Articles

Functionalized Organometallic Ligand (1) Synthesis of Some Ferrocene Derivatives of Cyclohexyl- and Cyclopentadienyl-phosphines

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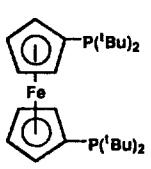
A series of new ferrocene derivatives containing cyclohexylphosphines have been prepared from the reactions of lithioferrocenes with corresponding chlorodicyclohexylphosphines. 1-diphenylphosphino-1'-dicyclohexylphosphinoferrocene has been prepared from [1]-ferrocenophane *via* a ring cleavage reaction. Chiral ferrocenylaminophosphines incorporating cyclohexyl- and cyclopentadienylphosphines have also been prepared from the chiral template 2-N,N-dimethylaminoethylferrocene (FA) *via* stereoselective lithiation followed by phosphination with corresponding R_2PCl($R=C_6H_{11}$, C_5H_5). The synthesis of cyclopentadienylphosphine derivative of (R)-FA (**6b**) led to the formation of a mixture of four diastereomers due to the presence of three chiral sources in the final product in addition to the fluxional behavior of the η^1-C_5H_5 group attached to the phosphorus. All these new compounds have been characterized by analytical and spectroscopic techniques.

Introduction

Ferrocenylphosphines are now well-known as efficient ligands for metal complexes in a wide range of homogeneous catalysis such as Rh(I)-catalyzed hydrogenation,[2-7] Pd(II)- and Ni(II)-catalyzed Grignard cross-coupling reactions,[8] Pt (II)-catalyzed hydrosilation of ketones,[9] and Au(II)-catalyzed aldol condensation.[10,11] Among others, most-widely used ligands are those containing ferrocenyl(ditertiaryaryl)phosphines such as 1,1'-bis(diphenylphosphino)ferrocene (BPPF), 1-(α-aminomethyl)ethyl)-2-diphenylphosphinoferrocene (PPFA), 1-(α-aminomethyl)ethyl)-2-bis(diphenylphosphino)ferrocene (BPPFA). This is due to the belief that the so-called chiral array of phenyl rings in an alternating face-and-edge manner around the metal would gurantee the high enantiomeric excess in asymmetric reactions.[13]

In this connection, however, it is worth noting that we have recently established[4,5] that equally efficient hydrogenation catalysts of the type [(L-L)Rh(diene)]ClO_4(diene=cyclooctadiene, norbornadiene) are also obtained even when (L-L) is a ferrocenylalkylphosphine such as **1-3**.



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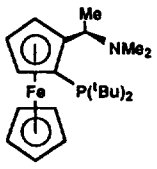

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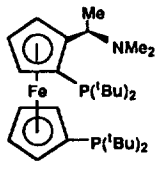

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The use of chiral **2** or **3** results in high optical yields, even though the ligand contains bulky, symmetrical P-^{t}Bu groups rather than P-Ph ones.[6] Also contrary to expectation, treatment of the cationic rhodium (I) precursors with hydrogen affords metal hydrides rather than a disolvate complex of the type $[Rh(L\text{-}L)(S)_2]^+$, usually formed when L-L is a typical chelating di(tertiaryarylphosphine) such as 1,2-(diphenylphosphino)ethane.[12,13] In view of these results it would be of interest to prepare ligands such as those containing bulky, basic cyclohexylphosphine moieties that are somewhat related to **1-3**. In addition, the synthesis of cyclopentadienylphosphines is also of interest since little is known about this class of compounds, especially the possibility of utilizing the C_5H_5 group for coordination to metals, Their synthesis and characterization are presented in this paper. The work described in this paper is part of our on-going projects for the synthesis and applications of functionalized organometallic ligands in a wide range of homogeneous catalysis.

