Chiral C_2-Symmetric α- and ω-Diimines with Bulky Substituents at Nitrogen: Synthesis and Catalytic Properties of Some Copper Complexes

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Two new C_2-symmetric chiral α- and ω-Diimines incorporating bulky ferrocenylethylamine and their copper(I) complexes have been synthesized and characterized by analytical and various spectroscopic techniques. The catalytic activities of these complexes have been tested in the asymmetric cyclopropanation of a series of olefins with some diazoacetates to achieve varying degree of dia- and enantio-selectivities depending on the nature of the ligand, the substrates, and the reagents. Some mechanistic implication has been made with regard to the interactions among all these chemical species.

Keywords : Chiral ferrocenes, Diimines, Copper catalyst, Cyclopropanation.

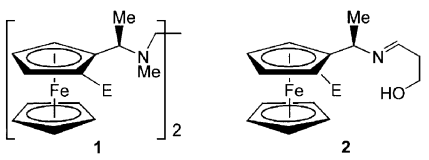
Introduction

The chelating α- or β-diimine ligands are now well-known to stablize organometallic comlexes[1] and have thus been widely employed in a number of catalytic reactions.[2] The recent resurgence of interest in this type of ligands incorporating bulky substituents at nitrogen stems from the observations that their late transition metal complexes are efficient catalysts for the polymerization of α-olefins and functionalized olefins under moderate conditions. Most notable are Brookhart's cationic Ni(II)- and Pd(II)-based catalysts of the type

$\{[ArN = C(R)C(R) = NAr]M\text{-}CH_3\}^+$ (Ar = 2,6-C_6H_3-$^iPr_2$), in which the metal center is efficiently shielded from associative displacement by bulky substituents on the diimine ligands.[2b,3]

In this regard, it is worth noting that replacement of the aromatic moieties in the diimine ligand with other bulky substituents such as ferrocene (or its derivatives) would provide essentially the same degree of steric influence. Further, these ferrocene groups may carry chirality thus making asymmetric catalysis feasible. The design and the synthesis of ferrocenes with various chirality are well-established, and consequently there are now available a great number of chiral ferrocenes.[4]

We have recently demonstrated the successful use of chiral C_2-symetric bisferrocenyl diamines such as **1** and a ferrocene-based Schiff base such as **2** in asymmetric catalytic reactions by achieving high enantiomeric excesses (Chart 1).[5,6]



1 **2**

E = H; $SiMe_3$; CH_2OH; PPh_2.

Chart 1

Prompted by our own success and motivated by the facts that various structural modification can be possible in the chelating α- or β-diimine ligands by employment of chiral ferrocenyl groups, we have decided to examine the related diimine analogues such as **3** and **4** as a potential source of chiral ligand in asymmetric cyclopropanation of olefins with diazoacetates.

Asymmetric cyclopropanation of olefins with diazoacetates catalyzed by chiral transition metal complexes is well-established, and as such a great number of catalysts are known. Palladium-, rhodium-, ruthenium-, and copper-based systems incorporating chiral dinitrogen bases such as salicylaldehydes, oxazolines, semicorrins, and polypyrazoles are among the most efficient with regard to both yields and enantioselectivity.[7,8] It would be thus desirable to compare the effectiveness of our new ligands **3** and **4** with the well-known nitrogen-based ligands in the same reaction. The work described in this paper deals with the synthesis, characterization, and catalytic application of these ferrocene-based diimines.

Experimental Section

Reagents and Instruments. All manipulations were carried out under an atmosphere of argon or nitrogen using a double manifold vacuum system and Schlenk techniques. Solvents were purified by standard methods and were freshly distilled prior to use. The progress of catalytic reaction was monitored using a GC-17A series equipped with a split mode capillary system, Shimadzu CR-3A data processor, and a flame ionization detector. Melting point was measured using an electrothermal model IA 9100 digital melting point apparatus. Microanalyses were performed by the Center for Instrumental Analysis, Kyungpook National University. ^{1}H NMR spectra were recorded on a Varian Unity Inova 300 WB Spectrometer and a Bruker Advance 400 Spectrometer. ^{1}H chemical shift were reported relative to internal TMS. Elemental analyses were conducted by using a Fisons EA 1108 model. Mass spectra were obtained

using a Micromass QUATTRO II GC8000 series model with electron energy of 20 or 70 eV. High resolution mass spectrometry (HRMS) was measured using a JMS 700 model. Optical rotations were measured on a JASCO DIP-370 digital polarimeter at ambient temperature.

Ethyl Diazoacetate (EDA),[9] *t*-Butyl Diazoacetate (*t*BDA),[10] and *l*-Menthyl Diazoacetate (MDA)[11] were prepared according to the literature methods.

