Synthesis of Chiral C_2-Symmetric Bisferrocenyldiamines. X-ray Crystal Structure of $Ru(2)Cl_2 \cdot 2CHCl_3$ (2 = *N*1,*N*2-Bis{(*R*)-1-[(*S*)-2-(diphenylphosphino)]ferrocenylethyl}-*N*1,*N*2-dimethyl-1,2-ethanediamine)

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A new class of chiral C_2-symmetrical bisferrocenyl diamines, *N*1,*N*2-bis[(*R*)-1-ferrocenylethyl]-*N*1,*N*2-dimethyl-1,2-ethanediamine (**1**) and *N*1,*N*2-bis{(*R*)-1-[(*S*)-2-(diphenylphosphino)]ferrocenylethyl}-*N*1,*N*2-dimethyl-1,2-ethanediamine (**2**), were prepared from the chiral template (*R*)-*N*,*N*-(dimethylamino)-1-ferrocenylethylamine ((*R*)-FA). Compound **1** was prepared from the reaction of (*R*)-FA with MeI followed by nucleophilic substitution with *N*,*N*′-dimethylethylenediamine, while **2** was formed from **1** via ortho lithiation followed by electrophilic substitution with chlorodiphenylphosphine. Compound **2** reacts with $Ru(DMSO)_4Cl_2$ to give *trans*-Ru(**2**)Cl_2 (**3**) in which the ligand is tetradentate. This complex crystallizes in the orthorhombic system: $P2_12_12_1$ (No. 19); $a = 11.7230(4)$ Å, $b = 16.5951(6)$ Å, $c = 27.853(1)$ Å; $Z = 4$; $R = 0.046$; $R_w = 0.104$. The geometry around the central metal is an octahedron with a pair of chlorine atoms trans to each other. This complex exhibits catalytic activity toward asymmetric cyclopropanation of some olefins and alkyl diazoacetates, giving enantioselectivity up to 95%.

Introduction

Since the pioneering work of Ugi and co-workers on the preparation and the resolution of *N*,*N*-dimethyl-1-ferrocenylethylamine (FA) and its derivatives nearly three decades ago,[1] 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.[2] Most of the chiral ferrocenes so far developed can be classified into two large groups: (i) 1,2-disubstituted planar-chiral monoferrocenes and (ii) C_2-symmetric chiral mono- or bisferrocenes. The syntheses of nearly all ligands belonging to the former group are based on Ugi's method that employs stereoselective ortho lithiation of FA followed by electrophilic substitution. These include aminophosphines,[3] diphosphines,[4] oxazolines,[5] pyrazoles,[6] hydroxyphosphines,[7] and hydroxyamines.[8] This method coupled with the fact that the ortho directing dimethylamine in FA can be exchanged by other nucleophiles in a stereoretentive S_N1-type[1a] reaction allows synthesis of further C_2-symmetric mono- and bisferrocene-based ligands such as amines,[9] diphosphines,[10] bisaminobisphosphines,[11] bisiminobisphosphines,[12] bisoxazolines,[13] and others.[14]

Most of these ligands have been tested with a great success in a number of asymmetric reactions such as hydrogenation,

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hydrosilylation, cross-coupling reactions, allylic substitution, aldol type condensation, cyclopropanation, and many others.[2,15]

Prompted by these observations and the fact that the C_2-symmetrical amines and diamines have great potential in asymmetric synthesis,[16] we have attempted the preparation of a new class of chiral C_2-symmetric bisferrocenylamine (**1**) and aminophosphine (**2**). Their synthesis, characterization, and the X-ray crystal structure of **3**·2$CHCl_3$ are presented in this paper. The catalytic activity of **3** for asymmetric cyclopropanation of some olefins with alkyl diazoesters has also been tested.

Experimental Section

General Information. All manipulations were carried out under an argon atmosphere using Schlenk techniques. Solvents were freshly distilled from sodium/benzophenone prior to use. Microanalyses were performed by The Center for Instrumental Analysis, Kyungpook National University. ^{1}H, ^{31}P NMR spectra were recorded on a Varian UNITY+ spectrometer operating at 300, 121.5 MHz, respectively. ^{1}H shifts are reported relative to internal TMS and ^{31}P shifts relative to 85% H_3PO_4. Mass spectra were obtained by using a Micromass QUATTRO II GC 8000 series model with electron energy of 20 or 70 eV and direct sample introduction. Optical rotations were determined using a JASCO model DIP-360 polarimeter. Melting points were determined using a Thomas-Hoover melting point apparatus and are not corrected.

