Importance of Planar Chirality in Chiral Catalysts with Three Chiral Elements: The Role of Planar Chirality in 2′-Substituted 1,1′-P,N-Ferrocene Ligands on the Enantioselectivity in Pd-Catalyzed Allylic Substitution

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Abstract: A series of novel planar chiral 2′-substituted 1,1′-P,N-ferrocene ligands **9**−**11**, **14**, and **16** were prepared with diastereopurity >99:1 and found to be effective in asymmetric allylic alkylation and amination reactions. Ligand **14** furnished the highest enantiomeric excess, 98.5% and 96.5% ee in alkylation and amination reactions, respectively. The role of planar chirality in asymmetric reactions has been examined, and decisive effects on enantioselectivity as well as the control of absolute configuration in palladium-catalyzed allylic alkylation and amination reactions were observed. To clarify why and how the planar chirality governed the stereochemical outcome, X-ray crystallographic structures of η^3-diphenylallyl Pd complexes, ^{1}H NMR, ^{31}P NMR spectra of palladium dichloride complexes, and η^3-diphenylallyl Pd complexes of three 1,1′-P,N-ferrocene ligands were analyzed with the aid of COSY and 2D NOESY experiments. All results led to the conclusion that planar chirality influences the stereochemical outcome by changing or even inverting the ratio of two rotamers because of the steric interaction between a planar chiral group and the coordination site.

Introduction

Catalytic enantioselective reactions have attracted great interest among synthetic chemists in recent years, and many efforts in preparing efficient ligands have been made.[1] It is noteworthy that most of the chiral ligands currently used consist of central chirality and/or axial chirality. Since the pioneering work of Hayashi and co-workers,[2a] the use of planar chiral ferrocene ligands has grown[2] rapidly, culminating recently in two industrial asymmetric hydrogenation processes.[3] Lately, several new approaches have appeared for the introduction of planar chirality to ferrocene, key contributors being Sammakia,[4a] Richards,[4b] Uemura[4c] (oxazoline system), Kagan[5] (acetal and sulfate system), Enders[6] (SAMP system), and Snieckus[7] (sparteine system). Ferrocene ligands have therefore received extremely intensive attention.[8] Although many excellent results were derived from planar chiral ferrocene ligands, the role of planar chirality was still unclear. Some examples showed that the planar chirality had a significant effect on the enantioselectivity,[9] while in other examples it was not so apparent.[10a,b] To date, there are only a few reports of attempts to investigate the role of planar

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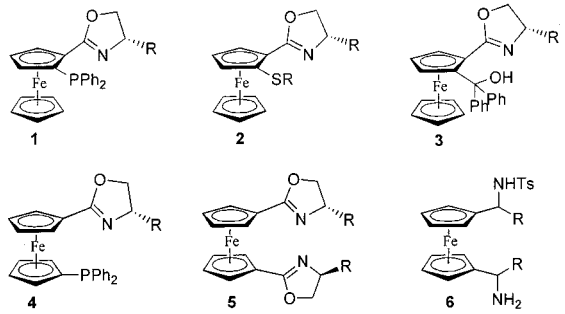
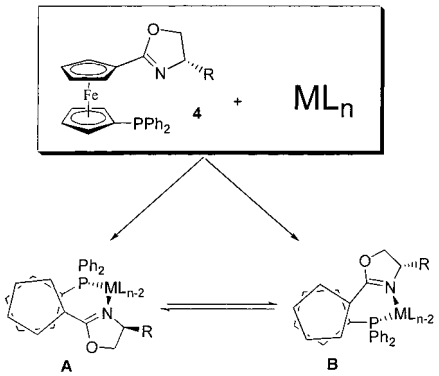
chirality on the stereochemical outcome in asymmetric synthesis.[9b,10a] Recently, the work of Fu and co-workers[11] on the single planar chiral ferrocene ligands revealed that they are highly efficient catalysts for asymmetric reactions. There is an urgent need to clarify the contradictory results on the role of planar chirality in ferrocene systems for the purpose of new efficient ligand design. In the literature, most ferrocene-based works dealt with 1,2-disustituted ferrocene ligands having two donor groups on the same Cp ring, e.g., **1**,[4b] **2**,[10a] and **3**.[9b] Recently, Ikeda,[12a,b] Ahn,[12c] and Knochel[13] reported the new 1,1′-disubstituted ferrocenyl ligands **4**, **5**, and **6**. From these catalysts, good enantioselectivities were obtained for several asymmetric reactions. However, the introduction of planar chirality has not been reported for this 1,1′-disubstituted ferrocene system prior to now.



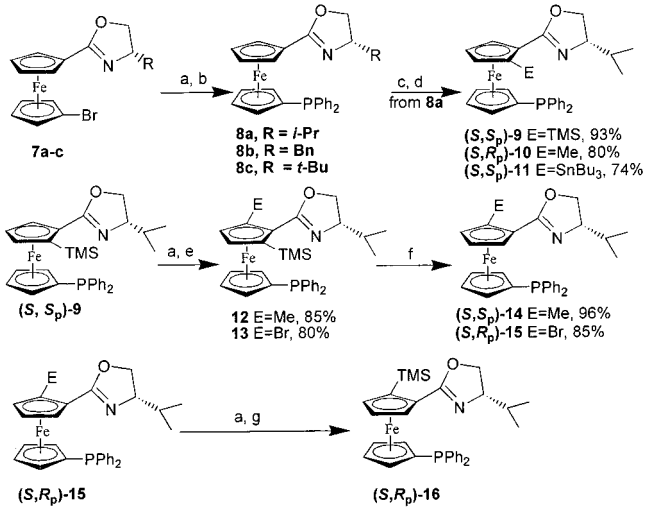
Ligand **4** has no planar chirality on the ferrocene backbone. However, coordination with a metal nevertheless leads to the formation of two rotamers, **A** and **B** (Scheme 1), due to the rotation of the Cp rings.[12b] This newly formed chirality is assigned as axial chirality.

Furthermore, it is worthy of note that, after introduction of planar chirality to ligand **4** and coordination with a metal, three kinds of chiral elements (central, axial, and planar chirality) in one catalyst will be installed. This interesting situation prompted us to explore the enantioselective ability of this three-chiral-elements catalyst in asymmetric reactions. As a part of our program[9c,10] aimed at the design of chiral ligands and their applications to asymmetric synthesis, we synthesized several novel planar chiral 1,1′-P,N-2′-substituted ferrocene ligands, **9**−**11**, **14**, and **16**. A preliminary communication[14] reported that these ligands were effective in Pd-catalyzed allylic alkylation reactions with excellent yield and excellent enantioselectivity. It was also apparent that planar chirality is decisive in exerting control over both absolute configuration and enantiomeric excess. In this report, we would like to answer the following three questions: (1) Are all three of these elements of chirality necessary for excellent enantioselectivity? (2) What is the role of each chirality on the stereo outcome? (3) Which chirality is more influential in the enantioselective control of the products?

Scheme 1



Scheme 2[a]



[a] Conditions: (a) *n*-BuLi/THF, −78 °C. (b) Ph_2PCl, 78%. (c) *n*-BuLi/Et_2O, TMEDA, −78 °C. (d) E^+ (MeI, TMSCl, or *n*-Bu_3SnCl). (e) E^+ (MeI or $BrCF_2CF_2Br$). (f) TBA/THF, reflux. (g) TMSCl, 73%.

In the meantime, we would like to provide detailed experimental evidence and extend the scope of application to allylic amination.

Results and Discussion

Synthesis of Ligands. As shown in Scheme 2, ferrocenyloxazoline derivatives **7a**−**c**, synthesized according to Bryce's method,[14,15] were treated with *n*-BuLi in THF at −78 °C for 0.5 h, followed by trapping with Ph_2PCl to afford 1-diphenylphosphino-1′-oxazolinylferrocenes **8a**−**c**. Directed diastereoselective ortho-lithiation of **8a** according to Richards's procedure,[16] followed by treatment with an electrophile (MeI, TMSCl, or Bu_3SnCl), gave 2′-substituted compound **9**, **10**, or **11**, respectively. Compound **9** was again lithiated in THF at −78 °C for 2 h, followed by trapping with an electrophile (MeI or $BrCF_2CF_2Br$), to afford ferrocene derivatives **12** and **13**. Conversion of **12** and **13** to **14** and **15**, respectively, was accomplished by protodesilylation with TBAF in 96% and 85% yields. A bromo-lithium exchange of **15** followed by quenching of the resulting lithium salt with TMSCl then furnished **16**. The diastereopurity of each of these planar chiral compounds as determined from 300 MHz ^{1}H NMR was >99:1. Ligands **14** and **16** have a sense of planar chirality opposite to that of ligands **10** and **9**.

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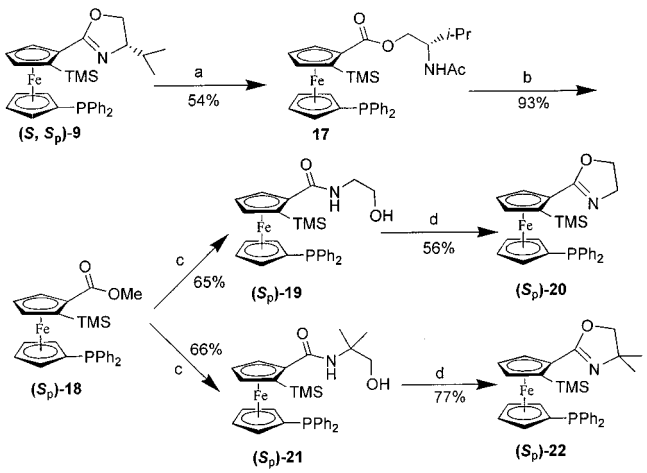
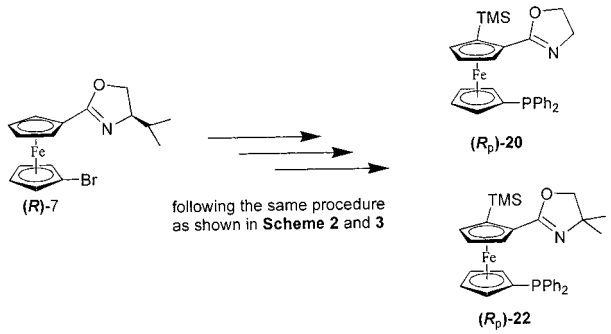
Scheme 3[a]



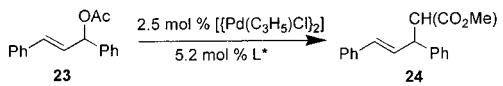
[a] Conditions: (a) (1) TFA/H_2O/Na_2SO_4; (2) Ac_2O/Py. (b) MeONa/MeOH, reflux. (c) Amino alcohol (neat)/Na. (d) Et_3N/CH_3SO_2Cl/DCM.

Scheme 4



To clarify the role of planar chirality on stereochemical outcome, we also synthesized ligands (S_p)-**20** and (S_p)-**22**, which contained only planar chirality. As shown in Scheme 3, compound (S,S_p)-**9** was converted into the corresponding ester (S,S_p)-**17** by employing Meyers's procedure.[17] The corresponding enantiomerically pure methyl ester (S_p)-**18** was easily formed in 93% yield from (S,S_p)-**17** through treatment with NaOMe. Compound **18** was allowed to react in neat amino alcohols at 100 °C for 1−1.5 h in the presence of a small amount of sodium metal, leading to the corresponding amides (S_p)-**19** and (S_p)-**21** in moderate yields. Further conversion of (S_p)-**19** and (S_p)-**21** was accomplished via the corresponding mesylate intermediates, which were cyclized in situ to our targets (S_p)-**20** and (S_p)-**22** in moderate yields. For the sake of comparison, the corresponding (R_p)-**20** and (R_p)-**22** were also prepared (Scheme 4).

Asymmetric Allylic Alkylation. Chiral P,N-ligands were proved to be effective in several kinds of metal-catalyzed asymmetric reactions,[18] especially in palladium-catalyzed allylic substitution.[18a−k] In particular, ligand **8a** gave 91% ee in palladium-catalyzed allylic substitution.[12b−d] In our previous work, we studied the role of planar chirality of 1,2-N,S-ferrocene ligands in the palladium-catalyzed allylic alkylation.[10a] To investigate the role of the planar chirality of our new kind of 1,1′-P,N-2′-disubstituted ferrocene ligands in metal-catalyzed asymmetric reactions, Pd-catalyzed allylic alkylation was also chosen as a model reaction (eq 1).[19] The results are summarized in Table 1.