Preparation of 3. A mixture of (*S*)-1-Ferrocenylethylamine (1.00 g; 4.36 mmol) and glyoxal (40% in water, 0.25 mL; 2.18 mmol) in ethanol (20 mL) was stirred in the presence of molecular sieves (2 g) at RT for 3 h. The solvent was removed under a reduced pressure and the oily residue was taken up in a minimum amount of dichloromethane to be chromatographed on silica gel with a mixture of hexane and diethyl ether (9 : 1) as an eluent. The product was obtained as dark brown crystals after crystallization from dichloromethane and hexane (720 mg, 72%). mp 78-80 °C. $[\alpha]_D^{20}$ = +27.8 (c = 0.01, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.53 (d, 6H, CH$\underline{CH_3}$), 4.13 (s, 10H, C_5H_5), 4.04-4.34 (AB quartet, 8H, C_5H_4), 4.32 (q, 2H, $\underline{CH}CH_3$), 7.95 (s, 2H, N=CH). Anal. Calcd for $C_{26}H_{28}FeN_2$: C, 65.04; H, 5.84; N, 5.84. Found: C, 64.80; H, 5.76; N, 6.04.

Preparation of 4. A mixture of (*S*)-1-Ferrocenylethylamine (1.00 g; 4.36 mmol) and ferrocene-1,1'-dicarboxaldehyde (0.53 g, 2.18 mmol) in ethanol (15 mL) was stirred in the presence of some molecular sieve at RT for 3 h. Following the procedure described for the synthesis of **3**, the product was obtained as brown crystals after recrystallization from dichloromethane and hexane after usual workups (440 mg, 44%). mp 159-161 °C. $[\alpha]_D^{20}$ = +197 (c = 0.001, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.55 (d, 6H, CH$\underline{CH_3}$), 4.14-4.21 (AB quartet, 8H, C_5H_4), 4.17 (s, 10H, C_5H_5), 4.32-4.57 (AB quartet, 8H, C_5H_4), 8.04 (s, 2H, N=CH). Anal. Calcd for $C_{36}H_{36}Fe_3N_2$: C, 65.09; H, 5.46; N, 4.22. Found: C, 65.66; H, 5.58; N, 4.19. HRMS (EI, *m/z*): 664.0919 (calc. 664.0927).

Preparation of 5. To a solution of 1-ferrocenylethylamine (5.00 g; 21.8 mmol) in ethanol (30 mL) was added 2,4-Pentanedione (2.24 mL; 21.8 mmol). The reaction mixture was stirred at RT for 3 h. The solvent was removed under reduced pressure, and the residue purified by column chromatography on silica gel with a mixture of hexane and diethyl ether (9 : 1) as an eluent. The product was obtained as a deep red oil (3.70 g, 74%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.52 (d, 3H, CH$\underline{CH_3}$), 1.99 (s, 3H, HN=C$\underline{CH_3}$), 2.05 (s, 3H, $\underline{CH_3}$CO), 4.08-4.15 (AB quartet, 4H, C_5H_4), 4.27 (s, 5H, C_5H_5), 4.39 (q, 1H, $CH_3\underline{CH}$), 4.97 (s, 1H, HN=CMe$\underline{CH}$), 11.08 (d, 1H, NH). ^{17}O NMR ($CDCl_3$, 500 MHz): δ 408.33 (COMe). Anal. Calcd for $C_{17}H_{21}FeNO$: C, 65.61; H, 6.80; N, 4.50. Found: C, 65.76; H, 6.92; N, 4.38. MS *m/z* (relative intensity): 311 (100, M^+), 213 (97).

Preparation of [Cu(3)]OTf. To a solution of $[Cu(OTf)]_2$-C_6H_6 (0.53 g, 1.05 mmol) in 1,2-dichloroethane (5 mL) was added dropwise a solution of **3** (1.00 g, 2.10 mmol) in 1,2-dichloroethane (5 mL). The solution was stirred for 3 h, after which any solid impurities were removed by filtration, the solvent removed under vacuum, and the residue washed with diethyl ether to remove excess ligand. The product was obtained as dark brown crystals after crystallization from dichloromethane and hexane (yield 82%). mp 90-92 °C. Anal. Calcd for $C_{27}H_{28}Fe_2N_2CuF_3SO_3$: C, 46.81; H, 4.07; N, 4.04. Found: C, 46.49; H, 4.44; N, 3.62. HRMS (EI, *m/z*): 875.9743 (calc. 875.9749).

Preparation of [Cu(4)]OTf. The reaction of Cu(OTf) with **4** under the conditions described above gave the title compound as brown crystals after crystallization from dichloromethane and hexane (yield 91%). mp 130-132 °C. Anal. Calcd for $C_{36}H_{36}Fe_3N_2$: C, 65.09; H, 5.46; N, 4.22. Found: C, 65.66; H, 5.58; N, 4.19. HRMS (EI, *m/z*): 664.0919 (calc. 664.0927).

