Chiral (Iminophosphoranyl)ferrocenes: A New Class of Practical Ligands for Rhodium-Catalyzed Asymmetric Hydrogenation

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

Department of Applied Chemistry, Kyungpook National University, Taegu, Korea 702-701

Sang Ook Kang, Won-Sik Han, and Jaejung Ko

Department of Chemistry, Korea University, 208 Seochang, Chochiwon, Chung-nam, Korea 339-700

Chung-Kyun Kim

Department of Chemistry, Dong-A University, 840 Hadan 2-Dong, Saha-Gu, Busan, Korea 604-714

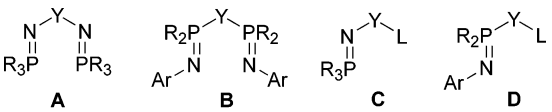
Received May 25, 2005

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)(Y)} (**1a**, Y = NMe_2, R = Me; **1b**, Y = NMe_2, R = ^{i}Pr; **1c**, Y = OMe, R = ^{i}Pr), {η^5-C_5H_4-(PPh_2=N-2,6-R_2-C_6H_3)}Fe{η^5-C_5H_3-1-(PPh_2=N-2,6-R_2-C_6H_3)-2-CH-(Me)(Y)} (**2a**, R = Me, Y = NMe_2; **2b**, R = ^{i}Pr, Y = NMe_2,; **2c**, R = Me, Y = OMe), and (η^5-C_5H_5)Fe{η^5-C_5H_4-1-PR_2-2-CH(Me)N=PPh_3} (**3a**, R = Ph; **3b**, R = C_6H_{11}), have been prepared from the reaction of 1,1′-bis(diphenylphosphino)-2-[(dimethylamino)ethyl]ferrocene with aryl azides (**1** and **2**) and the reaction of phosphine dichlorides (R_3PCl_2) with 1,1′-bis-(diphenylphosphino)-2-(aminoethyl)ferrocene (**3**), respectively. They form rhodium complexes of the type [Rh(NBD)(L)]ClO_4 (**4**−**6**; L = **1**−**3**), where the ligand (L) adopts an η^2(N,N) (**2**) or η^2(P,N) mode (**3**), as expected. In the case of **1**, a potential tridentate species, however, a chelating bidentate mode through the −CH(Me)NMe_2 and −PPh_2 groups is realized with the exclusion of the −P=NAr group from the coordination sphere, as confirmed by the X-ray crystal structure of [Rh(NBD)(**1b**)]ClO_4 (**4b**). The new ligands (**1**−**3**) exhibit exceptionally high enantioselectivity (up to 99%) and catalytic activity in the Rh-catalyzed asymmetric hydrogenation of (*E*)-2-methylcinnamic acid, (*Z*)-2-acetamidocinnamate, and (*Z*)-2-acetamidoacrylate.

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 synthesis of iminophosphoranes in the hope that they will offer a steric environment similar to that of diimines, while the electronic characteristics, such as donor strength and π-acceptor capacity, are clearly different.[5] Consequently, there are now known numerous transition-metal complexes of iminophosphoranes, and the most common are those incorporating the homobidentate (**A** and **B**) and heterobidentate (**C** and **D**) derivatives (Chart 1).[6]

Chart 1



Despite the availability of such a wide variety of iminophosphoranes, there have been limited studies on

* To whom correspondence should be addressed. E-mail: tjkim@knu.ac.kr. Fax: 82-53-950-6594.

(1) Staudinger, H.; Meyer, J. J. *Helv. Chim. Acta* **1919**, *2*, 635.

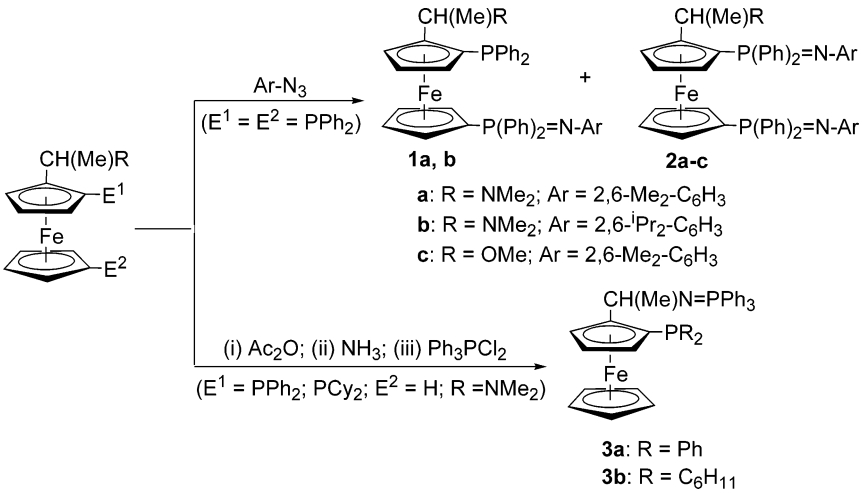
(2) (a) Johnson, A. V. *Ylides and Imines of Phosphorus*; Wiley: New York, 1993. (b) Gololobov, Y. G.; Kasukhin, L. F. *Tetrahedron* **1992**, *48*, 1353. (c) *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: Baffins Lane, England, 1994; Vol. 3.

(3) (a) Neilson, R. H.; Jinkerson, D. L.; Kucera, W. R.; Longlet, J. J.; Samuel, R. C.; Wood, C. E. 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; Chapter 18. White, M. L.; Matyjaszewski, K. *Ibid*., 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.

10.1021/om058028c CCC: $30.25
Publication on Web 09/02/2005

Scheme 1



the design and the synthesis of their chiral counterparts, not to mention their use in asymmetric catalysis. To the best of our knowledge, only two reports have appeared 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**, obtainable upon reacting R_3PBr_2 with 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**−**D**.