(1)

Table 1. Effect of Different Planar Chiral Ligands on Enantioselectivity and Configuration of the Product in Palladium-Catalyzed Allylic Alkylation[a]

entry	ligand	yield (%)[d]	ee value (%)[e]	configuration[f]
1	(*S*)-**8a**	99	91.0	*S*
2[b]	(*S*)-**8a**	98	92.8	*S*
3	(S,S_p)-**9**	98	69.7	*R*
4[b]	(S,S_p)-**9**	99	64.0	*R*
5[b]	(S,R_p)-**10**	98	34.2	*R*
6[b]	(S,S_p)-**14**	99	**98.5**	*S*
7	(S,S_p)-**14**	99	98.2	*S*
8[c]	(S,S_p)-**14**	99	87.8	*S*
9[b]	(S,R_p)-**16**	99	**98.6**	*S*
10	(S,R_p)-**16**	99	97.8	*S*
11	(S,S_p)-**11**	98	83.3	*R*
12[b]	(S,S_p)-**11**	98	77.7	*R*
13	(S_p)-**20**	99	79.4	*R*
14	(S_p)-**22**	99	81.9	*R*
15	(R_p)-**20**	98	79.6	*S*
16	(R_p)-**22**	98	84.1	*S*

[a] Molecular ratio: [Pd(η^3-C_3H_5)Cl]$_2$/ligand/**23**/dimethyl malonate/BSA/KOAc = 2.5/5.2/100/300/300/5. [b] No KOAc was used. [c] 10 equiv of KOAc was used vs ligand. [d] Isolated yield. [e] The ee value for **24** was determined by HPLC analysis using a Chiralcel OD column. [f] Configurations were assigned by comparison with the sign of optical rotation.

As can be seen in Table 1, a dramatic change of the enantioselectivity of the reaction was observed with **8a** and **9**; i.e., the enantiomeric excess of the reaction product **24** changed from 91% with *S* configuration by using ligand **8a** to 69.7% with *R* configuration by using ligand **9** (entries 1and 3). It therefore appears that the effect of the newly introduced TMS group is significant. This exciting result encouraged us to probe the effect of the newly introduced group with opposite planar chirality, which may result in the increase of ee values while keeping the same absolute configuration of the product. Therefore, (S,S_p)-**14** was subjected to the same reaction. As expected, a remarkable improvement of the ee value (entry 6, 98.5%, *S* configuration) was revealed. This result indicates that planar chirality is significant in the control of the stereochemical outcome. In an attempt to support our reasoning, ligands (S_p)-**20** and (S_p)-**22** with only planar chirality were tested for the same reaction. Good enantioselectivities (entries 13 and 14, 79.5% and 81.5% ee) were observed with both ligands, which

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Table 2. Enantioselective Allylic Amination[a]

entry	ligand	time (h)	solvent	yield (%)[b]	ee (%)[c] (configuration)[d]
1	(S,S_p)-**14**	8	THF	97	90.8 (*R*)
2	(S,S_p)-**14**	6	DME	99	92.4 (*R*)
3	(S,S_p)-**14**	6	dioxane	96	92.6 (*R*)
4	(S,S_p)-**14**	3	CH_3CN	99	88.5 (*R*)
5	(S,S_p)-**14**	3	DCM	98	94.5 (*R*)
6	(S,S_p)-**14**	1	DCE	99	**96.5 (*R*)**
7	(*S*)-**8a**	1.5	DCE	96	89.7 (*R*)
8	(S,S_p)-**9**	8	DCE	25	32.3 (*S*)
9	(S_p)-**20**	0.5	DCE	99	67.3 (*S*)
10	(S_p)-**22**	1	DCE	99	89.5 (*S*)

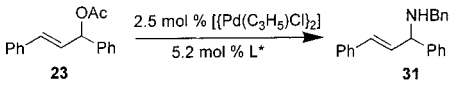
[a] Molecular ratio: [Pd(η^3-C_3H_5)Cl]$_2$/ligand/**23**/$BnNH_2$ = 2.5/5.2/100/200. [b] Isolated yields. [c] The ee value for **31** was determined by HPLC analysis using a Chiralcel OJ column. [d] Configurations were assigned by comparison with the sign of optical rotation.

indicate that the planar chirality should be decisive for the enantioselectivity. Furthermore, the antipodes of (S_p)-**20** and (S_p)-**22**, (R_p)-**20** and (R_p)-**22**, also afford good enantioselectivities (entries 15 and 16, 79.6% and 84.1% ee), as expected, but in the *R* configurations. This finding further indicates the decisive role of planar chirality in the control of enantioselectivity. To study the steric effect of the 2′-substituted group, (S,S_p)-**10** and (S,R_p)-**16** were also tested. Reasonable results were obtained to show a relationship between the steric bulkiness of the 2′-substituent and enantioselectivity; i.e., the bulkier the group is, the higher the ee value will be (viz. ligand **9** versus **10**, entries 4 versus 5, and **14** versus **16**, entries 6 versus 9). Consequently, it is anticipated that replacing the TMS group with a sterically bulkier 2′-substituent in ligand **9** will result in higher enantioselectivity. Because of the low electrophilicity of the Ph_3Si- group, which could not be introduced onto the Cp ring, finally Bu_3Sn- was chosen for this purpose. Also as expected, a higher ee value (83.3% ee of *R* configuration, entry 11) was obtained when ligand **11** was used for this reaction.

It was reported in the literature[20] that the addition of KOAc might sometimes increase the ee value. However, in our case, this is not true for some ligands. For ligands **9** and **11** having S_p planar chirality configuration, the addition of KOAc did increase the ee value of reaction product (comparing entries 4 to 3 and 12 to 11). Whereas for ligand **8a** and ligands **14** and **16**, having opposite planar chirality, almost the same results were obtained with the addition of KOAc (entries 2, 7, and 10).

The only difference between ligands **9** and **16** is the disposition of a TMS group. (S_p)-TMS for **9** and (R_p)-TMS for **16**, while the enantioselectivity of the reaction is 69.7% ee of product with *R* configuration by using **9** and 97.8% ee of *S* configuration for **16**.

Asymmetric Allylic Amination. To extend the scope of the application of these ligands, the most efficient ligand, (S,S_p)-**14**, as mentioned above, was employed in asymmetric allylic amination with benzylamine as a nucleophile. [21]



(2)

As shown in Table 2, different solvents obviously affected the reactivity as well as the enantioselectivity. The best result was obtained with 1,2-dichloroethane (DCE) as solvent, which showed the highest reaction rate and the highest enantiomeric excess of 96.5% (entry 6) in comparison with other solvents.

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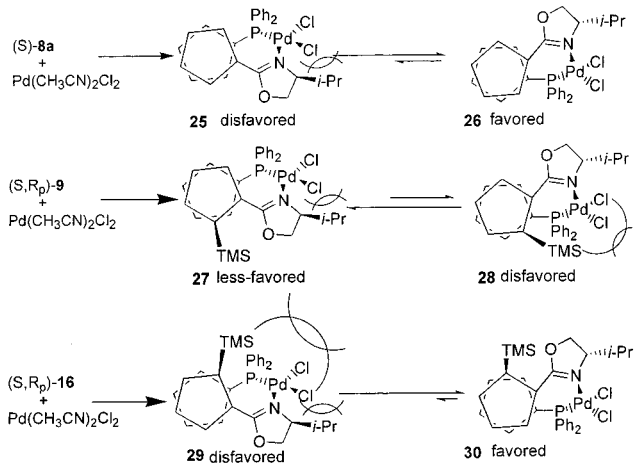
(21) Review for allylic amination: Johannsen, M.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689.

Scheme 5. Proposed Isomerism of $PdCl_2(CH_3CN)_2$ Complexes with Ferrocene Ligands **8a**, **9**, and **16**



Under the same reaction conditions, ligands (*S*)-**8a** and (S,S_p)-**9**, which has a configuration of planar chirality opposite to that of **14**, as well as ligands (S_p)-**20** and (S_p)-**22** with only planar chirality, were utilized for this reaction in order to test the role of planar chirality. The results in Table 2 demonstrate that planar chirality is also crucial to the stereochemistry of the reaction product when the results for ligand (S,S_p)-**9** are compared to those for ligand (S,S_p)-**14**. Furthermore, ligands **20** and **22**, having only planar chirality, also afforded good enantioselectivities (67.3% and 89.5%, respectively).

For the aforementioned allylic substitution reactions, all ligands are effective, and among them **14** and **16** are the two best ligands in terms of yield and enantioselectivity. Ligands **14** and **16** possess a (S_p)-Me group and a (R_p)-TMS group, respectively, situated at the counterclockwise neighboring position relative to the oxazoline group. As can be seen, **14** and **16** are better ligands than ligands **9** ((S_p)-TMS) and **10** ((R_p)-Me), having TMS and Me groups situated at the clockwise neighboring position. In addition, different dispositions of the neighboring groups also afforded different absolute configurations of the reaction products, i.e., *S* configuration from **14** and **16** but *R* configuration from **9** and **10**. It has also been shown that ligands (S_p)-**20** and (S_p)-**22** with only planar chirality also lead to good enantioselectivity (vide supra) and *R* configuration of the product, which is the same as that from ligand **9** that bears also a (S_p)-TMS group. Accordingly, the (R_p)-**20** and (R_p)-**22** afforded good ee values and *S* configuration of the product, which is the same with ligand **16** bearing a (R_p)-TMS group. Therefore, it appears that planar chiral groups play a decisive role in controlling enantioselectivities as well as the absolute configurations of the reaction products.

NMR Study of the Palladium Complexes of the Ligands. On complexation of **8a** (no planar chirality), **9** ((S_p)-TMS planar chirality), and **16** ((R_p)-TMS planar chirality) with dichlorobis(acetonitrile)-palladium(II) in acetonitrile-d_3, new axial chiralities will be formed. The existing central and planar chiralities may induce different ratios of the newly formed diastereomers, which could be examined with ^{1}H and ^{31}P NMR spectrometry. The ^{31}P NMR spectrum of the complex of **8a** with Pd $(CH_3CN)_2Cl_2$ exhibited two major peaks in a ratio of 62:38, which was consistent with the literature.[12b] The major one might be assigned to diastereomer **26** (Scheme 5), which has less steric interaction than **25**. However, for the complex with **9**, the ratio was changed to 42:58, and thus the major peak might be assigned to diastereomer **27**, on the basis of the assumption that a (S_p)-TMS group has a greater interaction on the coordination sites

Table 3. Selected 400 MHz ^{1}H NMR Chemical Shifts of Allylic Protons in Complexes **8aa**, **14a**, and **9a** in CD_2Cl_2

P- - -N	**8aa** (major)	**14a** (major)	**9a** (major)	**9a** (minor)
H^a	5.95	6.02	6.35	6.10
H^b	6.84	6.81[a]	6.65	6.65
H^c	4.55[a]	4.49	4.38[a]	4.59[a]

[a] Resonance could not be unequivocally assigned.

than an ^{i}Pr group in **28**. For the complex with **16** the ratio became 22:1, which might be assigned to diastereomers **30** (major) and **29** (minor) (Scheme 5). From the ^{31}P NMR data, it is evident that the addition of a third group in a proper position might change or even invert the ratio of the two rotamers. The above ratios are in parallel with the ee values of the product, i.e., 91% (*S*) for ligand **8a**, 69.7% (*R*) for ligand **9**, and 98.6% (*S*) for ligand **16**. Scheme 5 also illustrates that the linkage of N−Pd−P is clockwise in the preferred isomers of **8a** and **16**. For **9**, the above linkage of the preferred isomer is, however, altered to counterclockwise, and thus different absolute configurations of the product were obtained (cf. Table 1). By this consideration, a bulkier (S_p)-Bu_3Sn group in ligand **9** should further shift the equilibrium to the left. In agreement with this, ligand (S,S_p)-**11** increased the enantioselectivity of the reaction (entries 3 versus 11 in Table 1).

The ^{31}P NMR data revealed the ratio of diastereoisomers during the formation of axial chirality by complexation with Pd species. Furthermore, the enantioselectivity, especially the chiral sense of induction, in this allylic substitution was also related to the formation of endo or exo intermediates (W-type or M-type) of η^3-allylpalladium intermediates[22] as well as the trans effect of the ligating atom. It is known that the phosphorus atom is a better π-acceptor than the nitrogen atom in an π-allylpalladium complex bearing a P,N-bidentate ligand.[23] This preference consequently leads to a predominant nucleophilic attack at the allylic carbon terminus trans to the Pd−P bond.

To comprehensively understand this enantioselective reaction, solution NMR studies on the cationic palladium(II) 1,3-diphenylallyl intermediates were carried out, in the hope of getting some insight into the favored formation of endo or exo diastereomers in a rotamer and/or the ratio of two rotamers. The information garnered in this manner could be useful for future rational ligand design in this area.