Typical procedure for asymmetric cyclopropanation. To a solution of catalyst precursor (0.05 mmol) in 1,2-dichloroethane (10 mL) was added a ten molar excess of substrate, followed by dropwise addition of a diazoacetate (2.5 mmol) in 1,2-dichloroethane (10 mL) over 15 h with a syringe pump. The mixture was filtered through a short silica gel column, and the filtrate was concentrated in vacuo to leave an amber oil which was chromatographed on silica gel with hexane/ethyl acetate (92 : 8) to separate *trans*- and *cis*-cyclopropanated products. The ratio of the *trans*- and *cis*-products was determined by GC of the oil before chromatography with CBP-10 on a Schimadzu GC-17A. The enantiomeric excess (% ee) was determined by either chiral GC with ASTEC G-TA, B-DH, B-PH, or HPLC with Chiralcel OJ. The absolute configuration of enantiomers was determined by comparison of their specific rotation with the reported one.

The reaction of styrene with EDA. Isolated yield: 96%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.96 (t, *J* = 7.35, 3H, CH_3), 1.25-1.35 (m, 2H, CH_2), 1.27 (t, *J* = 7.2 Hz, 3H, CH_3), 1.56-1.62 (m, 1H, *trans*-CH), 1.68-1.74 (m, 1H, *cis*-CH), 1.86-2.16 (m, 1H, CH), 2.48-2.58 (m, 1H, CH), 3.87 (q, *J* = 7.1 Hz, 2H, *cis* -CH_2O), 4.15 (q, *J* = 7.1 Hz, *trans*-CH_2O), 7.08-7.30 (m, 5H, C_6H_5). MS *m/z* (relative intensity): 190 (M^+, 27), 162 (6), 144 (25), 133 (11), 117 (100), 116 (78), 106 (7), 91 (18), 65 (6), 52 (8). GC (CBP-10) conditions for diastereomeric separation:[12] t_R(*cis*), 30.27 min; t_R(*trans*), 32.12 min; oven temp., 70 °C; injection temp., 150 °C; initial time, 2 min; final temp., 230 °C; rate, 3 °C/min; detection temp., 250 °C; column pressure, 100 kPa. HPLC conditions for enantiomeric separation: t_R(*trans*), 7.43 (1*R*, 2*R*) and 9.70 (1*S*, 2*S*) min; t_R(*cis*), 12.96 (1*S*, 2*R*) and 17.93 (1*R*, 2*S*) min; eluent, 2.0% i-PrOH/hexane; flow rate, 1.0 mL/min; λ, 238nm.

The reaction of 1-hexene with EDA. Isolated yield: 85%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.66-0.69 (m, 2H, CH_2), 0.85-0.94 (m, 9H, $(CH_2)_3CH_3$), 0.95-1.02 (m, 2H, CH_2), 1.23-1.37 (m, 1H, CH), 1.26 (t, *J* = 7.2 Hz, 3H, CH_3), 1.41-1.56 (m, 1H, t*rans*-CH), 1.62-1.69 (m, 1H, *cis*-CH), 4.12 (q, *J* = 7.1 Hz, 2H, CH_2O). MS *m/z* (relative intensity): 170 (M^+, 0.3), 155 (0.6), 141 (2), 128 (10), 125 (18), 115 (3), 101 (31), 82 (30), 73 (60), 55 (100). GC (B-PH) conditions for diastereomeric separation:[13] t_R(*cis*), 5.46 min; t_R(*trans*), 5.88

min; oven temp., 120 °C; injection temp., 230 °C; initial time, 2 min; final temp., 200 °C; rate, 2 °C/min; detection temp., 270 °C; column pressure, 100 kPa. GC (B-PH) conditions for enantiomeric separation: t_R(*cis*), 13.54 (1*R*, 2*S*) and 13.56 (1*S*, 2*R*) min; t_R(*trans*), 14.86 (1*R*, 2*R*) and 15.13 (1*S*, 2*S*) min; oven temp., 70 °C; injection temp., 150 °C; initial time, 7 min; final temp., 180 °C; rate, 1.5 °C/min; detection temp., 250 °C; column pressure, 100 kPa after exchange of the ethyl group with the *t*-butyl group using 1.5 KO^{t}Bu in THF under reflux for 5 h.

The reaction of triethylvinylsilane with EDA. Isolated yield: 70%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.34-0.39, 0.73-0.79, 1.49-1.52 (3m, 1H, CH), 0.46-0.54 (q, 6H, ($\underline{CH_2}CH_3)_3$), 0.92-0.98 (t, 9H, ($CH_2\underline{CH_3}$)$_3$), 1.17-1.34 (m, 2H, $\underline{CH_2}CH_3$), 1.28 (t, 3H, $CH_2\underline{CH_3}$), 4.15 (q, J = 7.2 Hz, *cis*-CH_2O), 4.25 (q, J = 7.2 Hz, *trans*-CH_2O). MS *m/z* (relative intensity): 228 (M^+, 3), 199 (100), 171 (15), 75 (55), 55 (7). GC (CBP-10) conditions for diastereomeric separation: t_R(*cis*), 26.42 min; t_R(*trans*), 27.29 min; oven temp., 70 °C; injection temp., 150 °C; initial time, 2 min; final temp., 230 °C; rate, 3 °C/min; detection temp., 270 °C; column pressure, 100 kPa. GC (B-PH) conditions for enantiomeric separation:[14] t_R(*cis*), 20.07 (1*R*, 2*S*) and 20.29 (1*S*, 2*R*) min; t_R(*trans*), 20.77 (1*R*, 2*R*) and 21.20 (1*S*, 2*S*) min; oven temp., 70 °C; injection temp., 140 °C; initial time, 2 min; final temp, 250 °C; rate, 2 °C/min; detection temp., 250 °C; column pressure, 100 kPa.