Experimental

Generals. All manipulations of air-sensitive compounds were carried out under an inert (N_2 or argon) atmosphere using conventional Schlenk techniques. All commerical reagents were used as received unless otherwise mentioned. Solvents were predried by conventional methods and were distilled prior to use.[14] Microanalyses were performed by Microanalytical Laboratory, Kolon Company, Kumi, Korea. ^{1}H, ^{13}C, and ^{31}P-NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 300 MHz, 80.15 MHz, and 121.5 MHz, respectively. ^{1}H and ^{13}C shifts are reported relative to external TMS ($\delta=0$ ppm) and ^{31}P shifts relative to 85% H_3PO_4. Optical rotations were determined using a JASCO model DIP-360 polarimeter. The preparation and resolution of N,N-dimethylaminoethylferrocene (FA) was carried out using the method of Ugi and co-workers.[15]

Synthesis of 1,1'-bis(dicyclohexylphosphino)ferrocene (4). The TMEDA (TMEDA=N,N,N',N'-tetramethyle-

thylene diamine) adduct of 1,1'-dilithioferrocene (1.46 g, 4.65 mmol) prepared according to the literature method[16] was suspended in freshly distilled hexane (30 m*l*) in a 100 m*l* Schlenk tube maintained at −78℃. Chlorodicyclohexylphosphine (2.38 g, 10.2 mmol) was then added dropwise *via* syringe to the stirred suspension. The reaction mixture was allowed to warm slowly to room temperature and left to stir overnight. Following careful hydrolysis with aqueous sodium bicarbonate, the supernatant hexane layer was separated, dried over K_2CO_3. The dried solution then concentrated to a few m*l* to give an oil. The oil was chromatographed on silica gel. The major orange fraction eluted with a mixture of hexane and diethyl ether (3/1) was collected and concentrated to dryness. The product was isolated by crystallization from acetone at 0℃. Yield of **4**: 2.28 g, 84.9%. Anal. Calcd. for $C_{43}H_{52}P_2Fe$: C, 70.58, H, 9.06. Found: C, 70.70; H, 9.64.

Synthesis of (1-diphenylphosphino-1'-dicyclohexylphosphino)ferrocene (5). The title compound was prepared using the method of Seyferth[17] with a slight modification. A 250 m*l* three-necked, round-bottomed flask equipped with a magnetic stirrer, a pressure equalizing dropping funnel, an argon inlet was evacuated and refilled with argon. To this flask a solution of 2.7 M PhLi in benzene (1.4 m*l*, 3.8 mmol) was added *via* syringe. Separately, (1,1'-ferrocenediyl)phenylphosphine (0.5 g, 1.71 mmol) was dissolved in hexane (50 ml) in a Schlenk tube. A small amount of tan-insoluble material always resulted, so the mixture was filtered under argon and then transferred into the dropping funnel. The hexane solution of ferrocenophane was added dropwise to the phenyllithium during 30 min. As the addition proceeded, a tan-yellow precipitate formed while the solution became golden brown. The mixture was stirred for an additional hour after which the solvent was removed *in vacuo* to give a tan-yellow solid. This solid was then dissolved in diethyl ether (30 ml) and allowed to react with chlorodicyclohexylphosphine (0.93 g, 4 mmol). Upon addition of the phosphine the gold solution turned brownish orange and was stirred for 1 h at room temperature, then heated at reflux for 30 min, and finally allowed to cool and stir overnight. The solvent was removed under vacuum to leave a brown oil. The desired product was isolated by column chromatography on silica gel eluting with a mixture of hexane and diethyl ether (95/5), collecting the third major orange fraction. This gave orange crystals after crystallization from acetone at 0℃. Yield of **5**:, 20%. Anal. Calcd. for $C_{34}H_{40}O_2Fe$: C, 72.10; H, 7.07. Found: C, 72.27; H, 6.36.

