elemental analysis. Whereas the composition of the cation in (S_p)-**8** is clearly reflected in ESI-MS spectra, the O,P-bidentate coordination of the ferrocene ligand can be inferred from a low-field shift of the ^{31}P NMR resonance ($\Delta\delta_P$ ca. +39 ppm) and from a shift of the $\nu_{C=O}$ (amide I) band to lower energies ($\Delta\nu = -36$ cm^{-1}). Finally, the presence of the perchlorate counterion is manifested by its strong ν_3 (composite 1054−1113 cm^{-1}) and ν_4 (623 cm^{-1}) bands in the IR spectrum.

In solution, (S_p)-**8** exists as a mixture of isomers differing presumably by conformation of the allyl unit (*syn/syn* vs *syn/anti*) and its orientation toward the ferrocene unit (*exo/endo*), which is in line with observations made in similar systems.[23] Two sets of signals in ca. 2.7:1 ratio could be detected in the ^{1}H and ^{31}P NMR spectra. The major isomer was assigned an *exo-syn-syn* structure[24] (shown in Scheme 4) on the basis of

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Table 2. Selected Geometric Parameters for (S_p)-2 and (S_p)-8·Me_2CO (in Å and deg)

Coordination Geometry of (S_p)-**8**·Me_2CO			
Pd−P	2.2863(6)	P−Pd−O	93.52(6)
Pd−O	2.106(2)	P−Pd−C(31)	106.34(9)
Pd−C(31)	2.133(3)	P−Pd−C(33)	170.7(1)
Pd−C(32)	2.177(3)	O−Pd−C(33)	93.2(1)
Pd−C(33)	2.237(3)	O−Pd−C(31)	160.1(1)
C(31)−C(32)	1.424(5)	C(31)−Pd−C(33)	66.9(1)
C(32)−C(33)	1.389(5)	C(31)−C(32)−C(33)	117.9(3)
C(31)−C(34)	1.484(5)	C(32)−C(31)−C(34)	123.7(3)
C(32)−C(40)	1.466(5)	C(32)−C(33)−C(40)	126.1(3)

Geometry of the Free and Coordinated Ligand		
parameter	(S_p)-**2**	(S_p)-**8**·Me_2CO
Fe−Cg(1)	1.6407(8)	1.644(1)
Fe−Cg(1)	1.6441(9)	1.660(2)
∠Cp(1),Cp(2)	2.9(1)	4.9(2)
P−C(2)	1.823(2)	1.806(3)
P−C(12)	1.837(2)	1.824(3)
P−C(18)	1.841(2)	1.815(3)
C−C(11)	1.475(2)	1.483(4)
C(11)−O	1.238(2)	1.256(3)
C(11)−N	1.350(2)	1.256(3)
C−P−C	100.09(7)−102.77(8)	102.2(1)−105.7(1)
C(1)−C(2)−P	124.6(1)	128.3(2)
C(3)−C(2)−P	128.6(1)	124.8(2)
O−C(11)−N	122.0(2)	118.7(3)
C(2)−C(1)−C(11)	123.4(1)	126.9(3)
C(5)−C(1)−C(11)	128.5(2)	125.0(3)
P−C(2)−C(1)−C(11)	0.4(2)	−11.0(4)
O−C(11)−N−C(24)	2.9(2)	0.8(5)

[a] The ring planes are defined as follows: Cp(1) = C(1−5), Cp(2) = C(6−10); Cg(1,2) are the respective ring centroids.

2D NOESY spectra that showed correlations between the terminal allyl hydrogens, thus indicating a W-shape for the allyl moiety. Additionally, there is a cross-peak between the NH resonance and the adjacent hydrogen at the disubstituted ferrocene ring. NOE correlations between the allyl and phenyl protons are of limited diagnostic value due to extensive overlaps in the region of aromatic protons. Nevertheless, the cross-peaks at δ_H 5.00 × ∼7.20, 5.98 × ∼7.70, and 6.61 × ∼7.20, ∼7.70 support the mentioned conformation, where the terminal protons at the W-configured allyl group are directed toward different phenyl protons, while the *meso* CH in between correlates with both aromatic moieties. Although there is no such direct information about the minor isomer, it can tentatively be assigned the *endo-syn-syn* (or M-shaped) conformation, when considering the similarity of the chemical shifts and, particularly, the J_{HH} and J_{PH} coupling constants.

The solid-state structures of solvate (S_p)-**8**·Me_2CO and ligand (S_p)-**2** have been determined by single-crystal X-ray diffraction. The molecular structure of (S_p)-**2** is shown in Figure 1, and selected geometric data are collected in Table 2. The ferrocene unit in (S_p)-**2** has a regular geometry, showing a tilt of only 2.9(1)° and almost identical Fe−ring centroid distances. Likewise, the geometry of the amide group does not differ much from that in other structurally characterized secondary ferrocene carboxamides.[25] The amide plane is oriented so that the oxygen atom points toward the phosphine moiety and is rotated by 16.0(2)° from the Cp(1) plane (see Table 2 for definitions). The benzyl group is located above the ferrocene unit and together with one of the PPh_2 phenyl rings pointing in the same direction, C(12−17), which is almost perpendicular to the benzylic phenyl ring [dihedral angle = 83.0(1)°], shield the donor atoms from above the ferrocene moiety. In the crystal, the individual molecules of (S_p)-**2** associate into infinite linear chains along the crystallographic 2_1 screw axes via cooperative N−H(1N)···O and C(5)−H(5)···O hydrogen bonds (Figure 2).