The reaction of 1,1'-diphenylethylene with EDA. Isolated yield: 43%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.99 (t, J = 7.35, 3H, CH_3), 1.29-1.36 (m, 2H, CH_2), 1.31 (t, J = 7.2 Hz, 3H, CH_3), 2.17 (t, J = 5.4 Hz, 1H, CH), 3.86 (q, J = 7.1 Hz, 2H, *cis*-CH_2O), 4.17 (q, J = 7.1 Hz, 2H, *trans*-CH_2O), 7.11-7.35 (m, 10H, C_6H_5). MS *m/z* (relative intensity): 266 (M^+, 2), 237 (19), 221 (8), 192 (100), 178 (29), 165 (36), 152 (8), 115 (96), 105 (71), 91 (33). 77 (62), 51 (30). HPLC (Chiralcel OJ) conditions for enantiomeric separation:[15] t_R, 5.15 (*R*) min and 10.35 (*S*) min; eluent, 5.0% i-PrOH/hexane; flow rate, 2.0 mL/min; λ, 238 nm.

The reaction of styrene with ^{t}BDA. Isolated yield: 92%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.15, 1.49 (2s, 9H, $C(CH_3)_3$), 1.22-1.61 (m, 2H, CH_2), 1.82-1.88, 1.99-2.04 (2m, 1H, CH), 2.42-2.49, 2.51-2.59 (2m, 1H, CH), 7.10-7.32 (m, 5H, C_6H_5). MS *m/z* (relative intensity): 218 (M^+, 1), 145 (62), 117 (100), 91 (30), 57 (64). GC (CBP-10) conditions for diastereomeric separation: t_R(*cis*), 18.12 min; t_R(*trans*), 20.26 min; oven temp., 120 °C; injection temp., 230 °C; initial time, 2 min; final temp, 200 °C; rate, 2 °C/min; detection temp., 270 °C; column pressure, 100 kPa. GC (G-TA) conditions for enantiomeric separation:[12] t_R(*trans*), 11.09 (1*R*, 2*S*) and 12.11 (1*S*, 2*R*) min; t_R(*cis*), 12.18 (1*R*, 2*R*) and 12.23 (1*S*, 2*S*) min; oven temp., 120 °C; injection temp., 230 °C; initial time, 2 min; final temp., 200 °C; rate, 5 °C/min; detection temp., 250 °C; column pressure, 52 kPa.

The reaction of 1-hexene with ^{t}BDA. Isolated yield: 57%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.87-0.91 (m, 2H, CH_2), 1.06-1.07 (m, 1H, CH), 1.23-1.35 (m, 9H, $(CH_2)_3CH_3$), 1.44 (s, 9H, $(CH_3)_3$), 1.50-1.51 (m, 1H, *trans*-CH), 1.54-1.54 (m, 1H, *cis*-CH). MS *m/z* (relative intensity): 198 (M^+, 0.01), 183 (1), 142 (64), 125 (73), 100 (58), 79 (3), 57 (100). GC (CBP-10) conditions for diastereomeric separation: t_R(*cis*), 6.54 min; t_R(*trans*), 6.74 min; oven temp., 120 °C; injection temp., 230 °C; initial time, 2 min; final temp., 200 °C; rate, 2 °C/min; detection temp., 270 °C; column pressure, 100 kPa. GC (B-DA) conditions for enantiomeric separation:[13] t_R (*trans*), 10.12 (1*R*, 2*R*) and 10.33 (1*S*, 2*S*) min; oven temp., 120 °C; injection temp., 230 °C; initial time, 2 min; final temp., 200 °C; rate, 5 °C/min; detection temp., 250 °C; column pressure, 52 kPa.

The reaction of triethylvinylsilane with ^{t}BDA. Isolated yield: 60%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.45-0.53 (q, 6H, ($\underline{CH_2}CH_3)_3$), 0.59-0.61 (m, 2H, CH_2), 0.68-0.71, 1.11-1.15 (2m, 1H, CH), 0.92-0.97 (t, 9H, ($CH_2\underline{CH_3}$)$_3$), 1.44 (s, 9H, $(CH_3)_3$). MS *m/z* (relative intensity): 256 (M^+, 0.6), 200 (12), 171 (100), 127 (11), 75 (76), 53 (2). GC (CBP10) conditions for diastereomeric separation: t_R(*cis*), 15.02 min; t_R(*trans*), 15.99 min; oven temp., 120 °C; injection temp., 230 °C; initial time, 2 min; final temp., 200 °C; rate, 2 °C/min; detection temp., 270 °C; column pressure, 100 kPa. GC (B-PH) conditions for enantiomeric separation: t_R(*trans*), 11.92 (1*R*, 2*R*) and 12.03 (1*S*, 2*S*) min; t_R(*cis*), 12.70 (1*S*, 2*S*) and 14.48 (1*R*, 2*S*) min; oven temp., 120 °C; injection temp., 230 °C; initial time, 2 min; final temp, 200 °C; rate, 5 °C/min; detection temp., 270 °C; column pressure, 52 kPa.

