Organometallics **2001,** *20,* 5784−5787

A New Class of Planar-Chiral Ferrocenes: Serendipitous Formation of 1,2-Ferrocenediylazaphosphinines

Geun-Ho Hwang, Eun-Sook Ryu, Dong-Kyu Park, Sang Chul Shim,
Chan Sik Cho, and Tae-Jeong Kim*

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

Jong Hwa Jeong*

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

Minserk Cheong

Research Institute for Basic Sciences and Department of Chemistry, Kyung Hee University, Seoul, Korea 130-701

Received July 6, 2001

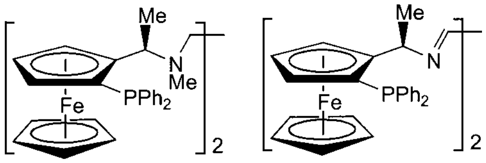
*Summary: The reaction of 1-(α-aminoalkyl)-2-diphenylphosphinoferrocene (**1**) with glyoxals gave via an unusual heterocyclization 1,2-ferrocenediylazaphosphinines (**3**) as a new class of planar-chiral ferrocenes. The products were fully characterized by analytical and various spectroscopic techniques. In particular, a complete assignment of all protons and carbons was made by various NMR techniques. A substantial degree of π-electron delocalization extending over the fused heterocyclic ring can be evidenced by IR and UV/vis spectra and in the case of **3a** by X-ray crystallographic data. Employment of rac-**3a** as ligand for Cu-catalyzed cyclopropanation of styrene by ethyl diazoacetate revealed a complete diastereo-discrimination leading to the formation of trans-product in 100% yield.*

Introduction

The recent resurgence of interest in 1,2-disubstituted planar-chiral ferrocenes has resulted in numerous interesting compounds which are finding widespread application in asymmetric catalysis.[1] Among others, those of the type (π-heterocycle)FeCp* developed by Fu deserve special attention due to their successful application not only as ligands but also as nucleophilic catalysts in a number of asymmetric cataytic reactions.[2−3]

Our recent success in the use of chiral C_2-symmetric bisferrocenyl diamine ligands such as **4** in asymmetric catalysis[4] has prompted us to examine the related diimine analogues such as **5** as a potential source of chiral ligand (Chart 1). Our rationale was straightforward: if the amino group can serve as an effective ligand for high enantiomeric excess, then the diimine derivatives could give better or at least comparable results. The α-diimine ligands are now well-known to stablize organometallic complexes[5] and have thus been widely employed in a number of catalytic reactions.[6]

Chart 1



4 **5**

We now wish to put into entry a completely new class of planar-chiral ferrocenes of the type (π-heteroaromatic ring)FeCp (**3**) that have been formed via an unusual cyclization from (*S*,*R*)-1-(α-aminoalkyl)-2-diphenylphosphinoferrocene (**1**) with glyoxals as illustrated in Scheme 1. Here the first (*S*) refers to the central chirality at the asymmetric carbon center and the second (*R*) to the planar chirality. In some cases, however, where R^1 = H, *rac*-**1** was employed for the reaction.

Results and Discussion

Synthesis and Characterization. In general, the synthesis of diimines involves the condensation of a diketone (or dialdehyde) with 2 equiv of an alkyl- or arylamine, often catalyzed by a Lewis or Bronsted acid. Surprisingly, however, the reaction between **1a** and glyoxal (R^2 = H) supposedly to give the bisferrocenyldiimine **5** proved futile. Instead, we ended up with obtaining **3a** as a single product regardless the reaction conditions employed. For instance, any change in the molar ratio between **1a** and glyoxal would not alter the result; neither would the change in the reaction temperatures.

---

(1) For recent reviews, see: (a) Richards, C. J.; Locke, A. J. *Tetrahedron: Asymmetry* **1998**, *9*, 2377. (b) Kagan, H. B.; Riant, O. In *Advances in Asymmetric Synthesis*; Hassner, A., Ed.; JAI Press Inc.: Greenwich, CT, 1997; Vol. 2, p 189.

(2) For a review, see: Fu, G. C. *Acc. Chem. Res.* **2000**, *33*, 412, and references therin.

(3) Shintani, R.; Lo, M. M.-C.; Fu, G. C. *Org. Lett.* **2000**, *2*, 3695.