Synthesis of 1. To a solution of 1,2−bis(methylamino)ethane (0.27 mL, 2.5 mmol) in 30 mL of dry acetonitrile were added K_2CO_3 (2.8 g, 20 mmol) and *(R)-N,N,N*-trimethyl-1-ferrocenylethylammonium iodide (2.1 g, 5.3 mmol), which was prepared by the literature method.[17] The solution was heated at 30 °C for 24 h with stirring. After cooling, K_2CO_3 was filtered off, the acetonitrile removed, and the yellow solid residue taken up in diethyl ether. The solution was washed with water (3 × 50 mL) to remove unreacted ferrocene quaternary ammonium salt, and the organic extracts were then dried over $MgSO_4$. Evaporation of the solvent left the crude product, which was recrystallized from acetone to give yellow-orange crystals. Yield: 1.2 g, 90%. Mp: 115 °C. $[\alpha]_D^{25} = -67$ ($c = 1.5$, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 1.39 (d, ^3J = 6.9 Hz, 6H, $-CH_3$), 2.03 (s, 6H, $-NCH_3$), 2.19 (m), 2.31 (m) (AA′BB′, 4H, $-CH_2$), 3.65 (q, ^3J = 6.9 Hz, 2H, −CH), 4.09 (s, 10H, C_5H_5), 4.13 (bs, 8H, C_5H_4). Anal. Calcd for $C_{28}H_{36}Fe_2N_2$: C, 65.64; H, 7.08; N, 5.46. Found: C, 65.33; H, 7.33; N, 5.42.

Synthesis of 2. To a solution of **1** (998.4 mg, 1.95 mmol) dissolved in THF (30 mL) in a Schlenk tube was added dropwise through a dropping−funnel 1.6 M *n*-BuLi (2.9 mL, 4.7 mmol) in hexane at −78 °C. After stirring 3 h as the tube gradually comes to room temperature, it was chilled again at −78 °C, to which was added dropwise a THF solution (10 mL) of Ph_2PCl (1.1 g, 4.9 mmol). The temperature was then raised gradually and the solution stirred for 10 h at room temperature. Following careful hydrolysis with aqueous sodium bicarbonate, the remaining reaction mixture was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane:CH_2Cl_2 = 90:10 (v/v)) and recrystallized from CH_2Cl_2/methanol to give a yellow solid. Yield: 1.0 g, 60%. Mp: 209 °C. $[\alpha]_D^{25} = -302$ ($c = 1.5$, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 1.08 (d, ^3J = 6.3 Hz, 6H, $-CH_3$), 1.51 (s, 6H, $-NCH_3$), 1.46 (m) and 1.82 (m) (AA′XX′, 4H, $-CH_2$), 3.78 (bs), 4.19 (bs), and 4.27 (bs) (ABC, 6H, C_5H_3), 3.92 (s, 10H, C_5H_5), 4.07 (q, ^3J = 6.3 Hz, 2H, −CH), 7.15−7.58 (m, 20H, Ph). ^{31}P NMR ($CDCl_3$): −23.35. Anal. Calcd for $C_{52}H_{54}Fe_2N_2P_2$: C, 70.92; H, 6.18; N, 3.18. Found: C, 70.67; H, 6.41; N, 3.17.

Table 1. Bond Lengths [Å] and Angles [deg] for **3**·2$CHCl_3$

Ru−P(1)	2.301(1)	C(3)−N(2)	1.474(7)
Ru−P(2)	2.313(1)	N(2)−C(7)	1.495(7)
Ru−N(2)	2.333(4)	N(2)−C(4)	1.517(7)
Ru−N(1)	2.374(4)	C(4)−C(31)	1.493(8)
Ru−Cl(2)	2.405(1)	C(4)−C(8)	1.538(8)
Ru−Cl(1)	2.415(1)	C(12)−P(1)	1.835(5)
C(1)−N(1)	1.497(8)	C(32)−P(2)	1.832(5)
C(1)−C(11)	1.523(7)	P(1)−C(51)	1.849(5)
C(1)−C(5)	1.536(7)	P(1)−C(61)	1.852(5)
N(1)−C(6)	1.479(7)	P(2)−C(71)	1.843(6)
N(1)−C(2)	1.495(7)	P(2)−C(81)	1.862(5)
C(2)−C(3)	1.508(8)		
P(1)−Ru−P(2)	98.02(5)	N(2)−Ru−Cl(2)	86.2(1)
P(1)−Ru−N(2)	170.6(1)	N(1)−Ru−Cl(2)	86.9(1)
P(2)−Ru−N(2)	91.4(1)	P(1)−Ru−Cl(1)	91.45(5)
P(1)−Ru−N(1)	90.4(1)	P(2)−Ru−Cl(1)	92.51(5)
P(2)−Ru−N(1)	171.5(1)	N(2)−Ru−Cl(1)	88.6(1)
N(2)−Ru−N(1)	80.2(2)	N(1)−Ru−Cl(1)	87.3(1)
P(1)−Ru−Cl(2)	92.88(5)	Cl(2)−Ru−Cl(1)	172.77(5)
P(2)−Ru−Cl(2)	92.61(5)		