The reaction of 1,1'-diphenylethylene with ^{t}BDA. Isolated yield: 58%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.11 (s, 9H, $C(CH_3)_3$), 1.36-1.42 (m, 1H, CH_2), 1.99-2.02 (m, 1H, CH_2), 2.34-2.38 (m, 1H, CH), 7.04-7.29 (m, 10H, C_6H_5). MS *m/z* (relative intensity): 294 (M^+, 0.4), 238 (96), 193 (100), 115 (82), 91 (25), 57 (41). HPLC (chiralcel OJ) conditions for enantiomeric separation:[15] t_R, 4.98 (*R*) min and 6.02 (*S*) min; eluent, 5.0% i-PrOH/hexane; flow rate, 2.0 mL/min; λ, 238 nm.

The reaction of styrene with MDA. Isolated yield: 94%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.47-2.10 (m, 21H), 2.48-2.61 (m, 1H, CH), 4.42, 4.73 (2td, J = 10.90, 4.35 Hz, 1H, CH), 7.11-7.33 (m, 5H, C_6H_5). MS *m/z* (relative intensity): 299 (M^+, 30), 255 (100), 197 (39), 165 (22), 121 (33), 91 (6), 59 (4). GC (CBP-10) conditions for enantiomeric separation:[11,12] t_R(*cis*), 34.68 (1*S*, 2*R*) and 35.14 (1*R*, 2*S*) min; t_R(*trans*), 36.94 (1*R*, 2*R*) and 37.71 (1*S*, 2*S*) min; oven temp., 150 °C; injection temp., 240 °C; initial time, 2 min; final temp., 230 °C; rate, 2 °C/min; detection temp., 270 °C; column pressure, 100 kPa.

The reaction of 1-hexene with MDA. Isolated yield: 60%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.89-0.93 (m, 9H, $(CH_2)_3CH_3$), 0.67-1.99 (m, 21H), 1.02-1.05, 1.07-1.12 (2m, 1H, CH). MS *m/z* (relative intensity): 281 (M^+, 1), 241 (37), 201 (8), 171 (100), 138 (80), 75 (46), 53 (3). GC (CBP-10) conditions for diastereomeric separation: t_R(*cis*), 19.90 min; t_R(*trans*), 20.79 min; oven temp., 150 °C; injection temp., 240 °C; initial time, 2 min; final temp, 230 °C; rate, 2 °C/min; detection temp., 270 °C; column pressure, 100 kPa. GC (B-PH) conditions for enantiomeric separation:[8g,16] t_R(*cis*), 21.16 (1*R*, 2*S*) and 21.41 (1*S*, 2*R*) min; t_R(*trans*), 23.04 (1*R*, 2*R*) and 23.21 (1*S*, 2*S*) min; oven temp., 120 °C; injection

temp., 240 °C; initial time, 2 min; final temp., 200 °C; rate, 1.5 °C/min; detection temp., 250 °C; column press, 100 kPa.

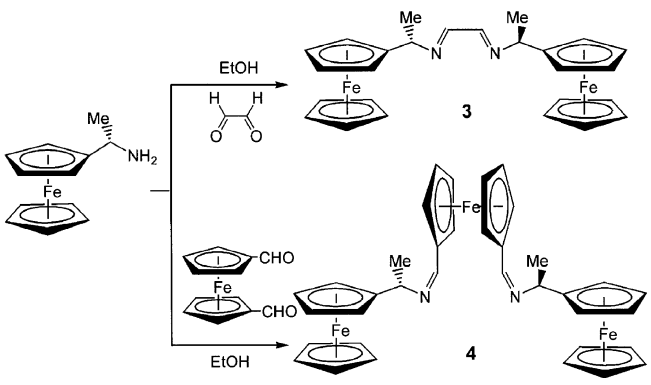
The reaction of triethylvinylsilane with MDA. Isolated yield: 83%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.28-0.32, 0.33-0.37 (2m, 1H, CH), 0.45-0.53 (m, 6H, $(CH_2CH_3)_3$), 0.74-0.78 (m, 9H, $(CH_2CH_3)_3$), 0.88-2.04 (m, 21H). MS *m/z* (relative intensity): 338 (M^+, 0.1), 309 (83), 241 (29), 201 (6), 171 (100), 138 (63), 75 (37), 53 (2). GC (CBP-10) conditions for enantiomeric separation: t_R(*cis*), 9.23 (1*R*, 2*S*) and 12.65 (1*S*, 2*R*) min; t_R(*trans*), 31.92 (1*S*, 2*S*) and 32.73 (1*R*, 2*R*) min; oven temp., 150 °C; injection temp., 240 °C; initial time, 2 min; final temp., 230 °C; rate, 2 °C/min; detection temp., 270 °C; column pressure, 100 kPa.