Synthesis of (S,R)-(1-(N,N-dimethylaminoethyl)-2-diclohexylphosphino)ferrocene (6a). (S)-FA(3 g, 11.7 mmol) was dissolved in diethyl ether (10 m*l*) in a Schlenk tube. To this solution was added *n*-BuLi (1.6 M, 10 m*l*) in hexane. After stirring 2 h, $(C_6H_{11})_2PCl$ (3 g, 13 mmol) was added dropwise by syringe. The mixture was stirred for 5 h. Following careful hydrolysis with aqueous sodium bicarbonate, the organic layer was separated, dried over K_2CO_3, filtered, and the filtrate reduced in volume to about 5 ml. The resulting oily solution was chromatographed on silica gel by eluting with a mixture of hexane and diethyl ether (90/10), collecting the first major orange band. After removal of solvents from the resulting orange solution afforded a dark oil which crystallized on adding ethanol to give orange crystals at 0℃. Yield of (S,R)-**6**: 3.97 g, 75%. $[\alpha]_D^{25}$-11.6°(c 5, $CHCl_3$). Anal. Calcd. for $C_{26}H_{40}NPFe$: C, 68.87; H, 8.89; N, 3.09. Found: C, 69.40; H, 9.04; N, 2.89.

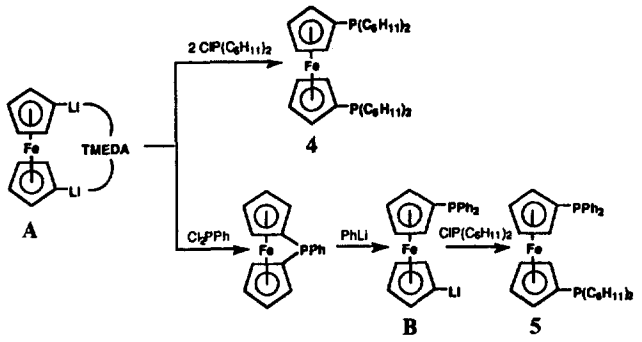
Synthesis of 1',2-bis(dicyclohexylphosphino)-1-(N,N-dimethylaminoethyl)ferrocene (7). (R)-FA(3 g, 11.7 mmol) was dissolved in diethyl ether (20 m*l*) in a Schlenk tube. To this solution was added *n*-BuLi (1.6 M, 9 m*l*) in hexane. After stirring 2 h, a mixture of *n*-BuLi (1.6 M, 10 m*l*) in hexane and TMEDA (1.5 g, 13 mmol) was added dropwise through a pressure equalizing dropping funnel. The reaction mixture was further stirred for 8 h at room temperature. This solution was added dropwise to a solution of $(C_6H_{11})_2PCl$(6.05 g, 26 mmol) in diethyl ether (30 m*l*) which was separately prepared in a 250 ml, round-bottomed, three-necked flask equipped with a condenser, an argon inlet, and a pressure equalized dropping funnel. After the initial exothermic reaction on addition of the $FALi_2 \cdot$ TMEDA solution, the mixture was allowed to boil under reflux for 3 h. Following hydrolysis with aqueous sodium bicarbonate, the organic layer was separated, dried over K_2CO_3, filtered, and reduced in volume to about 5 ml, the resulting oily solution was chromatographed on silica gel. After removal of the first yellow minor fraction with acetone/dichloromethane (1/3). Removal of solvents from the resulting orange solution afforded a dark oil which crystallized on adding ethanol or acetone to give the product as orange crystals. Yield of (R,S)-**7**: 4.94 g, 65%. $[\alpha]_D^{25}$+35.8°(c 5, $CHCl_3$). Anal. Calcd. For $C_{38}H_{61}NP_2Fe$: C, 70.25; H, 9.46; N, 2.16. Found: C, 70.00; H, 9.43; N, 1.95.