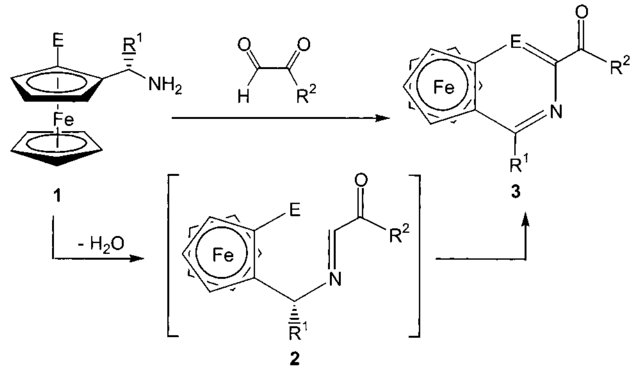
(4) (a) Song, J.-H.; Cho, D.-J.; Jeon, S.-J.; Kim, Y.-H.; Kim, T.-J. *Inorg. Chem.* **1999**, *38*, 893. (b) Cho, D.-J.; Jeon, S.-J.; Kim, H.-S.; Cho, C. S.; Shim, S. C.; Kim, T.-J. *Tetrahedron*: *Asymmetry* **1999**, *10*, 3833. (c) Cho, D.-J.; Jeon, S.-J.; Kim, H.-S.; Kim, T.-J. *Synlett* **1998**, 617.

(5) Van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151.

(6) For some leading references on the use of diimine ligands, see: (a) Fache, F.; Schulz, E.; Tommasino, M. L.; Lemaire, M. *Chem. Rev.* **2000**, *100*, 2159. (b) Ittel, S. D. L.; Johnson, K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (c) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (d) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497.

10.1021/om010603z CCC: $20.00

Scheme 1



1a, 2a, 3a: R^1 = Me; R^2 = H; E = PPh_2
1b, 2b, 3b: R^1 = Me; R^2 = Me; E = PPh_2
1c, 2c, 3c: R^1 = Me; R^2 = Ph; E = PPh_2
1d, 2d, 3d: R^1 = H; R^2 = H; E = PPh_2
1e, 2e, 3e: R^1 =H; R^2 = Me; E = PPh_2
1f, 2f, 3f: R^1 = H; R^2 = Ph; E = PPh_2

One of the most striking features of this reaction is the formation of a phosphorus ylide bond in a fused heteroaromatic ring. Pedagogically, the reaction bears some resemblance to the classical synthesis of phosphorus ylide compounds. One such example involves initially the nucleophilic attack of phosphorus to an alkyl halide to form a phosphonium salt followed by deprotonation by a base (or nucleophile).[7−8] The final stage of heterocyclization which accompanies the loss of the methine hydrogen may be the result of an oxidative aromatization occurring under aerobic workup conditions.[9] An activation and functionalization of the methine position in similar derivatives has recently been reported and exploited by Knochel.[10] In this connection, it is worth noting that the retentive S_N1 type reaction generating a remarkably stable α-ferrocenylalkyl carbocation is ubiquitous for this type of ferrocene derivatives.[11] A major driving force behind this reaction is believed to be resonance stabilization by the formation of a fused heteroaromatic ring through in situ generation of the aforementioned α-ferrocenylalkyl carbocation. Finally, in connection with the stereochemical change in the course of the reaction, the loss of the central chirality at the asymmetric cabon atom can be noted, while the planar chirality of the (*R*)-configuration around the disubstituted Cp ring still remains as confirmed by its X-ray crystal structure in Figure 1. Selected bond lengths and angles are listed in Table 1.

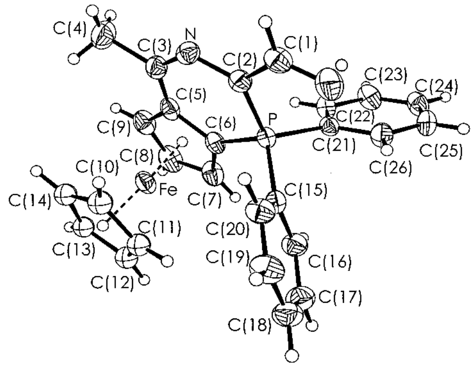


Figure 1. Crystal structure of (*R*)-**3a**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for (*R*)-3a