The reaction of 1,1'-diphenylethylene with (MDA). Isolated yield: 98%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.64-1.71 (m, 21H), 2.18, 2.54 (2m, 1H, CH), 7.15-7.35 (m, 10H, C_6H_5). MS *m/z* (relative intensity): 376 (M^+, 4), 238 (75), 192 (100), 115 (49), 83 (36), 55 (30). GC (CBP-10) conditions for enantiomeric separation:[16a] t_R, 40.31 (*R*) min and 41.13 (*S*) min; oven temp., 120 °C; injection temp., 230 °C; initial time, 2 min; final temp, 230 °C; rate, 3 °C/min; detection temp., 270 °C; column press, 100 kPa.

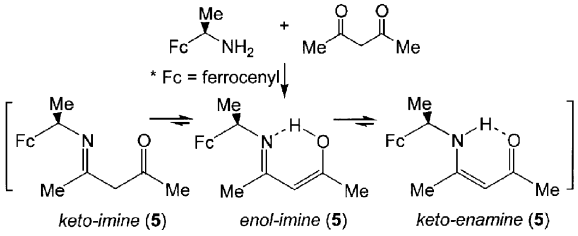
Results and Discussion

Synthesis and characterization. The synthesis of chiral diimines **3** and **4** requires initially the preparation and the resolution of (*S*)-*N*,*N*-dimethyl-1-ferrocenylethylamine (FA) reported by Ugi.[17] The reaction of FA with MeI (or acetanhydride) followed by amination of the resulting ammonium salt with liquid ammonia gives the starting primary amine, (*S*)-1-ferrocenylethylamine. Scheme 1 shows the synthetic routes leading to the formation of C_2-symmetric diimines **3** and **4**. The treatment of a two-fold excess of (*S*)-1-ferrocenylethylamine with glyoxal (40% in water) results in a α-diimine, **3** in a good yield. The same reaction with an equimolar amount of ferrocene-1,1'-dicarboxaldehyde led to the formation of a novel triferrocenyl ω-diimine **4**.

Both compounds were obtained as brown crystalline solids in good to moderate yields. Analytical and other spectroscopic data all agree with the formulations shown in this scheme. The presence of C_2-symmetry in both compounds can be easily confirmed by their ^{1}H NMR patterns. For instance, each compound exhibits only one set of signals for the equivalent pairs of protons.



Scheme 1



Scheme 2

The success of the preparation of these two compounds led us to attempt the synthesis of related bulky β-diimine from the reaction of 1-ferrocenylethylamine with 2,4-butadione as depicted in Scheme 2.[18] Surprisingly, however, the reaction gave the mono-condensation product **5** instead of the expected diimine, a double condensation product, regardless the reaction conditions employed. For instance, neither the change in the ratio of the reactants nor the reaction temperature would alter the results.

This unusual behavior of 1-ferrocenylethylamine may be explained in terms of steric congestion that would be felt in the double condensation product. These observations strongly demonstrate that our ferrocenylamine is sterically very demanding and bulkier than any of known substituents at nitrogen such as 2,6-disubstituted aniline derivatives. It is well known that 2,4-butadione reacts most of bulky anilines such as 2,6-diisopropylaniline or 2,6-di-*t*-butylaniline to yield the expected diimines.[1]

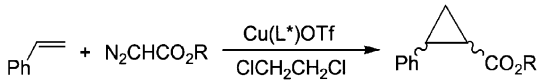
Of three possible resonance structures for **5**, the keto-enamine is the predominant species in the solution as evidenced by ^{17}O NMR data (δ = 408.3 ppm).[19] The unusual stability of **5** is realized by the fact that it resists any metallation reaction with RLi, R_2M (M = Mg, Zn), etc.

The compounds **3** and **4** react with Cu(OTf) to form the corresponding Cu(I) complexes of the type Cu(L)OTf, where the ligand (L = **3**, **4**) is believed to be coordinated in a typical bidentate manner. Both analytical and high-resolution mass spectral data support this formulation.

Asymmerric catalysis: Asymmetric cyclopropanation of simple olefins with alkyl diazoacetates catalyzed by chiral transition metal complexes is well-established, and as such a great number of catalysts are known.[5,20] In particular, copper complexes incorporating C_2-symmetric diimines deserve special attention in that they have achieved the cyclopropanation with moderate to high de and ee.[14,21] In this regard our ferrocene-based diimines may put a new entry into a mild, efficient system for the target reaction.