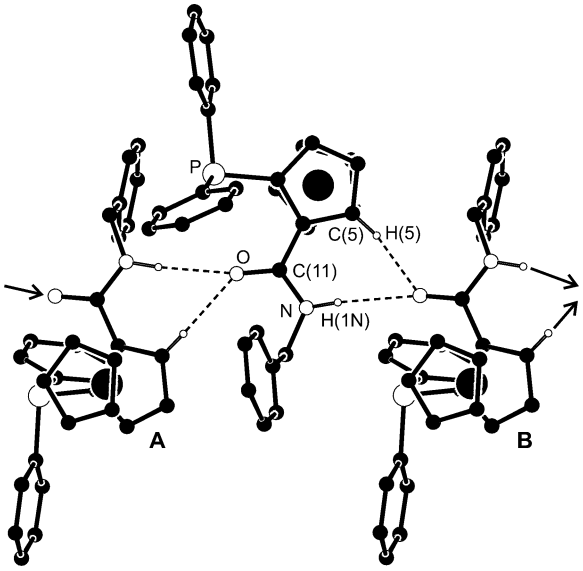


Figure 2. Section of the hydrogen-bonded assembly in the structure of (S_p)-**2** showing hydrogen bonds as dashed lines (only hydrogen-bonded H atoms are shown). Symmetry operations: **A**: $-x, y + 1/2, 1/2 - z$; **B**: $-x, y - 1/2, 1/2 - z$. Selected parameters: N···O = 3.284(2) Å, angle at H(1N) = 170°; C(5)···O = 3.150(2) Å, angle at H(5) = 151°.

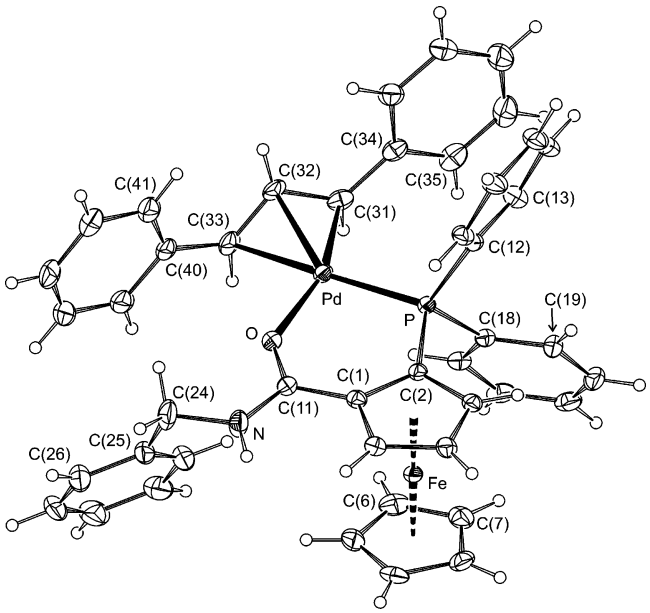


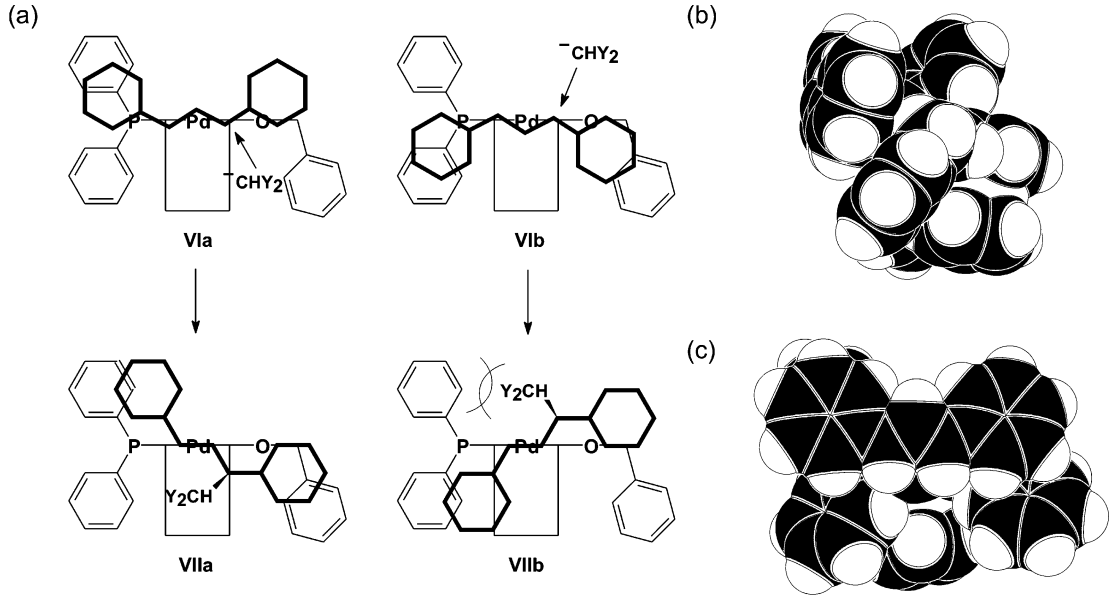
Figure 3. PLATON plot of the cation in the structure of (S_p)-**8**·Me_2CO. Displacement ellipsoids correspond to 30% probability. The ring atoms are numbered consecutively and, hence, the labels of only the pivotal and their adjacent carbon atoms are shown to avoid complicating the figure.

Crystals of solvate (S_p)-**8**·Me_2CO were obtained by recrystallization from acetone−diethyl ether.[26] The structure of the cation in (S_p)-**8**·Me_2CO is depicted in Figure 3, and selected

(24) Conformers are denoted *exo* (*endo*) when the *meso*-CH group of the allyl moiety is directed away from (toward) the ferrocene unit.

(25) FcC(O)NHCH$_2$R: (a) R = Ph: Hursthouse, M. B.; Coles, S. J.; Tucker, J. H. R. Private communication to CCDC (refcode BATLEO). (b) R = CH_2OH: Štěpnička, P.; Císařová, I. *CrystEngComm* **2005**, *7*, 37−43. (c) R = C≡CH: Brosch, O.; Weyhermueller, T.; Metzler-Nolte, N. *Eur. J. Inorg. Chem.* **2000**, 323−330. (d) R = Et: Oberhoff, M.; Duda, L.; Karl, J.; Mohr, R.; Erker, G.; Froehlich, R.; Grehl, M. *Organometallics* **1996**, *15*, 4005−4011.