Synthesis of (1-(N,N-dimethylaminoethyl)-2-phenylcyclopentadienylphosphino)ferrocene (6b). To a slurry of CpTl (2.5 g, 9.3 mmol) in diethyl ether (20 m*l*) at −70 ℃ was added dichlorophenylphosphine (1.26 m*l*, 9.3 mmol). The reaction mixture was allowed to warm to room temperature. After stirring 4 h the suspension was filtered, and the pale yellow filtrate was added dropwise to a stirred etheral solution of (R,R)-1-(N,N-dimethylaminoethyl)-2-(lithio)ferrocene (8.5 mmol) at −70℃ prepared from the reaction of (R)-FA with BuLi. Yellow precipitates formed immediately. The reaction mixture was left to stir overnight at room temperature, after which time the yellow preciptates were collected on a celite, washed with diethyl ether (20 m*l*), dissolved in CH_2Cl_2 (5 m*l*), and finally filltered to remove any solid impurity. The filtrate was evaporated to dryness. The remaining orange solid was dissolved in THF (10 m*l*) and filtered to remove some insoluble materials. The filtrate was reduced in volume to about 3 m*l* to which was added diethyl ether for attempted fractional crystallization of diastereomeric (R,S,S)-**6b** or (R,S,R)-**6b** at 0℃. On cooling, however, a diastereomeric mixture of products was obtained as yellow powders (1.81 g, 49.6%). Anal. Calcd. for $C_{25}H_{27}NPFe$: C, 70.11; H, 6.35. Found: C, 70.99; H, 6.44.

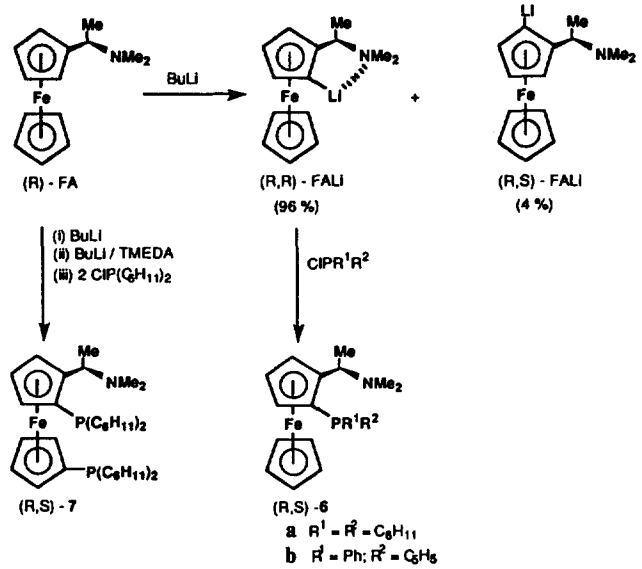
Results and Discussion

A series of chiral and achiral ferrocenylphosphine derivatives **4-7** were prepared by the direct reaction of lithioferrocenes with $ClP(C_6H_{11})_2$ or $ClP(Ph)(C_5H_5)$ as outlined in the synthetic Schemes 1 and 2.

The lithioferrocene derivatives were prepared as described in the literature.[17,18] As for the TMEDA adduct of dilithioferrocene (**A**), the orange precipitate separated from the reac-



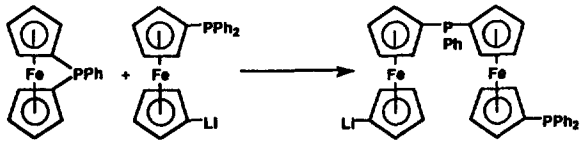
Scheme 1



Scheme 2

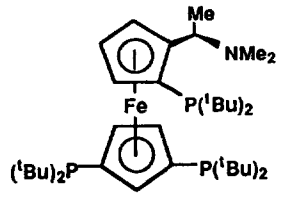
tion solution as a pyrophoric powder when ferrocene was lithiated with two equivalents of *n*-BuLi in the presence of one equivalent of TMEDA. There are distinct advantages in using these isolated TMEDA adduct rather than using the *in situ* solution of **A** in order to obtain high product yields of **4** with reduced amounts of side products, *i.e.*, monosubstituted phosphines.