Initially, three cationic palladium complexes, [Pd (η^3-1,3-diphenylallyl) (*S*-**8a**)]SbF_6 (**8aa**), [Pd (η^3-1,3-diphenylallyl) ((S,S_p)-**14**)]SbF_6 (**14a**), and [Pd (η^3-1,3-diphenylallyl) ((S,S_p)-**9**)]SbF_6 (**9a**), were prepared according to a literature method.[22a]

For complex **8aa** without planar chirality, two diastereomeric intermediates were observed in both its ^{1}H (Table 3) and ^{31}P NMR spectra, in a ratio of 14:1. The assignment of the major diastereomer as exo−syn−syn (M-type) (**8aa**) configuration is based on two critical NOEs experiments. First, a strong NOE between the two allyl terminal protons H^a and H^c indicates a syn−syn arrangement. The second key NOE, between the allyl terminal proton H^a trans to phosphorus and Cp ring proton H^2, confirms the exo configuration. [Nomenclature note: the endo isomer is defined as the isomer that is the central allyl proton and points to the ferrocene core]. Because the trans effect directs nucleophilic addition to the allyl terminus trans to phosphorus atom, the (*S*)-enantiomer should be the predominant product, which is consistent with our experimental results. For this rotamer, the W-type (**8aa** minor) would endure severe steric interaction between the allylic phenyl group and the bisphenylphosphino group as well as the *i*-Pr group. For complex **14a**, possessing a (S_p)-Me planar chiral group, there are also two diastereomeric intermediates observed from both ^{1}H (Table 3) and ^{31}P NMR spectra, present in a ratio of 14:1. The major diastereomer was assigned as exo−syn−syn (**14a**) configuration by NOE study (partial 2D NOESY spectra of **8aa** and **14a** are shown in Figure 1) similar to that of complex **8aa**. This is also consistent with the absolute configuration of the product of our experimental result. Scheme 6 shows that complexes **8aa** and **14a** also possess similar exo−syn−syn configurations and depicts that the (S_p)-Me in complex **14a** is away from the reaction site, which is consistent with its X-ray diffraction structure (vide infra).

However, for complex **9a**, in contrast to complexes **8aa** and **14a**, there are three diastereomeric intermediates, as shown in both ^{1}H (Table 3) and ^{31}P NMR spectra, present in a ratio of 59:36:5. To answer the question as to which one of these three intermediates belongs to the diastereomers due to axial chirality and which one belongs to the exo or endo intermediate, the ^{1}H NMR spectra were carefully analyzed. The full assignment of ^{1}H NMR of the **9a-A** and **9a-B** intermediates was facilitated by observing the characteristic pattern (a doublet) of the allylic proton H^a (or H$^{a\prime}$) trans to the phosphorus atom, and all other allyl protons signals were deduced from COSY experiments. However, it appears difficult to assign signals of the third intermediate (**9a-C**). To characterize the two major components, we carried out a 2D NOESY experiment (partial spectra of the 2D NOESY of **9a** are shown in Figure 1). In the NOESY spectrum, we observed three important NOEs for **9a-B**: (1) a NOE cross-peak between the two allylic terminal protons H$^{a\prime}$ and H$^{c\prime}$; (2) a NOE cross-peak between the ortho proton H$^{d\prime}$ of the phenyl group on the allylic moiety and the Cp ring proton H$^{5\prime}$; (3) a NOE cross-peak between the allylic proton H$^{a\prime}$ trans to phosphorus and the methine proton of the isopropyl group. These results led us to assign an endo−syn−syn configuration for **9a-B**. In addition, the absence of NOE cross-signal between the allylic proton H$^{a\prime}$ and the Cp ring proton H$^{5\prime}$ indicates that the minor diastereomer also possesses an endo configuration. The major diastereomer, **9a-A**, was assigned as exo−syn−syn due to two key NOEs: (1) a strong NOE between the two allylic terminal protons H^a and H^c; (2) the NOE between the allylic terminal proton H^a trans to phosphorus and the Cp ring proton H^5. Furthermore, a section of the phase-sensitive NOESY spectrum (Figure 1) showed that these two intermediates exchanged on the time scale of the NOE and particularly the interchange between the allylic proton H^a (or H$^{a\prime}$) of one diastereomer with the allylic proton H$^{c\prime}$ (or H^c) of the other, due to the rotation about the Pd−C bond in a σ-allyl intermediate.[22b,24] Therefore, these two major intermediates can be unambiguously assigned as **9a-A** (major) and **9a-B** (minor) as shown in Scheme 7. Similar to complex **14a**, the (S_p)-TMS of the two major components of complex **9a** are also away from the reaction site. Thus, the third tiny component may probably

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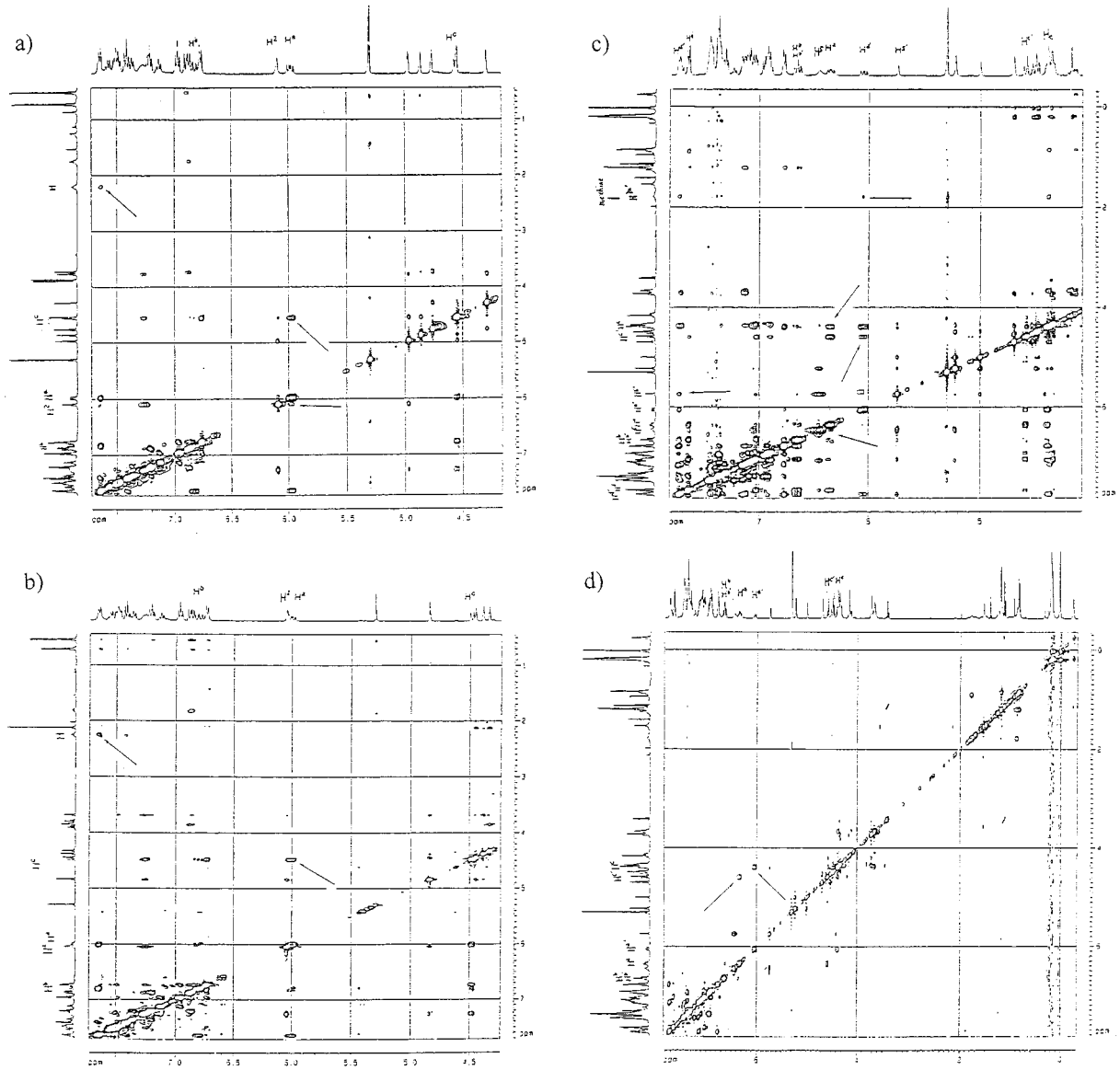
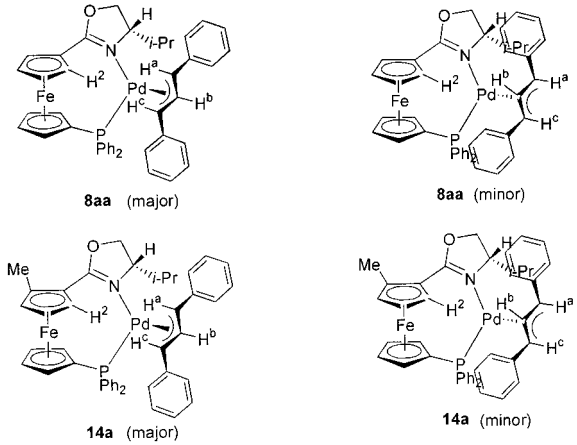
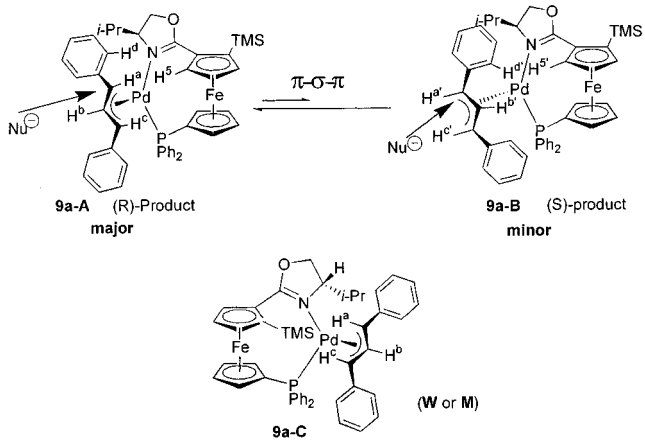


Figure 1. Sections of the phase-sensitive ^{1}H 2D NOESY spectra of compounds **8aa** (a), **14a** (b), and **9a** (c) and 2D exchange spectrum of **9a** (d). The square boxes mark the absence of cross-signals, which is also important for distinguishing between exo and endo configuration. The arrows show the NOE between two protons (see also text).

Scheme 6



Scheme 7



be assigned as **9a-C**. This result indicates that the introduction of planar chirality actually leads to an inversion of the axial chirality of complex **9a**, and hence leads to the inversion of the configuration of the reaction product. However, the low ee value of 69.7% observed with ligand **9** is consistent with the low ratio of its exo and endo diastereomers. The major intermediate **9a-A** is an endo−syn−syn isomer, which may lead to the product of *R* configuration. This is also consistent with our result. In

addition, the ee value of the product (69.7%) does not reflect the isomeric distribution of the intermediate allyl complex, which indicates that different isomers should display different rates for nucleophilic attack according to Bosnich's postulation.[25] That is, the major component should be a more reactive one in complex **9a**. As a result, the 69.7% ee value of the product is higher than the isomeric distribution (59% of **9a**) of the intermediate allyl complexes, and there should exist a fast equilibrium among different components. A kinetic study on complex **9a** was done by monitoring its ^{31}P NMR in order to confirm our postulation. The procedure is described as follows: complex **9a** was dissolved in CD_2Cl_2 at ambient temperature (**9a-A**/**9a-B**/**9a-C**: 1.59/1/0.07), and then 0.3 equiv of dimethylmalonate and 3 equiv of BSA were added, along with a catalytic amount of KOAc. We used ^{31}P NMR to detect the ratio of the three components **9a-A**/**9a-B**/**9a-C**: 5 min (1.47/1/0.06), 15 min (1.45/1/0.05), 30 min (1.51/1/0.07), 1 h (1.54/1/0.06), 3 h (1.61/1/0.09), 12 h (1.60/1/0.10). From the above data, the change of the ratio is not apparent, and fast equilibration between the isomers might exit. After 12 h the product was isolated, and the enantiomer excess was determined by HPLC as 64.6% in *R* configuration, which is almost the same result as that in entry 3 of Table 1. In addition, the assumption that **9a-A** is more more reactive could get support from ^{13}C NMR study. It has been reported that there is a correlation between downfield shifts and the relative positive charge of the carbon nucleus.[27] With such a correlation, ^{13}C NMR has been used to predict the reactivity of the palladium allylic complexes.[28] For the two major components in **9a**, **9a-A** and **9a-B** in the ratio of 1.6:1, the terminal ^{13}C allyl chemical shifts are $\delta = 110.8$ (allyl carbon terminus trans to P) and 72.1 (trans to N) for **9a-A** ($\Delta\delta = 38.7$) and $\delta = 103.2$ (allyl carbon terminus trans to P) and 71.7 (trans to N) for **9a-B** ($\Delta\delta = 31.5$), suggesting that **9a-A** is a more electrophilic allyl terminus than **9a-B**, and hence **9a-A** is more reactive.