Scheme 5. (a) Idealized Depiction of the Plausible Reaction Intermediates VI and VII (Y = CO_2Me); (b,c) Space-Filling Model of the Cation in (S_p)-8 as Viewed (b) along the C(33)−C(31) Line (i.e., from the benzyl group) and (c) Perpendicular to the η^3-Allyl Moiety



geometric parameters are given in Table 2. The allyl moiety adopts an *exo-syn-syn* arrangement, which is in line with the solution NMR data of the major isomer (see above). The dihedral angle of the allyl plane, C(31−33), and the plane defined by Pd and its two remaining ligating atoms (P,O) is 65.9(3)°, the *meso* carbon atom C(32) being most distant from the ferrocene axis. The Pd−C(allyl) distances increase gradually along the allyl moiety from C(31) to C(33), with the extreme values differing by as much as 0.10 Å. Nonetheless, this observation is in accordance with a stronger *trans*-influence[27] of the P-donor. Desymmetrization of the 1,3-diphenylallyl moiety is manifested also by the "interligand" angles involving the terminal allyl carbon atoms P−Pd−C(31) and O−Pd−C(33), which differ by about 13°.

The Pd−X (X = C, O, P) distances observed for (S_p)-**8**·Me_2-CO compare favorably with those reported for (η^3-1,3-diphenylallyl)palladium complexes bearing (*S*)-2-(diphenylphosphino)-2′-(diphenylphosphoryl)-1,1′-binaphthyl[7,28] and (1*R*,2*R*)-1-{2-(diphenylphosphino)benzoylamino}-2-{2-(diphenylamino)benzoylamino}cyclohexane[4,29] as the P,O-chelating ligands. The ligand bite angle P−Pd−O in (S_p)-**8**·Me_2CO of 93.52(5)° fits in between those of the reference compounds (98.5(2)° and 89.2(4)°, respectively). It is noteworthy that the bite angles correlate with the degree of asymmetric induction, the ligand with the lowest bite angle showing the highest ee under similar reaction conditions. Yet, any general conclusions would be inappropriate, as these structures represent the *only* three structurally characterized [Pd(η^3-1,3-$Ph_2C_3H_3$)(L−L′-κ^2*O,P*)]$^+$ cations.[30]

The ferrocene Cp(1) and [PdPO] planes in (S_p)-**8**·Me_2CO are nearly coplanar (the dihedral angle is only 3.4(1)°). When compared with the structure of the free ligand, the coordination leads to an elongation of the C(11)═O and C(1)−C(11) bonds by 0.018 and 0.026 Å, respectively, while the C(11)−N bond shrinks by 0.025 Å. A slight opening of the C(1)−C(11)−O angle (2.6°) is also observed and is compensated by a closure of the O−C(11)−N angle (3.3°). The amide plane in the complex is rotated from the Cp(1) plane by 8.7(3)°. Furthermore, the coordination brings about conformational changes that clearly aid the accommodation of the bulky (η^3-diphenylallyl)-Pd moiety into the chiral donor pocket. First, the PPh_2 moiety is rotated along the pivotal C(2)−P bond below the Cp(1) plane. Second, the amide benzyl substituent is moved below the Cp-(1) ring as if mirrored through the Cp(1) plane (cf. the torsion angles N−C(24)−C(25)−C(26) = −146.7(2)°/145.5(4)° and N−C(24)−C(25)−C(26) = 34.0(2)°/−40.5(5)° in (S_p)-**2**/(S_p)-**8**·Me_2CO).

Mechanistic Considerations. Because the symmetric allyl precursor **5** eliminates a possible bias due to unlike allyl substituents, the enantioselectivity is dictated predominantly by the steric and electronic properties of the coordinated chiral ligand. As discussed above, the collected structural data suggest the *exo-syn-syn* isomer of (S_p)-**8** (**VIa** in Scheme 5) to be the preferred species both in solution and in the solid state. In view of the fundamental mechanistic study by Bosnich et al.,[31] this intermediate should be the precursor to the major product. Indeed, **VIa** gives rise to (*R*)-**6** provided that the nucleophile attacks preferentially at the allyl terminus located *trans* to phosphorus as the donor with the stronger *trans*-influence.[32]

The preference of *exo-syn-syn* allyl intermediate (**VIa**) over

(26) Crystallization from chloroform−diethyl ether afforded the solvate (S_p)-**8**·$CHCl_3$. The crystal structures of (S_p)-**8**·Me_2CO and (S_p)-**8**·$CHCl_3$ are practically identical, differing only by the solvent molecules located in structural voids among the bulky complex molecules. Crystallographic data for (S_p)-**8**·$CHCl_3$: orthorhombic, space group $P2_12_12_1$ (no. 19), a = 9.5456(2) Å, b = 15.8592(5) Å, c = 28.4547(9) Å; V = 4307.6(2) Å^3, Z = 4 at 150 K.

(27) (a) Appleton, T. G.; Clark, H. C.; Manzer L. E. *Coord. Chem. Rev.* **1973**, *10*, 335−422. (b) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Applied Science: London, 1973; pp 299−303.

(28) Selected data: Pd−O 2.101(6) Å, Pd−P 2.321(2), Pd−C(allyl *trans*-P) 2.253(7), Pd−C(allyl *meso*) 2.139(8), and Pd−C(allyl *trans*-O) 2.113(9) Å at 293 K.

(29) Selected data: Pd−O 2.13(1) Å, Pd−P 2.286(6), Pd−C(allyl *trans*-P) 2.20(3), Pd−C(allyl *meso*) 2.10(2), and Pd−C(allyl *trans*-O) 2.07(2) Å at 213 K.

(30) Cambridge Structural Database, version 5.28 (November 2006) with updates of January and May 2007.

(31) Bosnich et al. have shown that the major allylic intermediate gives rise to the major product enantiomer: Mackenzie, P. B.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2046−2054.