Table 1 shows that our new C_2-symmetric chiral ferrocenyl diimines (**3** & **4**) can catalyze the asymmteric cyclopropanation of styrene to give the corresponding cyclopropanecarboxylates in a varying degree of diastereoselectivity (*trans*:*cis*, 86:14-72:28) and enantioselectivity (7-65% ee for *trans*- *vs* 49-92% ee for *cis*-products). As far as

Table 1. Asymmetric Cyclopropanation of styrene as a Function of Ligand[a]

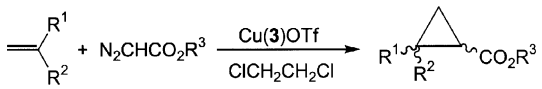


R	L*	yield (%)[b]	*trans*:*cis*[c]	% ee[d] (*trans*:*cis*)
Et	**3**	96	73:27	65:76
	4	58	79:21	53:57
^{t}Bu	**3**	92	77:23	20:59
	4	74	72:28	24:58
l-menthyl	**3**	94	86:14	21:92
	4	74	80:20	7:49

[a]Reaction conditions: [olefin]/[diazoester]/[catalyst] = 10/2.5/0.05. [b]Isolated yield based on diazoester. [c,d]Determined as described in the Experimental section.

total chemical yields and diastereoselectivity are concerned, these values may be comparable with those obtained by others employing the well-known nitrogen-based ligands such as semicorrins and oxazolines.[8f,8g,22] The strong dependence of not only chemical yields but stereoselectivity on the electronic as well as steric parameters from substrate, reagent, and the ligand is demonstrated once again. For instance, the increase in the steric congestion around the metal center by increasing steric bulk of the ligand definitely retards the reaction rates and lowers the chemical yields (entries 1/2, 3/4, and 5/6). These results are understandable considering the fact that with the ligand **5**, the substrate may experience a considerable amount of difficulty approaching the supposed metal carbene intermediate surrounded by three bulky ferrocene moities. However, little dependence of both diastereo- and enantio-selectivities on the structure of ligand can be noted. The observations concerning the diastereoselectivity do agree well with the general belief that diastereoselectivity depends rather on the interaction between the olefin and the diazo compound than on the structure of chiral ligand in the case of copper-catalysis incorporating C_2-symmetric diimines.[8f,23] On the other hand, enantioselectivity crucially depends on the interaction between the ester group and the substituent(s) of the ligand in a metal-carbenoid intermediate, thus the more discriminative the interaction between the ester group and the ligand substituent, the higher enantioselectivity becomes.[8f,24] According to the low ees shown in Table 1, however, such favorable discrimination does not seem to be effectively operating with our ligand systems. Although less dramatic, ees do show some dependence on the nature of the ligand with **3** proving to be more efficient than **4**. In general, as expected, ees depend more dramatically on the structure of the reagent to reveal the following order of % ees: EDA > ^{t}BDA > MDA. Finally, it is worth noting that contrary to the findings made by others,[11,14,23b,25] ees with *cis*-products are higher than *trans*-ones in all cases.

Table 2. Cycopropanation of Terminal Olefins with Diazoacetates[a]



R^1	R^2	R^3	yield (%)[b]	*trans*:*cis*[c]	% ee[d] (*trans*:*cis*)
Ph	Ph	Et	43	–	31
		^{t}Bu	58	–	47
		l-menthyl	98	–	27
^{n}Bu	H	Et	85	64:36	3:6
		^{t}Bu	57	99:1	26
		l-menthyl	60	91:9	62:51
$SiEt_3$	H	Et	70	96:4	21:39
		^{t}Bu	60	92:8	23:45
		l-menthyl	83	78:22	35:78

[a]Reaction conditions: [olefin]/[diazoester]/[catalyst] = 10/2.5/0.05. [b]Isolated yield based on diazoester. [c,d]Determined as described in the Experimental section.

Our ligands prove effective in the cyclopropanation of other terminal olefins to give excellent chemical yields and very high diastereoselectivities as shown in Table 2. In particular, almost complete diastereocontrol is achieved in the reactions of 1-hexene and triethylsilylethylene with ^{t}BDA and MDA. Here again, however, it is disappointing to observe low ees in most cases.

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References

1. Van Koten, G.; Vrieze, K. *Adv. Organoemet. Chem.* **1982**, *21*, 151.
2. 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.* **1994**, *33*, 497.
3. (a) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. (b) Mecking, S.; Johnson, L. K.; Wang, L.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888. (c) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (d) Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514.
4. (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. (c) Hayashi, T. In *Ferrocenes*: *Homogeneous Catalysis, Organic Synthesis, Materials Science*; Togni, A., Hayashi, T., Eds.; VCH: Weiheim, Germany, 1995; chapter 2.
5. (a) Song, J.-H.; Cho, D.-J.; Jeon, S.-J.; Jeong, J.-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.
6. Kim, T.-J.; Park, D.-K.; Ryu, E.-S.; Jeong, J. H. *J. Organomet. Chem.* **2002**, in press.
7. (a) Mass, G. *Top. Curr. Chem.* **1987**, *137*, 75. (b) Doyle, M. P. Asymmetric Cyclopropanation, In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: Weiheim, 1993; Chapter 3. (c) Noels, A. F.; Demonceau, A. Catalytic Cyclopropanation, In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornil, B., Hermann, W. A., Eds.: VCH: New York, 1996; chapter 3.
8. (a) Bedekar, A. V.; Anderson, P. G. *Tetrahderon Lett.* **1996**, *37*, 4073. (b) Park, S. B.; Sakata, N.; Nishiyama, H. *Chem. Eur. J.* **1996**, *2*, 303. (c) Uozumi, Y.; Kyota, H.; Kishi, E.; Kitayama, K.;