X-ray Crystallographic Study of the Intermediate Complex. From the NMR studies of the Pd complexes with ligands and the intermediate complexes of the reaction, the role of the planar chirality has almost been clarified. To obtain more in-depth and perceivable knowledge of their stereochemical interaction, the growth of single crystals of complexes **8aa**, **9a**, and **14a** has been attempted. Only a single crystal of complex **14a** was obtained by slow evaporation from dichloromethane/diethyl ether. In addition, a high-quality crystal of complex **8ca**, formed from the *trans*-1,3-diphenylpropenyl palladium chloride dimer and ligand **8c** in the presence of silver hexafluoroantimonate, was obtained by slow evaporation from dichloromethane/diethyl ether. The X-ray crystal structure analysis of **14a** confirms its exo−syn−syn configuration, which is similar to the result of solution NMR study. As shown in Figure 2, a pseudo-square-planar geometry around palladium was observed, and all bonding parameters fell in the expected ranges (see Supporting Information). However, several characteristics are worth noting. The planes of the two phenyl rings of the diphenylphosphino group are nearly perpendicular to each other,

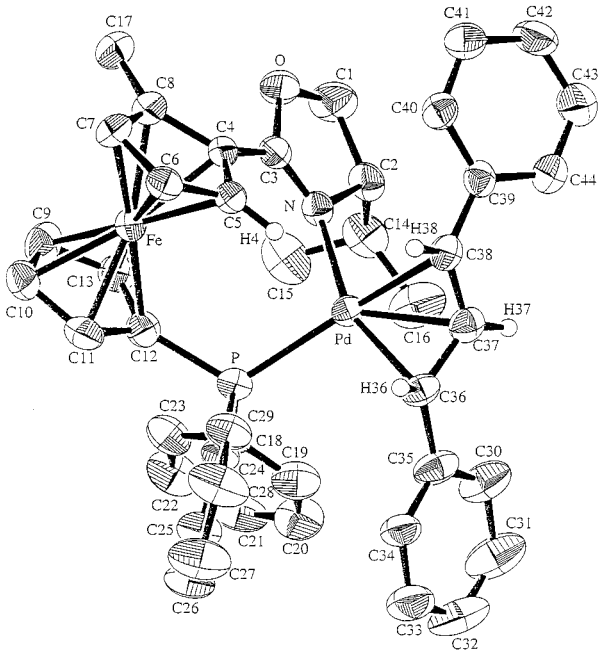


Figure 2. ORTEP view and atom numbering scheme for the cationic complexes **14a**.

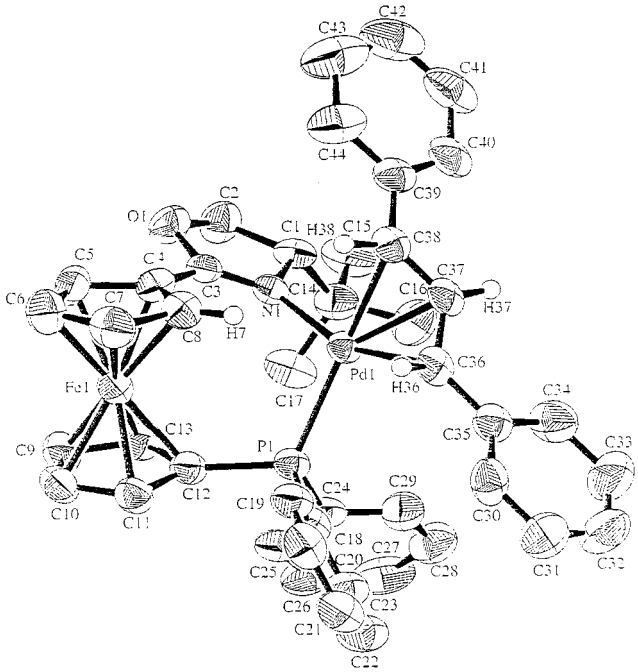


Figure 3. ORTEP view and atom numbering scheme for the cationic complexes **8ca**.

with one phenyl group directed downward and the other directed toward the allylic moiety. There is an interaction between the phenyl group at P and one of the allyl-phenyl groups (the spatial distance between protons at C34 and C29 is 2.92 Å). Minimization of this interaction is therefore the reason for the preference of the exo (M-type) over the endo isomer. X-ray diffraction of **8ca** shows that there are two molecules in an asymmetric unit which have the same configuration (see Supporting Information). As shown in Figure 3, the allyl ligand was also found to be of exo−syn−syn configuration. The general geometric features of the **8ca** are very similar to those found for **14a** (vide supra). In addition, it was found that, for complex **14a**, the spatial distance between the proton H^4 at C^8 and the allyl proton H^a trans to phosphorus is 2.46 Å; for complex **8ca**, the spatial distance

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between the proton H^7 at C^8 and the allyl proton H^a trans to phosphorus is 2.54 Å on average. This indicates that the two similar protons, H^4 and H^7, on the Cp ring in two different compounds are very close to the ligating center. Therefore, if a Me group or a bulkier TMS group is situated at this position instead of H^7 (like ligand **9** or **11**), there must be a strong steric repulsion between the substituent and the ligating center, thereby leading to the inversion of axial chirality in order to minimize the steric repulsion. This finding can also well explain why the planar chirality can control the enantioselectivity of the reaction course and the absolute configuration of the reaction products.

Conclusion

In summary, we have synthesized a new kind of planar chiral 2′-substituted 1,1′-P,N-ferrocene ligands, **9**−**11**, **14**, and **16**. Ligands **14** and **16** are very effective in enantioselective Pd-catalyzed allylic alkylation and amination reactions. These ligands possess central and planar chirality and a new axial chirality also formed during complexation with palladium. It is evident that the planar chirality resulted from the central chirality through a highly diastereoselective ortho-lithiation approach. From the NMR and crystallographic evidence, it is clear that the planar chirality of the newly introduced 2′-substituent determines the rotamer ratio of the Pd complexes as well as the stereo environment of the preferred rotamer. During the allylic substitution reaction, the whole stereo environment including central chirality shows a high preference for the diastereo intermediates with exo−syn−syn conformation. Consequently, high enantioselectivities are obtained in alkylation reaction up to 98.6%, and in amination reaction up to 96.5%. A similar result was observed in the asymmetric Heck reaction,[29] which further indicates that the significant role of planar chirality can be generalized to other reactions. In addition, this kind of ligand is unique for its multichirality (central, planar, and axial chirality on its coordination with Pd) and provides a new entry for the design of novel ligands.[30] Further study on exploring the scope of asymmetric reactions with these promising ligands is in progress.

Experimental Section

General Procedures. Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Brucker AMX-400 (400 MHz) spectrometer, and the chemical shifts were referenced to $CHCl_3$ (δ 7.27) in $CDCl_3$, $CHDCl_2$ (δ 5.32) in CD_2Cl_2, and CHD_2CN (δ 1.93) in CDCN. ^{31}P NMR spectra were recorded on a Bruker AMX-400 (162 MHz) spectrometer, and the chemical shifts were referenced to external 85% H_3PO_4. ^{13}C NMR spectra were recorded on a Bruker AMX-400 (100.6 MHz) spectrometer, and the chemical shifts were referenced to $CHDCl_2$ in CD_2Cl_2. Standard pulse sequences were employed for ^{1}H 2D NOESY and ^{1}H−^{1}H and ^{13}C−^{1}H correlations studies. Optical rotation was measured using a Perkin-Elmer 241 MC polarimeter with a thermally jacketed 10 cm cell at 25 °C (concentration *c* given as grams per 100 mL). IR spectra were recorded in KBr and measured in inverse centimeters, using a Shimadzu IR-440 infrared spectrophotometer. Mass spectra and high-resolution mass spectra were taken using HP5989A and Finnigan MAT mass spectrometers, respectively. Elemental analyses were performed on a Foss-Heraeus Vario EL instrument. Enantiomeric excess (ee) values were determined by chiral HPLC on a Chiralcel OD or OJ column.

All the reactions were performed under a dry argon atmosphere. Tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium under a dry argon atmosphere. Dichloromethane, TMEDA, and triethylamine were distilled from calcium hydride. Bis(μ-chloro)(1,3-diphenyl-η^3-allyl)dipalladium was prepared by a reported method.[22a] The commercially available reagents were used as received without further purification.

1-Diphenylphosphino-1′-[(*S*)-4-isopropyl-2,5-oxazolinyl]ferrocene, (*S*)-8a. Compound (*S*)-**7a** (188 mg, 0.5 mmol) was dissolved in freshly distilled THF (4 mL) under argon and cooled to −78 °C. At this temperature, *n*-BuLi (0.38 mL, 0.6 mmol, 1.6 M in *n*-hexane) was added, and the resulting deep red solution was stirred for 20 min. Chloro-diphenylphosphine (0.13 mL, 0.7 mmol) was then added, and the resulting mixture was continually stirred and warmed to room temperature over 30 min. The reaction mixture was diluted with ether (20 mL), washed with saturated aqueous $NaHCO_3$, and dried over $NaSO_4$. The solvent was removed under reduced pressure, and the resulting residue was chromatographed on silica gel with ethyl acetate:petroleum (1:4) as eluent to give 185 mg of (*S*)-**8a** (77%) as an orange oil. $[\alpha]^{20}_D = -84.5°$ (*c* 0.18, $CHCl_3$); lit.[12b,c] $[\alpha]^{20}_D = -85.0°$ (*c* 1.87, $CHCl_3$). ^{1}H NMR: δ 0.91 (d, J = 6.7 Hz, 3H), 0.99 (d, J = 6.7 Hz, 3H), 1.84 (m, 1H), 3.94−4.05 (m, 2H), 4.13 (m, 2H), 4.20 (m, 2H), 4.27 (dd, J = 8.0, 9.6 Hz, 1H), 4.39 (t, J = 1.8 Hz, 2H), 4.68 (m, 2H), 7.31−7.39 (m, 10H). MS: *m*/*z* (relative intensity) 481 (M^+, 100.0).

1-Diphenylphosphino-1′-[(*R*)-4-isopropyl-2,5-oxazolinyl]ferrocene, (*R*)-8a. Prepared from (*R*)-**7a** in 72% yield as an orange oil. $[\alpha]^{20}_D = 85°$ (*c* 0.29, $CHCl_3$). ^{1}H NMR: δ 0.90 (d, J = 6.7 Hz, 3H), 0.99 (d, J = 6.7 Hz, 3H), 1.83 (m, 1H), 3.94−4.04 (m, 2H), 4.12 (m, 2H), 4.19 (m, 2H), 4.25 (dd, J = 8.5, 9.1 Hz, 1H), 4.38 (t, J = 1.5 Hz, 2H), 4.68 (m, 2H), 7.31−7.36 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −17.26. MS: *m*/*z* (relative intensity) 481 (M^+, 100), 412 (51), 321 (41), 253 (23). IR (KBr): 2958, 1658, 1481, 1434, 1380, 1112, 1027. HRMS: calcd for $C_{28}H_{28}NOPFe$ 466.10228, found 466.09843.

1-Diphenylphosphino-1′-[(*S*)-4-benzyl-2,5-oxazolinyl]ferrocene, (*S*)-8b. Compound **7b** (212 mg, 0.5 mmol) was allowed to react according to the procedure for (*S*)-**8a** to afford (*S*)-**8b** (193 mg, 73%) as an orange oil. $[\alpha]^{20}_D = -15.6°$ (*c* 0.32, $CHCl_3$). ^{1}H NMR: δ 2.68 (dd, J = 9.0, 13.7 Hz, 1H), 3.19 (dd, J = 4.7, 13.7 Hz, 1H), 4.03 (dd, J = 7.5, 8.2 Hz, 1H), 4.08−4.12 (m, 2H), 4.18−4.25 (m, 3H), 4.34 (t, J = 1.8 Hz, 2H), 4.35−4.49 (m, 1H), 4.68 (t, J = 1.8 Hz, 2H), 7.20−7.46 (m, 15H). MS: *m*/*z* (relative intensity) 529 (M^+, 100), 412 (46), 328 (63), 253 (71), 91 (49). IR (KBr): 2926, 1655, 1480, 1434, 1116, 1026, 969, 744, 698, 504. Anal. Calcd for $C_{32}H_{28}NOPFe$: C, 72.58; H, 5.33; N, 2.65. Found: C, 72.55; H, 5.32; N, 2.54.