As part of our continuing effort in the design and the synthesis of new ferrocene-based chiral ligands for asymmetric catalysis,[8] we have undertaken the preparation of chiral iminophosphoranes derived from FA with a special emphasis on the types **B**−**D**. We now wish to introduce a new family of chiral iminophosphoranes such as those illustrated in Scheme 1. 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 should accomplish higher optical inductions in asymmetric reactions. We are now pleased to report that our new ligands exhibit excellent enantioselectivities in the Rh-catalyzed asymmetric hydrogenation of methyl (*Z*)-acetamidocinnamate, methyl (*Z*)-acetamidoacrylate, and methyl (*E*)-cinnamic acid.

Results and Discussion

Synthesis and Characterization. One of the most promising chiral templates for our purposes is *N*,*N*-dimethyl-1-ferrocenylethylamine (FA), whose synthesis and resolution have long been established.[9] Since the pioneering work of Hayashi and Kumada on the synthesis of the first chiral ferrocenylphosphine,[10] 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.[11] However, no chiral ferrocenes carrying the iminophosphorane moiety have ever been reported.

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*-dimethyl-1-ferrocenylethylamine (FA).[9] The preparation of PPFA (R = NMe_2; E^1 = PPh_2; E^2 =

(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. *Dalton Trans.* **2000**, 4247.

(6) Iminophosphoranes bonded to a transition metal in either an η^1 or an η^2(N,C) chelating fashion through metalation 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.

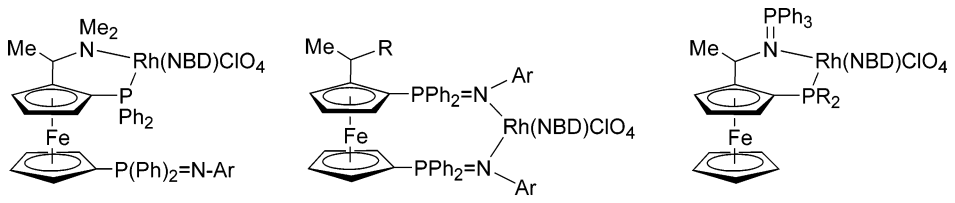
(8) (a) Co, T. T.; Paek, S. W.; Shim, S. C.; Cho, C. S.; Kim, T.-J.; Choi, D. W.; Kang, S. O.; Jeong, J. H. *Organometallics* **2003**, *22*, 1475. (b) Paek, S. H.; Shim, S. C.; Cho, C. S.; Kim, T.-J. *Synlett* **2003**, 849. (c) Hwang, G.-H.; Ryu, E.-S.; Park, D.-K.; Shim, S. C.; Cho, C. S.; Kim, T.-J.; 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.

(9) (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.

(10) (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.

(11) 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, Germany, 1995; pp 105−142.

Scheme 2



4a: Ar = 2,6-Me_2-C_6H_3
4b: Ar = 2,6-$^i Pr_2$-C_6H_3

5a: R = NMe_2; Ar = 2,6-Me_2-C_6H_3
5b: R = NMe_2; Ar = 2,6-$^i Pr_2$-C_6H_3
5c: R = OMe; Ar = 2,6-Me_2-C_6H_3

6a: R = Ph
6b: R = C_6H_{11}

H) and BPPFA (R = NMe_2; $E^1 = E^2 = PPh_2$) is followed simply by taking advantage of the highly stereoselective ortho metalation of enantiopure FA.[10] That is, 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* refers 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.

In general, 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 aryl azides 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 aryl azide 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 the 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.[12] In our case, PPFA 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 have come from spectroscopic and analytical techniques. The formation of **1** and **2** can be easily recognized by their characteristic downfield singlets (−6 to −10 ppm) in ^{31}P NMR assignable to the iminophosphoranes (P═NAr). The unreacted phosphines appear in a highly shielded (upfield) area such as −22 to −24 ppm in the case of **1**, for instance, thus making it feasible to differentiate **1** from **2**. The position of oxidation, namely P═NAr, 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═NAr 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 characteristic pairs of singlets and doublets arising from methyl and isopropyl groups in **1a**,**b**, respectively. The formation of **3** can be readily confirmed by a pair of characteristic ^{31}P NMR signals: an upfield singlet due to PR_2 (R = Ph, Cy) and a downfield singlet due to P═NAr.

Coordination Chemistry. Compounds **1** and **2** are potential tridentate ligands and thus await their coordination behaviors to be revealed. The reaction of (*S*,*R*)-**1b** with $[(NBD)RhCl]_2$ followed by treatment with $NaClO_4$ yielded a cationic Rh(I) complex of the type $[(NBD)Rh(S,R\text{-}\mathbf{1b})]ClO_4$ (**4b**), as expected. However, interestingly the cis-P,N chelation takes place through the $-PPh_2$ and $-NMe_2$ (not ═NAr) groups, as illustrated in Scheme 2. The iminophosphoranyl group seems to be sterically too demanding to be involved in coordination. The ^1H NMR spectrum confirms this fact by showing the presence of nonequivalent methyls in the $-NMe_2$ group. In addition, the ^{31}P NMR spectrum shows a significant coordination shift ($\Delta\delta \approx 45$ ppm) for the PPh_2 group, while the chemical shift for the iminophosphoranyl group remains almost unchanged.

