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Synthesis and crystal structure of novel planar chiral diferrocenylimine-diols X-ray crystal structure of $[(\eta^5\text{-}C_5H_5)\ Fe\{\ (\eta^5\text{-}C_5H_3)\ CPh_2OHCH\ (CH_3)\ N{=}CHC_6H_4CH{=}NCH\ (CH_3)\ CPh_2OH\ (\eta^5\text{-}C_5H_3)\ \}Fe\ (\eta^5\text{-}C_5H_5)]$

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Four novel planar chiral diferrocenylimine-diols **6 (6a, 6b, 6c, 6d)** have been designed and prepared, and the structure of **6a** determined by X-ray crystallography. Compound **6a** $[(\eta^5\text{-}C_5H_5)\ Fe\{\ (\eta^5\text{-}C_5H_3)\ CPh_2OHCH\ (CH_3)\ N{=}CHC_6H_4CH{=}NCH\ (CH_3)\ CPh_2OH\ (\eta^5\text{-}C_5H_3)\ \}Fe\ (\eta^5\text{-}C_5H_5)]$ is enantiomerically pure and crystallises in the noncentrosymmetric $P2_12_12_1$ space group, exhibiting a "∩" shape, phenyl ring as a bridge linking two ferrocenes on both sides via C=N, and the pair of ferrocenyl groups adopting the E-configuration.

Keywords: ferrocene, planar chirality, crystal structure, diferrocenylimine-diols

Because of their great success in catalytic asymmetric reactions, chiral ferrocene ligands incorporating both planar and central chirality have attracted considerable attentions in recent years,[1-3] and there is currently a surge of effort into the design and development of new enantiopure ferrocene derivatives.[4-8] Despite the large variety of planar-chiral ferrocene derivatives known to be highly effective in the asymmetric catalysis,[4-8] only a few examples have been developed into industrial processes. The lack of application of homogeneous asymmetric catalysis is partly due to the problems of separation and recycling of the expensive chiral catalysts. To facilitate the separation of the chiral catalyst from the reaction mixture, one of the current solutions is that ligands are anchored onto solid polymers; unfortunately, the immobilisation of chiral catalysts often results in lower activities and enantioselectivities as compared to those observed for their homogeneous counterparts.[9-12]

In order to discover effective and recoverable ferrocene catalysts, we have been interested in the design and synthesis of diferrocenylimines, which incorporate both planar and central chirality. The advantages of their binuclear cluster compounds are the characteristic of low polarity of the molecule and their low solubility in certain solvents, which aid in their recovery from the reaction system after use. Thus the reactions can be carried out in a homogeneous manner, and the catalyst can be separated by adding another solvent after the reaction completed. It is expected that the steric effect of the specific microenvironment created by the ferrocene skeleton structure could modulate the catalytic behaviour of the chiral diferrocenylimine-diols. Herein we report the synthetic and structural investigation of a novel chiral planar diferrocenylimine-diol **6**.

Experimental

General procedure

All reactions were carried out under argon and monitored by thin-layer chromatography (TLC). Diethyl ether was dried using Na under reflux. Melting points (uncorrected) were measured with a XT4 melting point apparatus. ^{1}H NMR spectra were recorded on a Varian EM-360 spectrometer, using $CDCl_3$ as solvent and TMS as the internal standard. Optical rotations were measured on a WZZ-3 polarimeter.

(R) -N, N-dimethyl-1-ferrocenylethylamine [(R) -**1**] $[\alpha]_D^{20} = +14.0$ (c 1.0, ethanol) and (R, S_p)-1-N,N-dimethylamino-1-(2-diphenylhydroxymethyl) ferrocenylethane [(R, S_p) -**2**] $[\alpha]_D^{20}$-171.1 (c 1.0, CH_2Cl_2); m.p. 160–162 °C. ^{1}H NMR spectrum ($CDCl_3$) δ_H: (ppm) 1.20 (d, *J* = 6.9, 3H, $CHCH_3$), 1.834 (s, 6H, N $(CH_3)_2$), 4.11 (s, 5H, Fc-unsubstituted ring), 4.12–4.23 (m, 3H, FeC_5H_3CH), 4.36 (q, 1H, CH), 7.09–7.68 (m, 10H, C_6H_5), 8.81 (s, 1H, OH) were prepared by literature methods and resolved according to the reported procedure.[13]

Chiral ferrocenylaminoalcohol **4** *$(\eta^5\text{-}C_5H_5)$ Fe{ $(\eta^5\text{-}C_5H_3)$ CPh_2OHCH (CH_3) NH_2}:*

Treatment of aminoalcohol **2** with methyl iodide in the presence of sodium azide (acetone solution) gave hydroxyazide **3** ($[\alpha]_D^{20}$ 25.0 (c 0.667, CH_2Cl_2) m.p. 159–161 °C (lit. 162–163 °C)[14]. ^{1}H NMR spectrum ($CDCl_3$) δ_H: (ppm) 1.48 (d, *J*=7, 3H, $CHCH_3$), 3.74 (s, 1H, OH), 4.28–4.45 (m, 9H, $C_5H_5FeC_5H_3CH$), 7.23–7.46 (m, 10H, C_6H_5).