P−C(2)	1.758(4)	P−C(6)	1.765(4)
P−C(15)	1.806(4)	P−C(21)	1.811(3)
N−C(2)	1.387(5)	N−C(3)	1.289(5)
C(1)−C(2)	1.406(5)	C(1)−O	1.240(5)
C(3)−C(5)	1.443(6)	C(5)−C(6)	1.444(5)
C(2)−P−C(6)	101.3(2)	C(2)−P−C(15)	114.6(2)
C(6)−P−C(15)	111.0(2)	C(2)−P−C(21)	115.1(2)
C(6)−P−C(21)	108.7(2)	C(15)−P−C(21)	106.2(2)
C(3)−N−C(2)	124.6(3)	N−C(2)−C(1)	119.0(3)
N−C(2)−P	125.7(3)	C(1)−C(2)−P	115.3(3)
N−C(3)−C(5)	123.8(3)	N−C(3)−C(4)	118.1(4)
C(5)−C(3)−C(4)	118.2(3)	C(3)−C(5)−C(6)	124.1(3)
C(5)−C(6)−P	120.5(3)	O−C(1)−C(2)	123.8(4)

The structure shows that P, C(2), N, C(3), C(5), C(6), C(7), C(8), and C(9) are coplanar within 0.041(4) Å deviation. The bond angles in the six-membered heterocycle are in the range 101.3(2)−125.6(3)°. The two heteroatoms, P and N, reveal two pairs of P−C(sp^2) bond distances and a pair of N−C(sp^2) bond distances, respectively. Namely, the pair of P−C(2) and P−C(6) in the six-membered ring have almost same bond lengths of 1.758(4) and 1.765(4) Å, which are a little longer than the traditional P−C (ylidic) bond distances such as 1.674(3) Å in $H_2C{=}PPh_2$ and 1.629(3) Å in $H_2C{=}P(Fc)_3$ (Fc = ferrocenyl).[7,8] The bond distances in the other pair of P−C(15) and P−C(21) with 1.806(4) and 1.811(3) Å fall within the range of typical P−C(sp^3) single bonds and are quite naturally longer than any of the above values. The N−C(3) distance of 1.289(5) Å is close to the normal C=N bond, and the N−C(2) distance of 1.387(5) Å is a little shorter than the value for the pure single N(sp^3)−C(sp^2).[12]

The IR and the UV−vis spectral data are quite informative in regard to extended resonance in this compound. For example, two IR stretching bands for C=N and C=O groups in **3a** move to lower frequency regions to appear at 1589 and 1543 cm^{-1}, respectively. The UV−vis spectrum of **3a** exhibits the expected bathochromic shift by showing two absorption maxima (λ_{max}, MLCT transition) at 325 and 375 nm, while the same λ_{max} value for **1a** appears at 275 nm. Here it is worth noting, for comparative purposes, that α-ferrocenylpolyenes of the type $(C_5H_5)Fe[C_5H_4(CH{=}CHR)_n]$ reveal the progressive bathochromic shifts upon increasing conjugation with $n = 1$ to 3. With R = 4′-$NO_2C_6H_4$, for instance, the absorption maxima appear at 354 nm ($n = 1$), 383 nm ($n = 2$), and 396 nm ($n = 3$).[13] Various techniques of ^1H and ^{13}C one- and two-dimensional NMR spectroscopy provide additional insight and make possible a complete assignment of every proton and carbon in **3a**.[14]

---

(7) Schmidbaur, H.; Jeong, J.; Schier, A.; Graf, W.; Wilkinson, L.; Muller, G. *New J. Chem.* **1989**, *13*, 341.

(8) Huang, Y. Z.; Shen, Y. C. *Adv. Organomet. Chem.* **1982**, *21*, 115.

(9) This reasoning was suggested by one of our referees, for which we are grateful.

(10) Ireland, T.; Perea, J. J. A.; Knochel, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 8, 1457.

(11) (a) Togni, A. In *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, Germany, 1995; p 175. (b) Allenmark, A. *Tetrahedron Lett.* **1974**, 371.

(12) Gilli, G.; Bertolasi, V.; Bellucci, F.; Ferretti, V. *J. Am. Chem. Soc.* **1986**, *108*, 2420.

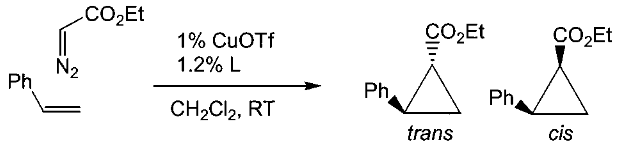
(13) Naskar, D.; Das, S. K.; Giribabu, L.; Maiya, B. G.; Roy, S. *Organometallics* **2000**, *19*, 1464.

