Chiral [Iminophosphoranyl]ferrocenes: Synthesis, Coordination Chemistry, and Catalytic Application

Thanh Thien Co, Sang Chul Shim, Chan Sik Cho, Dong-Uk Kim,† and Tae-Jeong Kim*

*Department of Applied Chemistry, Kyungpook National University, Daegu 702-701, Korea. *E-mail: tjkim@knu.ac.kr*
†Department of Science Education, Daegu National University of Education, Daegu 705-715, Korea
Received May 26, 2005

A series of new chiral [iminophosphoranyl]ferrocenes, {η^5-C_5H_4-(PPh_2=N-2,6-R_2-C_6H_3)}Fe{η^5-C_5H_3-1-PPh_2-2-CH(Me)NMe_2} (**1**: R = Me, ^{i}Pr), {η^5-C_5H_4-(PPh_2=N-2,6-R_2^1-C_6H_3)}Fe{η^5-C_5H_3-1-(PPh_2=N-2,6-R_2-C_6H_3)-2-CH(Me)R^2} (**2**: R^1 = Me, ^{i}Pr; R^2 = NMe_2, OMe), and (η^5-C_5H_5)Fe{η^5-C_5H_4-1-PR_2-2-CH(Me)N=PPh_3} (**3**: R = Ph, C_6H_{11}) have been prepared from the reaction of [1,1'-diphenylphosphino-2-(N,N-dimethylamino)ethyl]ferrocene with arylazides (**1** & **2**) and the reaction of phosphine dichlorides (R_3PCl_2) with [1,1'-diphenylphosphino-2-aminoethyl]ferrocene (**3**), respectively. They form palladium complexes of the type [Pd(C_3H_5)(L)]BF_4 (**4-6**: L = **1-3**), where the ligand (L) adopts an η^2-N,N (**2**) or η^2-P,N (**3**) as expected. In the case of **1**, a potential terdentate, an η^2-P,N mode is realized with the exclusion of the –P=NAr group from the coordination sphere. Complexes **4-6** were employed as catalysts for allylic alkylation of 1,3-diphenylallyl acetate leading to an almost stoichiometric product yield with modest enantiomeric excess (up to 74% ee). Rh(I)-complexes incorporating **1-3** were also prepared in situ for allylic alkylation of cinnamyl acetate as a probe for both regio- and enantioselectivities of the reaction. The reaction exhibited high regiocontrol in favor of a linear achiral isomer regardless of the ligand employed.

Key Words : Chiral ferrocenes, Iminophosphoranes, N ligand, Palladium catalysts, Allylic alkylation

Introduction

Iminophosphoranes (R_3P=NR), which make up an isoelectronic series with phosphorus ylides (R_3P=CR_2) and phosphine oxides (R_3P=O), have been the subject of extensive studies since their first appearance in the literature in 1919.[1] They have found numerous applications since then, which include their use as ylides in organic syntheses (aza-Wittig reaction),[2] as building blocks for P-N-backbone polymers (polyphosphazenes),[3] or as ligands for transition metals.[4] In addition, a recent breakthrough in the development of late-transition metal catalysts incorporating bulky α-and β-diimine ligands for olefin polymerization has spurred renewed interest in the design and the synthesis of iminophosphoranes in the hope that they offer a steric environment similar to diimines, while the electronic characteristics, such as donor strength and π-acceptor capacity, are clearly different.[5] In consequence, there are now known numerous transition metal complexes of iminophosphoranes, and the most common are those incorporating the homobidentate (**A** & **B**) and heterobidentate (**C** & **D**) derivatives (Chart 1).[6]

In spite of availability of such a wide variety of iminophosphoranes, there have been limited studies on the design and the synthesis of their chiral counterparts, not mention their use in asymmetric catalysis. To the best of our knowledge, there have appeared only two reports on the use of chiral iminophosphoranes in asymmetric catalytic reactions such as Pd-catalyzed allylic alkylation and Cu-catalyzed cyclopropanation.[7] The chiral ligands employed in these studies are 1,2-diiminophosphoranes of type **A**, and obtainable upon reacting R_3PBr_2 with the commercially available chiral 1,2-diaminoalkanes such as *cis*-(1*R*,2*R*)-diaminocyclohexane. Although relatively modest ee's have been achieved for the above-mentioned reactions,[7] these results encourage not only further investigation of the use of these ligands in other catalytic reactions but also the development of new types of ligands such as **B**, **C**, and **D**.

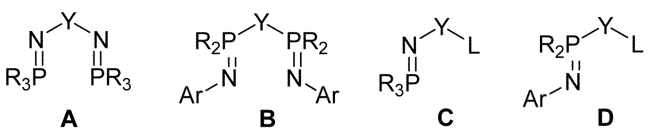


Chart 1

One of the most promising chiral templates for these purposes is N,N-dimethyl-1-ferrocenyl-ethylamine (FA) whose synthesis and resolution have long been established.[8] Since the pioneering work of Hayashi and Kumada on the synthesis of the first chiral ferrocenyl phosphine,[9] a great number of ferrocenes with various types of chirality have been prepared and used successfully as ligands for metal complexes in a variety of asymmetric catalytic reactions, and further development of new ligands is still in progress.[10] Yet no chiral ferrocenes carrying the iminophosphorane moiety have ever been reported. This is rather surprising considering the fact that with FA, diverse steric and electronic modifications are possible, leading to the formation of virtually all types of iminophosphoranes such as those listed in Chart 1.

We have recently undertaken the preparation of chiral iminophosphoranes and reported that our new ligands (**1-3**)

exhibit exceptionally high enantioselectivity (up to 99%) and catalytic activity in the Rh-catalyzed asymmetric hydrogenation of α,β-unsaturated carboxylic acid derivatives.[11] Encouraged by these observations and motivated by our continuing effort in the design and the synthesis of new ferrocene-based chiral ligands for asymmetric catalysis,[12] we have further pursued the coordination chemistry of **1-3** for their use as ligand in the Pd-catalyzed allylic alkylation. We anticipated that these compounds should act as tightly binding chelates and thus would be capable of stabilizing metal centers involved in catalytic cycles, even in rather low oxidation states. Furthermore, as sterically demanding and robust chelates, they are supposed to accomplish higher optical inductions in asymmetric reactions.

