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Synthesis and Crystal Structure of N-(2-Hydroxy-3,5-di*tert*butyl)benzylidene-1-(2-diphenyl hydroxy methyl)ferrocenylethylamine

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Novel planar chiral ferrocenylimine N-(2-hydroxy-3,5-di*tert*butyl)benzylidene-1-(2-diphenyl hydroxy methyl)ferrocenylethylamine was obtained by the reaction between 1-(2-diphenyl hydroxy methyl)ferrocenylethylamine and 2-hydroxy-3,5-di*tert*butylbenzaldehyde in anhydrous ethanol. Its structure was characterized by elemental analysis, ^{1}H NMR, MS and X-ray single-crystal diffraction techniques. The title compound comprises an 'U' shape of the molecule with the 2-hydroxy-3,5-di*tert*butylphenyl group and the 2-diphenylhydroxy methyl group.

Keywords: Ferrocene, Diferrocenylimine-diols, Crystal structure.

INTRODUCTION

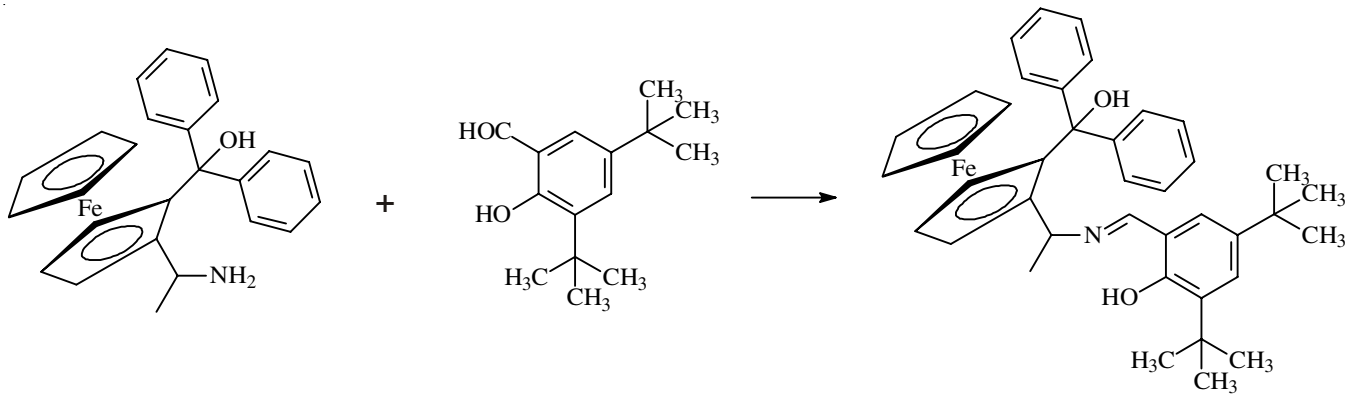
Well-known organometallic derivative of iron, ferrocene and it's derivatives, catalyzed coupling and carbonylation reactions with the transition metal, in the exploitation for the development of mechanically interlocked and non-interlocked synthetic molecular machines. In recent years a considerable amount of research has been devoted to the synthesis of various substituted ferrocenes. The use of chiral ferrocene based ligands with central and planar chirality and their applications in asymmetric catalyzed in the past several decades [1-3]. Especially transition metal complexes with chiral ferrocene ligands represent an important class of enantioselective catalysts. The design and synthesize chiral ferrocene catalyst which exhibits efficient and high stereoselective characterizations have attracted tremendous interest [4-7]. Numerous enantioselective transformations are successfully catalyzed by chiral ferrocenylimine, diphosphanes as well as other types of ligands. Such as asymmetric hydrogenation reaction, the chiral ferrocene substituted catalysts represents the efficient and 'green' way to access enantiomerically enriched secondary alcohols from inexpensive prochiral ketones, which are important pharmaceutical intermediates and building blocks in organic synthesis.

In order to discover effective and recoverable ferrocene catalysts, we designed and synthesized ferrocenylimineols with incorporates planar chirality. Recently, we synthesized a planar chiral ferrocenylimine N-(2-hydroxy-3,5-di*tert*butyl)-benzylidene-1-(2-diphenyl hydroxy methyl)ferrocenylethylamine by the reaction between 1-(2-diphenyl hydroxy methyl)ferrocenylethylamine and 2-hydroxy-3,5-di*tert*butylbenzaldehyde.

EXPERIMENTAL

All reagents were commercially available and used without further purification or purified by standard methods prior to use. Melting points were determined using a RY-1 apparatus and are uncorrected. ^{1}H NMR spectra were recorded on JNM-ECA-400 400 MHz instrument in the solvent indicated below. Chemical shift values are reported in parts per million (ppm) relative to those for tetramethylsilane used as an internal reference standard. Mass spectra were obtained from Micromass ZabSpec and API3000 instruments. Elemental analysis was carried at the CarloErba-1106. The synthetic pathway for the title compound is outlined in **Scheme-I**.