(32) Theoretical calculations: (a) Bloechl, P.; Togni, A. *Organometallics* **1996**, *15*, 4125−4132. (b) Ward, T. R. *Organometallics* **1996**, *15*, 2836−2838.

the *endo-syn-syn* form (**VIb**) as the most probable other component can be accounted for by steric reasons. The crystallographic data (Scheme 5) indicate the diphenylallyl moiety in **VIa** to better avoid sterically congested space. Besides, both **VIa** and the η^2-alkene species **VIIa** resulting by addition of the nucleophile and rotation of the formed alkene retain better the possibility of stabilization via $\pi-\pi$ interactions of the aromatic rings than the intermediates occurring along the pathway involving the *endo-syn-syn* isomer (**VIb** → **VIIb**). It should be noted, however, that this explanation represents a summary of the available data, neglecting a possible structural reorganization of the ligand and individual reaction rates of the isomeric intermediates.

Introduction of a methyl group at the benzylic α-carbon destabilizes all intermediates whose phenyl group attached to the allylic terminus *trans* to the phosphorus is oriented upward with respect to the ferrocene unit, including the *exo-syn-syn* isomer. This holds particularly true for (S,S_p)-**4**, where the methyl groups point into the donor pocket. Accordingly, (S,S_p)-**4** shows the lowest ee among the donors derived from (S_p)-**1** (Table 1). A similar observation was made with C-chiral amides (*R*)- and (*S*)-(2-$Ph_2PC_6H_4$)C(O)NHCH(Me)Ph.[5c] It is also worth noting that the dominating role of planar chirality in amides obtained from (S_p)-**1** contrasts with the conclusions presented for the structurally related [2-(diphenylphosphino)ferrocenyl]-oxazolines, where the central chirality has been recognized as the main stereodiscriminating factor.[2e,19,33]

Conclusions

In summary, amides derived from planar-chiral acid (S_p)-**1** are efficient ligands for palladium-catalyzed, enantioselective allylic alkylation of 1,3-diphenylallyl acetate, producing the alkylated product preferably as the *R*-isomer. Their catalytic efficiency is much better than that achieved with analogous compounds derived from acid **V**[13] and similar to donors **I**[8,34] and **IV**.[11] The collected catalytic results indicate that the course of the catalyzed reaction is determined largely by the planar chirality. However, the N-substituents can be used to tune the catalyst properties through changing steric properties of the chiral pocket.

Experimental Section

Materials and Methods. The syntheses were performed under argon atmosphere with exclusion of direct daylight. Dichloromethane was dried by standing over anhydrous potassium carbonate and then distilled from calcium hydride. Hdpf,[35] (S_p)-**1**,[36] 1,3-diphenylallyl acetate (**5**),[37] and di-μ-chloridobis(η^3-1,3-diphenylallyl)dipalladium(II) (**7**)[38] were prepared following the literature procedures. Other chemicals (Lachema, Fluka) and solvents used for crystallizations and chromatography (Lach-Ner) were used without further purification.

NMR spectra were measured on a Varian Unity Inova 400 spectrometer at 25 °C. $^1H\{^{31}P\}$ NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer. Chemical shifts (δ/ppm) are given relative to internal $SiMe_4$ (^{13}C and ^1H) or to external 85% aqueous H_3PO_4 (^{31}P). The assignment of the NMR signals is based on COSY, ^{13}C gHSQC, and ^{13}C gHMBC spectra. IR spectra were recorded on an FT IR Nicolet Magna 650 spectrometer. Positive ion electron impact (EI) and fast atom bombardment (FAB) mass spectra (including high-resolution (HR) measurements) were obtained with a ZAB SEQ spectrometer. Electrospray (ESI) mass spectra were recorded on a Bruker Esquire 3000 spectrometer for methanol solutions. Optical rotations were determined with an Autopol III automatic polarimeter (Rudolph Research) at room temperature.

Safety Note. CAUTION! Although we have not encountered any problems, it should be noted that perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled only in small quantities and with great care.

General Procedure for the Preparation of the Amides. 1-Hydroxybenzotriazole (HOBt) and the respective acid were suspended in dichloromethane (15 mL), and the reaction mixture was stirred at 0 °C for 5 min. Then, *N*-[3-(dimethylamino)propyl]-*N*′-ethylcarbodiimide (EDC) was slowly added, and the formed solution was stirred at 0 °C for 30 min. Finally, the appropriate amine was introduced (diluted with a small amount of dichloromethane), and stirring was continued at room temperature for another 20 h. The mixture was extracted with 3 M HCl (10 mL), a saturated aqueous $NaHCO_3$ solution (2 × 10 mL), and brine (10 mL). The organic phase was separated, dried over $MgSO_4$, and evaporated under vacuum, leaving an orange residue, which was purified by column chromatography on silica gel using a dichloromethane−methanol mixture (20:1) as the eluent.