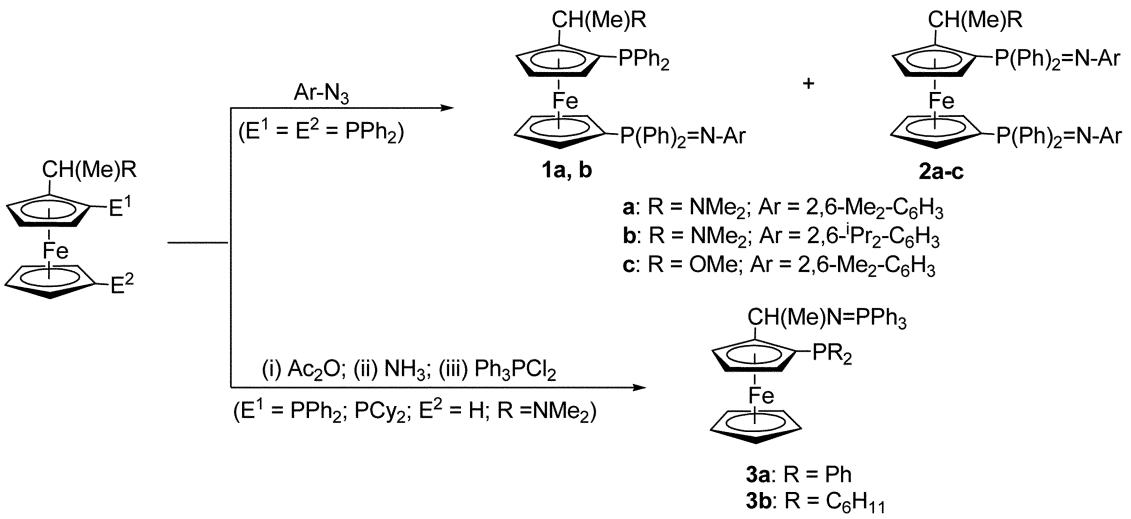
Results and Discussion

Synthesis and Characterization. Scheme 1 shows the synthetic routes leading to the formation of our target compounds (**1-3**) for the present studies. All routes require initially the preparation and resolution of N,N-dimethylaminoethylferrocene (FA).[8] The preparation of PPFA (R = NMe_2; $E^1 = PPh_2$; $E^2 = H$) and BPPFA (R = NMe_2; $E^1 = E^2 = PPh_2$) is followed simply by taking advantage of the highly stereoselective ortho-metallation of enantiopure FA.[9] Namely, monolithiation of (*S*)- or (*R*)-FA followed by treatment with chlorodiphenylphosphine yields (*S*,*R*)- or (*R*,*S*)-PPFA, respectively. In the same vein, dilithiation leads to (*S*,*R*)- or (*R*,*S*)-BPPFA. Here, the first (*S*) or (*R*) referes to the central chirality located on the asymmetric carbon atom and the second (*R*) or (*S*) to the ferrocene planar chirality created by electrophilic substitution at the ortho-position.

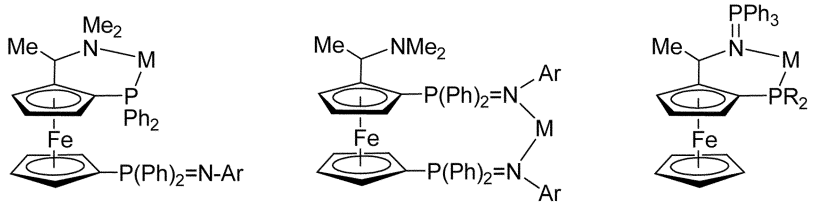
Iminophosphoranes are best prepared through one of two major routes, namely the reaction of azides with phosphines (the Staudinger reaction) and the reaction of phosphine dibromides (R_3PBr_2) with primary amines followed by treatment with a base (the Kirsanov reaction).[2a,b] We employed the former method to prepare **1** and **2**, and the latter to prepare **3**. Thus, treating BPPFA with arylazides led to the formation of a mixture of **1** and **2**, whose relative yields depended upon the choice of azides and the reaction conditions. For instance, an equimolar mixture of arylazide and BPPFA yielded preferentially the mono(iminophosphorane) derivatives (**1a**, **b**), while a 4-5 molar excess of azides was normally required for the formation of bis(iminophosphorane) derivatives (**2a**, **b**) as major products. Here it is worth noting that during the course of the formation of **1**, it is the phosphine at 1'-position (not α-PPh_2 to ethylamine) that undergoes oxidation by azide for some steric reason.

The Kirsanov reaction leading to the formation of **3** has one advantage over the other in that it avoids tedious preparative steps and the use of hazardous azides. Even more intriguing with this method is the fact that optically active 1,2-diamines are now readily accessible.[13] In our case, FA had to be converted initially to its primary amines by acetylation with acetanhydride followed by amination with ammonia. This was then reacted with PPh_3Cl_2 to form **3**.

Structural confirmations of new compounds come from spectroscopic and analytical techniques. The formation of **1** and **2** can be easily recognized by their characteristic downfield singlets (−6 ~ −10 ppm) on ^{31}P NMR assignable to the iminophosphoranes (P=NAr). The unreacted phosphines appear in the highly shielded (up-field) area such as −22 ~ −24 ppm in the case of **1**, for instance, thus making it feasible to differentiate **1** from **2**. The position of oxidation, namely P=N-Ar, in **1** can be easily identified by comparison with ^{31}P NMR patterns of parent BPPFA. As deduced from their structures, both **1** and **2** must be sterically quite demanding, and the free rotation along the axis of P=N-Ar is prohibited. As a result, pairs of methyl (**1a**) and isopropyl groups (**1b**) become diastereotopic within each pair. Their ^1H NMR spectra confirm this statement by showing characteristically pairs of singlets and doublets arising from methyl and isopropyl groups in **1a** and **1b**, respectively. The formation of **3** can be readily confirmed by a pair of characteristic ^{31}P NMR signals: an up-field singlet due to



Scheme 1



4: M = $Pd(C_3H_5)BF_4$ **5**: M = $Pd(C_3H_5)BF_4$ **6**: M = $Pd(C_3H_5)BF_4$

Scheme 2

PR_2 (R = Ph, Cy) and a down-field singlet due to P=NAr.

Coordination Chemistry. Compounds **1** and **2** are potential terdentate ligands, and thus await their coordination behaviors to be revealed. We have reported in our previous paper that the reaction of (*S,R*)-**1b** with $[(NBD)RhCl]_2$ followed by treatment with $NaClO_4$ yields a cationic Rh(I) complex of the type $[(NBD)Rh(S,R\text{-}\mathbf{1b})]ClO_4$ as expected.[11] Yet, interestingly the cis-*P,N*-chelation takes place through $-PPh_2$ and $-NMe_2$ (not =N-Ar). The iminophosphoranyl group seems to be sterically too demanding to be involved in coordination.

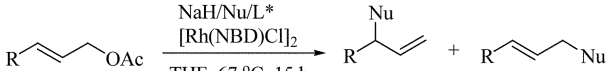
Such a coordination behavior as that found with **1** proves to be universal. Thus, for example, the reaction of both **1a** and **1b** with $[Pd(C_3H_5)Cl]_2$ followed by treatment with $AgBF_4$ resulted in $[Pd(C_3H_5)(L)]BF_4$ (**4a**: L = **1a**; **4b**: L = **1b**), where palladium binds to the ligand (L) in the same fashion as rhodium as illustrated in Scheme 2. Analytical and NMR data confirm their formation, and in particular a pair of phosphorus signals are the most straightforward revealing the up-field signal ($\delta \approx -11$ ppm) due to P=N-Ar and a down-field signal ($\delta \approx 11$ ppm) with a coordination shift ($\Delta\delta$) of approximately 34-35 ppm due to the coordinated PPh_2 group.