1-Diphenylphosphino-1′-[(*S*)-4-*tert*-butyl-2,5-oxazolinyl]ferrocene, (*S*)-8c. Compound **7c** (195 mg, 0.5 mmol) was allowed to react according to the procedure for (*S*)-**8a** to afford (*S*)-**8c** (176 mg, 71%) as a yellow solid. $[\alpha]^{20}_D = -132.6°$ (*c* 0.35, $CHCl_3$); lit.[12b,c] $[\alpha]^{20}_D = -131.8°$ (*c* 0.32, $CHCl_3$).^{1}H NMR: δ 0.92 (s, 9H), 3.87 (dd, J = 7.7, 10.1 Hz, 1H), 4.09−4.24 (m, 6H), 4.40 (br, 2H), 4.65−4.68 (m, 2H), 7.30−7.40 (m, 10 H).

1-Diphenylphosphino-1′-[(*S*)-4-isopropyl-2,5-oxazolinyl]-2′(S_p)-(trimethylsilyl)-ferrocene, (S,S_p)-9. A solution of **8a** (3.13 g, 6.5 mmol) and TMEDA (1.2 mL, 8.0 mmol) in ether (40 mL) under argon was cooled to −78 °C. To this solution was added dropwise *n*-BuLi (5.0 mL, 8.0 mmol). After the resultant solution was stirred at −78 °C for 2 h, TMSCl (1.2 mL, 9.6 mmol) was added, and the dry ice bath was removed. The resulting mixture was continually stirred for 20 min, and then quenched with saturated $NaHCO_3$, diluted with ether, washed with brine, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The resulting residue was purified by column chromatography with ethyl acetate:petroleum (1:20) as an eluent to afford 3.34 g of compound (S,S_p)-**9** as an orange oil (yield, 93%). $[\alpha]^{20}_D = 64°$ (*c* 0.20, $CHCl_3$). ^{1}H NMR: δ 0.26 (s, 9H), 0.90 (d, J = 6.7 Hz, 3H), 1.01 (d, J = 6.7 Hz, 3H), 1.78 (m, 1H), 3.85−4.02 (m, 2H), 4.10−4.17 (m, 3H), 4.18 (t, J = 2.5 Hz, 1H), 4.27 (td, J = 7.3, 1.4 Hz, 1H), 4.34 (m, 1H), 4.39 (m, 1H), 4.79 (s, 1H), 7.24−7.40 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −17.17. MS: *m*/*z* (relative intensity) 553 (M^+, 38), 538 (33), 368 (100), 353 (65), 268 (55), 149 (53). IR (KBr): 2957, 1656, 1434, 1242, 1154, 990, 836, 742, 697, 503. Anal. Calcd for $C_{31}H_{36}NOSiPFe$: C, 67.27; H, 6.55; N, 2.53. Found: C, 67.42; H, 6.68; N, 2.40.

1-Diphenylphosphino-1′-[(*R*)-4-isopropyl-2,5-oxazolinyl]-2′(R_p)-(trimethylsilyl)-ferrocene, (R,R_p)-9. Prepared from (*R*)-**8a** in 92% yield as an orange oil. $[\alpha]^{20}_D = -65°$ (*c* 0.16, $CHCl_3$). ^{1}H NMR: δ 0.26 (s,

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9H), 0.90 (d, $J = 6.7$ Hz, 3H), 1.01 (d, $J = 6.7$ Hz, 3H), 1.79 (m, 1H), 3.89−3.98 (m, 2H), 4.10−4.17 (m, 3H), 4.19 (t, $J = 2.3$ Hz, 1H), 4.26 (t, $J = 8.0$ Hz, 1H), 4.33 (m, 1H), 4.38 (m, 1H), 4.78 (s, 1H), 7.25−7.35 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −16.98. MS: *m*/*z* (relative intensity) 553 (M^+, 100), 538 (72), 481 (39), 412 (20), 321 (33). IR (KBr): 2957, 1658, 1479, 1434, 1242, 988, 835. Anal. Calcd for $C_{31}H_{36}NOSiPFe$: C, 67.27; H, 6.55; N, 2.53. Found: C, 67.66; H, 6.75; N, 2.57.

1-Diphenylphosphino-1′-[(*S*)-4-isopropyl-2,5-oxazolinyl]-2′(*R*$_p$)-(methyl)-ferrocene, (*S*,*R*$_p$)-10. Compound **8a** (242 mg, 0.5 mmol) was allowed to react according to the procedure for **9** to afford (*S*,*R*$_p$)-**10** (193 mg, 78%) as an orange oil. $[\alpha]^{20}_D = -162°$ (*c* 0.19, $CHCl_3$). ^{1}H NMR: δ 0.93 (d, $J = 6.7$ Hz, 3H), 1.0 (d, $J = 6.7$ Hz, 3H), 1.81 (m, 1H), 2.14 (s, 3H), 3.94−4.07 (m, 4H), 4.10−4.13 (m, 2H), 4.20−4.26 (m, 2H), 4.30 (m, 1H), 4.54 (dd, $J = 1.5$, 1.6 Hz, 1H), 7.25−7.48 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −17.15. MS: *m*/*z* (relative intensity) 495 (M^+, 100), 426 (24), 321 (39), 294 (24), 267 (34), 171 (25). IR (KBr): 2958, 1653, 1480, 1434, 1070, 1025, 743, 697, 505. Anal. Calcd for $C_{29}H_{30}NOPFe$: C, 70.31; H, 6.10; N, 2.83. Found: C, 70.62; H, 6.22; N, 2.82.

1-Diphenylphosphino-1′-[(*S*)-4-isopropyl-2,5-oxazolinyl]-2′(*S*$_p$)-(methyl)-ferrocene, (*S*,*S*$_p$)-14. Under an argon atmosphere, a yellow solution of 1 M TBAF in THF (20 mL) containing approximately 5% H_2O and compound **13** (567 mg, 1 mmol) was heated at reflux for 10 h. The resultant orange solution was evaporated in vacuo to low volume and diluted with ether (30 mL), washed with water, dried over $MgSO_4$, filtered, and evaporated in vacuo. The resulting residue was column chromatographed with ethyl acetate:petroleum (1:5) as eluent to give (*S*,*S*$_p$)-**14** as an orange oil (475 mg, 96%). $[\alpha]^{20}_D = -59.0°$ (*c* 0.35, $CHCl_3$). ^{1}H NMR: δ 0.90 (d, $J = 6.7$ Hz, 3H), 0.98 (d, $J = 6.7$ Hz, 3H), 1.91 (m, 1H), 2.10 (s, 3H), 3.87−4.33 (m, 9H), 4.56 (t, $J = 1.55$ Hz, 1H), 7.24−7.39 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −17.25. MS: *m*/*z* (relative intensity) 495 (M^+, 100), 427 (21), 321 (33), 267 (27), 171 (25). IR (KBr): 2958, 1652, 1480, 1434, 1070, 1025, 743, 697, 505. Anal. Calcd for $C_{29}H_{30}NOPFe$: C, 70.31; H, 6.10; N, 2.83. Found: C, 70.40; H, 6.09; N, 2.69.

1-Diphenylphosphino-1′-[(*S*)-4-isopropyl-2,5-oxazolinyl]-2′(*R*$_p$)-(trimethylsilyl)-ferrocene, (*S*,*R*$_p$)-16. Compound **15** (205 mg, 0.37 mmol) was dissolved in freshly distilled THF (4 mL) under argon and cooled to −78 °C. At this temperature, *n*-BuLi (0.3 mL, 0.48 mmol, 1.6 M in *n*-hexane) was added, and the resulting deep red solution was stirred for 20 min. TMSCl (0.07 mL, 0.56 mmol) was then added, and the resulting mixture was continually stirred and warmed to room temperature over 30 min. The reaction mixture was diluted with ether (20 mL), washed with saturated aqueous $NaHCO_3$, and dried over $NaSO_4$. The solvent was removed under reduced pressure, and the resulting residue was chromatographed on silica gel with ethyl acetate:petroleum (1:10) as eluent to give 149 mg of (*S*,*R*$_p$)-**16** (73%) as an orange oil. $[\alpha]^{20}_D = -203°$ (*c* 0.19, $CHCl_3$). ^{1}H NMR: δ 0.24 (s, 9H), 0.91 (d, $J = 6.7$ Hz, 3H), 0.99 (d, $J = 6.7$ Hz, 3H), 1.75 (m, 1H), 3.80−3.99 (m, 2H), 4.10−4.20 (m, 4H), 4.25 (dd, $J = 7.9$, 9.2 Hz, 1H), 4.32 (m, 1H), 4.37 (m, 1H), 4.78 (dd, $J = 1.4$, 2.4 Hz, 1H) 7.25−7.41 (m, 10H). MS: *m*/*z* (relative intensity) 553 (M^+, 100), 538 (75), 469 (43), 171 (35), 149 (56), 73 (34), 43 (43). IR (KBr): 2957, 1656, 1434, 1242, 1154, 990, 836, 743, 697. Anal. Calcd for $C_{31}H_{36}NOPSiFe$: C, 67.27; H, 6.55; N, 2.53. Found: C, 67.64; H, 6.68; N, 2.49.

1-Diphenylphosphino-1′-[(*S*)-4-isopropyl-2,5-oxazolinyl]-2′(*R*$_p$)-(bromo)-ferrocene, (*S*,*R*$_p$)-15. Under an argon atmosphere, a yellow solution of 1 M TBAF in THF (16 mL) containing approximately 5% H_2O and compound **13** (500 mg, 0.79 mmol) was heated at reflux for 5 h. The resulting orange solution was evaporated in vacuo to low volume, diluted with ether (30 mL), washed with water, dried over $MgSO_4$, filtered, and evaporated in vacuo. The resulting residue was column chromatographed with ethyl acetate:petroleum (1:10) as an eluent to give (*S*,*R*$_p$)-**15** as an orange oil (377 mg, 85%). $[\alpha]^{20}_D = -75.6°$ (*c* 0.33, $CHCl_3$). ^{1}H NMR: δ 0.92 (d, $J = 6.8$ Hz, 3H), 1.00 (d, $J = 6.8$ Hz, 3H), 1.85 (m, 1H), 4.03 (m, 1H), 4.08−4.15 (m, 2H), 4.18 (s, 1H), 4.21 (s, 1H), 4.30 (t, $J = 9.4$ Hz, 1H), 4.38−4.48 (m, 3H), 4.62 (m, 1H), 7.31−7.39 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −18.10. MS: *m*/*z* (relative intensity) 561 (M^+, 4), 559 (4), 142 (100), 100 (79). IR (KBr): 2957, 2896, 1650, 1479, 1434, 1245, 1162, 985, 832, 742, 697. Anal. Calcd for $C_{28}H_{27}NOPBrFe$: C, 60.03; H, 4.86; N, 2.50. Found: C, 60.12; H, 5.00; N, 2.47.

1-Diphenylphosphino-1′-[(*S*)-4-isopropyl-2,5-oxazolinyl]-2′(*S*$_p$)-(trimethylsilyl)-5′(*S*$_p$)-(methyl)-ferrocene, (*S*,*S*$_p$,*S*$_p$)-12. Compound **9** (553 mg, 1.0 mmol) was dissolved in freshly distilled THF (8 mL) under argon and cooled to −78 °C. At this temperature, *n*-BuLi (0.76 mL, 1.2 mmol, 1.6 M in *n*-hexane) was added, and the resulting deep red solution was stirred for 2 h. Methyl iodide (0.2 mL, 3.0 mmol) was then added, and the resulting mixture was continually stirred and warmed to room temperature over 40 min. The reaction mixture was diluted with ether (20 mL), washed with saturated aqueous $NaHCO_3$, and dried over $NaSO_4$. The solvent was removed under reduced pressure, and the resulting residue was chromatographed on silica gel with ethyl acetate:petroleum (1:30) as eluent to give 482 mg of (*S*,*S*$_p$,*S*$_p$)-**12** (85%) as an orange oil. $[\alpha]^{20}_D = 97°$ (*c* 0.24, $CHCl_3$). ^{1}H NMR: δ 0.21 (s, 9H), 0.89 (d, $J = 6.7$ Hz, 3H), 1.02 (d, $J = 6.7$ Hz, 3H), 1.75 (m, 1H), 2.06 (s, 3H), 3.87−4.02 (m, 4H), 4.10−4.13 (m, 2H), 4.21−4.28 (m, 2H), 4.37 (s, 1H), 7.24−7.40 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −17.06. MS: *m*/*z* (relative intensity) 567 (M^+, 100), 552 (28), 171 (21), 73 (34). IR (KBr): 2957, 1649, 1434, 1244, 1064, 1027, 837, 742, 697. Anal. Calcd for $C_{32}H_{38}NOSiPFe$: C, 67.72; H, 6.75; N, 2.47. Found: C, 67.74; H, 6.99; N, 2.50.