(S_p)-2-(Diphenylphosphino)-1-(*N*-benzylcarbamoyl)ferrocene [(S_p)-2]. Starting with acid (S_p)-**1** (104 mg, 0.25 mmol), HOBt (38 mg, 0.28 mmol), EDC (0.05 mL, 0.3 mmol), and benzylamine (29 mg, 0.27 mmol), the general procedure gave amide (S_p)-**2** as an orange, solid foam. Yield: 91 mg (72%). ^1H NMR ($CDCl_3$): δ 3.80 (m, 1 H, C_5H_3), 4.07 (s, 5 H, C_5H_5), 4.46 (m, 1 H, C_5H_3), 4.54 (d, $^3J_{HH}$ = 5.5 Hz, 2 H, CH_2), 5.19 (m, 1 H, C_5H_3), 7.10−7.53 (m, 15 H, 3 × *Ph*), 7.70 (br dt, $J_{PH} \approx 13$ Hz, $J_{HH} \approx 6$ Hz, 1 H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 43.58 (CH_2), 70.73 (C_5H_5), 71.49 (C_5H_3 *C*H), 73.76 (d, J_{PC} = 2 Hz, C_5H_3 *C*H), 74.41 (d, J_{PC} = 4 Hz, C_5H_3 *C*H), 74.98 (d, $^2J_{PC}$ = 9 Hz, C_5H_3 *C*−CONH), 80.70 (d, $^1J_{PC}$ = 19 Hz, C_5H_3 *C*−PPh_2), 127.06, 127.49 (2 × Ph *C*H); 128.3−128.6 (m, 4 × PPh_2 and Ph *C*H), 129.72 (PPh_2 and Ph *C*H), 132.13 (d, J_{PC} = 18 Hz, PPh_2 *C*H), 135.06 (d, J_{PC} = 21 Hz, PPh_2 *C*H), 135.76 (d, $^1J_{PC}$ = 6 Hz, PPh_2 C_{ipso}), 137.68 (d, $^1J_{PC}$ = 6 Hz, PPh_2 C_{ipso}), 138.69 (Ph C_{ipso}), 170.20 (d, $^3J_{PC}$ = 3 Hz, *C*ONH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −20.4 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} 3362 (m, N−H), 1628 (vs, amide I), 1530 (vs, amide II), 1285 (m), 1179 (m), 1105 (m), 1002 (m), 936 (m), 843 (m), 823 (m), 748 (vs), 694 (vs), 499 (s), 481 (s). EI-MS: *m*/*z* (relative abundance) 503 (100, $M^{+\bullet}$), 438 (90, $[M - C_5H_5]^+$), 412 (40, $[M - CH_2Ph]^+$), 346 (25, $[412 - C_5H_6]^+$), 302 (14, $[M - Ph_2PO]^+$), 256 (7), 222 (8), 201 (90, $[Ph_2PO]^+$), 183 (10), 170 (11), 129 (10), 111 (11), 97 (19), 91 (19, $[C_7H_7]^+$), 83 (22), 69 (32), 57 (39), 43 (34). HR-MS: calcd for $C_{30}H_{26}NOP^{56}Fe$ ($M^{+\bullet}$) 503.1101, found 503.1120. $[\alpha]_D$ = −236.5 (*c* 1.0, $CHCl_3$).

(R,S_p)-2-(Diphenylphosphino)-1-[*N*-(1-phenylethyl)carbamoyl]ferrocene [(R,S_p)-3]. Starting with (S_p)-**1** (104 mg, 0.25 mmol), HOBt (38 mg, 0.28 mmol), EDC (0.05 mL, 0.3 mmol), and (*R*)-(1-phenylethyl)amine (33 mg, 0.27 mmol), the above procedure gave amide (R,S_p)-**3** as an orange, solid foam. Yield: 97 mg (75%). ^1H NMR ($CDCl_3$): δ 1.58 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, $CHCH_3$), 3.74 (m, 1 H, C_5H_3), 4.15 (s, 5 H, C_5H_5), 4.44 (m, 1 H, C_5H_3), 5.17 (m, 1 H, C_5H_3), 5.20 (m, 1 H, $CHCH_3$), 6.98−7.56 (m, 15 H, 3 × *Ph*), 7.62 (dd, J = 7.9 Hz, J = 13.0 Hz, 1 H, CON*H*). $^{13}C\{^1H\}$ NMR

(33) You, S.-L.; Hou, X.-L.; Dai, L.-X.; Yu, Y.-H.; Xia, W. *J. Org. Chem.* **2002**, *67*, 4684−4695.

(34) It is worth noting that **I**-based catalysts produce preferably (*R*)-**6** under similar conditions.

(35) Podlaha, J.; Štěpnička, P.; Císařová, I.; Ludvík, J. *Organometallics* **1996**, *15*, 543−550.

(36) Štěpnička, P. *New J. Chem.* **2002**, *26*, 567−575.

(37) Acetate **5** was prepared by acetylation of 1,3-diphenylallyl alcohol, which results from reduction of chalcone: (a) Kohler, E. P.; Chadwell, H. M. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, pp 78−80. (b) Leung, W.; Cosway, S.; Jonmes, R. H. V.; McCann, H.; Wills, M. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2588−2594. (c) Watson, I. D. G.; Styler, S. A.; Yudin, A. K. *J. Am. Chem. Soc.* **2004**, *126*, 5086−5087.

(38) Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301−6311.

($CDCl_3$): δ 22.74 (CH*C*H_3), 48.98 (*C*HCH_3), 70.84 (C_5H_5), 71.28 (C_5H_3 *C*H), 73.96 (d, J_{PC} = 3 Hz, C_5H_3 *C*H), 74.40 (d, J_{PC} = 3 Hz, C_5H_3 *C*H), 74.91 (d, $^2J_{PC}$ = 9 Hz, C_5H_3 *C*−CONH), 80.70 (d, $^1J_{PC}$ = 18.9 Hz, C_5H_3 *C*−PPh_2), 125.88, 126.69 (2 × Ph *C*H); 128.2−128.6 (m, 4 × PPh_2 and Ph *C*H), 129.68 (PPh_2 and Ph *C*H), 132.38 (d, J_{PC} = 17 Hz, PPh_2 *C*H), 134.99 (d, J_{PC} = 20 Hz, PPh_2 *C*H), 135.55 (d, $^1J_{PC}$ = 7 Hz, PPh_2 C_{ipso}), 137.39 (d, $^1J_{PC}$ = 6 Hz, PPh_2 C_{ipso}), 143.33 (Ph C_{ipso}), 169.21 (d, $^3J_{PC}$ = 3 Hz, *C*ONH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −20.4 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} 3311 (br m, N−H), 1629 (s composite, amide I), 1528 (s, amide II), 1278 (w), 1260 (m), 1211 (w), 1107 (w), 1002 (w), 837 (w), 749 (vs composite), 700 (vs), 498 (s), 487 (s). EI-MS: *m*/*z* (relative abundance) 517 (100, $M^{+\bullet}$), 452 (66, $[M - C_5H_5]^+$), 412 (57, $[M - PhCHMe]^+$), 346 (21, $[412 - C_5H_6]^+$), 316 (15, $[M - Ph_2PO]^+$), 222 (5), 201 (53, $[Ph_2PO]^+$), 183 (5), 170 (5), 121 (6), 105 (12, $[PhCHMe]^+$), 56 (5). HR-MS: calcd for $C_{31}H_{28}NOP^{56}Fe$ ($M^{+\bullet}$) 517.1258, found 517.1242. $[\alpha]_D$ = −208.5 (*c* 1.0, $CHCl_3$).