Further structural confirmation comes from X-ray crystallography, and the absolute configuration is shown in Figure 1. A summary of crystallographic data and selected bond lengths and angles for **4b** are listed in Tables 1 and 2, respectively. The Rh atom can be viewed as having a square-planar environment (assuming that each NBD C═C bond is filling a single coordination site). The Rh−P distance of 2.2756(10) Å is similar to that reported in the analogous complex $[(NBD)Rh(PPFA)]ClO_4$ (2.28(1) Å) and those in $[Rh(COD)(S,S\text{-Chiraphos})]ClO_4$ (2.275 and 2.266(1) Å).[14] The Rh−N distance of 2.185(3) Å is slightly shorter than that found in the analogous species $[(NBD)Rh(PPFA)]ClO_4$ (2.26(3) Å).[14a]

Scheme 2 shows additional coordination modes when employed in the reactions involving **2** and **3**. The coordination nature of ligands **2a**−**c** in $[(NBD)Rh(L)]ClO_4$ (**5a**−**c**) can be confirmed straightforwardly by not only ^{31}P NMR but also ^1H NMR spectra. In the case of **2a**,**b**, coordination through both iminophosphoranyl groups can be confirmed by the presence of the charac-

(12) (a) Bennani, Y. L.; Hanessian, S. *Chem. Rev.* **1997**, *97*, 3161. (b) Corey, E. J.; Pikul, S. *Org. Synth.* **1992**, *71*, 22.

(13) Cossío, F. P.; Ganboa, I.; Palomo, C. *Tetrahedeon Lett* **1985**, *26*, 3041.

(14) (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.

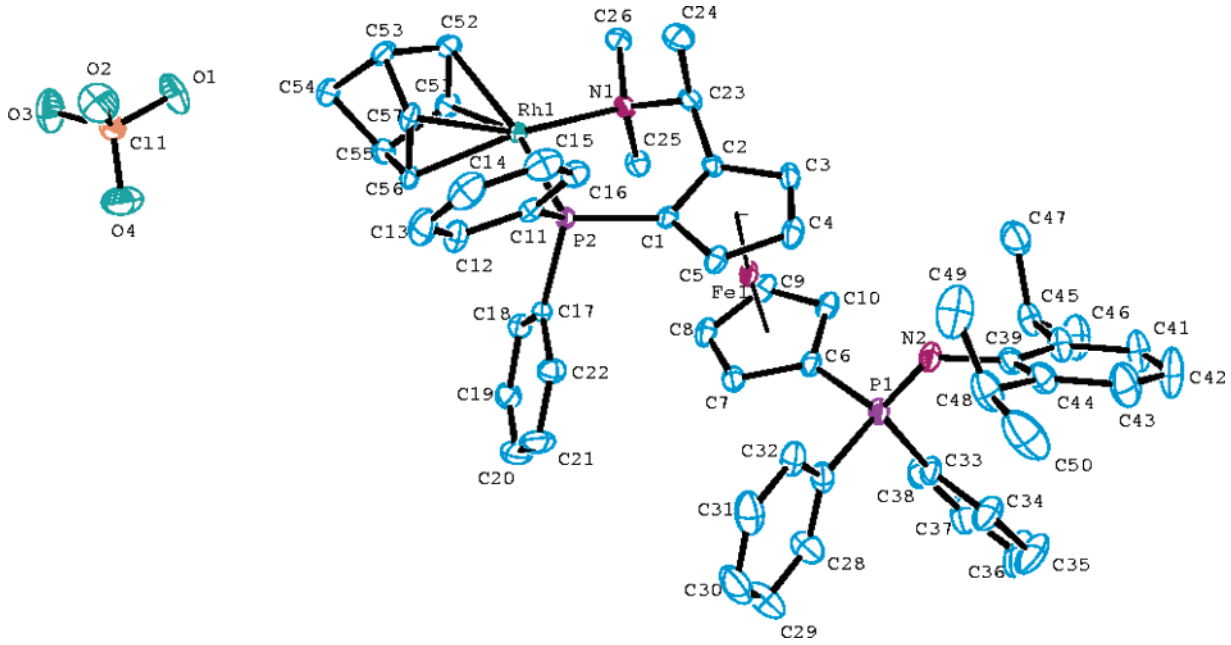


Figure 1. Crystal structure of **4b**. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Summary of Crystallographic Data for 4b

empirical formula	$C_{57}H_{62}ClFeN_2O_4P_2Rh$
formula wt	1095.24
temp	293(2) K
wavelength	0.71073
cryst syst	monoclinic
space group	$P2_1$
unit cell dimens	
a	9.2019(7) Å
b	14.1308(10) Å
c	19.7275(14) Å
α	90
β	92.1920(10)
γ	90
V	2563.3(3) Å^3
Z	2
density (calcd)	1.419 Mg/m^3
abs coeff	0.768 mm^{-1}
F(000)	1136
cryst size	0.432 × 0.291 × 0.107 mm^3
θ range for data collecn	1.03−28.32°
index ranges	$12 \le h \le 12$, $-18 \le k \le 18$, $-26 \le l \le 26$
no. of rflns collected	25 531
no of indep rflns	12 440 (R(int) = 0.0371)
completeness to θ = 28.32°	99.7%
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	12 440/1/621
goodness of fit on F^2	1.067
final R indices ($I > 2\sigma(I)$)	R1 = 0.0431, wR2 = 0.0944
R indices (all data)	R1 = 0.0618, wR2 = 0.1062
abs structure param	0.040(17)
extinction coeff	0.0020(3)
largest diff peak and hole	1.087 and −0.718 e/Å^3

teristic singlet on ^{1}H NMR, assignable to the equivalent pair of methyls in the −NMe$_2$ group due to free rotation. The same coordination pattern can also be realized in the case of **2c**, where the −NMe$_2$ group is replaced with OMe. In addition, all three ligands exhibit similar ^{31}P NMR signals, demonstrating the same type of coordination. Thus, there can be no ambiguity about the coordination chemistry of these three ligands.