Table 2. Summary of Crystallographic Data for (*R*)-3a

empirical formula	$C_{26}H_{22}FeNOP$
fw	451.27
cryst size	0.35 × 0.40 × 0.50
space group	$P2_12_12_1$
a (Å)	8.6289(6)
b (Å)	13.4215(5)
c (Å)	18.5382(9)
V (Å^3)	2147.0(2)
Z	4
T (K)	293(2)
radiation, λ(transmn range)	Mo Kα 0.71073
2θ range (deg)	3.74−50.94
data collected: *h; k; l*	−10, 0; 0, 16; 0, 22
no. of unique reflns	2290
μ (mm^{-1})	0.795
transmn range	93−100
refinement	FMLS on F^2
goodness of fit	1.05
R indices ($I > 2\sigma(I)$)[a]	$R_1 = 0.032$; $wR_2 = 0.79$
absolute structure param	0.02(3)
max. residue density (e/Å^3)	0.27

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = [\sum w_i(F_o^2 - F_c^2)/w_i(F_o^2)]^{1/2}$.

Table 3. Catalytic Cyclopropanation of Styrene: Diastereoselectivity as a Function of *rac*-3a[a]



L	*trans*:*cis*	yield (%)
blank	61:39	80
rac-**3a**	100:0	>99

[a] All data represent the average of two runs, and all yields are GC yields.

Reaction Scope and Catalytic Application. Structural modification with R^1 and R^2 has also allowed us to obtain an array of the same type of products (**3b**−**f**). The detailed procedure for NMR assignment for **3a** provides the basis for the structural confirmation for all other compounds (**3b**−**f**) because of their spectral similarities. Other spectroscopic (IR, UV−vis) features of all these compounds are quite similar to those of **3a**, and thus their structural confirmation can be readily performed by comparison and by analogy.[14] Although the test for the reaction scope has so far been far from being comprehensive, the reagent bearing R^2 seems to be limited to glyoxal derivatives (R^2 = H, Me, Ph) for the product formation. Employment of simple aldehydes and ketones such as 2-pyridinecarboxaldehyde, *o*-anisaldehyde, formaldehyde, 2,3-butadione, pyruvonitrile, and formic hydrazide simply yielded corresponding condensation imine products.

Preliminary results on the use of *rac*-**3a** as ligand in Cu-catalyzed cyclopropanation of styrene with ethyl diazoacetate reveal that a perfect diastereo-discrimination in favor of *trans* product can be achieved (Table 3). These results demonstrate that our ligand is far more excellent in diastereoselectivity than the well-known C_2-symmetric diimines such as semicorrins, bisoxazolines, and bisazaferrocene.[15] Although the origin of diastereocontrol has yet to be illucidated, the formation of a Cu(**3a**)$_2$ species, where **3a** coordinates through nitrogen, may be envisaged in the initial stage of the reaction.

In conclusion, the present work describes the synthesis of a series of 1,2-ferrocendiylazaphosphinines as a new family of planar-chiral ferrocenes formed serendipitously from the reaction of 1-(α-aminoalkyl)-2-diphenylphosphinoferrocene (**1**) with various glyoxals. Further work is underway to investigate the reaction chemistry of **3** including potential application in asymmetric nucleophilic catalysis as well as the asymmetric version of the reaction described Table 3. The outcome will appear elsewhere in due course.

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 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 internal standard. GC−mass spectra were obtained by using a Micromass QUATTRO II GC8000 series model with electron energy of 20 or 70 eV. Optical rotations were measured on a JASCO DIP-370 digital polarimeter at ambient temperature. IR spectra were run on a Mattson FT-IR Galaxy 6030E spectrophotometer. UV−visible spectra were obtained in CH_2Cl_2 on a Varian CARY 5G spectrophotometer. All commercial reagents were purchased from Aldrich and used as received. (*S*,*R*)-**1a** and *rac*-**1d** were prepared according to the literature methods.[16−17]