1-(2-Diphenyl hydroxy methyl)ferrocenylethylamine (**1**) (410 g, 10 mmol) and 2-hydroxy-3,5-di*tert*butylbenzaldehyde (**2**) (280 mg, 12 mmol) were dissolved in anhydrous ethanol and the molecular sieve (5 g) was added, then the mixture was reflux for 4 h. The mixture was washed with hot water, then concentrated *in vacuo*, the crude material recrystallized from *n*-hexane giving yellow crystals **3** (0.51 g, 81 %). m.p.: 142-144 °C, $[\alpha]_D^{20}$ = -114.4 (c = 0.125, CH_2Cl_2). ^{1}H NMR spectrum ($CDCl_3$) δ_H: (ppm) 1.27 (m, 3H), 1.38 (m, 18H), 3.52 (s, 1H), 3.87-4.30 (m, 9H, $C_5H_5FeC_5H_3CH$), 4.98 (s, 1H), 7.14-7.54 (m, 12H), 8.30 (s, 1H). Calcd. for $C_{40}H_{45}NO_2Fe$: C, 76.55; H, 7.23; N, 2.23. Anal. found: C, 76.52; H, 7.28; N, 2.25; MS (TOF): 627.6.



Scheme-I: Synthesis procedure of the title compound

Crystallographic study: An orange crystal of the title compound with dimensions of 0.57 mm × 0.38 mm × 0.21 mm was mounted on a glass fiber in a random orientation. The data were collected by a rigaku r-axis rapid IP area detector with a graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) by using an ω scan mode in the range of $3.06 \leq \theta \leq 27.48°$ at 293(2) K. The structure was solved by direct methods and all data were corrected by using SHELXL-97 program [8]. Unit cell dimensions were obtained with least-squares refinements. A total of 33189 reflections were collected with 7739 unique ones ($R_{int} = 0.0367$), of which 6876 with $I > 2\sigma(I)$ were considered as observed and used in the succeeding refinements. All the other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was carried out by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were added theoretically and allowed to ride on the concerned atoms and refined with fixed thermal factors. The final refinement gave R = 0.0337 and wR = 0.0906 for 397 observed reflections ($w = 1/[\sigma^2(F_o)^2 + (0.0631\ P)^2 + 0.1002\ P]$, where $P = (F_o^2 + 2F_c^2)/3$), S = 1.001, $(\Delta/\sigma)_{max} = 0.103$, $(\Delta\rho)_{max} = 0.258$ and $(\Delta\rho)_{min} = -0.287$ e/ Å^3.

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT SUMMARY FOR THE TITLE COMPOUND

CCDC deposit No.	662839
Empirical formula	$C_{40}H_{45}NO_2Fe$
Molecular weight	627.62
Measured temperature	293(2) K
Crystal size (mm^3)	0.57 × 0.38 × 0.21
Crystal system	Orthorhombic
Space group	$P2_1\ P2_1\ P2_1$
Unit cell dimensions	a = 9.2252(18) Å b = 12.725(3) Å c = 28.820(6) Å
Volume V (Å^3)	3383.2(12)
Z	4
D_{calcd} (g cm^{-3})	1.232
μ (mm^{-1})	0.480
F (000)	1336
θ range (°)	3.06 – 27.48°
Completeness to θ	99.6 %
h/k/l	-11/11, -16/16, -37/37
Reflection unique	7739
Parameters refined	397
R(int)	0.0367
Final R indices [$I \geq 2\sigma(I)$]	R1 = 0. 0337, wR2 = 0.0906
Goodness of fit	0.998
Residual electron densities (e Å^{-3})	0.258 and -0.287

RESULTS AND DISCUSSION

In order to discover effective and recoverable ferrocene catalysts, we designed and synthesized the desired planar chiral diferrocenylimine-ols, which has not been described in literature so far. N-(2-Hydroxy-3,5-di*tert*butyl)benzylidene-1-(2-diphenyl hydroxy methyl)ferrocenylethylamine was obtained by the reaction between 1-(2-diphenyl hydroxy methyl)ferrocenylethylamine and 2-hydroxy-3,5-di*tert*-butylbenzaldehyde in anhydrous ethanol. To mixed with 4 Å molecular sieve in water separator in order to remove the water in reagents, we applied the modified general synthesis procedure.

The ^{1}H NMR, MS and elemental analysis for the product are in good agreement with the title compound. Crystallographic data and experimental details for structural analyses are summarized in Table-1. The selected bond distances and angles are listed in Table-2, respectively. Fig. 1 shows the molecular structure of the title compound.