Reduction of **3** with H_2 at 4Mp in methanol gave aminoalcohol **4** (R, S_p) -1- (2-diphenyl hydroxyl methyl) ferrocenylethylamine (Scheme 1). ($[\alpha]_D^{20}$-171.3) (c 0.633, CH_2Cl_2) m.p. 176–178 °C (lit. 159–160 °C) [14]. ^{1}H NMR spectrum ($CDCl_3$) δ_H: (ppm) 0.72 (d, *J*=7, 3H, $CHCH_3$), 1.26 (s, 2H, NH_2), 3.50 (s, 1H, OH), 3.89–4.31 (m, 9H, $C_5H_5FeC_5H_3CH$), 7.14–7.54 (m, 10H, C_6H_5).

Chiral ferrocenyl bis-imine diols **6**

6a: Ferrocenylaminoalcohol **4** (860 mg, 2.1 mmol) and *p*-phthaldehyde (560 mg, 4.17 mmol) were dissolved in anhydrous ethanol, mixed with molecular sieve (5 g) and refluxed for 4 h, then concentrated *in vacuo* and washed with hot water (10 ml × 2). The solution was then filtered and evaporated to dryness, the crude material **5a** and ferrocenylaminoalcohol **4** (860 mg, 2.1 mmol) were dissolved in anhydrous ethanol, refluxed for 2 h, filtered, and the crude material was recrystallised from dichloromethane/petroleum ether giving orange crystals **6a** (1.66 g, 86%). m.p. 172–174 °C, ($[\alpha]_D^{20}$-237.3) (c 0.153, CH_2Cl_2). The IR spectrum indicated the presence of the unsubstituted cyclopentadienyl ring (1103.9 and 996.6 cm^{-1}), 1022.0–1147.6 cm^{-1} (single substituted cyclopentadienyl), 486.1 cm^{-1} and 509.9 cm^{-1} ($\nu_{Fe\text{-}C}$), 1621 and 1639 cm^{-1} (N=CH); ^{1}H NMR spectrum ($CDCl_3$) δ_H: (ppm) 0.72 (d, *J*=6.7, 6H, $CHCH_3$), 3.48 (s, 2H, OH), 4.10 (s, 10H, Fc-unsubst. Ring), 4.06–4.22 (m, 8H, FeC_5H_3CH), 7.22–7.60 (m, 40H, C_6H_5), 8.06 (s, 4H, C_6H_4), 8.31 (s, 1H, N=CH), 8.84 (s, 1H, N=CH); Calc. for $C_{58}H_{52}Fe_2N_2O_2$: C, 75.7; H, 5.7; N, 3.0. Anal. Found: C, 75.6; H, 5.6; N, 3.0; MS (TOF): 920.6.

6b: This complex was prepared in similar manner to that for the preparation of **6a,** starting with isophthalaldehyde (1.45 g, 75.1%). m.p. 158–160 °C, ($[\alpha]_D^{20}$-160.2 °C (c 0.4, CH_2Cl_2). The IR spectrum indicated the presence of the unsubstituted cyclopentadienyl ring (1100.1 and 996.0 cm^{-1}), 1021.0–1145.6 cm^{-1} (single substituted cyclopentadienyl), 486.5 cm^{-1} and 509.7 cm^{-1} ($\nu_{Fe\text{-}C}$), 1620 and 1638 cm^{-1} (N=CH); ^{1}H NMR spectrum ($CDCl_3$) δ_H: (ppm) 0.84 (d, *J*=6.7, 6H, $CHCH_3$), 3.52 (s, 2H, OH), 4.15 (s, 10H, Fc-unsubst. Ring), 4.08–4.24 (m, 8H, FeC_5H_3CH), 7.19–7.58 (m, 40H, C_6H_5), 7.86 (m, 4H, C_6H_4), 8.30 (s, 1H, N=CH), 8.79 (s, 1H, N=CH).