The preparative route for the symmetrical ligand, **4** is a simple extension of the preparation of 1,1′-bis(diphenylphosphino)ferrocene (BPPF) replacing Ph_2PCl with $(C_6H_{11})_2PCl$. The unsymmetrically 1,1′-disubstituted ligand, **5** was prepared *via* the ring cleavage reaction of the [1]-ferrocenophane which was prepared from the reaction of **A** with $PPhCl_2$.[17,19] The subsequent synthetic route involved the reaction of the intermediate, 1-diphenylphosphino-1′-lithioferocene (**B**) with $(C_6H_{11})_2PCl$. Although this is an extremely useful method of activating the second ring for further substitution, care must be taken to minimize the formation of byproducts. For example, the initial product **B** may compete with PhLi for the substrate [1]-ferrocenophane, thus giving a monolithioferrocenyl derivative as shown in Eq. (1).



In order to avoid this potential complication, we adopted the procedure of Seyferth[17] involving the slow addition of the [1]-ferrocenophane to an equimolar amount of PhLi in hexane as described in the Experimental section. The success of this procedure lies in the fact that the intermediate **B** is insoluble in hexane and thus its reaction with the ferrocenopane is minimized. An alternative route may involve the slow addition of 1.5 molar excess of PhLi to the [1]-ferrocenophane in diethyl ether maintained at −78℃ as described by Cullen *et al.*[19]

The synthetic routes for the formation of chiral aminophosphines such as **6** and **7** are described in Scheme 2. The monolithiation of α-dimethylaminoethylferrocene (FA) is well-known to be highly stereospecific affording (R,R)- or (S,S)-2-lithio-1-dimethylaminoethylferrocene in high optical yield (96%) form (R)- or (S)-FA, respectively, due to the attractive interaction between lithium and the nitrogen lone pair electrons.[15] Subsequent treatment with $ClP(C_6H_{11})_2$ of this 96 : 4 diastereometric mixture of dilithiated intermediates affords pure (R,S)-**6a** or (S,R)-**6a**. The small amount of minor diastereomer (R,R)-**6a** or (S,S)-**6a** can be easily removed by fractional crystallization. Here the first R (or S) refers to the central chirality on the asymmetric carbon (*CHMe-NMe_2) and the second S (or R) to the planar chirality due to the presence of two differernt substituents on the same ring. In a likewise manner stepwise dilithiation of (R)-FA or (S)-FA easily affords the substitute (R,R)- or (S,S)-1,1′-dilithioferrocene derivative, respectively, which can also be isolated as a pyrophoric TMEDA adduct. Subsequent reaction of this intermediate with $ClP(C_6H_{11})_2$ led to the formation of the disubstituted compound (R,S)-**7** or (S,R)-**7**. No sign of the formation of a trisphosphine derivative analogous to that found for the case of tertiarybutylphosphine[6] has been observed (*vide infra*).



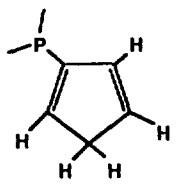
The synthesis of cyclopentadienylphosphine derivative **6b** is of interest because little is known about this class of compounds, especially the possibility of utilizing the C_5H_5 group for coordination to metals. In principle, this synthesis should lead to the formation of a mixture of a number of diastereomeric products due to the nature of this compound. Namely, this compound has two chiral centers on both the asymmetric carbon (*$CHMeNMe_2$) and the asymmetric phosphorus (*$PR^1R^2R^3$) as well as the planar chirality, thus giving rise to a pair of diastereomers, (R,S,S)-**6b** and (R,S,R)-**6b** from (R)-FA alone. In addition, as shown below, the Cp ligand can be attached to phosphorus in two different manners thus resulting in another pair of diastereomers from each diastereomeric **6b**. Thus, in theory, all possible isomers that should be contained in the mixture are (R,S,S)-**6b-1**, (R,S,S)-**6b-2**, (R,S,R)-**6b-1**, and (R,S,R)-**6b-2**.