Scheme 2 shows additional coordination modes when employed in the reactions involving **2** and **3**. Thus the reaction of **2** with $[Pd(C_3H_5)Cl]_2$ followed by treatment with $AgBF_4$ led to the formation of $[Pd(C_3H_5)(L)]BF_4$ (**5**), where **2** binds to palladium through both phosphoranylimines. This moves the ^{31}P NMR signals for both groups to deshielding areas. The coordination chemistry of **3** should be quite obvious and deserves little attention. Thus complexes $[Pd(C_3H_5)(\mathbf{3})]BF_4$ (**6**) have in common a pair of down-field phosphorus signals on ^{31}P NMR spectrum.

Asymmetric Allylic Alkylation (AAA). AAA is one of well-known test reactions to examine enantio- and regioselection of new chiral ligands. It looks quite obvious that the steric demand of **1-3** should be directly influenced by the nature of the ferrocene backbone as well as the steric hindrance of both N- and P-substituents. It is well-known that the P-substituents also concurrently influence the electronic properties as well by exerting a significant influence on the basicity of these ylides.[2a,c] Thus our ligands meet most of our requirements.

Table 1 shows the results on the Rh(I)-catalyzed allylic alkylation of cinnamyl acetate employing **1-3** as ligands. The use of rhodium complexes may be justified by the fact

Table 1. Regioselective allylic alkylation of cinnamyl acetate as a function of ligand[a]



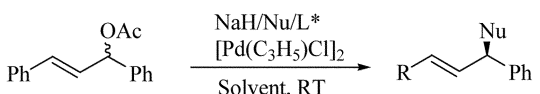
Entry	Ligand (L*)	Yield (%)[b]	Ratio[c] **7** : **8**	*ee* (**7**)[d]
1	(*S,R*)-**1a**	53	18:82	80 (*R*)
2	(*S,R*)-**1b**	70	14:86	88 (*R*)
3	(*S,R*)-**2a**	65	16:84	78 (*R*)
4	(*S,R*)-**2b**	75	15:85	90 (*R*)
5	(*S,R*)-**2c**	64	15:85	91 (*R*)
6	(*S,R*)-**3a**	12	13:87	84 (*R*)
7	(*S,R*)-**3b**	32	11:89	74 (*R*)

[a]Detailed procedure provided in Experimental Section: Nu = dimethyl malonate. [b]Isolated yield. [c]Determined by GC (CBP-10). [d]Determined by HPLC (Chiralpak IA).

that non-Pd catalysts such as those incorporating Mo, W, Rh, or Ir have been known for some time to exhibit high regiocontrol in favor of a branched chiral isomer such as **7**.[16] With most palladium catalysts, such substrates react with soft nucleophiles preferentially at the less substituted terminus, giving rise to an achiral linear product,[17] although we have recently demonstrated that the rule of thumb stated above is no longer universal.[12a] Contrary to our expectation, however, all reactions under the standard set of reaction conditions exhibit high regiocontrol in favor of a linear achiral isomer (**8**) regardless of the ligand employed. Relatively high enantiomeric excesses (up to 91% ee) for the branched isomer (**7**) are obtained.

Table 2 shows that the palladium complexes of the same series of ligands work better for the alkylation of 1,3-diphenylallyl acetate to produce the product (**9**) almost quantitatively. Yet the enantiomeric excess is unsatisfactory as compared with that reported using other well-known ligands in the literature.[16] It is a little disappointing to find that the ligands **2a-c** capable of providing a sterically demanding environment around the central metal as seen from **5** (Scheme 2) led only to modest % ee's. A partial explanation for these observations may be given in terms of the so called 'proximity rule' (the chirality is far removed from the reaction center in **5**) as well as the conformational flexibility as deduced from the structure. In this regard the ligands **3** are expected to be the most efficient considering

Table 2. Asymmetric Allylic Alkylation of 1,3-Diphenylallyl Acetate[a]



(**9**)

Entry	Ligand (L*)	Solvent	Time (h)	Yield (%)[b]	*ee* (%)[c]	Config.
1	(*S,R*)-**1a**	THF	8	97	48	R
2	(*S,R*)-**1a**	CH_2Cl_2	8	97	46	R
3	(*S,R*)-**1b**	CH_2Cl_2	3	96	51	R
4	(*S,R*)-**2a**	CH_2Cl_2	24	54	31	R
5	(*S,R*)-**2b**	CH_2Cl_2	3	96	50	R
6	(*S,R*)-**2c**	CH_2Cl_2	24	40	25	R
7	(*S,R*)-**3a**	CH_2Cl_2	3	97	74	R
8	(*S,R*)-**3b**	CH_2Cl_2	15	88	52	R

[a]Detailed procedure provided in Experimental Section: Nu = dimethyl malonate. [b]Isolated yield. [c]Determined by GC (CBP-10). [d]Determined by HPLC (Chiralpak IA).

the fact that, in the resultant complexes **6** (Scheme 2), both the steric demand around the metal and the proximity rule seem to work cooperatively. Indeed the ligand **3a** gives the highest ee (74%) as well as the highest yield (97%).

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of nitrogen using the standard Schlenk techniques. Solvents were dried using standard procedures. The ^{1}H and ^{13}C NMR experiments were performed on a Bruker Advance 400 or 500 Spectrometer. The ^{31}P NMR spectra were recorded on a Varian Unity Invova 300 WB Spectrometer. Chemical shifts were given as δ values with reference to tetramethylsilane (TMS) as an internal standard. Coupling constants are in Hz. GC-Mass spectra were obtained by using a Micromass QUATTRO II GC8000 series model with electron energy of 20 or 70 eV. IR spectra were run on a Mattson FT-IR Galaxy 6030E spectrophotometer. All commercial reagents were purchased from Aldrich and used as received. FA,[8] BPPFA,[9] BPPFA-NH_2,[9] BPPFA-OMe,[9] 2,6-^{i}Pr$_2$C$_6$H$_3$N$_3$ and 2,6-Me$_2$C$_6$H$_3$N$_3$,[5a] Ph_3PCl_2[13] were prepared according to the literature methods.