1-Diphenylphosphino-1′-[(*S*)-4-isopropyl-2,5-oxazolinyl]-2′(*R*$_p$)-(bromo)-5′(S$_p$)-(trimethylsilyl)-ferrocene, (*S*,*R*$_p$,*S*$_p$)-13. Compound **9** (553 mg, 1.0 mmol) was dissolved in freshly distilled THF (8 mL) under argon and cooled to −78 °C. At this temperature, *n*-BuLi (0.76 mL, 1.2 mmol, 1.6 M in *n*-hexane) was added, and the resulting deep red solution was stirred for 2 h. 1,2-Dibromo-tetrafluoroethane ($BrCF_2$-CF_2Br) (0.24 mL, 2.0 mmol) was then added, and the resulting mixture was continually stirred and warmed to room temperature over 30 min. The reaction mixture was diluted with ether (20 mL), washed with saturated aqueous $NaHCO_3$, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the resulting residue was chromatographed on silica gel with ethyl acetate:petroleum (1:30) as eluent to give 506 mg of (*S*,*R*$_p$,*S*$_p$)-**13** (80%) as an orange oil. $[\alpha]^{20}_D = 25°$ (*c* 0.19, $CHCl_3$). ^{1}H NMR: δ 0.23 (s, 9H), 0.91 (d, $J = 6.7$ Hz, 3H), 1.04 (d, $J = 6.7$ Hz, 3H), 1.81 (m, 1H), 3.92−4.16 (m, 3H), 4.17−4.22 (m, 2H), 4.28−4.42 (m, 3H), 4.52 (m, 1H), 7.25−7.48 (m, 10H). MS: *m*/*z* (relative intensity) 633 (M^+, 100), 631 (91), 446 (54), 448 (54), 296 (56), 171 (50). IR (KBr): 2958, 1660, 1648, 1479, 1434, 1127, 1027, 977, 743, 697. Anal. Calcd for $C_{31}H_{35}NOSiPBrFe$: C, 58.87; H, 5.58; N, 2.21. Found: C, 58.78; H, 5.64; N, 2.13.

1-Diphenylphosphino-1′-[(*S*)-4-isopropyl-2,5-oxazolinyl]-2′(*S*$_p$)-(tributylstannyl)-ferrocene, (*S*,*S*$_p$)-11. Compound **8a** (242 mg, 0.5 mmol) was allowed to react according to the procedure for **9** to afford (*S*,*S*$_p$)-**11** (285 mg, 74%) as an orange oil. $[\alpha]^{20}_D = 33°$ (*c* 0.27, $CHCl_3$). ^{1}H NMR: δ 0.80−1.20 (m, 21H), 1.25−1.42 (m, 6H), 1.48−1.62 (m, 6H), 1.82 (m, 1H), 3.85−4.0 (m, 2H), 4.07 (m, 2H), 4.13 (m, 1H), 4.25−4.36 (m, 4H), 4.81 (m, 1H), 7.25−7.40 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −17.35. MS: *m*/*z* (relative intensity) 714 (M^+ − Bu, 100), 600 (20). IR (KBr): 2955, 2922, 1652, 1434, 1128, 1028, 984, 741, 697, 504. Anal. Calcd for $C_{40}H_{54}NOPSnFe$: C, 62.36; H, 7.07; N, 1.82. Found: C, 62.16; H, 7.16; N, 1.73.

1-Diphenylphosphino-1′-[*N*-acetyl-(*S*)-2-isopropyl-2-aminoethoxycarbonyl]-2′(*S*$_p$)-(trimethylsilyl)-ferrocene, (*S*,*S*$_p$)-17. A solution of **9** (5.53 g, 10 mmol) in freshly distilled THF (100 mL) was successively treated with water (10 mL) and 74 g (0.52 mol) of sodium sulfate and cooled to 0 °C before trifluoroacetic acid (4 mL) was added via a syringe. The reaction mixture was stirred for 3 days at room temperature, and then 20 g sodium sulfate was further added, and the reaction mixture was filtered under argon. The organic solvent was removed in vacuo to leave a dark oil, which was immediately dissolved in freshly distilled dichloromethane (150 mL). The resulting solution was cooled to 0 °C, and acetic anhydride (35 mL, 0.37 mol) was added followed by pyridine (55 mL, 0.7 mol). Stirring was continued overnight, and the resulting dark solution was quenched with 3 M HCl (750 mL), washed with saturated sodium bicarbonate solution, and dried over anhydrous $MgSO_4$. The resulting deep red solution was removed in vacuo and then purified by column chromatography with ethyl acetate:petroleum (1:1) as an eluent to afford 3.34 g of ester amide (*S*,*S*$_p$)-**17**

as a yellow solid (yield, 54%). Mp: 85−86 °C. $[\alpha]^{20}_D = -132.0°$ (*c* 0.315, $CHCl_3$). ^1H NMR: δ 0.27 (s, 9H), 1.01 (d, $J = 6.8$ Hz, 3H), 1.03 (d, $J = 6.8$ Hz, 3H), 1.87 (s, 3H), 1.99 (m, 1H), 4.07−4.28 (m, 7H), 4.35 (m, 1H), 4.45 (s, 1H), 4.85 (m, 1H), 6.05 (d, $J = 8.9$ Hz, 1H) 7.24−7.40 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −17.29. MS: *m*/*z* (relative intensity) 613 (M^+, 27), 486 (100), 442 (29), 321 (28), 170 (25), 86 (18). IR (KBr): 3285, 2960, 1714, 1649, 1550, 1434, 1247, 1157, 835, 696. Anal. Calcd for $C_{33}H_{40}NO_3PSiFe$: C, 64.60; H, 6.57; N, 2.28. Found: C, 64.02; H, 6.46; N, 2.19.

1-Diphenylphosphino-1′-[*N*-acetyl-(*R*)-2-isopropyl-2-aminoethoxycarbonyl]-2′(*R*$_p$)-(trimethylsilyl)-ferrocene, (*R*,*R*$_p$)-17. Prepared from (*R*,*R*$_p$)-**7a** in 52% yield as a yellow solid. Mp: 85−86 °C. $[\alpha]^{20}_D = 145.0°$ (*c* 0.59, $CHCl_3$). ^1H NMR: δ 0.28 (s, 9H), 1.01 (d, $J = 6.8$ Hz, 3H), 1.03 (d, $J = 6.8$ Hz, 3H), 1.88 (s, 3H), 1.99 (m, 1H), 4.08−4.29 (m, 7H), 4.35 (m, 1H), 4.46 (s, 1H), 4.86 (dd, $J_1 = 1.2$ Hz, $J_2 = 1.9$ Hz, 1H), 6.02 (d, $J = 8.9$ Hz, 1H) 7.24−7.40 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −17.25. MS: *m*/*z* (relative intensity) 613 (M^+, 28), 486 (100), 442 (23), 321 (11). IR (KBr): 3284, 2960, 1714, 1650, 1549, 1434, 1247, 1157, 835. HRMS: calcd for $C_{33}H_{40}NO_3PSiFe$ 613.18642, found, 613.18829.

1-Diphenylphosphino-1′-(methoxycarbonyl)-2′(*S*$_p$)-(trimethylsilyl)-ferrocene, (*S*$_p$)-18. To a solution of ester amide (*S*,*S*$_p$)-**17** (613 mg, 1.0 mmol) in THF (15 mL) was added a sodium methoxide solution prepared by the addition of sodium metal (1.0 g, 46 mmol) to methanol (60 mL). After being stirred for 5 h at reflux temperature, the mixture was neutralized with methanolic acetic acid, and the solvent was removed by evaporation in vacuo. The residue was dissolved in dicholromethane, and the resulting solution was washed with water and then with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified by silica gel column chromatography with ethyl acetate:petroleum (1:20) as eluent to afford ester (*S*$_p$)-**18** as an orange solid (465 mg, 93%). Mp: 108−109 °C. $[\alpha]^{20}_D = 55.8°$ (*c* 0.425, $CHCl_3$). ^1H NMR: δ 0.27 (s, 9H), 3.76 (s, 3H), 4.14 (s, 1H), 4.19 (s, 1H), 4.23 (m, 1H), 4.27 (t, $J = 2.4$ Hz, 1H), 4.36 (s, 1H), 4.39 (m, 1H), 4.85 (m, 1H), 7.29−7.37 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −17.32. MS: *m*/*z* (relative intensity) 500 (M^+, 33), 485 (23), 226 (24), 149 (28), 84 (37), 56 (100), 43 (46), 41 (70). IR (KBr): 2951, 1716, 1447, 1249, 1159, 836, 743, 697, 502. Anal. Calcd for $C_{27}H_{29}O_2PSiFe$: C, 64.80; H, 5.84. Found: C, 65.01; H, 6.04.

1-Diphenylphosphino-1′-(methoxycarbonyl)-2′(*R*$_p$)-(trimethylsilyl)-ferrocene, (*R*$_p$)-18. Prepared from (*R*,*R*$_p$)-**17** in 92% yield as an orange solid. Mp: 109−110 °C. $[\alpha]^{20}_D = -58°$ (*c* 0.18, $CHCl_3$). ^1H NMR: δ 0.27 (s, 9H), 3.76 (s, 3H), 4.14 (s, 1H), 4.19 (s, 1H), 4.23 (m, 1H), 4.27 (t, $J = 2.3$ Hz, 1H), 4.36 (s, 1H), 4.39 (m, 1H), 4.85 (m, 1H), 7.29−7.37 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −17.26. MS: *m*/*z* (relative intensity) 500 (M^+, 100), 485 (45), 321 (8), 305 (11), 226 (16). IR (KBr): 2948, 1708, 1583, 1444, 1340, 1248, 1158, 842. Anal. Calcd for $C_{27}H_{29}O_2PSiFe$: C, 64.80; H, 5.84. Found: C, 64.60; H, 6.08.

1-Diphenylphosphino-1′-[*N*-(2-hydroxyethyl)amido]-2′(*S*$_p$)-(trimethylsilyl)-ferrocene, (*S*$_p$)-19. A mixture of (*S*$_p$)-**18** (100 mg, 0.2 mmol), 2 mL of 2-aminoethanol, and a small amount of sodium was heated at 100 °C for 1 h. The mixture was diluted with dichloromethane 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 ethyl acetate:petroleum (1:2) as eluent to afford amide (*S*$_p$)-**19** as a yellow solid (68 mg, 68%). Mp: 52−53 °C. $[\alpha]^{20}_D = -138°$ (*c* 0.175, $CHCl_3$). ^1H NMR: δ 0.29 (s, 9H), 2.91 (t, $J = 5.2$ Hz, 1H), 3.36 (m, 1H), 3.57−3.83 (m, 3H), 4.03 (m, 1H), 4.14 (m, 1H), 4.20 (m, 1H), 4.23 (t, $J = 2.5$ Hz, 1H), 4.36 (m, 1H), 4.49−4.52 (m, 2H), 6.53 (br, 1H), 7.32−7.49 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −16.76. MS: *m*/*z* (relative intensity) 529 (M^+, 7), 514 (7), 484 (8), 86 (67), 84 (100), 47 (28). IR (KBr): 3354, 2961, 1649, 1526, 1262, 1091, 1027, 833, 804, 742, 697. Anal. Calcd for $C_{28}H_{32}NO_2PSiFe$: C, 63.52; H, 6.09; N, 2.65. Found: C, 63.18; H, 5.94; N, 2.72.

1-Diphenylphosphino-1′- [*N*-(2-hydroxyethyl)amido]-2′(*R*$_p$)-(trimethylsilyl)-ferrocene, (*R*$_p$)-19. Prepared from (*R*$_p$)-**18** in 70% yield as a yellow solid. Mp: 51−52 °C. $[\alpha]^{20}_D = 141°$ (*c* 0.55, $CHCl_3$). ^1H NMR: δ 0.29 (s, 9H), 2.97 (br, 1H), 3.33−3.39 (m, 1H), 3.60−3.68 (m, 1H), 3.71−3.82 (m, 2H), 4.03 (s, 1H), 4.13 (s, 1H), 4.21 (m, 1H), 4.23 (t, $J = 2.4$ Hz, 1H), 4.36 (m, 1H), 4.49−4.52 (m, 2H), 6.55 (br, 1H), 7.32−7.49 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$) δ −16.86. MS: *m*/*z* (relative intensity) 529 (M^+, 27), 514 (49), 496 (31), 484 (100), 456 (22), 321 (7). IR (KBr): 3358, 2953, 1738, 1529, 1479, 1434, 1244, 1160. HRMS: calcd for $C_{28}H_{32}NO_2PSiFe$ 529.12890, found 529.12801.