Our initial hope was to separate all of these isomers by a chromatographic technique. In practice, however, we were unable to achieve our goal to obtain a series of chiral orga-

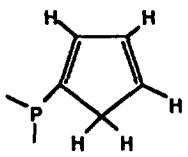
Table 1. NMR (^{1}H and ^{31}P) Data for **4-7**[a-d]

Compound	^{1}H	^{31}P
4	4.24 (s), 4.12 (s) (8H, -(C_5H_4)$_2$), 1.04-1.93 (m, 44H, -(C_6H_{11})$_4$)	−9.65 (s)
5	7.00-7.85 (m, 10H, Ph), 4.24, 4.10, 3.98, 3.96 (8H, -(C_5H_4)$_2$), 0.65-1.95 (m, 22H, -(C_6H_{11})$_4$)	-9.64 (s) −19.14 (s)
6a	4.27, 4.22, 4.09 (m, 3H, -C_5H_3), 4.04 (s, 5H, C_5H_5), 2.10 (s, 6 H, -NMe_2), 4.00 (qdt, ^{3}J=3 Hz, 1H, -CH), 2.07-1.03 (m, 22H, -C_6H_{11}), 1.32 (d, ^3J= Hz, 3H, -CMe)	−12.88 (s)
6b	7.41-7.22 (m, 5H, Ph) 6.47/2.90 (b, 3H/2H, P (C_5H_5)) 4.42, 4.35, 4.29 (m, 3 H, C_5H_3) 4.22 (s, 5H, π-C_5H_5), 2.23 (s, 6H, NMe_2) 1.69 (d, ^{3}J=3 Hz, 3H, CMe)	2.08 (b)/0.07 (b) −23.3 (b)/−26.1 (b) 9.83 (b)/7.25 (b) −29.3 (b)/−34.0 (b)
7	4.28, 4.17, 4.10 (m, 3H, -C_5H_3), 4.08, 4.01 (m, 4H, -C_5H_4), 3.98 (qdt, ^{3}J=3 Hz, 1H, -CH), 2.08 (s, 6H, -NMe_2), 1.27 (d, ^{3}J=3 Hz, 3H, -CMe), 0.96-2.15 (m, 44H, -C_6H_{11})	−10.57 (s) −12.73 (s)

[a]In $CDCl_3$. [b]Chemical shifts are in ppm and coupling constants in Hz. [c]Key: s=singlet; d=doublet; m=multiplet; qdt=quartet of doublets; b=broad. [d]The methyne proton concealed in the Cp region.



6b-1



6b-2

nometallic ligands functionallized by a Cp group since the yellow powders which are believed to be a whole mixture of the above-mentioned diasteromers refused to be eluted at all.

The NMR data for the new ligands **4-7** are listed in Table 1. The ^{1}H-NMR pattern for the cyclopentadienyl (Cp) ring protons in **4** and **5** exhibit a simple A_2B_2 pattern with the coupling constants $J_{AA'}$, $J_{BB'}$, J_{AB} being negligibly small. Thus, as shown in Table 1, a symmetric two-line pattern from **4** and a non-symmetrical four-line pattern from **5** are exhibited for the AB portions. These patterns are almost the same as those found for the BPPF ligand and its iron complexes.[7b] The cyclohexyl protons in both compounds show complex multiplets in the region 1-2 ppm. The phosphorus signal for the equivalent pair of the -$P(C_6H_{11})_2$ moiety in **4** is as expected except for its appearance in the less-shielded area (δ= −9.65 ppm) as compared with that of the ligand BPPF which appears at −17.61 ppm.[4] What has also been noticed is the same trend that the resonance peak for the phosphorus atoms moves to a less-shielded region as the substitution of the phenyl groups by other alkyl groups proceeds.[5,20] Thus, for example, the compound **1** shows a phosphorus signal at 26.48 ppm. The ^{31}P-NMR pattern for the compound **5** is also as expected to give two singlets at −9.64 ppm and −19.14 ppm for the diastereotopic PCy_2 and PPh_2 groups, respectively. No coupling between the two phosphorus atoms is observed.