6c: Ferrocenylaminoalcohol **4** (860 mg, 2.1 mmol) and glutaric dialdehyde (50wt% solution in water) (840 mg, 4.2 mmol) were dissolved in anhydrous benzene, refluxed for 4 h with molecular sieve in a water separator then concentrated *in vacuo*. The crude material **5c** and ferrocenylaminoalcohol **4** (860 mg, 2.1 mmol) were dissolved in anhydrous ethanol, refluxed for 2 h, concentrated *in vacuo*, and the crude material was recrystallised from *n*-hexane giving yellow crystals **6c** (0.53 g, 36.8%). m.p. 184–186 °C, ($[\alpha]_D^{20}$-206.3 °C) (c 0.4, CH_2Cl_2). The IR spectrum indicated the presence of the unsubstituted cyclopentadienyl ring (1105.8 and 995.6 cm^{-1}), 1023.0–1149.6 cm^{-1} (single substituted cyclopentadienyl), 486.1 cm^{-1}

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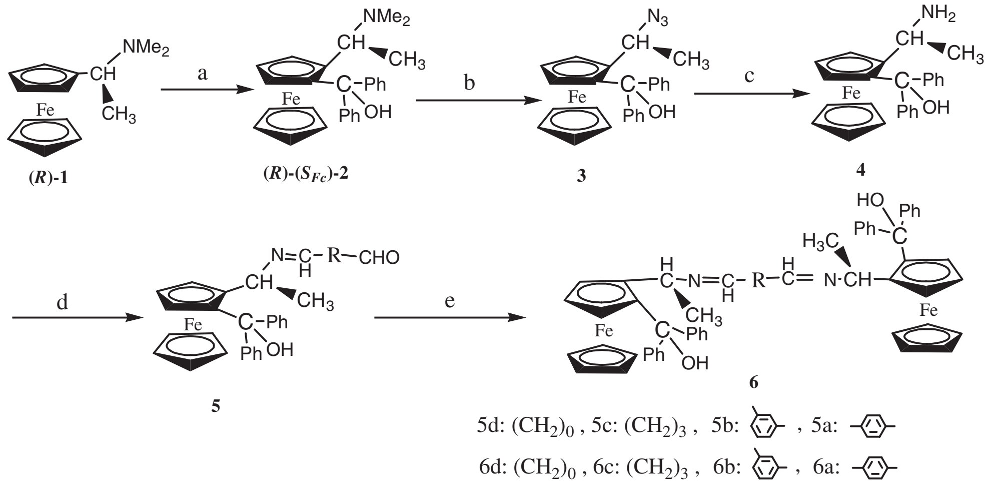

a. 1) *n*-BuLi 2) Ph$_2$CO b. CH$_3$I, NaN$_3$ c. H$_2$/Raney Ni, 4Mpa d. HOC-R CHO, benzene or ethanol, 4A MS, reflux e. 4, benzene or ethanol, 4A MS, reflux

Scheme 1 Synthesis of chiral planar diferrocenylimine-diols **6**.

and 509.9 cm^{-1} ($\nu_{Fe\text{-}C}$), 1622 and 1637 cm^{-1} (N=CH); ^{1}H NMR spectrum (CDCl$_3$) δ_H: (ppm) 0.807 (d, J=6.8, 6H, CHCH$_3$), 1.168 (6H CH2), 3.474 (s, 2H, OH), 4.176 (s, 10H, Fc-unsubst. Ring), 4.03–4.216 (m, 8H, FeC$_5$H$_3$CH), 6.242 (s, 2H, N=CH),7.10–7.47 (m, 40H, C$_6$H$_5$).

6d: This compound was prepared in similar manner to **6c,** starting with glyoxal dialdehyde (40wt% solution in water), (0.39 g, 46.7%). m.p. 186–188 °C, ([α]$_D$^{20}-197.2 °C (c 0.4, CH$_2$Cl$_2$). The IR spectrum indicated the presence of the unsubstituted cyclopentadienyl ring (1102.7 and 994.8 cm^{-1}), 1022.0–1146.6 cm^{-1} (single substituted cyclopentadienyl), 485.1 cm^{-1} and 509.6 cm^{-1} ($\nu_{Fe\text{-}C}$), 1621 and 1637 cm^{-1} (N=CH); ^{1}H NMR spectrum (CDCl$_3$) δ_H: (ppm) 0.837 (d, J=6.9, 6H, CHCH$_3$), 3.49 (s, 2H, OH), 4.175 (s, 10H, Fc-unsubst. Ring), 4.03–4.28 (m, 8H, FeC$_5$H$_3$CH), 6.152 (s, 2H, N=CH), 7.10–7.360 (m, 40H, C$_6$H$_5$).