{η^5-C_5H_4-(PPh$_2$=N-2,6-Me$_2$-C_6H_3)}Fe{η^5-C_5H_3-1-PPh$_2$-2-CH(Me)NMe$_2$} (1a). To a solution of BPPFA (1.00 g, 1.60 mmol) in diethyl ether (15 mL) was added dropwise an equimolar amount of 2,6-dimethylbenzoylazide (0.24 g, 1.60 mmol). Bubbles of N_2 gas evolved during the addition. The mixture was further stirred overnight at ambient temperature, after which time the solvent was removed. The oily residue dissolved in a minimum amount of CH_2Cl_2 was transferred into a column of silica gel for chromatographic separation. A single orange band was eluted with a mixture of hexane and ethyl acetate (8 : 2) to give orange solids after removal of solvents. Recrystallization from CH_2Cl_2/hexane yielded 0.49 g of **1a** (41%) in two crops as yellow solids. ^{31}P NMR ($CDCl_3$): δ −22.56 (s, PPh_2), -6.32 (s, P=N). ^{1}H NMR ($CDCl_3$): δ 0.98 (d, J = 6.6, 3H, CH*CH$_3$*), 1.62 (s, 3H, *Me*-Ph), 1.66 (s, 3H, *Me*-Ph), 2.06 (s, 6H, N*Me$_2$*), 3.50, 3.58 (br, 4H, C_5H_4), 4.21-4.42 (m, 3H, C_5H_3), 3.98 (q, J = 7.2, 1H, CH), 6.60 (t, J = 6.3, 1H, *p*-N-*C$_6$H$_3$*), 6.88 (d, J = 6.6, 2H, *m*-N-*C$_6$H$_3$*), 7.57-7.26 (m, 20H, PPh_2). Anal. Calcd for $C_{46}H_{46}FeN_2P_2$: C 73.99; H 6.23; N 3.76. Found: C 74.19; H 6.28; N 3.60. MS (EI, m/z): Calcd for $C_{46}H_{46}FeN_2P_2$: 744.24. Found: 744.24 (M^+).

{η^5-C_5H_4-(PPh$_2$=N-2,6-^{i}Pr$_2$-C_6H_3)}Fe{η^5-C_5H_3-1-PPh$_2$-2-CH(Me)NMe$_2$} (1b). The title compound was prepared in the same manner as described above for the synthesis of **1a** by replacing 2,6-dimethylbenzoylazide with 2,6-diisopropylbenzoylazide. Yield: 1.08 g (85%). ^{31}P NMR ($CDCl_3$): δ −23.76 (s, PPh_2), −9.11 (s, P=N). ^{1}H NMR ($CDCl_3$): δ 0.88 (d, J = 6.9, 6H, CH*Me$_2$*), 0.96 (d, J = 6.9, 6H, CH*Me$_2$*), 1.11 (d, J = 6.9, 3H, CH*Me*), 1.68 (s, 6H, NMe_2), 3.40 (sept, J = 6.6, 2H, *CH*Me$_2$), 3.50, 3.63 (br, 4H, *C$_5$H$_4$*), 4.02 (qt, J = 4.8, 1H, *CH*Me), 4.28-4.46 (m, 3H, *C$_5$H$_3$*), 6.76 (t, J = 7.5, 1H, *p*-N-*C$_6$H$_3$*), 6.93 (d, J = 7.5, 2H, *m*-N-*C$_6$H$_3$*), 7.57-7.12 (m, 20H, PPh_2). Anal. Calcd for $C_{50}H_{54}FeN_2P_2$: C, 74.99; H, 6.80; N, 3.50. Found: C, 74.54; H, 6.66; N, 3.39.

{η^5-C_5H_4-(PPh$_2$=N-2,6-Me$_2$-C_6H_3)}Fe{η^5-C_5H_3-1-(PPh$_2$=N-2,6-Me$_2$-C_6H_3)-2-CH(Me)NMe$_2$} (2a). The title compound was prepared by essentially the same method for the preparation of **1a** except the use of excess of 2,6-dimethylbenzoylazide (1.14 g, 9.60 mmol) as compared with the amount of BPPFA (1.00 g, 1.60 mmol). The product was obtained as yellow solids after chromatographic separation (silica gel; hexane/ethyl acetate, 8/2). Yield: 1.03 g (75%). ^{31}P NMR ($CDCl_3$): δ −7.72, −6.12 (s, P=N-Ar). ^{1}H NMR ($CDCl_3$): δ 0.91 (d, J = 6.7, 3H, CH*Me*), 1.49 (s, 6H, N*Me$_2$*), 2.02, 2.04 (s, 12H, *Me$_2$*-C_6H_3), 4.12 (qt, J = 7.2, 1H, C*H*Me), 4.05-4.23 (m, 4H, C_5H_4), 4.20-4.96 (m, 3H, C_5H_3), 6.58 (t, J = 9.9, 2H, *p-C$_6$H$_3$*), 6.90 (t, J = 9.9, 4H, *m-C$_6$H$_3$*), 7.31-7.61 (m, 20H, *C$_6$H$_5$*). Anal. Calcd for $C_{54}H_{55}FeN_3P_2$: C 75.08; H 6.42; N 4.86. Found: C 75.26; H 6.26; N 4.67.

{η^5-C_5H_4-(PPh$_2$=N-2,6-^{i}Pr$_2$-C_6H_3)}Fe{η^5-C_5H_3-1-(PPh$_2$=N-2,6-^{i}Pr$_2$-C_6H_3)-2-CH(Me)NMe$_2$} (2b). The title compound was prepared by essentially the same method for the preparation of **1b** except the use of excess of 2,6-diisopropylbenzoylazide (1.92 g, 9.60 mmol) as compared with the amount of BPPFA (1.00 g, 1.60 mmol). The product was obtained as yellow solids after chromatographic separation (silica gel; hexane/ethyl acetate, 8/2). Yield: 0.84 g (54%). In this case **1b** was also obtained as a minor product (0.22 g, 17%). ^{31}P NMR ($CDCl_3$): δ −9.66, −7.89 (s, P=N-Ar). ^{1}H NMR ($CDCl_3$): δ 0.75, 0.89, 0.95, 1.01 (d, J = 6.3, 24H, CH*Me$_2$*), 1.01 (d, J = 6.6, 3H, CH*Me*), 1.55 (s, 6H, N*Me$_2$*), 3.40 (m, 4H, C*H*Me$_2$), 3.56-4.85 (m, 7H, (*C$_5$H$_4$*)Fe(*C$_5$H$_3$*)), 4.07 (qt, J = 7.2, 1H, C*H*Me), 6.78 (t, J = 7.2, 2H, *p-C$_6$H$_3$*), 6.90 (t, J = 7.2, 4H, *m-C$_6$H$_3$*), 7.31-7.61 (m, 20H, *C$_6$H$_5$*). Anal. Calcd for $C_{62}H_{71}FeN_3P_2$: C 76.29; H 7.33; N 4.31. Found: C 76.04; H 7.22; N 4.17.