Table 2. Crystal Data and Structure Refinement for **3**·2$CHCl_3$

$C_{52}H_{54}Cl_2Fe_2N_2P_2Ru$·2$CHCl_3$	1291.32
$a = 11.7230(4)$ Å	$P2_12_12_1$ (No. 19)
$b = 16.5951(6)$ Å	$T = -85$ °C
$c = 27.853(1)$ Å	$\lambda = 0.710\ 73$ Å
$\rho_{calcd} = 1.583$ g/cm^3	$\mu = 12.96$ cm^{-1}
$V = 5418.6(3)$ Å^3	$R(F_o2) = 0.046^a$
$Z = 4$	$R_w(F_o2) = 0.104^b$

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum_w(F_o^2 - F_c^2)^2/\sum_w(F_o^2)^2]^{1/2}$.

Synthesis of 3. A solution of **2** (0.17 g, 0.2 mmol) and *trans*−Ru(DMSO)$_4$Cl$_2$[18] (0.1 g, 0.2 mmol) in toluene (15 mL) was stirred at 110 °C for 18 h, after which time the crude product was passed through a short silica gel column with CH_2Cl_2 to remove any solid impurities. The red solid remaining after the removal of the solvent was dissolved in $CHCl_3$/isooctane (1:3, v/v) to give red crystals on cooling in a refrigerator. Yield: 87%. ^{1}H NMR ($CDCl_3$): 1.47 (d, ^3J = 6.3 Hz, 6H, $-CH_3$), 2.33 (bd), 3.45 (bd) (A_2X_2, J = 9.3 Hz, 4H, $-CH_2$), 2.41 (s, 6H, $-NCH_3$), 3.39 (s, 10H, C_5H_5), 3.92 (bs), 4.12 (bs), and 4.31 (bs) (ABC, 6H, C_5H_3), 6.15 (q, ^3J = 6.3 Hz, 2H, −CH), 6.92−7.86 (m, 20H, Ph). ^{31}P NMR ($CDCl_3$): 38.55.

X-ray Structure Determination of 3·2CHCl$_3$. One of the X-ray quality single crystals, 0.30 × 0.20 × 0.20 mm, was mounted on a Siemens Smart system equipped a CCD area detector and a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.710\ 73$ Å) at −85 °C. The final cell parameters and specific data collection parameters are summarized in Table 2. A total of 9236 independent reflections were obtained after Lorentz and polarization correction. An empirical absorption correction was applied using SADABS[19] based on equivalent reflections(T_{max}/T_{min} = 1.00/0.75). The structure was determined by direct methods and refined by full-matrix least-squares on F^2 using SHELX-97.[20] All non-hydrogen atoms were refined anisotropically except the two disordered carbon atoms at one of the two unsubstituted Cp rings, which were refined isotropically with half occupancies. All hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms ($B_{iso} = 1.2B_{eq}$). The final refinement with 620 parameters gave error indices of R1 = 0.046 and wR2 = 0.104. The final difference Fourier map revealed that a couple of peaks had heights of 1.26 e/Å^3.

Catalytic Cyclopropanation. Complex **3** (50.0 mg, 5.0 × 10^{-2} mmol) was dissolved in 10 mL of 1,2-dichloroethane, and 10 equiv of the olefin was added. Diazoester (2.5 mmol) was diluted in 10 mL of

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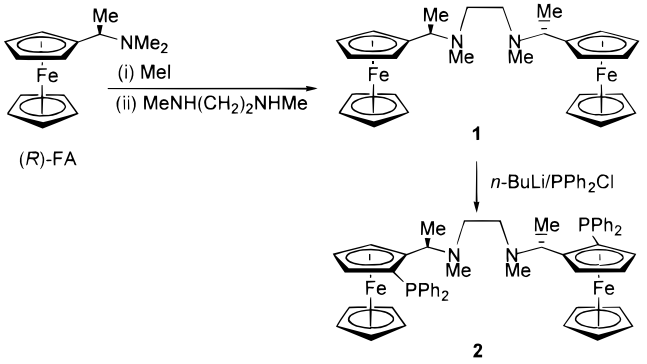
Scheme 1