(*S*,*S*$_p$)-2-(Diphenylphosphino)-1-[*N*-(1-phenylethyl)carbamoyl]-ferrocene [(*S*,*S*$_p$)-3]. Starting with (S_p)-**1** (104 mg, 0.25 mmol), HOBt (38 mg, 0.28 mmol), EDC (0.05 mL, 0.3 mmol), and (*S*)-(1-phenylethyl)amine (33 mg, 0.27 mmol), the general procedure afforded amide (*S*,S_p)-**3** as an orange, gummy material. Yield: 102 mg (79%). ^1H NMR ($CDCl_3$): δ 1.31 (d, $^3J_{HH}$ = 7.0 Hz, 3 H, C*H*$_3$), 3.77 (m, 1 H, C_5H_3), 3.98 (s, 5 H, C_5H_5), 4.43 (apparent t, $J \approx$ 2.7 Hz, 1 H, C_5H_3), 5.15 (m, 1 H, C*H*CH_3), 5.16 (m, 1 H, C_5H_3), 7.18−7.58 (m, 15 H, 3 × *Ph*), 7.77 (dd, J = 8.2 Hz, J = 14.3 Hz, 1 H, CON*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.90 (CH*C*H_3), 49.21 (*C*HCH_3), 70.66 (C_5H_5), 71.39 (C_5H_3 *C*H), 73.90 (d, J_{PC} = 3 Hz, C_5H_3 *C*H), 74.43 (d, J_{PC} = 3 Hz, C_5H_3 *C*H), 74.81 (d, $^2J_{PC}$ = 9 Hz, C_5H_3 *C*−CONH), 80.75 (d, $^1J_{PC}$ = 19 Hz, C_5H_3 *C*−PPh_2), 126.24, 127.16 (2 × Ph *C*H); 128.3−128.7 (m, 4 × PPh_2 and Ph *C*H), 129.75 (PPh_2 and Ph *C*H), 132.25 (d, J_{PC} = 18 Hz, PPh_2 *C*H), 135.0 (d, J_{PC} = 20 Hz, PPh_2 *C*H), 135.53 (d, $^1J_{PC}$ = 6 Hz, PPh_2 C_{ipso}), 137.42 (d, $^1J_{PC}$ = 6 Hz, PPh_2 C_{ipso}), 144.30 (Ph C_{ipso}), 169.21 (d, $^3J_{PC}$ = 3 Hz, *C*ONH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −20.1 (s). IR (RAS): $\tilde{\nu}$/cm^{-1} 3304 (br m, N−H), 1644 (vs, amide I), 1522 (s, amide II), 1310 (w), 1261 (m), 1211 (w), 1183 (w), 1157 (m), 1106 (m), 1093 (m), 1028 (w), 1002 (m), 821 (m), 744 (s), 697 (vs), 482 (m). EI-MS: *m*/*z* (relative abundance) 517 (100, $M^{+\bullet}$), 452 (66, $[M - C_5H_5]^+$), 412 (57, $[M - PhCHMe]^+$), 346 (21, $[412 - C_5H_6]^+$), 316 (15, $[M - Ph_2PO]^+$), 222 (5), 201 (53, $[Ph_2PO]^+$), 183 (5), 170 (5), 121 (6), 105 (12, $[PhCHMe]^+$), 56 (5). HR-MS: calcd for $C_{31}H_{28}NOP^{56}Fe$ ($M^{+\bullet}$) 517.1258, found 517.1264. $[\alpha]_D$ = −179 (*c* 1.0, $CHCl_3$).