Single crystal X-ray diffraction

Crystal data: C$_{63}$H$_{64}$Fe$_2$N$_2$O$_2$', Mr = 992.86, orthorhombic, P2$_1$2$_1$2$_1$, a = 11.1510 (17) Å, b = 21.222 (3) Å, c = 23.948 (4) Å, V = 5667.2 (15) Å^3, D_x = 1.164 g cm^{-3}, Z = 4, T = 293 (2) K. Absolute structure parameter is –0.02 (2). Slow evaporation of the compound **6a** in petroleum ether and ethyl acetate yielded single crystals suitable for X-ray analysis. An orange block crystal with approximate dimensions of 0.22 × 0.20 × 0.18 mm was mounted on a BRUKER SMART 1000 CCD diffractometer equipped with a graphite monochromator data collection. The determination of unit cell parameters and data collections were performed at 293 (2) K, using graphite monochromated MoKα (λ = 0.71073 A) radiation. A total of 33258 independent with 11598 independent ones with Rint = 0.0470 reflections were measured in the range of $1.28 \leq \theta \leq 26.50°$ with an Oscillation method. All data were corrected using SADABS method. The structure was solved by direct methods using SHELXL-97 program and refined by full-matrix least-squares on F^2.[15] All non–hydrogen atoms were refined anisotropically, and hydrogen atoms were added according to theoretical modes. The final cycle of refinement gave R = 0.0564, wR = 0.1452 (The weighting scheme was $w = 1/[s^2(F_0^2) + (0.0995P)^2]$ where $P = (F_0^2 + 2F_c^2)/3$). The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. Molecular graphics were drawn with the program package XP. Full crystallographic details have been deposited with the Cambridge Crystallographic Data Center and allocated the deposition number CCDC-251130.

Results and discussion

Synthesis, IR and NMR spectroscopy

In order to discover effective and recoverable ferrocene catalysts, we designed and synthesised the desired planar chiral diferrocenylimine-diols **6**, which has not been described in literature so far. We applied a modified general procedure to synthesise **6**,[16] in that in order to remove the water in the reagents, we mixed them with 4Å molecular sieve in water separator. To avoid the difficulty in separating mono- and diferrocenylimines, it is better to obtain the mono-imine **5** before transformation to the corresponding diimine **6** (Scheme 1).

During our study of the synthetic procedure for chiral ferrocenylaminoalcohol **4**, the effect of the reducing agent was investigated. Experimental results showed that the yields of the reduction step were 65% with LiAlH$_4$, 90% with SnCl$_2$/KOH, 94% with H$_2$/Raney Ni respectively. Hence, we chose H$_2$/Raney Ni for the scaled-up preparation of chiral ferrocenylaminoalcohol **4**.

The structure of the compound **6** was unambiguously confirmed by spectroscopic analysis. The imine function of the compounds was registered as strong absorptions at about 1620 and 1640 cm^{-1} in IR spectra, as well as resonances at about 8.35 and 8.84 ppm in the ^{1}H NMR. Signals at 7.22–7.60 ppm in ^{1}H NMR spectra of compound **6** belonged to phenyl protons.

Description of crystal structure

Single crystal X-ray diffraction analysis reveals that the molecular structure of compound **6** is essentially as expected and confirms the formulation of the compound (shown in Fig. 1). This compound is enantiomerically pure and crystallises in the noncentrosymmetric P2$_1$2$_1$2$_1$ space group. A view of compound **6a** perpendicular to the central phenyl plane demonstrates the "∩" shape of the molecule, with the phenyl ring as the bridge linking two ferrocenes on both sides via C=N, and all substituents attached adopting the stable E-configuration. Another view parallel to the central phenyl plane demonstrates that the substituents of the molecule exhibit the *trans* arrangement due to steric bulk (shown in Figs 2 and 3).

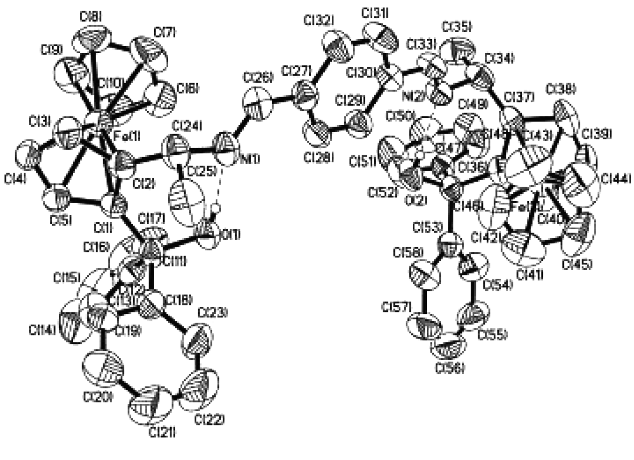

Fig. 1 ORTEP drawing of the structure of **6**, *n*-pentane as well as H atoms have been omitted for clarity except the H atoms on the OH. Thermal ellipsoids are drawn at 50% probability level.