1,2-dichloroethane and added slowly (12 h) with a syringe pump to the [Ru]−olefin mixture, which was under reflux. After the addition was completed, the solvent and excess olefin were removed under vacuum. The oily residue was passed through a short silica gel column to remove catalyst using a 95:5 hexanes/EtOAc mixture as an eluent. The cis- and trans-diastereomers and enantiomers were separated by chiral GC (column Astect B-DA & G-TA; oven temp 120 °C; injection temp 230 °C; detection temp 250 °C; column head pressure 52 kpa; flow rate 0.4 mL/min; split ratio −1).

Results and Discussion

Synthesis and Characterization. The synthetic strategy and reaction conditions adopted in this work are described in Scheme 1. The resolution of FA with L-*(+)*-tartaric acid is achieved using the well-known Ugi's procedure from which both antipodes are obtained.[1]

The preparation of bisferrocenyldiamine, **1**, is quite straightforward simply by taking advantage of the fact that FA with a suitable leaving group such as trimethylammonium or acetate in the α-position undergoes nucleophilic substitution of S_N1-type with complete retention of configuration as mentioned above. Thus, treatment of a 2-fold excess of *(R)-N,N,N*-trimethy-1-ferrocenylethylammonium iodide with 1,2-bis(methylamino)-ethane in the presence of anhydrous K_2CO_3 in acetonitrile resulted in **1**. Here it is worth noting that employment of K_2-CO_3 into the reaction mixture is essential to ensure maximum product yields.[17] Lithiation with *n*-BuLi of **1** followed by electrophilic substitution with $ClPPh_2$ resulted in the formation **2**. Here the first (*R*) designates the carbon central chirality originating from (*R*)-FA, and the second (*S*) designates the ferrocene planar chirality generated at the stereoselective lithiation.

The structural characterization of these new compounds was performed by elemental analysis, NMR(^{1}H, ^{31}P) spectroscopy, and mass spectrometry. The ^{1}H NMR patterns of **1** and **2** are straightforward and reveal the signals expected from their structures. The presence of the electrophile PPh_2 in **2** does not alter significantly the NMR patterns of the FA moiety.

The reaction of **2** with $Ru(DMSO)_4Cl_2$ yielded the complex **3**. Figure 1 presents an ORTEP[21] drawing and atomic labeling scheme for **3**.

The geometry of the complex is a distorted octahedron. The ligand occupies a square plane in a tetradentate manner with two chloride ligands being trans to each other. The angle of Cl(1)−Ru−Cl(2) is almost linear, 172.78(5)°. The four atoms P(1), P(2), N(2), and N(1) are nearly in a plane with less than 0.005(2) Å deviations. The Ru atom is located on the plane. The ring conformation for the 1,2-bis(methylamino)ethane fragment of the ligand is δ in the solid state. Ru−P(1) and Ru−P(2) distances are 2.301(1) and 2.313(1) Å and Ru−Cl(1) and Ru−Cl(2) distances are 2.415(1) and 2.405(1) Å, which are comparable to the distances observed in the *trans*-$RuCl_2$ complex of *N,N′*-bis[*o*-(diphenylphosphino)benzyl]cyclohexane-1,2-diamine.[22] However, Ru−N(1) and Ru−N(2) [2.374(4) and 2.333(4) Å] are longer than those in the literature compound, which results from the aminoalkyl groups at the Cp rings instead of those at phenyl rings in the complex. Selected bond distances and angles are reported in Table 1.

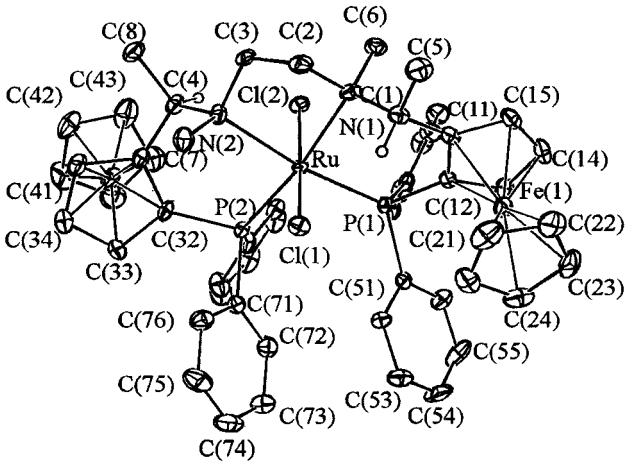


Figure 1. ORTEP drawing of **3**. The atoms are represented by 40% probability thermal ellipsoids.