The coordination chemistry of **3** is quite obvious and warrants little attention. Thus, complexes **6a**,**b** have in common a pair of downfield phosphorus signals in ^{31}P NMR spectrum.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4b

Bond Lengths (Å)					
Rh(1)−C(56)	2.112(4)	Rh(1)−C(51)	2.222(4)	Rh(1)−N(1)	2.185(3)
Rh(1)−C(57)	2.140(4)	Rh(1)−C(52)	2.246(4)	Rh(1)−P(2)	2.2756(10)
P(1)−N(2)	1.559(4)	P(1)−C(6)	1.794(4)	P(2)−C(1)	1.798(4)
N(1)−C(23)	1.503(5)	N(2)−C(39)	1.415(6)		

Bond Angles (deg)			
N(1)−Rh(1)−P(2)	93.84(9)	C(57)−Rh(1)−C(52)	65.88(17)
C(56)−Rh(1)−C(51)	66.11(16)	C(56)−Rh(1)−N(1)	157.94(14)
C(51)−Rh(1)−P(2)	150.39(12)	C(1)−P(2)−Rh(1)	115.25(14)
C(17)−P(2)−C(11)	103.42(18)	C(39)−N(2)−P(1)	127.7(3)
N(2)−P(1)−C(33)	113.9(2)	N(2)−P(1)−C(6)	111.7(2)
C(27)−P(1)−C(33)	102.1(2)		

Asymmetric Hydrogenation. Hydrogenation of α,β-unsaturated carboxylic acids and α-dehydroamino acid derivatives has been a typical reaction to test the efficiency of new chiral ligands. Indeed, a number of chiral phosphorus ligands with great structural diversity are found to be effective for Rh-catalyzed hydrogenation of these acid derivatives.[15−17] It seems 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, we expect that our ligands meet most of these requirements.

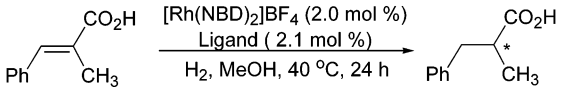
In the first set of experiments, we performed the Rh-catalyzed asymmetric hydrogenation of (*E*)-2-methylcinnamic acid to benchmark the potential of our ligands **1**−**3** for asymmetric catalysis. Hydrogenation was conducted at ambient temperature under a H$_2$ pressure of

(15) For the latest and the most comprehensive reviews on chiral phosphorus ligands for use in asymmetric hydrogenation, see: (a) Tang, W.; Zhang, X. *Chem. Rev.* **2003**, *103*, 3029. (b) *Tetrahedron: Asymmetry* **2004**, *15*, 2099−2100.

(16) Brown, J. M., In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; pp 121−182.

(17) Ohkuma, T.; Kitamura, M.; Noyori, R., In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH: New York, 2000; pp 1−110.

Table 3. Asymmetric Hydrogenation of (*E*)-2-Methylcinnamic Acid[a]



entry	ligand	$P(H_2)$ (atm)	yield (%)[b]	ee (%)[c]
1	(*S*,*R*)-**1a**	1	7	97
2	(*S*,*R*)-**1b**	1	12	98
3	(*S*,*R*)-**1c**	1	6	98
4	(*S*,*R*)-**1a**	10	18	92
5	(*S*,*R*)-**1b**	10	35	96
6	(*S*,*R*)-**1c**	10	90	93
7	(*S*,*R*)-**2a**	1	94	98
8	(*S*,*R*)-**2b**	1	62	96
9	(*S*,*R*)-**2c**	1	87	97
10	(*S*,*R*)-**2a**	10	100	92
11	(*S*,*R*)-**2b**	10	97	88
12	(*S*,*R*)-**2c**	10	100	91
13	(*S*,*R*)-**3a**	1	93	94
14	(*S*,*R*)-**3b**	1	91	92
15	(*S*,*R*)-**3a**	10	100	90
16	(*S*,*R*)-**3b**	10	100	89

[a] All data represent the average of two runs. [b] GC yield. [c] Percent ee determined by chiral capillary GC on a Chiraldex γ-TA column (30 m). The product configuration was determined by comparison with the literature values; it was *S* in all cases.

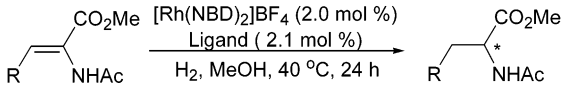
1 or 10 bar in the presence of 2 mol % of catalysts prepared in situ from $[Rh(NBD)_2]BF_4$ and 1.1 equiv of chiral ligand, and the results are summarized in Table 3. The results are remarkable in that exceptionally high enantioselectivity (up to 98%) and catalytic activity are achieved. It should be pointed out that few systems have been reported on Rh-catalyzed hydrogenation of α,β-unsaturated carboxylic acids such as (*E*)-2-methylcinnamic acid, although some successful results have been obtained with Ru-based catalysts.[18] Optimization experiments revealed that enantioselection is dependent on both the H_2 pressure and the reaction temperature. Table 3 shows that an increase in the H_2 pressure is accompanied by an increase in the chemical yield yet causes simultaneously a slight drop in the percent ee value. These observations may be as expected, if one presupposes that the cationic Rh(I) catalyst incorporating **1**, **2**, or **3** exhibits the same mechanistic behavior as that incorporating a typical chelating diphos ligand.[19,20] As far as the chemical yield is concerned, the ligand **1** is the least active of all, regardless of the hydrogen pressure, although its enantioselectiviy reaches the highest (entries 1−3). The reactivity of **1** may be better compared with that of the parent PPFA, in that hydrogenation of the related substrates has to be carried out under even harsher conditions (>50 atm) only to result in much lower optical yields (<58% ee).[14a] It should be noted that another class of related P,N donors such as BPPFA is more effective than PPFA, achieving optical yields as high as those obtained by **1** under elevated temperature and higher pressure.[15−17]

(18) Hayashi, T.; Kawamura, N.; Ito, Y. *J. Am. Chem. Soc.* **1987**, *109*, 7876.

(19) (a) Halpern, J.; Riley, D. P.; Chan, A. S. C.; Pluth, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 8055. (b) Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 838. (c) Halpern, J. *Science* **1982**, *217*, 401.