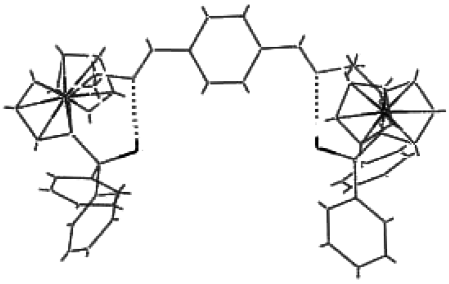

Fig. 2 View of compound **6** perpendicular to the central phenyl plane.

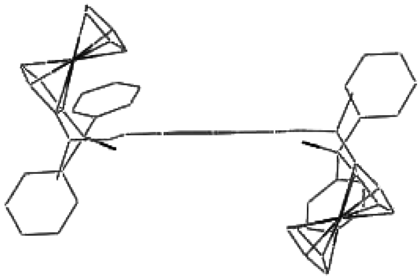

Fig. 3 View of compound **6** parallel to the central phenyl plane.

Table 1 Hydrogen-bonding geometry [Å, deg] for 6a

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O1–H1...N1	0.820	1.886	2.702	173.09
O2–H2...N	0.820	1.950	2.747	163.78

The Fe–C contact lengths range from 2.029 (5) (Fe1–C5) to 2.052 (5) (Fe1–C7) and from 2.018 (6) (Fe2–C45) to 2.066 (5) (Fe2–C37) in the molecule. The Fe atoms are almost at the center of the two cyclopentadienyl rings, with the Fe (1) –Cg (1) and Fe (1) –Cg (2) distances 1.6442 Å, 1.6551 Å, Fe (2) –Cg (1) and Fe (2) –Cg (2) distances 1.6433 Å, 1.6428 Å, respectively, where Cg (1) and Cg (2) are the centroids of the $\eta5$ (C_5H_4) and $\eta5$ (C_5H_4) rings. The iron atoms are in molecules slightly closer to plane of the unsubstituted rings. The two cyclopentadienyl rings are not parallel, they deviate from an eclipsed geometry in compound **6**, as evidenced by the interplanar angles of 2.1° and 2.6° respectively between the η^5 (C^5H^4) and η^5 (C^5H^4) rings. The C (26) –C (27) and C (30) –C (33) bond lengths are 1.462 (7) and 1.465 (6) Å, in good agreement with values reported for other ferrocenylimine derivatives,[17] which are shorter than the common distance of the C–C single bond 1.540Å.[18] This is in keeping with the suggestion that some delocalisation of electron density is found over the N=C-C6H4-C=N fragment indicating that there is conjugation between C=N unit and the phenyl groups. There are two intramolecular hydrogen bonds O1–H1…N1and O2– H2…N2 in unit cell [H1…N1=1.886Å, H2…N2=1.950Å, O1–H1…N1 =173.09°, O2–H2…N2 =163.78°] (Table 1).

Interestingly, the packing diagram (Fig. 4) shows that the *n*-pentane molecule arranged in the unit cell, which showed that the title compound can selectively enfold the *n*-pentane molecule from petroleum ether when crystallising.

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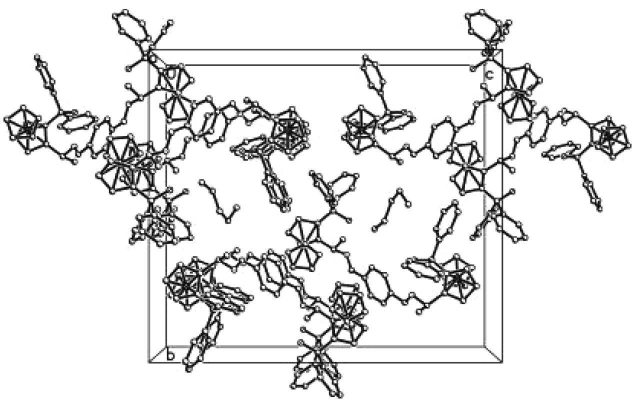

Fig. 4 Three-dimensional molecular-packing diagram of the title compound.

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