The ^{1}H-NMR patterns for the chiral ligands **6a** and **7** are as expected. They give rise to singlets for the six equivalent NMe_2 protons due to free rotation at 2.10 and 2.08 ppm, respectively, and doublets at 1.32 and 1.27 ppm for the methyl protons on the chiral center coupling with the methine proton, and complex multiplets for the cyclohexyl protons in the expected region of 1-2 ppm. A significant difference between the two spectra arises due to the Cp ring protons. Namely, the monophosphine derivative **6a** shows a singlet (δ=4.04 ppm) for the unsubstituted Cp ring protons (C_5H_5) and three multiplets (δ=4.27, 4.22, and 4.09 ppm) for the ABC protons in the disubstitituted ring (C_5H_3), while the diphosphine derivative **7** shows an AB doublet for the disubstituted ring protons (C_5H_4) in addition to the three multiplets for the ABC protons in the disubstuted ring (C_5H_3) at chemical shifts almost the same as those found for **6a**. Other interesting feature of the ^{1}H-NMR patterns regarding the methine protons in both **6a** and **7** is that the methine protons couple not only with the germinal methyl protons ($^3J_{HH}$=3 Hz) but also with the phosphorus in the same ring through space (coupling through space), thus resulting in quartets of doublets although the coupling constants for the doublets are too small to be measured. These same observations have also been made in our previous work in connection with the ^{1}H-NMR spectra of **2** and **3**[6,20] Two ^{31}P signals at −10.57 and −12.73 ppm confirm the presence of two diastereotopic phosphine groups in **7**. An assignment of two signals can be readily made by simple comparison between the spectra of **6a** and **7**. Thus the signal at −10.57 ppm is due to the -($C_5H_4PCy_2$) group and provides a supporting evidence for the electron donating ability of the α-aminoethyl group.

The ^{1}H-NMR spectrum of **6b** shows some interesting features in that this compound exhibits not only all signals expected for the parent ferrocenylethylamine moiety but also a pair of broad signals at 6.47 and 2.90 ppm with the intensity ratio of 3 : 2 due to the η^1-C_5H_5 group on the phosphorus. This line broadning may be explained in terms of fluxional behavior of the Cp group, *i.e.*, site exchange of phosphorus around the η^1-C_5H_5 moiety. Cyclopentadiene derivatives containing the $P(CH_2)_nC_5H_5$(n=0-2) group have been the subject of intense research by a number of workers,[21-23] and to our knowledge, this is the second example next to $F_2P(C_5H_5)$[21] that has been found to be fluxional. This fluxional behavior is confirmed by the $^{31}P\{^1H\}$ NMR that shows four broad signals at 2.08, 0.07, −23.3, and −26.1 ppm indicating the presence of four major diastremeric isomers of **6b** as mentioned above. In addition to these signals, however, there also arises a second set of minor signals centered at 9.83, 7.25, −29.3, and −34.0 ppm in a similar fashion. This fact indicates the presence of (R,R,S)-**6b-1**, (R,R,R)-**6b-1**, (R,R,S)-**6b-2**, and (R,R,R)-**6b-2** that have been originally resulted from the monor(4%) diastereomeric intermediate, (R,S)-FALi

(see Scheme 2). An attempt to carry out more extensive variable temperature NMR studies was unsuccessful due to the low solubility of the compound at low temperatures, and neither did we make any attempt to assign each pair of signals to the corresponding isomer. All in all, there seem to be eight stereoisomers, thus making the solution nearly recemic. The reason for the existence minor diastereomeric pairs is that fractional crystallization to remove them could not be applied since both pairs were obtained as powders. The coordination chemistry of the ligands reported in this paper will be the subject of our future communication.