Catalysis. Asymmetric cyclopropanation of olefins with alkyl diazoacetates catalyzed by chiral transition metal complexes is well-established, and as such a great number of catalysts are known. Palladium-, rhodium-, and copper-based systems incorporating chiral diamine bases such as salicylaldehydes, oxazolines, semicorrins, and polypyrazoles are among the most efficient with regard to both yields and enantioselectivity.[23,24] In comparison, however, only a limited number of examples are available for asymmetric Ru catalysis.[25]

We now wish to report results that show that our Ru complex (**3**) is an efficient catalyst for the asymmetric cyclopropanation under the standard set of reaction conditions (eq 1).

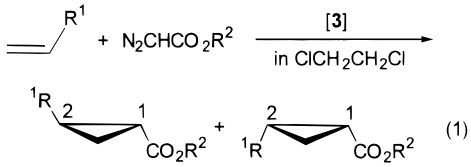


Table 3 shows the results of cyclopropanation of a variety of olefins. Good to high diastereoselectivity as well as enantio-

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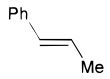
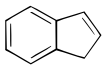
Table 3. Asymmetric Cyclopropanation of Olefins and Diazoesters with **3**[a]

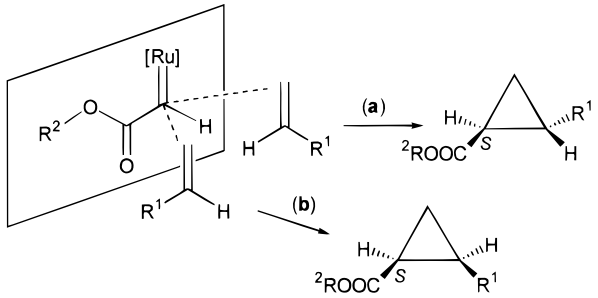
Olefin	Diazoester[b]	Yield(%)	*Trans*:*Cis*[c]	% ee[d] (*trans/cis*)
	EDA	73	66:34	72/74
	EDA	71	68:32	87/79
	BDA	66	93:7	87/84
	EDA	65	-	81
	EDA	67	70:30	64/60
	BDA	51	98:2	82/55
	EDA	75	72:28	89/75
	BDA	50	98:2	95/82

[a] Yields are isolated ones based on diazoester. [b] EDA: R^2 = Et. BDA: R^2 = 2,6-di-^{t}Bu-4-methylphenyl in $N_2CHCO_2R^2$. [c] The trans/cis ratio was determined by ^{1}H NMR and GC analysis. [d] The % ee's were determined by chiral capillary GLPC (column: Astec B-DA & G-TA, 30 m) with corresponding methyl ester on a Shimadzu GC-17A instrument. Absolute configurations for products: *trans*-(1*S*,2*S*)/*cis*-(1*S*,2*R*) from styrene and *trans*-β-methylstyrene; *trans*-(1*S*,2*R*)/*cis*-(1*S*,2*S*) from 1-hexene; (1*S*) from 1,1-diphenylethene; unknown from indene.

selectivity is observed regardless of the type of olefins. In particular, the extremely high trans-selectivity (98:2) and enantioselectivity (95% ee) from the reaction of indene with 2,6-di-*tert*-butyl-4-methylphenyl diazoacetate (BDA) is quite impressive. These results are comparable to those obtained by others employing the well-known chiral oxazoline ligands incorporated in copper, rhodium,[23,24] or ruthenium.[25a]

Comparative studies show that both diastereo- and enantioselectivity increase with increase in the steric congestion in the diazoacetate. These observations may be explained by the ability of the hypothetical Ru-carbene intermediate to discriminate between the two enantiotopic faces of the olefin as shown in Scheme 2. According to this scheme, as the size of substituent

Scheme 2



(R^2) in the diazoacetate increases, the olefin should approach the Ru-carbene in an anti-fashion (route a), leading to the formation of a trans-isomer. The scheme may also explain the creation of absolute configuration of 1*S* in the cyclopropanated products from styrene, 1-hexene, 1,1-diphenylethene, and *trans*-β-methylstyrene if these olefins are supposed to approach from the less hindered face of the Ru-carbene intermdediate.

We were unable to determine the absolute configuration of the product obtained from indene due to the lack of reference in the literature.

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Supporting Information Available: X-ray crystallographic files in CIF format for the complex **3**·2$CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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