(*R*)-1′-(Diphenylphosphino)-1-[*N*-(1-phenylethyl)carbamoyl]-ferrocene [(*R*)-4]. Following the general procedure with Hdpf (415 mg, 1.0 mmol), HOBt (161 mg, 1.2 mmol), EDC (0.22 mL, 1.25 mmol), and (*R*)-(1-phenylethyl)amine (133 mg, 1.1 mmol) gave amide (*R*)-**4** as an orange solid. Yield: 486 mg (94%). ^1H NMR ($CDCl_3$): δ 1.56 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, CH*Me*), 3.92, 4.00 (2 × m, 1 H, C_5H_4); 4.19 (apparent t, $^3J_{HH}$ = 1.9 Hz, 2 H, C_5H_4), 4.31, 4.34 (2 × dt, $J \approx$ 1.3, 2.5 Hz, 1 H, C_5H_4); 4.54−4.59 (m, 2 H, C_5H_4); 5.25 (virtual p, $J \approx$ 7.1 Hz, 1 H, C*H*Me), 6.17 (br d, $^3J_{HH}$ = 8.1 Hz, 1 H, N*H*), 7.18−7.42 (m, 15 H, *Ph*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.87 (CH*Me*), 48.75 (*C*HMe), 69.60 (d, J_{PC} = 2 Hz, C_5H_4 *C*H), 69.73 (d, J_{PC} = 1 Hz, C_5H_4 *C*H), 71.46 (2C, C_5H_4 *C*H), 72.64 (d, J_{PC} = 4 Hz, C_5H_4 *C*H), 72.78 (d, J_{PC} = 3 Hz, C_5H_4 *C*H), 74.14 (d, J_{PC} = 5 Hz, C_5H_4 *C*H), 74.27 (d, J_{PC} = 4 Hz, C_5H_4 *C*H), 126.38 (2C, Ph *C*H), 127.28 (Ph *C*H), 128.27 (d, J_{PC} = 7 Hz, PPh_2 *C*H), 128.28 (d, J_{PC} = 7 Hz, PPh_2 *C*H), 128.59 (PPh_2 *C*H), 128.75, 128.80 (2 × Ph *C*H); 133.35 (d, J_{PC} = 19 Hz, PPh_2 *C*H), 133.45 (d, J_{PC} = 20 Hz, PPh_2 *C*H), 138.04, 138.20 (2 × d, $^1J_{PC}$ = 9 Hz, PPh_2 C_{ipso}); 143.56 (Ph C_{ipso}), 168.91 (*C*O); the signal due to C_5H_4 *C*−CONH was not found due to overlaps. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.9 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} 1625 (vs, amide I), 1527 (vs, amide II), 1307 (m), 1275 (m), 1209 (w), 1175 (w), 1160 (m), 1092 (w), 1026 (s), 832 (m), 820 (m), 741 (vs), 697 (vs), 493 (s), 452 (m). EI-MS: *m*/*z* (relative abundance) 518 (9), 517 (26, $M^{+\bullet}$), 413 (20), 412 (72, $[M - PhCHMe]^+$), 322 (12), 321 (48), 316 (18, $[M - 201]^+$), 226 (8), 202 (15), 201 (100, $[Ph_2PO]^+$), 197 (9), 183 (8), 171 (15), 170 (11), 141 (6), 121 (6, $[FeC_5H_5]^+$), 105 (24), 79 (8), 77 (8), 56 (12, Fe^+). HR-MS: calcd for $C_{31}H_{28}{}^{56}FeNOP$ ($M^{+\bullet}$) 517.1258, found 517.1237. $[\alpha]_D$ = +48 (*c* 1.0, $CHCl_3$).

(*S*)-1′-(Diphenylphosphino)-1-[*N*-(1-phenylethyl)carbamoyl]-ferrocene [(*S*)-4]. Following the general procedure with Hdpf (415 mg, 1.0 mmol), HOBt (161 mg, 1.2 mmol), EDC (0.22 mL, 1.25 mmol), and (*S*)-(1-phenylethyl)amine (133 mg, 1.1 mmol) gave amide (*S*)-**4** as an orange solid. Yield: 465 mg (90%). The spectroscopic data are identical with those of the *R*-isomer, $[\alpha]_D$ = −47 (*c* 1.0, $CHCl_3$).

Asymmetric Allylic Alkylation: General Procedure.[39,14] Ligand (25 μmol), [{Pd(η^3-C_3H_5)Cl}$_2$] (4.8 mg, 13 μmol), and base (0.05 mmol) were mixed with dry dichloromethane (3 mL), and the mixture was stirred at room temperature for 30 min. Then, *rac*-1,3-diphenylprop-2-en-1-yl acetate (**5**; 126 mg, 0.5 mmol) was introduced followed, after stirring for another 5 min, by *N*,*O*-bis-(trimethylsilyl)acetamide (BSA; 0.37 mL, 1.5 mmol) and dimethyl malonate (0.17 mL, 1.5 mmol). The reaction mixture was stirred at the reaction temperature for 20 h. Then, it was washed with a saturated aqueous NH_4Cl solution (2 × 5 mL), and the organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. Subsequent purification by column chromatography (silica gel; hexane−ethyl acetate, 3:1) afforded the alkylation product. Optimization of the reaction conditions (Table 2) was performed at half scale.

Enantiomeric excesses were determined from ^1H NMR spectra recorded in C_6D_6 in the presence of chiral lanthanide shift reagent tris(3-trifluoroacetyl-*d*-camphorato)europium(III), Eu(facam)$_3$, while the configuration of the major component was assigned on the basis of optical rotation of the mixture.[40]

Preparation of (η^3-1,3-Diphenylallyl)[(S_p)-2-(diphenylphosphino)-1-(*N*-benzylcarbamoyl)ferrocene-κ^2*O*,*P*]palladium(II) Perchlorate [(S_p)-8]. A suspension of (S_p)-**2** (21 mg, 0.04 mmol) and **7** (13.4 mg, 0.02 mmol) in dichloromethane (3 mL) was stirred at room temperature for 15 min to give a clear orange solution. Then, silver perchlorate (8.5 mg, 0.04 mmol) was added, causing immediate formation of a white precipitate (AgCl). After stirring for 1 h, the precipitate was filtered off (PTFE syringe filter, 45 μm pore size) and the yellow-orange filtrate was layered with diethyl ether and allowed to crystallize at 4 °C for several days. The orange crystalline product was isolated by suction and dried *in vacuo*. Yield: 27 mg (75%). Anal. Calcd for $C_{45}H_{39}ClFeNO_5PPd\cdot 1.8CH_2Cl_2$: C 53.26, H 4.07, N 1.33. Found: C 53.32, H 3.77, N 1.30. ESI+: *m*/*z* 802 ($[Pd(\mathbf{2})(Ph_2C_3H_3)]^+$); the observed isotopic distribution fits the calculated one. (In the MS/MS spectrum, the ion at *m*/*z* 802 fragments to give ions *m*/*z* 609, corresponding to $[Pd(\mathbf{2})]^+$.) IR (Nujol): $\tilde{\nu}$/cm^{-1} 1592 (vs, C═O), 1553 (s), 1281 (m), 1208 (w), 1167 (m), 1113 (br vs, ClO_4), 1067 (vs, ClO_4), 1054 (s, ClO_4), 1026 (m), 1010 (w), 916 (m), 840 (m), 821 (m), 755 (s), 695 (s), 688 (s), 623 (s, ClO_4), 548 (s), 523 (s), 513 (s), 490 (m), 465 (s), 456 (s).