(20) (a) Brown, J. M.; Chaloner, P. A. *J. Chem. Soc., Chem. Commun.* **1978**, 321. (b) Brown, J. M.; Chaloner, P. A.; Kent, A. G.; Murrer, B. A.; Nichoson, P. M.; Parker, D. P.; Sidebottom, P. J. *J. Organomet. Chem.* **1981**, *216*, 263. (c) Brown, J. M.; Chaloner, P. A. *J. Am. Chem. Soc.* **1980**, *102*, 3040. (d) Brown, J. M.; Parker, D. P. *Organometallics* **1982**, *1*, 950. (e) Brown, J. M.; Chaloner, P. A.; Parker, D. P. *Adv. Chem.* **1982**, *196*, 355.

Table 4. Asymmetric Hydrogenation of Methyl (*Z*)-2-Acetamidocinnamate and Methyl (*Z*)-2-Acetamidoacrylate[a]



entry	ligand	R	$P(H_2)$ (atm)	yield (%)[b]	ee (%)[c]
1	(*S*,*R*)-**1a**	H	1	100	99
2	(*S*,*R*)-**1b**	H	1	100	99
3	(*S*,*R*)-**1c**	H	1	3	92
4	(*S*,*R*)-**1c**	H	10	100	88
5	(*S*,*R*)-**2a**	H	1	100	88
6	(*S*,*R*)-**2b**	H	1	100	95
7	(*S*,*R*)-**2c**	H	1	100	83
8	(*S*,*R*)-**3a**	H	1	100	82
9	(*S*,*R*)-**3b**	H	1	100	74
10	(*S*,*R*)-**1a**	Ph	1	78	97
11	(*S*,*R*)-**1b**	Ph	1	72	99
12	(*S*,*R*)-**1b**	Ph	10	100	96
13	(*S*,*R*)-**1c**	Ph	1	27	99
14	(*S*,*R*)-**1c**	Ph	10	100	97
15	(*S*,*R*)-**2a**	Ph	1	82	99
16	(*S*,*R*)-**2a**	Ph	10	100	91
17	(*S*,*R*)-**2c**	Ph	1	80	93
18	(*S*,*R*)-**2c**	Ph	10	100	86
19	(*S*,*R*)-**3a**	Ph	1	86	73
20	(*S*,*R*)-**3b**	Ph	1	70	68
21	(*S*,*R*)-**3b**	Ph	10	100	65

[a] All data represent the average of two runs. [b] GC yield. [c] Percent ee determined by chiral capillary GC on a Chiraldex γ-TA column (30 m). The product configuration was determined by comparison with the literature values; it was *S* in all cases.

As deduced from the structural features illustrated in Scheme 2, the presence of the iminophosphoranyl group in the coordination sphere seems to play a certain role in the catalytic activity. Finally, in connection with the findings listed in Table 3, it is observed that an increase in the steric bulk around rhodium slightly reduces catalytic activity with regard to chemical yield (entries 7 vs 8 and 10 vs 11). However, it is worth noting that optical yields are still very high with ligand **2**, although the chirality is far removed from the reaction center, as deduced from the structure of **5** (Scheme 2).

Remarkable enantioselectivity and catalytic activity were also observed in the Rh-catalyzed asymmetric hydrogenation of (*Z*)-2-acetamidocinnamate and (*Z*)-2-acetamidoacrylate (Table 4). Near-perfect enantioselection as well as quantitative conversion demonstrated by ligands **1**−**3** may well be compared with other ligands well-documented in the literature.[15−17] Again, the same trend in the dependence of enantioselection and the product yield on the H_2 pressure can be recognized: the higher the H_2 pressure, the higher the product yield and the lower the percent ee. Ligands **1a**,**b**, the least effective in the hydrogenation of (*E*)-2-methylcinnamic acid, prove to be the most effective with regard to both enantioselectivity and catalytic activity for the hydrogenation of (*Z*)-2-acetamidocinnamate and (*Z*)-2-acetamidoacrylate (entries 1, 2, and 10−12). Here, the role of the acylamino group for high asymmetric induction through a secondary interaction with rhodium seems to be minimal, as one compares the results listed in both tables. That is, any significant change in the optical yield can hardly be recognized.

Conclusions

The preparation of new series of ferrocene-based chiral iminophosphoranyls **1**−**3** is described. They form

rhodium complexes of the type $[Rh(NBD)(L)]ClO_4$ (L = **1**−**3**), where the ligand (L) adopts various coordination modes: η^2(N,N) (**2**) or η^2(P,N) (**3**), as expected. The ligand **1** adopts the same coordination mode (η^2(P,N)) as **3**, yet with a chelation through the −CH(Me)NMe_2 and $-PPh_2$ groups with the exclusion of the −P═NAr group. The X-ray crystal structure of **4b** confirms this fact. The new ligands (**1**−**3**) exhibit exceptionally high enantioselectivity (up to 99% ee) and catalytic activity in the Rh-catalyzed hydrogenation of some olefinic acids.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of nitrogen using 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 Inova 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 an 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] PPFA,[9] BPPFA,[9] PPFA-NH_2,[9] BPPFA-NH_2,[9] BPPFA-OMe,[9] 2,6-^{i}Pr$_2$$C_6H_3N_3$ and 2,6-$Me_2C_6H_3N_3$,[5a] and 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-dimethylbenzoyl azide (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 onto 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, *P*Ph_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, C*H*), 6.60 (t, J = 6.3, 1H, p-N-C_6H_3), 6.88 (d, J = 6.6, 2H, m-N-C_6H_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-dimethylbenzoyl azide with 2,6-diisopropylbenzoyl azide. Yield: 1.08 g (85%). ^{31}P NMR ($CDCl_3$): δ −23.76 (s, *P*Ph_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_5H_3), 6.76 (t, J = 7.5, 1H, p-N-C_6H_3), 6.93 (d, J = 7.5, 2H, m-N-C_6H_3), 7.57−7.12 (m, 20H, P*Ph*$_2$). 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-^{i}Pr_2-C_6H_3)}Fe{η^5-C_5H_3-1-PPh_2-2-CH(Me)(OMe)} (1c). The title compound was prepared in the same manner as described above for the synthesis of **1b** by replacing BPPFA with BPPF−OMe. Yield: 0.95 g (75%). ^{31}P NMR ($CDCl_3$): δ −23.12 (s, *P*Ph_2), −9.61 (s, *P*═N). ^{1}H NMR ($CDCl_3$): δ 0.86 (d, J = 6.9, 6H, CH*Me*$_2$), 0.92 (d, J = 6.9, 6H, CH*Me*$_2$), 1.41 (d, J = 6.9, 3H, CH*Me*), 2.85 (s, 3H, OMe), 3.34 (sept, J = 6.6, 2H, *CH*Me_2), 3.62−4.51 (m, 7H, $C_5H_3FeC_5H_4$), 4.47 (qt, J = 4.7, 1H, *CH*Me), 6.75 (t, J = 7.2, 1H, p-N-C_6H_3), 6.91 (d, J = 7.0, 2H, m-N-C_6H_3), 7.17−7.49 (m, 20H, P*Ph*$_2$). Anal. Calcd for $C_{49}H_{51}FeNOP_2$: C, 74.71; H, 6.53; N, 1.78. Found: C, 74.80; H, 6.56; N, 1.85.