{η^5-C_5H_4-(PPh$_2$=N-2,6-^{i}Pr$_2$-C_6H_3)}Fe{η^5-C_5H_3-1-(PPh$_2$=N-2,6-^{i}Pr$_2$-C_6H_3-2-CH(Me)OMe} (2c). To a solution of BPPFA-OMe (1.00 g, 1.18 mmol) in CH_2Cl_2 (10 mL) was added dropwise 2,6-dimethylbenaoylazide (0.50 g, 2.58 mmol). Bubbles of N_2 gas evolved during the addition. The

mixture was stirred for 6 h at ambient temperature, after which the solvent was removed under vacuum. The oily residue dissolved in a minimum amount of CH_2Cl_2 was transferred into a column of silica gel for chromatographic separation. A single orange band was eluted with a mixture of hexane and ethyl acetate (7 : 3) to give orange solids after removal of solvents. Recrystallization from CH_2Cl_2/hexane yielded 1.03 g of **2c** (79%) in two crops as orange solids. ^{31}P NMR ($CDCl_3$): δ −8.96, −8.20 (s, P=N). ^{1}H NMR ($CDCl_3$): δ 1.23 (d, J = 6.3, 3H, CH*Me*), 2.02, 2.05 (s, 12H, *Me*$_2$CH), 2.55 (s, 3H, O*Me*), 4.13 (qt, J = 7.2, 1H, CH*Me*$_2$), 4.49, 4.53 (m, 4H, *C*$_5$*H*$_4$), 3.82, 4.51, 4.85 (br, 3H, *C*$_5$*H*$_3$), 6.02 (m, 2H, *C*$_6$*H*$_3$), 6.90 (m, 4H, *C*$_6$*H*$_3$), 7.28-7.60 (m, 20H, PPh_2). Anal. Calcd for $C_{53}H_{52}FeN_2OP_2$: C, 74.82; H, 6.16; N, 3.29. Found: C, 74.86; H, 6.45; N, 3.02.

(η^5-C_5H_5)Fe{η^5-C_5H_4-1-PPh_2-2-CH(Me)N=PPh_3} (3a). To a solution of BPPF-NH_2 (1.00 g, 2.42 mmol) in CH_2Cl_2 (15 mL) were added Ph_3PCl_2 (0.85 g, 2.42 mmol) and Et_3N (2.42 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 16 h. The Solvent was removed under a reduced pressure. The residue was washed with diethyl ether (15 mL) and extracted with THF (15 mL) to eliminate the triethyl ammonium salt. NaH (0.17 g, 7.26 mmol) was added to the THF extract in portions at 0 °C. The solution was then stirred for 2 h at room temperature, after which diethyl ether was added until precipitation was complete. The precipitate was isolated by filtration, washed several times with diethyl ether, and dried under vacuum to give a yellow solid (0.70 g, 47%). ^{31}P NMR ($CDCl_3$): δ −25.40 (s, PPh_2), 35.00 (s, P=N). ^{1}H NMR ($CDCl_3$): δ 1.95 (d, J = 6.9, 3H, CH*Me*), 4.13 (qt, J = 6.0, 1H, C*H*Me), 3.82 (s, 5H, *C*$_5$*H*$_5$), 3.87-4.57 (m, 3H, *C*$_5$*H*$_3$), 6.92-7.65 (m, 25H, *C*$_6$*H*$_5$). HRMS (EI, *m/z*): Calcd for $C_{42}H_{38}FeNP_2$: 674.1830 (M^+). Found: 674.1905. Anal. Calcd for $C_{42}H_{38}FeNP_2$: C, 62.66; H, 4.90; N, 1.66. Found: C, 62.40; H, 4.40; N, 1.93.

(η^5-C_5H_5)Fe{η^5-C_5H_4-1-PCy_2-2-CH(Me)N=PPh_3} (3b). The title compound was prepared in the same manner as described for the preparation of **3a** by replacing BPPF-NH_2 with BCP-NH_2. Yield (0.48 g, 30%). ^{31}P NMR ($CDCl_3$): δ −16.62 (s, PCy_2), 36.57 (s, P=N). ^{1}H NMR ($CDCl_3$): δ 0.73-2.03 (m, 22H, *C*$_6$*H*$_{11}$), 1.97 (d, J = 6.3, 3H, CH*Me*), 3.75 (qt, J = 6.0, 1H, C*H*Me), 4.35 (s, 5H, *C*$_5$*H*$_5$), 4.05-4.63 (m, 3H, *C*$_5$*H*$_3$), 7.44-7.87 (m, 15H, *C*$_6$*H*$_5$). HRMS (EI, *m/z*): Calcd for $C_{42}H_{38}FeNP_2$: 686.2700 (M^+). Found: 686.3100. Anal. Calcd for $C_{42}H_{49}FeNP_2$: C, 73.57; H, 7.20; N, 2.04. Found: C, 73.37; H, 7.17; N, 2.16.

[Pd(C_3H_5)(1a)]BF_4 (4a). To a stirred solution of [Pd(C_3H_5)Cl]$_2$ (0.036 g, 0.10 mmol) and **1a** (0.150 g, 0.20 mmol) in CH_2Cl_2 (10 mL) was added $AgBF_4$ (0.040 g, 0.25 mmol) at room temperature. After stirring 1 h, the mixture was filtered on celite. The filtrate was dried under vacuum to leave a reddish brown solid which was then washed with diethyl ether several times to give **4a**. Yield (0.148 g, 76%). ^{31}P NMR ($CDCl_3$): δ −11.15 (s, P=N), 11.72 (s, PPh_2). ^{1}H NMR ($CDCl_3$): δ 0.91 (d, J = 7.8, 3H, CH*Me*), 1.28, 1.30 (s, 6H, *Me*$_2$-C_6H_3), 2.11 (s, 6H, NMe_2), 2.92 (m, 2H, *anti*-C_3H_5), 3.45-4.57 (m, 7H, $C_5H_4FeC_5H_3$), 4.03 (m, 2H, *syn*-C_3H_5), 5.86 (m, 1H, *center*-C_3H_5), 6.27 (t, J = 6.9, 1H, *p*-C_6H_3), 6.88 (d, J = 7.2, 2H, *m*-C_6H_3), 7.01-7.89 (m, 20H, C_6H_5). Anal. Calcd for $C_{49}H_{51}BF_4FeN_2P_2Pd$: C, 60.12; H, 5.55; N, 2.86. Found: C, 60.75; H, 5.20; N, 2.96.

[Pd(C_3H_5)(1b)]BF_4 (4b). The title compound was prepared in the same manner as described for the preparation of **4a** by replacing **1a** with **1b**. Yield (0.186 g, 90%). ^{31}P NMR ($CDCl_3$): δ −11.84 (s, P=N), 11.33 (s, PPh_2). ^{1}H NMR ($CDCl_3$): δ 0.92 (d, J = 6.0, 6H, CH*Me*$_2$), 0.95 (d, J = 6.6, 6H, CH*Me*$_2$), 1.35 (d, J = 6.3, 3H, CH*Me*), 2.88 (s, 6H, NMe_2), 2.89 (m, 2H, *anti*-C_3H_5), 3.37 (m, 2H, C*H*Me$_2$), 3.52-4.83 (m, 7H, $C_5H_4FeC_5H_3$), 4.22 (qt, J = 4.8, 1H, C*H*Me), 4.32 (m, 2H, *syn*-C_3H_5), 5.89 (m, 1H, *center*-C_3H_5), 6.78 (t, J = 7.8, 1H, *p*-C_6H_3), 6.95 (d, J = 6.9, 2H, *m*-C_6H_3), 7.02-7.90 (m, 20H, C_6H_5). Anal. Calcd for $C_{53}H_{59}BF_4FeN_2P_2Pd$: C, 61.50; H, 5.75; N, 2.71. Found: C, 61.99; H, 5.20; N, 2.56.