Preparation of (*R*)-3a. To a solution of (*S*,*R*)-**1a** (500 mg, 1.2 mmol) in MeOH (10 mL) was added an aqueous solution (40%) of glyoxal (0.2 mL, 1.2 mmol). The mixture was stirred for 5 h at room temperature, after which the solution was dried over anhydrous $MgSO_4$. Removal of any solids through filtration followed by concentration in vacuo gave the crude product. Recrystallization from hexane/acetone (4:1) afforded the product as orange crystals (540 mg, 90%). $[\alpha]_D^{23}$ −1700 (c = 0.1 in $CHCl_3$). The following numbering scheme for NMR characterization is based on Figure 1. ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4): δ −4.2 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.6 (d, H1, J_{PH} = 25.5), 2.36 (s, H4), 4.56 (m, H7), 4.63 (m, H8), 4.84 (m, H9), 3.70 (s, H10−H14), 7.66−7.58 (m, H16/H20), 7.89−7.84 (m, H17/H19), 7.66−7.58 (m, H18), 7.35−7.30 (m, H22/H26), 7.54−7.47 (m, H23/H25), 7.45−7.39 (m, H24). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 185.0 (d, C1, J = 22.3), 89.5 (d, C2, J = 74.4), 136.3 (d, C3, J = 12.6), 23.0 (s, C4), 83.6 (d, C5, J = 4.8), 61.1 (d, C6, J = 93.7), 70.8 (d, C7, J = 6.8), 73.7 (d, C8, J = 11.6), 67.5 (d, C9, J = 4.8), 70.9 (s, C10−C14), 126.0 (d, C15, J = 93.7), 133.1 (d, C16/C20, J = 10.6), 129.0 (d, C17/C19, J = 12.6), 132.6 (d, C18, J = 2.9), 129.1 (d, C21, J = 86.9), 128.3 (d, C22/C26, J = 12.6), 133.5 (d, C23/C25, J = 11.6), 131.9 (d, C24, J = 2.9). IR (KBr): 1589 cm^{-1} (vs), 1543 cm^{-1} (vs). UV/vis (MeCN): λ_{max} nm 375. EIMS m/z (rel intensity): 451 (M$^+$, 100), 238 (30), 183 (22), 149 (38), 59 (53). Anal. Calcd for

---

[14] The detailed procedure for NMR assignment and relevant NMR spectra of **3a**−**f** are provided in the Supporting Information.

[15] (a) Lo, M. M.-C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 10270. (b) Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1005. Lowenthal, R. E.; Abiko, A.; Masamune, S. *Tetrahedron Lett* **1990**, *31*, 6005. (c) Evans, D. A.; Woerpel, K. A.; Hinman, M. A.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726.

[16] (a) Hayashi, T.; Hayashi, C.; Uozumi, Y. *Tetrahedron: Asymmetry* **1995**, *6*, 2503. (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. Jpn.* **1980**, *53*, 1138. (c) Marr, G.; Hunt, T. *J. Chem. Soc.* (*C*) **1969**, 1070. (d) Honeychuck, R. V.; Okoroafor, M. O.; Shen, L.-H.; Brubaker, C. H., Jr.; *Organometallics* **1986**, *5*, 482.

[17] Sheldrick, G. M. *SHELXS-86*; Universität Göttingen, 1986; *SHELXS-97*, Universität Göttingen, 1997.

$C_{26}H_{22}NPOFe$: C, 69.20; H, 4.88; N, 3.11. Found: C, 69.26; H, 5.04; N, 2.98.

X-ray Structure Determination. Crystallogrphic data for **3a** are collected in Table 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 CAD4 diffractometer using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Lorentz and polarization reflections were applied and absorption corrections made with three Ψ scans. The structures were solved by direct methods and refined by full-matrix least-squares methods based on F^2 using SHELXS-97 and SHELXL-97.[16] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in calculated positions. Additional crystallographic data are available in the Supproting Information.

Acknowledgment. T.J.K. is grateful to KOSEF for financial support (Grant No.: 2000-2-12200-001-3), to Ms. Y. S. Park for the NMR experiments, and to Prof. S.-O. Kang, Korea University, for the generous donation of chlorodimethylphosphine.

Supporting Information Available: The detailed procedure for NMR assignment and relevant NMR spectra of **3a**−**f**, compound characterization data for **3b**−**f**, and tables of positional parameters and B_{iso}/B_{eq}, H atom coordinates, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **3a**. This material is avaiable free of charge via the Internet at http://pubs.acs.org.

OM010603Z