{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 as for the preparation of **1a**, except for the use of an excess of 2,6-dimethylbenzoyl azide (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*═NAr). ^{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_6H_3), 6.90 (t, J = 9.9, 4H, m-C_6H_3), 7.31−7.61 (m, 20H, C_6H_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-diisopropylbenzoyl azide (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*═NAr). ^{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_5H_4)Fe(C_5H_3)), 4.07 (qt, J = 7.2, 1H, C*H*Me), 6.78 (t, J = 7.2, 2H, p-C_6H_3), 6.90 (t, J = 7.2, 4H, m-C_6H_3), 7.31−7.61 (m, 20H, C_6H_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-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)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-dimethylbenzoyl azide (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 time 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*$_2$−Ph), 2.55 (s, 3H, O*Me*), 4.13 (qt, J = 7.2, 1H, C*H*Me), 4.49, 4.53 (m, 4H, C_5H_4), 3.82, 4.51, 4.85 (br, 3H, C_5H_3), 6.02 (m, 2H, C_6H_3), 6.90 (m, 4H, m-C_6H_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 PPFA-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 warmed to room temperature and stirred for 16 h. The solvent was removed under reduced pressure. The residue was washed with diethyl ether (15 mL) and extracted with THF (15 mL) to eliminate the triethylammonium 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, *P*Ph_2), 35.00 (s, *P*═N). ^{1}H NMR

($CDCl_3$): δ 1.95 (d, J = 6.9, 3H, CH*Me*), 3.74 (qt, J = 6.0, 1H, C*H*Me), 3.82 (s, 5H, C_5H_5), 3.87−4.57 (m, 3H, C_5H_3), 6.92−7.65 (m, 25H, C_6H_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 PPFA-NH_2 with P(Cy_2P)-FA-NH_2 (yield 0.48 g, 30%). ^{31}P NMR ($CDCl_3$): δ −16.62 (s, *P*Cy_2), 36.57 (s, *P*=N). ^{1}H NMR ($CDCl_3$): δ 0.73−2.03 (m, 22H, C_6H_{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_5H_5), 4.05−4.63 (m, 3H, C_5H_3), 7.44−7.87 (m, 15H, C_6H_5). HRMS (EI, *m/z*): calcd for $C_{42}H_{49}FeNP_2$, 686.2793 (M^+); found, 686.3101. 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.

[(NBD)Rh(1a)]ClO_4 (4a). To a solution of [(NBD)RhCl]$_2$ (0.046 g, 0.10 mmol) in CH_2Cl_2 (5 mL) in a Schlenk tube was added **1a** (0.160 g, 0.22 mmol). The mixture was stirred at room temperature for 30 min, after which $NaClO_4$ (0.024 g, 0.20 mmol) was added. The solution turned dark red, and any solid impurities were removed by filtration. The solvent was removed to give red solids. Recrystallization from CH_2Cl_2/hexane yielded **4a** (0.150 g, 78%) in two crops as red crystals. ^{31}P NMR ($CDCl_3$): δ −8.51 (s, *P*=N), 21.06 (d, J_{P-Rh} = 169, *P*Ph_2). ^{1}H NMR ($CDCl_3$): δ 0.95 (d, J = 6.6, 3H, CH*Me*), 1.44 (s, 2H, C_7H_8), 1.57 (s, 6H, NMe_2), 2.09, 2.12 (s, 6H, *Me*−Ph), 2.94 (br, 2H, C_7H_8), 3.75 (qt, J = 7.0, 1H, C*H*Me), 3.87−4.96 (m, 7H, $C_5H_3FeC_5H_4$), 5.54 (br, 4H, C_7H_8), 6.62 (t, J = 7.2, 1H, *p*-C_6H_3), 6.87 (d, J = 6.0, 2H, *m*-C_6H_3), 7.31−7.86 (m, 20H, C_6H_5). Anal. Calcd for $C_{53}H_{54}ClFeN_2O_4P_2Rh$: C, 61.26; H, 5.24; N, 2.70. Found: C, 61.30; H, 5.22; N, 2.80.

