

Synthesis and Crystal Structures of Schiff Bases Bearing Ferrocenylphenyl Groups

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Abstract: The Schiff bases bearing ferrocenylphenyl and diferrocenylphenyl groups were synthesized by the reactions of *m*-ferrocenylaniline with salicylaldehyde or 1, 4-bis (2'-formylphenyl)-1, 4-dioxabutane. The title compounds were characterized by elemental analysis, IR, ¹H NMR and X-ray structural determination.

Keywords: Ferrocene, Schiff base, single crystal diffraction, synthesis.

Ferrocene derivatives could be used as electroactive polymers¹, thermotropic liquid crystal² and non-linear optical materials³. Of particular interest is the redox chemistry of the iron center with the sandwich structure⁴. Substituent on the Cp-ring would influence the redox behaviour by changing energy level of the HOMO⁵⁻⁶. Ferrocene groups containing aliphatic imine could cause hydrolysis when they reacted with metal ions and related analogues have been widely investigated⁷. However, unlike the aliphatic imines, the condensation products of arylamines and carbonyl compounds are quite stable. In order to overcome the hydrolytic problems, maintain the coordinating ability of the Schiff base and the electrochemical properties of the ferrocene, a new kind of Schiff base analogues bearing ferrocenylphenyl and diferrocenylphenyl groups were synthesized (**Scheme 1**) and their single crystal structures were also determined. Ferrocenylphenyl group was also an excellent electron transfer mediator⁸, and could be used to evaluate the effect of the extended π interaction in the ligand and lowered symmetry of the molecules on the ion states⁹. So the new compounds could potentially serve as efficient mediators for biosensors and new bioorganometallic mediators⁸.

Experimental

Synthesis and spectral data for compound **3**: *m*-ferrocenylaniline **2** was prepared according to literature¹¹. *m*-Ferrocenylaniline (0.277 g, 1 mmol) and salicylal (0.135 g, 1.1 mmol) were dissolved in 20 mL of dry ethanol, the mixture was refluxed until the ν_{N-H} vibration of *m*-ferrocenylaniline disappeared according to the IR spectra. The

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yellow precipitate was filtered after cooling to room temperature, washed with cooled ethanol, and dried under the vacuum. Yield: 81%(0.31 g), yellow solid, m.p. 144-145°C. Calcd. for $C_{23}H_{19}FeNO$: C, 72.46; H, 5.02; N, 3.67%; Found: C, 72.38; H, 5.25; N, 3.42; IR (KBr, cm^{-1}): 3369 (s, -OH), 1616 (s, -C=N), 1104 (m, Fc) and 1000 (w, Fc), 1283(m, -Ar-N). 1H NMR ($CDCl_3$, δ ppm): 4.07(s, 5H, -Fc), 4.35 (s, 2H,-Fc), 4.69 (s, 2H, -Fc), 6.93~7.46(m, 8H, H-Ar.), 8.67(s, 1H, CH=N), 13.36(s, 1H, -ArOH).

Synthesis and spectroscopic data for compound **4**: 1,4-Bis(2'-formylphenyl)-1,4-dioxabutane was prepared according to literature¹². Compound **4** was synthesized in the similar way as described previously, yield: 32%. Yellow solid, m.p. 222-223°C. Calcd. for $C_{48}H_{40}Fe_2N_2O_2$: C, 73.11; H, 5.11; N, 3.55%; Found: C, 72.29; H, 5.30; N, 3.40; IR (KBr, cm^{-1}): 1619 (s, -C=N), 1241 (m, Ar-O-CH₂) 1053 (m, Ar-O-CH₂), 1105 (m, Fc) and 1000 (w, Fc), 1288 (m, Ar-N). 1H NMR ($CDCl_3$, δ ppm): 4.02-4.05 (t, 5H, J=6.1Hz, -Fc), 4.29-4.30(m, 2H, -Fc), 4.60-4.64 (t, 2H, J=2Hz, -Fc), 4.52-4.54 (d, 2H, J=7.48Hz, CH₂), 6.94-7.48 (m, 8H, H-Ar), 10.45-10.48 (d, 1H, J=10.2Hz, CH=N).

Yellow single crystals of the title compounds were used for structural determinations by X-ray structure analysis. All calculations were performed using the SHELXL-97 crystal graphic software package¹³.

Crystal data for compound **3** $C_{23}H_{19}FeNO$: $M=381.24$, monoclinic, space group $P2_1/n$, $a=10.130(2)$, $b=7.7015(15)$, $c=23.386(5)$ Å, $\beta=93.51(3)^\circ$, $Z=4$, $V=1821.0(6)$ Å³, $F(000)=792$, 3841 reflections measured and 2242 unique ($R_{int}=0.0533$) were used in all calculations. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 . The final R factor was 0.0892 and wR 0.2178.