[Pd(C_3H_5)(2a)]BF_4 (5a). The title compound was prepared in the same manner as described for the preparation of **4a** by replacing **1a** with **2a**. Yield (0.162 g, 74%). ^{31}P NMR ($CDCl_3$): δ 23.86, 17.91 (s, P=N). ^{1}H NMR ($CDCl_3$): δ 0.98 (d, J = 6.6, 6H, CH*Me*), 1.47 (s, 6H, NMe_2), 1.86, 1.88, 2.18, 2.21 (s, 12H, *Me*$_2$-C_6H_3), 3.02 (m, 2H, *anti*-C_3H_5), 3.94-4.49 (m, 7H, $C_5H_4FeC_5H_3$), 3.98 (m, 2H, *syn*-C_3H_5), 4.21 (qt, J = 5.7, 1H, C*H*Me), 5.43 (m, 1H, *center*-C_3H_5), 6.71 (t, J = 7.5, 2H, *p*-C_6H_3), 6.85 (d, J = 6.0, 4H, *m*-C_6H_3), 7.11-7.77 (m, 20H, C_6H_5). Anal. Calcd for $C_{57}H_{60}BF_4FeN_3P_2Pd$: C, 62.34; H, 5.51; N, 3.83. Found: C, 62.49; H, 5.94; N, 3.90.

[Pd(C_3H_5)(2b)]BF_4 (5b). The title compound was prepared in the same manner as described for the preparation of **5a** by replacing **2a** by **2b**. Yield (0.180 g, 75%). ^{31}P NMR ($CDCl_3$): δ 24.06, 24.71 (s, P=N). ^{1}H NMR ($CDCl_3$): δ 0.71 (d, J = 6.9, 6H, CH*Me*$_2$), 0.90 (d, J = 7.5, 6H, CH*Me*$_2$), 0.93 (d, J = 7.2, 6H, CH*Me*$_2$), 1.06 (d, J = 6.6, 3H, CH*Me*), 1.42 (d, J = 4.8, 6H, CH*Me*$_2$), 1.50 (s, 6H, NMe_2), 2.82 (m, 2H, *anti*-C_3H_5), 3.02-4.52 (m, 7H, C_5H_4-Fe-C_5H_3), 3.38 (m, 4H, C*H*Me$_2$), 3.78 (qt, J = 6.3, 1H, C*H*Me), 4.22 (m, 2H, *syn*-C_3H_5), 5.46 (m, 1H, *center*-C_3H_5), 6.74 (t, J = 7.2, 2H, *p*-C_6H_3), 6.89 (d, J = 4.2, 4H, *m*-C_6H_3), 7.15-8.00 (m, 20H, C_6H_5). Anal. Calcd for $C_{65}H_{76}BF_4FeN_3P_2Pd$: C, 64.50; H, 6.33; N, 3.47. Found: C, 64.31; H, 6.54; N, 3.94.

[Pd(C_3H_5)(2c)]BF_4 (5c). The title compound was prepared in the same manner as described for the preparation of **5a** by replacing **2a** by **2c**. Yield (0.182 g, 84%). ^{31}P NMR ($CDCl_3$): δ 22.55, 23.78 (s, P=N). ^{1}H NMR ($CDCl_3$): δ 1.23 (d, J = 6.0, 3H, CH*Me*), 1.87, 1.89, 2.19, 2.22 (s, 12H, *Me*$_2$-C_6H_3), 2.49 (s, 3H, OMe), 2.94 (m, 2H, *anti*-C_3H_5), 3.05 (qt, J = 6.3, 1H, C*H*Me), 3.97-5.98 (m, 7H, $C_5H_4FeC_5H_3$), 4.11 (m, 2H, *syn*-C_3H_5), 5.45 (m, 1H, *center*-C_3H_5), 6.72 (t, J = 3.6, 2H, *p*-C_6H_3), 6.89 (d, J = 7.2, 4H, *m*-C_6H_3), 7.13-8.13 (m, 20H, C_6H_5). Anal. Calcd for $C_{56}H_{57}BF_4FeN_2OP_2Pd$: C, 61.99; H, 5.29; N, 2.58. Found: C, 62.06; H, 5.74; N, 2.83.

[Pd(C_3H_5)(3a)]BF_4 (6a). The title compound was prepared in the same manner as described for the preparation of **5a** by replacing **2a** by **3a**. Yield (0.105 g, 58%). ^{31}P NMR ($CDCl_3$): δ 12.13 (s, PPh_2), 33.87 (s, PPh_3). ^{1}H NMR ($CDCl_3$): δ 1.56 (d, J = 6.0, 3H, CH*Me*), 3.04 (m, 2H, *anti*-

C_3H_5), 3.89 (qt, J = 6.0, 1H, C*H*Me), 4.70 (m, 2H, *syn*-C_3H_5), 3.57-4.47 (m, 8H, C_5H_5-Fe-C_5H_3), 5.46 (m, 1H, *center*-C_3H_5), 7.27-8.08 (m, 25H, C_6H_5). Anal. Calcd for $C_{45}H_{42}BF_4FeNP_2Pd$: C, 59.53; H, 4.66; N, 1.54. Found: C, 59.49; H, 4.94; N, 1.90.

[Pd(C_3H_5)(3b)]BF_4 (6b). The title compound was prepared in the same manner as described for the preparation of **5a** by replacing **2a** by **3b**. Yield (0.136 g, 74%). ^{31}P NMR ($CDCl_3$): δ 28.61 (s, PCy_2), 36.65 (s, PPh_3). ^{1}H NMR ($CDCl_3$): δ 1.03-1.92 (m, 22H, C_6H_{11}), 1.61 (d, J = 6.5, 3H, CH*Me*), 3.02 (m, 2H, *anti*-C_3H_5), 3.78 (qt, J = 3.7, 1H, C*H*Me), 4.20 (m, 2H, *syn*-C_3H_5), 4.06-4.77 (m, 8H, C_5H_5-Fe-C_5H_3), 5.56 (m, 1H, *center*-C_3H_5), 7.67-7.77 (m, 15H, C_6H_5). Anal. Calcd for $C_{45}H_{54}BF_4FeNP_2Pd$: C, 58.75; H, 5.92; N, 1.52. Found: C, 58.49; H, 5.94; N, 1.65.

Typical Procedure for Allylic Alkylation. To a solution of cinnamyl acetate (0.17 mL, 1.0 mmol) and dimethyl-sodium malonate (prepared from dimethyl malonate (0.26 mL, 2.0 mmol) and NaH (48 mg, 2.0 mmol)) was added catalyst generated *in situ* from [Rh(NBD)Cl]$_2$ (0.01 mmol) and ligand (0.02 mmol) in THF (2 mL). The mixture was stirred at 67 °C until the reaction was complete (as evidenced by TLC), then diluted with ether (2 mL), and washed successively with 5% aqueous $NaHCO_3$ and water. The organic phase was dried with $MgSO_4$, and the solvent was evaporated under reduced pressure. The oily residue was passed through a short silica gel column to remove catalyst using a 9 : 1 hexane-ethyl acetate mixture as an eluent. The diastereometic excess (% de) was determined by GC equipped with a CBP-10 column on a Shimadzu GC-17A.