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References

1. (a) Department of Chemistry, Kyungpook National University; (b) Department of Chemistry, Youngnam University; (c) Department of Chemical Education, Hyosung University; (d) Department of Chemistry, Keimyung University.
2. M. Kumada, T. Hayashi, and K. Tamao, Fundamental Research in Homogeneous Catalysis, Plenum Press, New York, 1982, p. 175.
3. T. Hayashi and M. Kumada, *Acc. Chem. Res.*, 15, 395 (1982).
4. W. R. Cullen, F. W. B. Einstein, T. Jones, and T. J. Kim, *Organometallics*, **2**, 741 (1983).
5. W. R. Cullen, F. W. B. Einstein, T. Jones, and T. J. Kim, *Organomeatllics*, **4**, 346 (1985).
6. T. G. Appleton, W. R. Cullen, S. V. Evans, T. J. Kim, and J. Trotter, *J. Organomet. Chem.*, **279**, 5 (1985).
7. (a) T. J. Kim and K. C. Lee, *Bull. Korean Chem.*, **10**, 279 (1989). (b) T. J. Kim, K. H. Kwon, S. C. Kwon, J. O. Baeg, S. C. Shim, and D. H. Lee, *J. Organomet. Chem.*, **389**, 205 (1990).
8. T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, and K. Hirotsu, *J. Am. Chem. Soc.*, **106**, 158 (1984).
9. W. R. Cullen, S. V, Evans, N, F. Han, and J. Trotter, *Inorg. Chem.*, **26**, 514 (1987).
10. Y. Ito, M. Sawamura, and T. Hayashi, *J. Am. Chem.*, **108**, 6405 (1986).
11. Y. Ito, M. Sawamura, and T. Hayashi, *Tetrahedron Lett.*, **289**, 6215 (1987).
12. I. R. Butler, W. R. Cullen, T. J. Kim, F. W. B. Einstein, and T. Jones, *J. Chem. Soc., Chem. Commun.*, 719 (1984).
13. W. S. Knowles, *Acc. Chem. Res.*, **16**, 106 (1983).
14. T. J. Kim, *Bull. Korean Chem. Soc.*, **11**(2), 134 (1990).
15. D. D. Perin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals", 2nd ed., Pergamon Press, New York, 1980.
16. (a) D. Marquarding, H. Klusacek, G. Gokel, P. Hoffman, and I. Ugi, *J. Am. Chem. Soc.*, **92**, 5389 (1970); (b) G. Gokel and I. Ugi, *J. Chem. Educ.*, **49**, 294 (1972).
17. T. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merril, and J. C. Smart, *J. Organomet. Chem.*, **27**, 241 (1971).
18. D. Seyferth and H. P. Withers, Jr., *Organometallics*, **1**, 1275 (1982).
19. T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, M. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, Y. Yamamoto, and M. Kumada, *Bull. Chem. Soc. Jpn.*, **53**, 1138 (1980).
20. I. R. Butler, W. R. Cullen, F. W. B. Einstein, S. J. Rettig, and A. J. Willis, *Organometallics*, **2**, 128 (1983).
21. T. J. Kim, Ph. D. Dissertation, University of British Columbia, 1984.
22. J. E. Bentham, E. A. V. Ebsworth, H. Moretto, and D. W. H. Rankin, *Angew. Chem. Int. Ed. Engl.*, **11**, 640 (1972).
23. (a) F. Mathey and J. D. Lampin, *Tetrahedron* **31**, 2685 (1975); (b) F. Mathey and J. D. Lampin, *J. Organomet. Chem.*, **128**, 287 (1977); (c) C. Charrier and F. Mathey, *Tetrahedron Lett.*, **240**, 7 (1978); (d) C. Charrier and F. Mathey, *J. Organomet. Chem.*, **120**, C41 (1979); (e) S. G. Baxter, R. L. Collins, A. H. Cowley, and S. F. Sena, *Inorg. Chem.*, **22**, 3475. (1983).
24. I. R. Butler, W. R. Cullen, and S. J. Rettig, *Organometallics*, **6**, 872 (1987).