Hayashi, T. *Tetrahedron: Asymmetry* **1996**, *7*, 1603. (d) Gant, T. G.; Noe, M. C.; Corey, E. J. *Tetrahedron Lett.* **1995**, *36*, 8745. (e) Leutenegger, U.; Umbricht, G.; Fahrni, C.; Matt, P.; Pfaltz, A. *Tetrahedron* **1992**, *48*, 2143. (f) Evans, D. A.; Woerpel, K. A.; Hinman, M. N.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726. (g) Lowenthal, R. E.; Abiko, A.; Masamune, S. *Tetrahedron Lett.* **1990**, *31*, 6005.

9. Doyle, M. P.; Bagheri, V.; Wandless, T. T.; Harn, N. K.; Brinker, D. A.; Eagle, C. T.; Loh, K. L. *J. Am. Chem. Soc.* **1990**, *112*, 1906.
10. Reigitz, M.; Hocker, J.; Liedhegener, A. *Org. Synth. Coll.* **1973**, *V*, 179.
11. Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Helv. Chim. Acta* **1988**, *71*, 1553.
12. Kim, S.-G.; Cho, C.-W.; Ahn, K.-H. *Tetranhedron: Asymmetry* **1999**, *10*, 1903.
13. Ito, K.; Katsuki, T. *Tetrahedron Lett.* **1993**, *34*, 2661.
14. Lo, M. M.-C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 10270.
15. Kwong, H.-L.; Lee, W.-S. *Tetrahedron: Asymmetry* **2000**, *11*, 2299.
16. (a) Nishiyama, H.; Itoh, Y.; Matsumoto, H.; Park, S.-B.; Itoh, K. *J. Am. Chem. Soc.* **1994**, *116*, 2223. (b) Nishiyama, H.; Itoh, Y.; Sugawara, Y.; Matsumoto, H.; Aoki, K.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1247.
17. (a) Gokel, G. W.; Marquarding, D.; Ugi, I. K. *J. Org. Chem.* **1972**, *37*, 3052. (b) Marquarding, D.; Gokel, G. W.; Hoffmann, P.; Ugi, I. K. *J. Am. Chem. Soc.* **1970**, *92*, 5389.
18. Bhattacharyya, S. *Synth. Commun.* **1994**, *24*, 2713.
19. Zhuo, J.-C. *Magnetic Resonance in Chemistry* **1997**, *35*, 21.
20. (a) Aratani, T.; Yoneyoshi, Y.; Nagase, T. *Tetrahedron Lett.* **1982**, *23*, 685. (b) Kanemasa, S.; Hamura, S.; Harada, E.; Yamamoto, H. *Tetrahedron Lett.* **1994**, *35*, 7985. (c) Doyle, M. P.; Protopopova, M. N.; Pouller, C. D.; Rogers, D. H. *J. Am. Chem. Soc.* **1995**, *117*, 7281.
21. (a) Nozaki, H.; Moriuti, S.; Takaya, H.; Noyori, A. *Tetrahedron Lett.* **1966**, *7*, 5239. (b) Aratani, T. *Pure Appl. Chem.* **1985**, *57*, 1839. (c) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911.
22. Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1005.
23. (a) Pfaltz, A. In *Comprehensive Asymmetric Catalysis II*; Jacobsen, E. N., Yamamoto, H., Eds.; Springer: Berlin, Germany, 1999; p 533. (b) Aratani, T.; Yoneyoshi, Y.; Nagase, T. *Tetrahedron Lett.* **1977**, *18*, 2599. (c) Ichiyanagi, T.; Shimizu, M.; Fujisawa, T. *Tetrahedron* **1997**, *53*, 9599.
24. (a) Pfaltz, A. In *Comprehensive Asymmetric Catalysis II*; Jacobsen, E. N., Yamamoto, H., Eds.; Springer: Berlin, Germany, 1999; p 534. (b) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; Wiley: New York, 1998. (c) Calter, M. A. *Curr. Org. Chem.* **1997**, *1*, 37. (d) Pfaltz, A. *Adv. Catal. Proc.* **1995**, *1*, 61.
25. Fritschi, H.; Leutenegger, U.; Siegmann, K.; Pfaltz, A.; Keller, W.; Kratky, C. *Helv. Chem. Acta* **1988**, *71*, 1541.