1-Diphenylphosphino-1′-(2,5-oxazolinyl)-2′(*S*$_p$)-(trimethylsilyl)-ferrocene, (*S*$_p$)-20. To a solution of amide (*S*$_p$)-**19** (158 mg, 0.3 mmol) and triethylamine (0.23 mL, 1.5 mmol) in dichloromethane (3 mL) was added of methanesulfonyl chloride (0.02 mL, 0.3 mmol) at 0 °C. After being stirred at room temperature for 5 h, the reaction solution was washed with chilled water (10 mL) and then with brine, dried over Na_2SO_4, and concentrated under reduced pressure to provide a residue which was purified by column chromatography with ethyl acetate: petroleum (1:5) as eluent to afford oxazoline (*S*$_p$)-**20** as a yellow solid (86 mg, 56%). Mp: 82−83 °C. $[\alpha]^{20}_D = 209°$ (*c* 0.14, $CHCl_3$). ^1H NMR: δ 0.26 (s, 9H), 3.80−3.95 (m, 2H), 4.13−4.17 (m, 3H), 4.21 (t, $J = 2.4$ Hz, 1H), 4.26−4.35 (m, 3H), 4.39 (m, 1H), 4.82 (s, 1H), 7.26−7.34 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −17.18. MS: *m*/*z* (relative intensity) 511 (M^+, 90), 496 (100), 497 (40), 326 (42), 171 (19). IR (KBr): 2954, 1656, 1434, 1243, 1137, 835, 743, 697, 502. Anal. Calcd for $C_{28}H_{30}NOPSiFe$: C, 65.75; H, 5.91; N, 2.74. Found: C, 65.37; H, 6.01; N, 2.69.

1-Diphenylphosphino-1′-(2,5-oxazolinyl)-2′(*R*$_p$)-(trimethylsilyl)-ferrocene, (*R*$_p$)-20. Prepared from (*R*$_p$)-**19** in 53% yield as a yellow solid. Mp: 82−84 °C. $[\alpha]^{20}_D = -208.0°$ (c 0.63, $CHCl_3$). ^1H NMR: δ 0.26 (s, 9H), 3.88−3.92 (m, 2H), 4.14−4.20 (m, 4H), 4.27−4.33 (m, 3H), 4.39 (m, 1H), 4.81 (s, 1H), 7.26−7.34 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −17.28. MS: *m*/*z* (relative intensity) 511 (M^+, 100), 496 (95), 468 (11), 452 (5), 326 (20). IR (KBr): 2947, 1644, 1477, 1431, 1166, 982, 752. HRMS: calcd for $C_{28}H_{30}NOPSiFe$ 511.11833, found 511.11860.

1-Diphenylphosphino-1′-[*N*-(1,1-dimethyl-2-hydroxyethyl)amido]-2′(*S*$_p$)-(trimethylsilyl)-ferrocene, (*S*$_p$)-21. A mixture of (*S*$_p$)-**18** (170 mg, 0.34 mmol), 2,2-dimethyl-2-aminoethanol (2 mL), and a small amount of sodium was heated at 100 °C for 1.5 h. The mixture was diluted with dichloromethane 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 ethyl acetate: petroleum (1:2) as eluent to afford amide (*S*$_p$)-**21** as a yellow solid (125 mg, 66%). Mp: 67−68 °C. $[\alpha]^{20}_D = -115°$ (*c* 0.12, $CHCl_3$). ^1H NMR: δ 0.28 (s, 9H), 1.39 (s, 6H), 3.63−3.65 (m, 2H), 3.98 (s, 1H), 4.09 (s, 1H), 4.17−4.18 (m, 2H), 4.33 (s, 1H), 4.44 (d, $J = 5.4$ Hz, 2H), 5.17 (br, 1H), 6.41 (br, 1H), 7.24−7.44 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −17.18. MS: *m*/*z* (relative intensity) 557 (M^+, 18), 527 (22), 484 (100), 485 (38), 321 (31), 285 (20), 171 (19). IR (KBr): 3335, 2952, 1662, 1641, 1515, 834, 742, 696. Anal. Calcd for $C_{30}H_{36}NO_2PSiFe$: C, 64.63; H, 6.51; N, 2.51. Found: C, 64.32; H, 6.41; N, 2.32.

1-Diphenylphosphino-1′-[*N*-(1,1-dimethyl-2-hydroxyethyl)amido]-2′(*R*$_p$)-(trimethylsilyl)-ferrocene, (*R*$_p$)-21. Prepared from (*R*$_p$)-**18** in 69% yield as a yellow solid (125 mg, 66%). Mp: 68−70 °C. $[\alpha]^{20}_D = 116.0°$ (*c* 0.72, $CHCl_3$). ^1H NMR: δ 0.28 (s, 9H), 1.39 (s, 6H), 3.64 (m, 2H), 3.97 (m, 1H), 4.09 (m, 1H), 4.17−4.18 (m, 2H), 4.33 (m, 1H), 4.44−4.45 (m, 2H), 5.26 (t, $J = 6.2$ Hz, 1H), 6.44 (br, 1H), 7.24−7.44 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −17.32. MS: *m*/*z* (relative intensity) 557 (M^+, 26), 511 (31), 484 (100), 468 (17), 452 (11), 321 (15). IR (KBr): 3335, 2955, 1739, 1663, 1642, 1516, 1244, 1161, 835. HRMS: calcd for $C_{30}H_{36}NO_2PSiFe$ 557.16020, found 557.16357.

1-Diphenylphosphino-1′-(4,4-dimethyl-2,5-oxazolinyl]-2′(*S*$_p$)-(trimethylsilyl)-ferrocene, (*S*$_p$)-22. To a solution of amide (*S*$_p$)-**21** (100 mg, 0.18 mmol) and 0.14 mL (0.9 mmol) of triethylamine in 2 mL of dichloromethane was added methanesulfonyl chloride (0.014 mL, 0.18 mmol) at 0 °C. After being stirred at room temperature for 5 h, the reaction solution was washed with chilled water (10 mL) and then with brine, dried over Na_2SO_4, and concentrated under reduced pressure to provide a residue which was purified by column chromatography with ethyl acetate:petroleum (1:10) as an eluent to afford oxazoline (*S*$_p$)-**22** as a yellow solid (75 mg, 77%). Mp: 112−113 °C. $[\alpha]^{20}_D = 179°$ (*c*

0.20, $CHCl_3$). ^1H NMR: δ 0.25 (s, 9H), 1.31 (d, $J = 4.5$ Hz, 6H), 3.94 (d, $J = 7.9$ Hz, 1H), 3.96 (d, $J = 7.9$ Hz, 1H), 4.12−4.19 (m, 4H), 4.31 (d, $J = 1.1$ Hz, 1H), 4.36 (m, 1H), 4.81 (dd, $J = 1.3$, 2.2 Hz, 1H), 7.26−7.37 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −17.17. MS: *m*/*z* (relative intensity) 539 (M^+, 100), 524 (16), 468 (10), 452 (33), 339 (9), 305 (9), 171 (15). IR (KBr): 2961, 1661, 1434, 1240, 1132, 837, 749, 695, 517. Anal. Calcd for $C_{30}H_{34}NOPSiFe$: C, 66.79; H, 6.35; N, 2.60. Found: C, 66.66; H, 6.23; N, 2.51.

1-Diphenylphosphino-1′-(4,4-dimethyl-2,5-oxazolinyl]-2′(R_p)-(trimethylsilyl)-ferrocene, (R_p)-22. Prepared from (R_p)-**21** in 75% yield as a yellow solid. Mp: 110−112 °C. $[\alpha]^{20}_D = -180.0°$ (*c* 0.58, $CHCl_3$). ^1H NMR: δ 0.25 (s, 9H), 1.31 (d, $J = 5.2$ Hz, 6H), 3.94 (d, $J = 7.9$ Hz, 1H), 3.96 (d, $J = 7.9$ Hz, 1H), 4.13−4.19 (m, 4H), 4.31 (s, 1H), 4.37 (s, 1H), 4.82 (s, 1H), 7.26−7.37 (m, 10H). ^{31}P NMR (161.92 MHz, $CDCl_3$): δ −17.30. MS: *m*/*z* (relative intensity) 539 (M^+, 93), 524 (14), 452 (22), 339 (4), 57 (100). IR (KBr): 2959, 1644, 1430, 1255, 1128, 982, 757, 702. HRMS: calcd for $C_{30}H_{34}NOPSiFe$ 539.14964, found 539.14869.

General Procedure for Palladium-Catalyzed Allylic Alkylation. A mixture of ligand **9** (11.6 mg, 0.02 mmol) and [Pd(η^3-C_3H_5)Cl]$_2$ (3.7 mg, 0.01 mmol) in dry dichloromethane (4 mL) was stirred at room temperature for 1 h, and to the resulting yellow solution were added potassium acetate (2.0 mg 0.02 mmol) and **23** (100 mg, 0.4 mmol). After an additional 10 min of stirring, to the resulting solution were added dimethyl malonate (0.12 mL, 1.2 mmol) and BSA (0.3 mL, 1.2 mmol). The reaction was carried out at room temperature and monitored by TLC for the disappearance of **23**. When all of the **23** had been converted to the product, the reaction mixture was diluted with ether, washed with saturated aqueous NH_4Cl solution, and then dried over Na_2SO_4. After removal of the solvent, the residue was purified by preparative TLC with ethyl acetate:petroleum (1:10) as eluent to afford pure **24**. ^1H NMR (400 MHz, $CDCl_3$): δ 3.52 (s, 3H), 3.70 (s, 3H), 3.95 (d, $J = 10.8$ Hz, 1H), 4.27 (dd, $J = 8.8$, 10.8 Hz, 1 H), 6.30 (dd, $J = 8.8$, 15.8 Hz, 1 H), 6.44 (d, $J = 15.8$ Hz, 1 H), 7.19−7.34 (m, 10H). The enantiomeric excess was determined by HPLC analysis (Chiralcel OD, hexane:2-propanol (80:20); flow rate = 0.7 mL/min; t_R = 18.7 min, t_S = 20.4 min). The absolute configuration of the product was assigned by comparing the sign of its specific rotation with literature data.[26]

General Procedure for Palladium-Catalyzed Allylic Amination. A mixture of ligand **14** (9.9 mg, 0.02 mmol) and [Pd(η^3-C_3H_5)Cl]$_2$ (3.7 mg, 0.01 mmol) in dry 1,2-dichloroethane (4 mL) was stirred at room temperature for 1 h, and to the resulting yellow solution was added **23** (100 mg, 0.4 mmol). After an additional 10 min of stirring, to the resulting solution was added benzylamine (0.1 mL, 0.8 mmol). The reaction was carried out at room temperature and monitored by TLC for the disappearance of **23**. When all of the **23** had been converted to the product, the reaction mixture was diluted with ether, washed with saturated aqueous NH_4Cl solution, and then dried over Na_2SO_4. After removal of the solvent, the residue was purified by preparative TLC with ethyl acetate:petroleum (1:10) as eluent to afford pure product **29**. ^1H NMR (300 MHz, $CDCl_3$): δ 3.75−3.81 (AB, $J = 13.3$ Hz, 2 H), 4.39 (d, $J = 7.4$ Hz, 1 H), 6.31 (dd, $J = 7.4$, 15.9 Hz, 1 H), 6.58 (d, $J = 15.9$ Hz, 1 H), 7.17−7.45 (m, 15H). The enantiomeric excess was determined by HPLC analysis (Chiralcel OJ, flow rate = 0.6 mL/min, *n*-hexane:*i*-PrOH = 87:13, t_S = 20.3 min, t_R = 24.3 min). The absolute configuration of the product was assigned by comparing the sign of its specific rotation with literature data.[22a]

Complexation Behavior of 8a with Dichlorobis(acetonitrile)-palladium(II). A mixture of **8a** (9.7 mg, 0.02 mmol) and dichlorobis-(acetonitrile)palladium(II) (5.2 mg, 0.02 mmol) was dissolved in acetonitrile-d_3 (0.5 mL). The resulting solution gave two sets of signals in the ^1H NMR spectrum and presented a ratio of 62:38 in the ^{31}P NMR spectrum at room temperature, which might be assigned as diastereomers **26** and **25**, respectively.

26 (Major). ^1H NMR (400 MHz): δ 0.64 (d, $J = 6.7$ Hz, 3H), 0.83 (d, $J = 6.7$ Hz, 3H), 2.86 (m, 1H), 3.22 (t, $J = 9.2$ Hz, 1H), 3.96 (dd, $J = 6.8$, 9.2 Hz, 1H), 4.46 (s, 1H), 4.72−4.96 (m, 5H), 5.10 (s, 1H), 5.81 (s, 1H), 6.48 (m, 1H), 7.34−7.89 (m, 10H).

25 (Minor). ^1H NMR (400 MHz): δ 0.44 (d, $J = 6.2$ Hz, 3H), 1.67 (d, $J = 6.2$ Hz, 3H), 2.50 (m, 1H), 3.66 (dd, $J = 9.2$, 12.2 Hz, 1H), 4.00 (m, 1H), 4.50 (t, $J = 9.2$ Hz, 1H), 4.72−4.96 (m, 6H), 5.05 (m, 1H), 6.36 (m, 1H), 7.34−7.89 (m, 10H).