[(NBD)Rh(1b)]ClO_4 (4b). This compound was prepared in the same manner as described for the synthesis of **4a** by replacing **1a** with **1b**. Recrystallization from CH_2Cl_2/hexane yielded **4b** (0.180 g, 82%) in two crops as red crystals. ^{31}P NMR ($CDCl_3$): δ −9.70 (s, *P*=N), 20.98 (d, J_{P-Rh} = 175, *P*Ph_2). ^{1}H NMR ($CDCl_3$): δ 0.88 (d, J = 6.8, 6H, CHMe_2), 0.95 (d, J = 6.8, 6H, CHMe_2), 1.24 (d, J = 6.8, 3H, CH*Me*), 1.45 (s, 2H, C_7H_8), 1.68 (s, 6H, NMe_2), 3.37 (m, 2H, 2 C*H*Me_2), 3.42 (br, 2H, C_7H_8), 3.77 (qt, J = 7.2, 1H, C*H*Me), 3.89−4.69 (m, 7H, $C_5H_3FeC_5H_4$), 4.70 (br, 4H, C_7H_8), 6.79 (t, J = 7.8, 1H, *p*-C_6H_3), 6.95 (d, J = 6.3, 2H, *m*-C_6H_3), 7.26−7.57 (m, 20H, C_6H_5). Anal. Calcd for $C_{57}H_{62}ClFeN_2O_4P_2Rh$: C, 62.51; H, 5.71; N, 2.56. Found: C, 62.97; H, 5.24; N, 2.36.

[(NBD)Rh(1c)]ClO_4 (4c). This compound was prepared in the same manner as described for the synthesis of **4a** by replacing **1a** with **1c**. Recrystallization from CH_2Cl_2/hexane yielded **4b** (0.130 g, 68%) in two crops as red crystals. ^{31}P NMR ($CDCl_3$): δ 27.88 (d, J_{P-Rh} = 145, *P*Ph_2), 28.30 (s, *P*=N). ^{1}H NMR ($CDCl_3$): δ 0.88 (d, J = 7.2, 6H, CHMe_2), 0.93 (d, J = 7.2, 6H, CHMe_2), 1.36 (d, J = 6.7, 3H, CH*Me*), 2.52 (s, 2H, C_7H_8), 2.75 (s, 3H, O*Me*), 3.46 (sept, J = 6.8, 2H, C*H*Me_2), 3.81 (br, 2H, C_7H_8), 3.86−4.97 (m, 7H, $C_5H_3FeC_5H_4$), 4.35 (qt, J = 5.5, 1H, C*H*Me), 5.55 (br, 4H, C_7H_8), 6.77 (t, J = 7.0, 1H, *p*-C_6H_3), 6.93 (d, J = 6.9, 2H, *m*-C_6H_3), 7.35−7.73 (m, 20H, C_6H_5). Anal. Calcd for $C_{56}H_{59}ClFeNO_5P_2Rh$: C, 62.15; H, 5.50; N, 1.29. Found: C, 62.07; H, 5.14; N, 1.42.

[(NBD)Rh(2a)]ClO_4 (5a). This compound was prepared in the same manner as described for the synthesis of **4a** by replacing **1a** with **2a**. Recrystallization from CH_2Cl_2/hexane yielded **5a** (0.150 g, 70%) in two crops as red crystals. ^{31}P NMR ($CDCl_3$): δ 9.31, 34.95 (s, *P*=N), ^{1}H NMR ($CDCl_3$): δ 1.08 (d, J = 7.8, 3H, CH*Me*), 1.50 (s, 6H, NMe_2), 1.59 (s, 2H, C_7H_8), 1.83, 1.86 (s, 12H, Me_2−Ph), 3.74 (br, 2H, C_7H_8), 3.85 (qt, J = 5.1, 1H, C*H*Me), 3.88−5.08 (m, 7H, $C_5H_3FeC_5H_4$), 6.52 (br, 4H, C_7H_8), 6.60 (t, J = 5.4, 2H, *p*-C_6H_3), 6.88 (d, J = 7.2, 4H, *m*-C_6H_3), 7.22−7.79 (m, 20H, C_6H_5). Anal. Calcd for $C_{61}H_{63}ClFeN_3O_4P_2Rh$: C, 63.25; H, 5.48; N, 3.63. Found: C, 63.49; H, 5.55; N, 3.50.

[(NBD)Rh(2b)]ClO_4 (5b). This compound was prepared in the same manner as described for the synthesis of **5a** by replacing **2a** with **2b**. Recrystallization from CH_2Cl_2/hexane yielded **5b** (0.150 g, 70%) in two crops as red crystals. ^{31}P NMR ($CDCl_3$): δ 12.35, 30.56 (s, *P*=N). ^{1}H NMR ($CDCl_3$): δ 0.75, 0.94, 0.99, 1.12 (d, J = 7.2, 24H, CHMe_2), 1.43 (d, J = 7.0, 3H, CH*Me*), 1.61 (s, 6H, NMe_2), 1.65 (s, 2H, C_7H_8), 3.37 (m, 4H, 2 C*H*Me_2), 3.75 (qt, J = 5.1, 1H, C*H*Me), 3.95 (br, 2H, C_7H_8), 3.81−4.56 (m, 7H, $C_5H_3FeC_5H_4$), 6.58 (br, 4H, C_7H_8), 6.72 (t, J = 6.5, 2H, *p*-C_6H_3), 6.95 (d, J = 7.0, 4H, *m*-C_6H_3), 7.20−7.80 (m, 20H, C_6H_5). Anal. Calcd for $C_{69}H_{79}ClFeN_3O_4P_2Rh$: C, 65.23; H, 6.27; N, 3.31. Found: C, 65.02; H, 5.98; N, 3.50.

[(NBD)Rh(2c)]ClO_4 (5c). The title compound was prepared in the same manner as described for the preparation of **4b** by replacing **1b** with **2c** (yield 0.170 g, 64%). ^{31}P NMR ($CDCl_3$): δ 13.76, 31.45 (s, *P*=N). ^{1}H NMR ($CDCl_3$): δ 1.32 (d, J = 6.5, 3H, CH*Me*), 1.65, 1.87 (s, 12H, Me_2−C_6H_3), 2.45 (m, 2H, C_7H_8), 2.50 (s, 3H, O*Me*), 3.11 (qt, J = 6.5, 1H, C*H*Me), 4.01−5.89 (m, 7H, $C_5H_4FeC_5H_3$), 6.56 (t, J = 6.0, 2H, *p*-C_6H_3), 6.63 (d, J = 7.5, 4H, *m*-C_6H_3), 6.78 (m, 4H, C_7H_8), 6.89 (m, 2H, C_7H_8), 7.20−8.07 (m, 20H, C_6H_5). Anal. Calcd for $C_{60}H_{59}ClFeN_2O_5P_2Rh$: C, 64.42; H, 5.98; N, 2.28. Found: C, 64.49; H, 5.94; N, 2.90.