Typical Procedure for Asymmetric Allylic Alkylation. A mixture of chiral ligand (0.02 mmol) and [Pd(C_3H_5)Cl]$_2$ (0.01 mmol) in a dry solvent (2 mL) was stirred at RT in a Schlenk tube. To this catalyst generated *in situ* was added a solution of 1,3-diphenyl-2-propenyl acetate (0.13 g, 0.50 mmol) in the same solvent (2 mL), followed by the addition of dimethyl malonate (0.17 mL, 1.50 mmol), KOAc (0.01 g, 0.10 mmol), and *N*,*O*-bis(trimethylsilyl)acetamide (0.37 mL, 1.50 mmol). The mixture was stirred at RT until the reaction was complete (as evidenced by TLC), then the reaction mixture was diluted with diethyl ether (10 mL) and water. The organic layer was washed with brine and dried over $MgSO_4$. After evaporation of solvent in vacuo, the residue was purified by column chromatography on silica gel (eluent : hexane-ethyl acetate, 9 : 1). The enantioselectivity was determined by HPLC analysis with a chiral column (Chiralpak IA; hexane/*i*-PrOH, 95 : 5; flow rate, 0.7 mL/min; t_R, 12.406; t_S, 14.765 min).

Dimethyl 2-(1-phenylprop-2-enyl)propanedioate (7). This was obtained as the product from the reaction of cinnamyl acetate with dimethyl sodium malonate. GC (CBP-10) conditions for diastereomeric separation: t_R, 16.2 min; oven temp, 100 °C; injection temp, 220 °C; initial time, 2 min; final temp, 200 °C; rate, 10 °C/min; detection temp, 250 °C; column pressure, 100 kPa. HPLC (Chiralpak IA) conditions for enantiomeric excess separation: hexane/2-propanol (95 : 5); flow rate = 0.7 mL/min; t_R = 7.48 min; t_S = 8.10 min. IR (KBr): 3031 (w), 1760 (s), 1740 (s), 1639 (w), 1602 (w), 1494 (w), 1435 (m), 1263 (m), 1198 (m), 1163 (m), 1027 (w), 765 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.19 (m, 5H), 5.99 (ddd, J = 17.0, 10.2, 8.1, CH), 5.15-5.06 (m, 2H), 4.14-4.08 (m, CH), 3.87 (d, J = 11.0, CH), 3.74, 3.49 (2s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.2, 167.8, 139.9, 137.8, 128.7, 127.9, 127.1, 116.6, 57.4, 52.6, 52.4, 49.7. MS: m/z (%) 248 (2, M$^+$), 217 (2), 189 (100), 156 (19), 129 (43), 117 (100), 91 (19).

Dimethyl 2-[(*E*)-3-phenylprop-2-enyl)propanedioate (8). This was also obtained as the product from the reaction of cinnamyl acetate with dimethyl sodium malonate. GC (CBP-10) conditions for diastereomeric separation: t_R, 23.4 min; oven temp, 100 °C; injection temp, 220 °C; initial time, 2 min; final temp, 200 °C; rate, 10 °C/min; detection temp, 250 °C; column pressure, 100 kPa. R_f = 0.32 (hexane/EtOAc, 6 : 1). IR (KBr): 3448 (s), 2359 (w), 1734 (m), 1635 (s), 1435 (w), 1261 (w), 1153 (m), 966 (w), 749 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20-7.34 (m, 5H), 6.48 (d, J = 15.6, CH), 6.16 (dt, J = 15.8, 7.2, CH), 3.74 (s, 2OCH_3), 3.53 (t, J = 14.7, CHCO), 2.80 (dt, J = 15.9, 1.2, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.1 (C=O), 136.9 (arom. C), 132.8 (CH), 128.4 (CH), 127.3 (CH), 126.1 (CH), 125.3 (CH), 52.4, 51.6 (CH, Me), 32.2 (CH_2). MS: m/z (%) 248 (30, M$^+$), 188 (38), 157 (20), 129 (100), 117 (61), 84 (19).

Dimethyl 2-(1,3-Diphenylprop-2-enyl)propanedioate (9). This was obtained as the product from the reaction of 1,3-diphenyl-2-propenyl acetate with dimethyl sodium malonate. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.51 (s, OCH_3), 3.70 (s, OCH_3), 3.95 (d, J = 11, CHCO), 4.26 (dd, J = 9 and 11, PhCH), 6.33 (dd, J = 9 and 16, PhCH=C*H*), 6.47 (d, J = 16, PhC*H*=CH), 7.18-7.33 (m, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 49.2 (*C*HPh), 52.5 (OCH_3), 52.6 (OCH_3), 57.6 (*C*HCO), 126.4/127.2 (PhCH=CH), 127.6/127.9/128.4/128.7/129.1/131.8/136.8/140.2 (Ph), 167.6/167.8 (C=O).

Acknowledgment. TJK gratefully acknowledges KRF for financial support (Grant No.: PBRG 070-C00055). NMR and mass spectral measurements were performed by KBSI.

References

1. Staudinger, H.; Meyer, J. J. *Helv. Chim. Acta* **1919**, *2*, 635.
2. (a) Johnson, A. V. *Ylides and Imines of Phosphorus*; Wiley: New York, 1993. (b) Gololobov, Y. G.; Kasukhin, L. F. *Tetrahedron* **1992**, *48*, 1353. (c) *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; John Wiley and Sons: Baffins Lane, England, 1994; Vol. 3.
3. (a) In *Inorganic and Organic Polymers II. Advanced Materials and Intermediates*; Wisian-Neilson, P., Allcock, H. R., Wynne, K. J., Eds.; ACS Symposium Series 572; American Chemical Society: Washington, DC, 1994; Neilson, R. H., Jinkerson, D. L., Kucera, W. R., Longlet, J. J., Samuel, R. C., Wood, C. E., Chapter 18; White, M. L., Matyjaszewski, K., Chapter 24. (b) Allcock, H. R. *Science* **1992**, *255*, 1106. (c) For a review article, see: Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602.
4. For recent reviews, see: (a) Dehnicke, K.; Krieger, M.; Massa, W. *Coord. Chem. Rev.* **1999**, *182*, 19. (b) Roesky, H. W.; Witt, M. *Chem. Rev.* **1994**, *94*, 1163.
5. (a) Spencer, L. P.; Altwer, R.; Wei, P.; Gelmini, L.; Gauld, J.;

Stephan, D. W. *Organometallics* **2003**, *22*, 3841 and references therein. (b) Stephan, D. W.; Stewart, J. C.; Guérin, F.; Courtenay, S.; Kickham, J.; Hollink, E.; Beddie, C.; Hoskin, A.; Graham, T.; Wei, P.; Spence, R. E. v. H.; Xu, W.; Koch, L.; Gao, X.; Harrison, D. G. *Organometallics* **2003**, *22*, 1937. (c) Sauthier, M.; Leca, F.; de Souza, R. F.; Bernardo-Gusmâo, K.; Queiroz, L. F. T.; Toupet, L.; Réau, R. *New. J. Chem.* **2002**, *26*, 630. (d) Al-Benna, S.; Sarsfield, M. J.; Thornton-Pett, M.; Ormsby, D. L.; Maddox, P. J.; Brés, P.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **2000**, 4247.