^{31}P NMR (161.9 MHz): δ 16.82 (major), 14.47 (minor).

Complexation Behavior of 9 with Dichlorobis(acetonitrile)-palladium(II). A mixture of **9** (11.2 mg, 0.02 mmol) and dichlorobis-(acetonitrile)palladium(II) (5.2 mg, 0.02 mmol) was dissolved in acetonitrile-d_3 (0.5 mL). The resulting solution gave two sets of signals in the ^1H NMR spectrum and presented a ratio of 42:58 in the ^{31}P NMR spectrum at room temperature, which might be assigned as diastereomers **28** and **27**, respectively.

27 (Major). ^1H NMR (400 MHz): δ 0.20 (s, 9H), 0.67 (d, $J = 6.6$ Hz, 3H), 0.91 (d, $J = 7.1$ Hz, 3H), 2.73 (m, 1H), 3.53 (m, 1H), 3.78 (t, $J = 9.3$ Hz, 1H), 4.24 (dd, $J = 5.2$, 9.3 Hz, 1H), 4.52−4.60 (m, 2H), 4.76 (m, 1H), 4.86 (m, 1H), 4.95 (m, 1H), 5.07 (t, $J = 2.4$ Hz, 1H), 7.10 (s, 1H), 7.24−7.80 (m, 10H).

28 (Minor). ^1H NMR (400 MHz): δ 0.20 (s, 9H), 1.00 (d, $J = 5.6$ Hz, 3H), 1.01 (d, $J = 5.6$ Hz, 3H), 2.91 (m, 1H), 4.35 (t, $J = 7.3$ Hz, 1H), 4.48−4.60 (m, 4H) 4.63 (m, 1H), 4.76 (m, 1H), 5.61 (br, 2H), 5.81 (s, 1H), 7.24−7.80 (m, 10H).

^{31}P NMR (161.9 MHz): δ 17.17 (major), 18.29 (minor).

Complexation Behavior of 16 with Dichlorobis(acetonitrile)-palladium(II). A mixture of **16** (11.2 mg, 0.02 mmol) and dichlorobis-(acetonitrile)palladium(II) (5.2 mg, 0.02 mmol) was dissolved in acetonitrile-d_3 (0.5 mL). The resulting solution gave two sets of signals in the ^1H NMR spectrum and presented a ratio of 22:1 in the ^{31}P NMR spectrum at room temperature, which might be assigned as diastereomers **30** and **29**, respectively.

30 (Major). ^1H NMR (400 MHz): δ 0.27 (s, 9H), 0.44 (d, $J = 6.8$ Hz, 3H), 1.13 (d, $J = 6.9$ Hz, 3H), 2.10 (m, 1H), 3.92 (s, 1H), 4.06 (m, 1H), 4.09 (dd, $J = 8.7$, 12.2 Hz, 1H), 4.46 (m, 1H), 4.50 (m, 1H), 4.58 (dd, $J = 8.7$, 10.1 Hz, 1H), 4.68 (m, 1H), 4.83 (m, 1H), 5.03 (t, $J = 2.5$ Hz, 1H), 7.13 (s, 1H), 7.27−7.88 (m, 10H).

^{31}P NMR (161.9 MHz): δ 15.75 (major), 18.51 (minor).

[Pd(η^3-PhCHCHCHPh)(8a)][SbF_6] (8aa). To a solution of ligand **8a** (96 mg, 0.2 mmol) in dichloromethane (20 mL) was added [Pd(η^3-PhCHCHCHPh)(μ-Cl)]$_2$ (69 mg, 0.1 mmol). After the solution turned clear again, $AgSbF_6$ (69 mg, 0.2 mmol) was added and stirring continued for 2 h at room temperature. The suspension was filtered over Celite, and the solvent was evaporated in vacuo, to afford a yellow foamy solid. The resulting solid was recrystallized from dichloromethane/ethyl ether, yielding 183 mg (90%) of complex **8aa** as a yellow amorphous solid.

8aa (Major). ^1H NMR (400 MHz, CD_2Cl_2): δ 0.52 (d, $J = 6.7$ Hz, 3H), 0.73 (d, $J = 6.7$ Hz, 3H), 1.76 (m, 1H), 2.21 (m, 1H), 3.73 (d, $J = 1.1$ Hz, 1H), 3.77 (s, 1H), 3.88 (d, $J = 10.6$ Hz, 2H), 4.29 (d, $J = 0.9$ Hz, 1H), 4.51−4.60 (m, 2H), 4.77 (t, $J = 1.2$ Hz, 1H), 4.87 (d, $J = 1.1$ Hz, 1H), 4.97 (d, $J = 1.2$ Hz, 1H), 5.95 (dd, $J = 13.4$, 8.5 Hz (J_{P-H}), 1H), 6.12 (s, 1H), 6.84 (dd, $J = 13.3$, 11.5 Hz, 1H), 6.75−7.04 (m, 6H), 7.10−7.71 (m, 14H). ^{31}P NMR (161.9 MHz): δ 14.79. ^{13}C NMR (100.58 MHz): δ 73.9 (allyl trans to N), 109.0 (central allyl), 102.0 (allyl trans to P). IR (cm^{-1}): 1626, 695, 658, 507. ESI: *m*/*z* 780 ($M^+ - SbF_6$). Anal. Calcd for $C_{43}H_{41}NF_6OPFePdSb$: C, 50.80; H, 4.06; N, 1.38. Found: C, 50.41; H, 3.79; N, 1.39.

[Pd(η^3-PhCHCHCHPh)(9)][SbF_6] (9a). To a solution of ligand **9** (110 mg, 0.2 mmol) in dichloromethane (20 mL) was added [Pd(η^3-PhCHCHCHPh)(μ-Cl)]$_2$ (69 mg, 0.1 mmol). After the solution turned clear again, $AgSbF_6$ (69 mg, 0.2 mmol) was added and stirring continued for 2 h at room temperature. The suspension was filtered over Celite, and the solvent was evaporated in vacuo, to afford a yellow foamy solid. The resulting solid was recrystallized from dichloromethane/ethyl ether and yielded 187 mg (86%) of complex **9a** as a yellow amorphous solid.

9a (Major). ^1H NMR (400 MHz, CD_2Cl_2): δ 0.17 (d, $J = 6.7$ Hz, 3H), 0.2 (s, 9H), 0.87 (m, 1H), 1.21 (d, $J = 6.7$ Hz, 2H), 3.61−3.77 (m, 3H), 4.15 (m, 1H), 4.35 (m, 1H), 4.49 (m, 1H), 4.32−4.43 (m, 3H), 4.69 (s, 1H), 5.23 (s, 1H), 6.35 (dd, $J = 13.9$, 8.7 (J_{P-H}) Hz, 1H), 6.44 (br, 1H), 6.65 (t, 12.8 Hz, 1H), 6.75−7.85 (m, 20H). ^{31}P NMR (161.9 MHz): δ 18.24. ^{13}C NMR (100.58 MHz): δ 72.1 (allyl trans to *N*), 113.7 (central allyl), 110.8 (allyl trans to *P*).

9a (Minor). ^1H NMR (400 MHz, CD_2Cl_2): δ −0.22 (d, $J = 6.7$ Hz, 3H), 0.03 (s, 9H), 0.85 (d, $J = 6.7$ Hz, 3H), 1.80 (m, 1H), 3.61−

3.77 (m, 1H), 4.17 (s, 1H), 4.30−4.42 (m, 3H), 4.46 (s, 1H), 4.52 (s, 1H), 4.58−4.62 (m, 2H), 5.00 (t, J = 2.5 Hz, 1H), 5.74 (s, 1H), 6.10 (dd, J = 13.4, 8.7 (J_{P-H}) Hz, 1H), 6.65 (t, 12.8 Hz, 1H), 6.75−7.85 (m, 20H). ^{31}P NMR (161.9 MHz): δ 16.34. ^{13}C NMR (100.58 MHz): δ 71.7 (allyl trans to *N*), 110.6 (central allyl), 103.2 (allyl trans to *P*). ^{31}P NMR (161.9 MHz): δ 15.54 (the isomer of 5%). IR (cm^{-1}): 2959, 1616, 1437, 1249, 836, 695, 658. ESI: *m*/*z* 852 ($M^+ - SbF_6$). Anal. Calcd for $C_{46}H_{49}NF_6OSiPFePdSb$: C, 50.74; H, 4.54; N, 1.29. Found: C, 51.23; H, 4.68; N, 1.23.

[Pd(η^3-PhCHCHCHPh)(14)][SbF$_6$] (14a). To a solution of ligand **14** (99 mg, 0.2 mmol) in dichloromethane (20 mL) was added [Pd(η^3-PhCHCHCHPh)(μ-Cl)]$_2$ (69 mg, 0.1 mmol). After the solution turned clear again, $AgSbF_6$ (69 mg, 0.2 mmol) was added and stirring continued for 2 h at room temperature. The suspension was filtered over Celite, and the solvent was evaporated in vacuo, to afford a yellow foamy solid. The resulting solid was recrystallized from dichloromethane/ethyl ether and yielded 177 mg (86%) of complex **14a** as a yellow amorphous solid.

14 (Major). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.56 (d, J = 4.8 Hz, 3H), 0.74 (d, J = 4.8 Hz, 3H), 1.81 (m, 1H), 2.20 (s, 3H), 2.26 (td, J = 5.6, 10.3 Hz, 1H), 3.73 (s, 1H), 3.76−3.93 (m, 3H), 4.32 (m, 1H), 4.38 (m, 1H), 4.46 (s, 1H), 4.49 (d, J = 11.1 Hz, 1H), 4.85 (t, J = 2.6 Hz, 1H), 6.02 (dd, J = 13.6, 8.6 (J_{P-H}) Hz, 1H), 6.05 (s, 1H), 6.70−7.71 (m, 21H). ^{13}C NMR (100.58 MHz): δ 73.4 (allyl trans to *N*), 108.7 (central allyl), 102.6 (allyl trans to *P*). ^{31}P NMR (161.9 MHz): δ 15.33 (major), 19.25 (minor). IR (cm^{-1}): 1624, 1482, 1146, 760, 695, 658, 507. ESI: *m*/*z* 794 ($M^+ - SbF_6$). Anal. Calcd for $C_{44}H_{43}NF_6OPFePdSb$: C, 51.27; H, 4.20; N, 1.36. Found: C, 51.43; H, 3.89; N, 1.39.

[Pd(η^3-PhCHCHCHPh)(8)][SbF$_6$] (8ca). To a solution of ligand **8c** (99 mg, 0.2 mmol) in dichloromethane (20 mL) was added [Pd(η^3-PhCHCHCHPh)(μ-Cl)]$_2$ (69 mg, 0.1 mmol). After the solution turned clear again, $AgSbF_6$ (69 mg, 0.2 mmol) was added and stirring continued for 2 h at room temperature. The suspension was filtered over Celite, and the solvent was evaporated in vacuo, to afford a yellow foamy solid. The resulting solid was recrystallized from dichloromethane/ethyl ether and yielded 181 mg (88%) of complex **8ca** as a yellow amorphous solid.

8ca (Major). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.76 (s, 9H), 2.01 (t, J = 11.1 Hz, 1H), 3.74 (s, 1H), 3.82−3.95 (m, 2H), 4.32 (m, 2H), 4.53 (d, J = 10.9 Hz, 1H), 4.57 (m, 1H), 4.80 (m, 1H), 4.88 (m, 1H), 4.99 (m, 1H), 6.15 (dd, J = 13.6, 7.8 (J_{P-H}) Hz, 1H), 6.23 (m, 1H), 6.63−6.73 (m, 5H), 6.75 (dd, J = 13.6, 11.0 Hz, 1H), 7.05 (t, J = 7.8 Hz, 2H), 7.10−7.31 (m, 3H), 7.34−7.69 (m, 10H). ^{31}P NMR (161.9 MHz): δ 13.24 (major), 18.77 (minor). ^{13}C NMR (100.58 MHz): δ 71.9 (allyl trans to *N*), 108.7 (central allyl), 103.6 (allyl trans to *P*). IR (cm^{-1}): 1623, 1484, 1146, 760, 695, 658, 509. ESI: *m*/*z* 794 ($M^+ - SbF_6$). Anal. Calcd for $C_{44}H_{43}NF_6OPFePdSb$: C, 51.27; H, 4.20; N, 1.36. Found: C, 51.11; H, 4.06; N, 1.35.

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Supporting Information Available: Full spectral characterization for all new ferrocene compounds and Pd complexes, and crystallographic data of two Pd complexes (PDF). X-ray crystallographic data, in CIF format, are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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