[(NBD)Rh(3a)]ClO_4 (6a). The title compound was prepared in the same manner as described for the preparation of **4b** by replacing **1b** with **3a** (yield 0.105 g, 54%). ^{31}P NMR ($CDCl_3$): δ 18.29 (d, J = 167, *P*Ph_2), 33.85 (s, =*P*Ph_3). ^{1}H NMR ($CDCl_3$): δ 1.27 (s, 2H, C_7H_8), 1.48 (d, J = 6.9, 3H, CH*Me*), 3.48 (br, 2H, C_7H_8), 3.77 (qt, J = 7.8, 1H, C*H*Me), 4.22−4.62 (m, 8H, $C_5H_5FeC_5H_3$), 5.14 (br, 4H, C_7H_8), 7.22−7.97 (m, 25H, C_6H_5). Anal. Calcd for $C_{49}H_{45}ClFeNO_4P_2Rh$: C, 60.80; H, 4.69; N, 1.45. Found: C, 60.72; H, 4.94; N, 1.76.

[(NBD)Rh(3b)]ClO_4 (6b). The title compound was prepared in the same manner as described for the preparation of **6a** by replacing **3a** with **3b** (yield 0.156 g, 80%). ^{31}P NMR ($CDCl_3$): δ 15.08 (d, J = 160, *P*Cy_2), 32.73 (s, *P*Ph_3). ^{1}H NMR ($CDCl_3$): δ 0.98−1.90 (m, 22H, C_6H_{11}), 1.19 (br, 2H, C_7H_8), 1.36 (d, J = 6.6, 3H, CH*Me*), 3.85 (br, 2H, C_7H_8), 3.93 (qt, J = 2.7, 1H, C*H*Me), 4.13−4.64 (m, 8H, $C_5H_5FeC_5H_3$), 4.93 (br, 4H, C_7H_8), 7.44−7.85 (m, 15H, C_6H_5). Anal. Calcd for $C_{49}H_{57}ClFeNO_4P_2Rh$: C, 60.05; H, 5.86; N, 1.43. Found: C, 60.37; H, 5.64; N, 1.52.

X-ray Structure Determination. Selected crystallographic data for **4b** are collected in Tables 1 and 2. An ORTEP drawing showing the numbering scheme used in refinement is presented in Figure 1. Intensity data were collected at room temperature with a Bruker SMART 1000 CCD diffractometer using monochromated Mo Kα radiation (λ = 0.710 73 Å). Lorentz and polarization reflections were applied and absorption corrections made with three ψ scans. The structure was solved by direct methods and refined by full-matrix least-squares methods based on F^2 using SHELXS-97 and SHELXL-97.[21] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in calculated positions. Additional crystallographic data are available in the Supporting Information.

Typical Procedure for Asymmetric Hydrogenation. (a) Hydrogenation under 1 bar. To a reaction tube (Carousel 12 Place Reaction Station) equipped with a stirring bar were added $Rh(NBD)_2BF_4$ (7.5 mmg, 0.02 mmol), substrate (1.00 mmol), and methanol (10 mL) under an inert atmosphere. The inert atmosphere was then replaced by three H_2/release cycles, and the reaction mixture was stirred under 1 bar of H_2 pressure at 40 °C for 24 h. After this, the solvent was evaporated and the residue passed through a short silica column and submitted to GC analysis for conversion and ee values.

(21) Sheldrick, G. M. SHELXS-86; Universität Göttingen, Göttingen, Germany, 1986. SHELXS-97; Universität Göttingen, Göttingen, Germany, 1987.

(b) Hydrogenation under 10 bar. The whole procedure was the same, except the reaction was carried out in an autoclave.

2-Benzylpropanoic Acid. This was obtained as the product from the hydrogenation reaction of (*E*)-2-methylcinnamic acid. GC (Chiraldex γ-TA, 30 m $\times$ 0.25 mm) conditions for enantiomeric excess separation: oven temperature, 80 °C; injection temperature, 220 °C; detection temperature, 250 °C; initial time, 2 min; final temperature, 150 °C; rate, 3 °C/min; column pressure, 100 kPa; t_R, 27.58 min; t_S, 30.03 min.

Methyl 2-Acetamido-3-phenylpropionate. This was obtained as slightly brown crystalline solids from the reaction of methyl (*Z*)-2-acetamidocinnamate. GC (Chiraldex γ-TA, 30 m $\times$ 0.25 mm) conditions for enantiomeric excess separation: oven temperature, 90 °C; injection temperature, 220 °C; detection temperature, 250 °C; initial time, 2 min; final temperature, 160 °C; rate, 5 °C/min; column pressure, 100 kPa; t_R, 23.61 min; t_S, 27.32 min.

Methyl 2-Acetamidopropionate. This was obtained as slightly brown crystalline solids from the reaction of methyl (*Z*)-2-acetamidoacrylate. GC (Chiraldex γ-TA, 30 m $\times$ 0.25 mm) conditions for enantiomeric excess separation: oven temperature, 80 °C; injection temperature, 220 °C; detection temperature, 250 °C; initial time, 2 min; final temperature, 160 °C; rate, 2 °C/min; column pressure, 100 kPa; t_R, 29.07 min; t_S, 30.26 min.

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

Supporting Information Available: Tables giving atomic coordinates, displacement parameters, and bond distances and angles for **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM058028C