Solution NMR spectra show the presence of two isomers in ca. 2.7:1 ratio. NMR data for the major isomer (*exo-syn-syn*). ^1H NMR ($CDCl_3$): δ 3.91, 3.97 (2 × dd, $^2J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 6.4 Hz, 1 H, NHC*H*$_2$Ph), 3.97 (m, 1 H, C_5H_3), 4.17 (s, 5 H, C_5H_5), 4.66 (apparent t, J = 2.7 Hz, 1 H, C_5H_3), 5.00 (d, $^3J_{HH}$ = 10.7 Hz, 1 H, allyl CH *trans*-O), 5.58 (m, 1 H, C_5H_3), 5.98 (dd, $^3J_{HH}$ = 13.3 Hz, $^3J_{PH}$ = 8.4 Hz, 1 H, allyl CH *trans*-P), 6.61 (dd, $^3J_{HH}$ = 13.3 Hz, $^3J_{HH}$ = 10.9 Hz, 1 H, allyl CH *meso*), 6.12 and 6.86−7.76 (m, 25 H, 5 × Ph), 8.36 (t, $^3J_{HH}$ = 6.7 Hz, 1 H, NH). $^{31}P\{^1H\}$ NMR

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Table 3. Crystallographic Data, Data Collection, and Structure Refinement Parameters for (S_p)-2 and (S_p)-8·Me$_2$CO

	(S_p)-**2**	(S_p)-**8**·Me$_2$CO
formula	$C_{30}H_{26}FeNOP$	$C_{48}H_{45}ClFeNO_6PPd$[f]
M (g mol^{-1})	503.34	960.52
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)
T (K)	150(2)	150(2)
a (Å)	9.8424(1)	9.4409(1)
b (Å)	10.6075(1)	15.8585(2)
c (Å)	23.6117(4)	28.5158(3)
V (Å^3)	2465.14(5)	4269.34(8)
Z	4	4
D_{calc} (g mL^{-1})	1.356	1.494
μ(Mo Kα) (mm^{-1})	0.700	0.912
T[a]	*e*	0.673−0.860
total no. of diffractions	32 793	52 778
no. of unique/obsd[c] diffractions	5637/5298	9761/8985
R_{int} (%)[b]	4.8	6.25
R (obsd data) (%)[c,d]	2.68	3.30
R, R_w (all data) (%)[d]	3.11, 6.11	3.90, 8.09
Flack's parameter	−0.00(1)	−0.01(2)
$\Delta\rho$ (e Å^{-3})	0.18, −0.32	0.65, −0.47
CCDC entry	649277	649278

[a] The range of transmission coefficients. [b] $R_{int} = \sum|F_o^2 - F_o^2(\text{mean})|/\sum F_o^2$, where F_o^2(mean) is the average intensity of symmetry-equivalent diffractions. [c] Diffractions with $I_o > 2\sigma(I_o)$. [d] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum w(F_o^2)^2]^{1/2}$. [e] Not corrected. [f] $[C_{45}H_{39}FeNOPPd]ClO_4 \cdot C_3H_6O$.

($CDCl_3$): δ +18.6. NMR data for the minor isomer. ^{1}H NMR ($CDCl_3$): δ 3.82 (m, 1 H, C_5H_3), 4.02 (s, 5 H, C_5H_5), 4.07 (dd, $^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 6.2 Hz, 1 H, NHCH_2Ph), 4.61 (apparent t, J = 2.7 Hz, 1 H, C_5H_3), 4.92 (d, $^3J_{HH}$ = 11.6 Hz, 1 H, allyl CH *trans*-O), 5.56 (m, 1 H, C_5H_3), 5.75 (dd, $^3J_{HH}$ = 12.9 Hz, $^3J_{PH}$ = 8.6 Hz, 1 H, allyl CH *trans*-P), 6.12 and 6.86−7.76 (m, 25 H, 5 × Ph), 8.40 (t, $^3J_{HH}$ = 6.5 Hz, 1 H, NH); signals due to NHCH_2Ph and allylic *meso*-CH (δ_H ca. 6.9 ppm) are obscured by other signals. ^{31}P{^{1}H} NMR ($CDCl_3$): δ +19.1.

X-ray Crystallography. Crystals suitable for single-crystal X-ray diffraction analysis were grown from ethyl acetate−hexane ((S_p)-**2**: orange plate, 0.03 × 0.18 × 0.42 mm^3) and from acetone−diethyl ether ((S_p)-**8**·Me$_2$CO: orange prism, 0.20 × 0.30 × 0.55 mm^3). Full-set diffraction data ($\pm h \pm k \pm l$; $2\theta \le 55°$) were collected on a Nonius KappaCCD diffractometer equipped with a Cryostream Cooler (Oxford Cryosystems) at 150(2) K using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) and analyzed with the HKL program package.[41] The data for (S_p)-**8**·Me$_2$CO were corrected for absorption by using a Gaussian method. The range of transmission factors is given in Table 3.

The structures were solved by direct methods (SIR97[42]) and refined by full-matrix least-squares on F^2 (SHELXL97[43]). The non-hydrogen atoms were refined with anisotropic displacement parameters. The amide hydrogen atom [H(1N)] in (S_p)-**2** and (S_p)-**8**·Me$_2$CO as well as the allylic hydrogens [H(31), H(32), and H(33)] in (S_p)-**8**·Me$_2$CO were located on the electron density maps and refined as riding atoms. All other hydrogen atoms were included in the calculated positions and refined as riding atoms with U_{iso}(H) assigned to a multiple of U_{eq} of their bonding atom. Selected crystallographic data are given in Table 3. Geometric parameters and structural drawings were obtained by using a recent version of Platon program.[44] The calculated numerical values are rounded with respect to their estimated standard deviations (esd's) given with one decimal; parameters involving hydrogen atoms in calculated positions are given without esd's.

Full crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and can be obtained free from http://www.ccdc.cam.ac.uk/conts/retrieving.html. The deposition numbers are quoted in Table 3.

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Supporting Information Available: Complete crystallographic data in CIF format for compounds (S_p)-**2** and (S_p)-**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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