The mean deviations from planes C(1)-C(5) (Cp1), C(6)-C(10) (Cp2) are 0.0089Å, 0.0041Å respectively. The Cp rings in ferrocenyl fragment are planar and nearly parallel with a dihedral angle of 1.1°. The dihedral angle of the phenyl ring C(11)-C(16) and cyclopentadienyl ring (Cp2) is 8.5° and the two phenyl rings is 49.8°. The torsion angle is 170.3(9)° for C(15)-N(1)-C(17)-C(18). The intramolecular hydrogen bond originates from hydroxy with iminic forming a six membered ring. The distance of N(1)⋯O(1) is 2.606, H(1)⋯N(1) is 1.678Å, and the angle of N(1)⋯H(1)-O(1) is 143.41°. Obviously, the N⋯H-O interaction is strong. The distance of C(10)-C(11) is 1.473(12)Å and C=N double bond is 1.269(13) Å.

Scheme 1

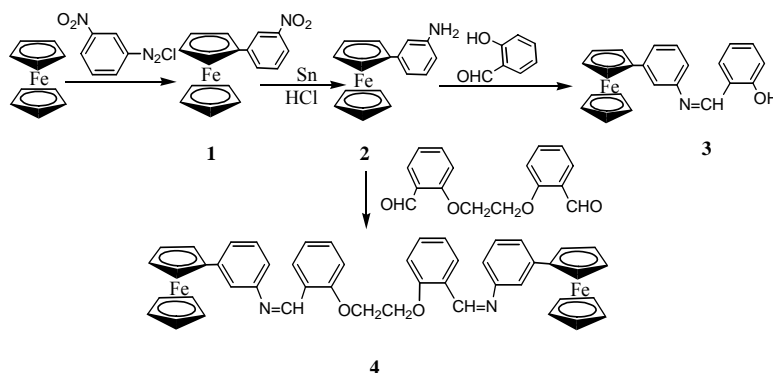


Figure 1 The molecular structure of compound **3**.

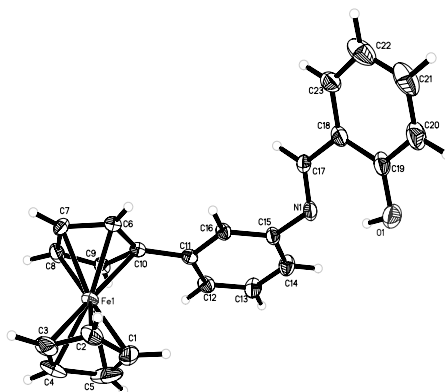
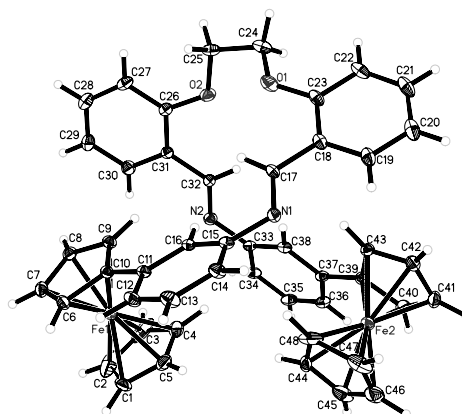


Figure 2 The molecular structure of compound **4**



Crystal data for compound **4**, $C_{48}H_{40}Fe_2N_2O_2$: $M=788.52$, monoclinic, space group $P2_1/c$, $a=10.106(2)$, $b=19.433(4)$, $c=19.714(4)$ Å, $\beta=96.59(3)^\circ$, $Z=4$, $V=3846.3(13)$ Å³, $F(000)=1640$, 7770 reflections measured and 4590 unique ($R_{int}=0.0588$) were used in all calculations. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 . The final R factor was 0.0763 and wR 0.1576.

Compound **4** features a helical shape structure. The mean deviations from planes C(1)-C(5) (Cp1), C(6)-C(10) (Cp2), C(39)-C(43) (Cp3), C(44)-C(48) (Cp4) are 0.0074, 0.058, 0.0037, 0.0126Å respectively. The Cp4 ring and phenyl ring C(33)-C(38) are nearly parallel with a dihedral angle of 2.6° and the dihedral angle of Cp2-ring and phenyl ring C(11)-C(16) is 8.8°. This is not similarly to those reported in the literature⁸. The dihedral angle of the two phenyl rings C(11)-C(16), C(18)-C(23) is 37.3° and C(26)-C(31), C(33)-C(38) is 27.5°. The torsion angles are $-179.5(6)^\circ$ and $-178.1(6)^\circ$ for C(15)-N(1)-C(17)-C(18) and C(33)-N(2)-C(32)-C(31). The Cp rings in ferrocenyl groups are planar and nearly parallel with a dihedral angle of 1.3°(Cp1, Cp2) and

2.9°(Cp3, Cp4). The distance of C(10)-C(11) is 1.478(9) Å, C(37)-C(39) 1.481(9)Å. The distance of C=N double bond is N(1)-C(17) 1.252(8) Å and N(2)-C(32) 1.266(8) Å.

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