6. Iminophosphoranes bonded to a transition metal in either η^1 or an η^2-N,C-chelating fashion through metallation of some of the R (or Ar) groups in $R(Ar)_2P{=}NR'$ (R = alkyl, Ar = aryl, R' = aryl) are also widely known. See for example: (a) Kubo, K.; Nakazawa, H.; Inagaki, H.; Miyoshi, K. *Organometallics* **2002**, *21*, 1942. (b) Vicente, J.; Abad, J.-A.; Clemente, R.; López-Serrano, J.; de Arellano, M. C. R.; Jones, P. G.; Bautista, D. *Organometallics* **2003**, *22*, 4248. (c) Leeson, M. A.; Nicholson, B. K.; Olsen, M. R. *J. Organomet. Chem.* **1999**, *579*, 243. (d) Avis, M. W.; van der Boom, M. E.; Elsevier, C. J.; Smeets, W. J.; Spek, A. L. *J. Organomet. Chem.* **1997**, *527*, 263. (e) Avis, M. W.; Goosen, M.; Elsevier, C. J.; Veldman, N.; Kooijman, H.; Spek, A. L. *Inorg. Chim. Acta* **1997**, *264*, 43.
7. (a) Sauthier, M.; Forniés-Cámer, J.; Toupet, L.; Réau, R. *Organometallics* **2000**, *19*, 553. (b) Reetz, M.; Bohres, E.; Goddard, R. *Chem. Commun*. **1998**, 935.
8. (a) Marquarding, D.; Gokel, G. W.; Hoffman, P.; Ugi, I. K. *J. Am. Chem. Soc.* **1970**, *92*, 5389. (b) Gokel, G. W.; Ugi, I. K. *J. Chem. Educ. Chem.* **1972**, *49*, 294.
9. (a) Hayashi, T.; Yamamoto, K.; Kumada, M. *Tetrahedron Lett.* **1974**, 4405. (b) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138.
10. For representative recent reviews on chiral ferrocenes, see: (a) Colacot, T. J. *Chem. Rev.* **2003**, *103*, 3101. (b) Hayashi, T. *Acc. Chem. Res*. **2000**, *33*, 354. (c) Boudier, A.; Bromm, L. O.; Lotz, M.; Knochel, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 4414. (d) Fu, G. C. *Acc. Chem. Res*. **2000**, *33*, 412. (e) Richards, C. F.; Lock, A. J. *Tetrahedron: Asymmetry* **1998**, *9*, 2377. (f) Schwink, L.; Knochel, P. *Chem. Eur. J*. **1998**, *4*(5), 950. (g) Togni, A. In *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley: New York, 1998; pp 685-721. (h) Kagan, H. B.; Riant, O. *Adv. Asymmetric Synth.* **1997**, *2*, 189-235. (i) Hayashi, T. In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995; pp 105-142.
11. Kim, T.-J.; Shim, S. C.; Cho, C. S.; Thanh, T. C.; Kang, S. O.; Ko, J. J.; Han, W. S. *Organometallics* **2005**, *24*, 4824.
12. (a) Co, T. T.; Paek, S. W.; Shim, S. C.; Cho, C. S.; Kim, T.-J.; Choi, D. W.; Kang, S. O.; Jeong, J. H. *Organometallics* **2003**, *22*, 1475. (b) Paek, S. H.; Shim, S. C.; Cho, C. S.; Kim, T.-J. *Synlett* **2003**, 849. (c) Hwang, G.-H.; Ryu, E.-S.; Park, D.-K.; Shim, S. C.; Cho, C. S.; Kim, T.-J.; Jeong, J. H.; Cheong, M. *Organometallics* **2001**, *20*, 5784. (d) Song, J.-H.; Cho, D.-J.; Jeon, S.-J.; Kim, Y.-H.; Kim, T.-J. *Inorg. Chem.* **1999**, *38*, 893. (e) Cho, D.-J.; Jeon, S.-J.; Kim, H.-S.; Shim, S. C.; Cho, C. S.; Kim, T.-J. *Tetrahedron: Asymmetry* **1999**, *10*, 3833.
13. (a) Bennani, Y. L.; Hanessian, S. *Chem. Rev.* **1997**, *97*, 3161. (b) Corey, E. J.; Pikul, S. *Org. Synth*. **1992**, *71*, 22.
14. Cossío, F. P.; Ganboa, I.; Palomo, C. *Tetrahedeon Lett.* **1985**, *26*, 3041.
15. (a) Cullen, W. R.; Einstein, F. W. B.; Huang, C.-H.; Willis, A. C.; Yeh, E.-S. *J. Am. Chem. Soc.* **1980**, *102*, 988. (b) Ball, R. G.; Payne, N. C. *Inorg. Chem.* **1977**, *16*, 1187.
16. (a) Lloyd-Jones, G. C.; Pfaltz, A. *Angew. Chem. Int. Ed.* **1995**, *34*, 462. (b) Trost, A. M.; Hachiya, I. *J. Am. Chem. Soc.* **1998**, *120*, 1104. (c) Glorius, F.; Pfaltz, A. *Organic Lett.* **1999**, *1*, 142. (d) Belda, O.; Kaiser, N.-F.; Bremberg, U.; Larhed, M.; Hallberg, A.; Moberg, C. *J. Org. Chem.* **2000**, *65*, 5868. (e) Glorius, F.; Neuburger, M.; Pfaltz, A. *Helv. Chim. Acta* **2001**, *84*, 3178. (f) Trost, M.; Dogra, K.; Hayachi, I.; Emura, T.; Hughes, D. L.; Krska, S.; Reamer, R. A.; Palucki, M.; Yasuda, N.; Reider, P. J. *Angew. Chem. Int. Ed.* **2002**, *41*, 1929. (g) Evans, P. A.; Nelson, J. D. *Tetrahedron Lett.* **1998**, *39*, 1725. (h) Evans, P. A.; Kennedy, L. J. *J. Am. Chem. Soc.* **2001**, *123*, 1234. (i) Takeuchi, R.; Kashio, M. *J. Am. Chem. Soc.* **1998**, *120*, 8647.
17. Godleski, S. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Semmelhack, M. F., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol 4, pp 585-662. (b) However, for recent interesting exceptions with Pd catalysis, see: Hayashi, T.; Kawatsura, M.; Uozumi, Y. *Chem. Commun*. **1997**, 561.; Prétôt, R.; Pfaltz, A. *Angew. Chem. Int. Ed.* **1998**, *37*, 323.