Single crystal X-ray diffraction analysis reveals that the molecular structure of the title compound is essentially as expected and confirms it's formulation (Fig. 1). This compound is enantiomerically pure and crystallizes in the non-centrosymmetric

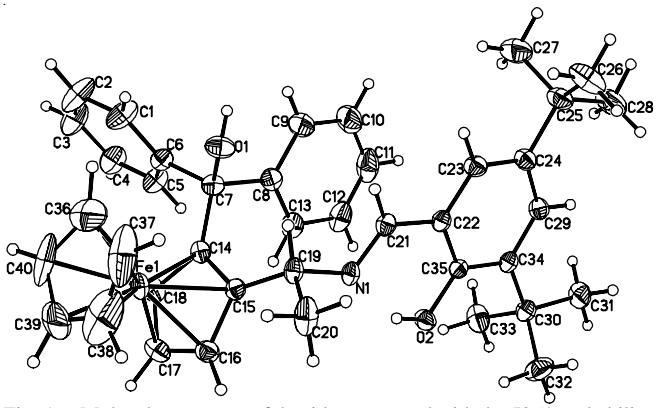


Fig. 1. Molecular structure of the title compound with the 50 % probability of the thermal ellipsoids

$P2_12_12_1$ space group. View of the title compound perpendicular to the ferrocene, the 2-hydroxy-3,5-di*tert*butylphenyl group and the 2-diphenylhydroxy methyl group demonstrates the 'U' shape of the molecule.

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Bond	Dist.	Angle	(°)
Fe1-C14	2.0410(17)	C14-Fe1-C18	41.02(7)
Fe1-C17	2.033(2)	C16-Fe1-C17	40.32(9)
C15-C16	1.428(3)	C15-C19-N1	110.31(14)
C14-Cl8	1.431(3)	O1-C7-C14	107.87(15)
N1-C21	1.277(3)	C6-C7-C8	108.32(14)
O2-C35	1.352(2)	C15-C19-C20	112.88(17)
C3-C4	1.362(4)	O1-C35-C34	120.43(15)
Fe1-C15	2.0457(17)	C14-Fe1-C15	41.09(7)
Fe1-C18	2.0442(18)	C17-Fe1-C18	40.65(9)
C16-C17	1.400(3)	C19-N1-C21	116.28(16)
C15-Cl9	1.514(3)	O1-C7-C6	109.76(15)
N1-C19	1.480(2)	C14-C7-C6	112.02(16)
C1-C2	1.384(4)	N1-C19-C20	107.46(15)
C21-C22	1.453(2)	C26-C25-C27	110.0(3)
Fe1-C16	2.031(2)	C15-Fe1-C16	41.02(8)
C14-C15	1.434(2)	C16-C15-C19	124.65(17)
C17-C18	1.416(3)	N1-C21-C22	123.86(16)
C7-C14	1.529(3)	O1-C7-C8	106.88(15)
O1-C7	1.444(2)	C8-C7-C14	111.86(15)
C2-C3	1.378(4)	O1-C35-C22	119.63(15)
C30-C31	1.532(3)	C26-C25-C28	109.0(2)

The Fe-C contact lengths are ranged from 1.979(4) (Fe1-C38) to Fe1 C15 2.0457(17) (Fe1-C15) 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 are 1.641 Å and 1.661 Å, respectively, where Cg(1)and Cg(2)are the centroids of the η5(C_5H_4) and η5(C_5H_4) rings. The iron atoms are in molecules slightly closer to plane of the unsubstituted rings. And the two cyclopentadienyl rings are not parallel, the two cyclopentadienyl rings deviate from an eclipsed geometry in compound **6**, as evidenced by the interplanar angles of 6.7º and 2.6º respectively between the two $\eta^5(C_5H_4)$ rings.

The distance of N(1)-C(21) is 1.277(3) Å, which is very shorten than C(19)-N(1) (1.480(2) Å) indicated that it is C=N double bonds. The C(21)-C(22) bond lengths is 1.453(2) Å which is in good agreement with values reported for other ferrocenylimine derivatives, which are shorter than the common distance of the C-C single bond 1.540 Å [9]. The shorten C(21)-C(22) bond lengths is in keeping with the suggestion that some delocalization of electron density is found over the N=C-C_6H_5 fragment indicating that there is conjugation between C=N unit and the phenyl groups. The torsion angles of C(19)-N(1)=C(21)-C(22) [178.27(15) Å] and N(1)=C(21)-C(22)-C(23) (-179.67(17) Å) are very closed to 180° indicated that C=N imine is coplanar with aromatic ring. The interplanar angle of η^4C(19)-N(1)=C(21)-C(22) and η^6(C(22)-C(23)-C(24)-C(29)-C(3)-C(35)) is 0.4°. One aromatic ring in the 2-diphenylhydroxy methyl group is almost parallel to coplanar of the C=N imine and aromatic ring in the *N*-(2-hydroxy-3,5-di*tert*butyl) phenyl group. The interplanar angle is 5.4°. There is an intramolecular hydrogen bonds O(2)-H(2A)···N(1) in unit cell [H1···N1=1.88 Å, O(2)-H(2A)···N(1)=149.6°].

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