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Synthesis, structures and electrochemistry of two Schiff base compounds bearing phenylferrocene

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Abstract

Two novel ferrocene derivatives, FcL_1 and FcL_2, were prepared and characterized. The X-ray crystal structure of FcL_1 was also described. The electrochemical studies reveal that oxidation of the substituents on the ferrocene moiety leads to an electrode passivation process.

Keywords: Ferrocenyl Schiff base derivatives; Synthesis; Crystal structure; Electrochemical property

Since its discovery [1,2], ferrocene and its derivatives are among the most thoroughly studied compounds in organometallic chemistry. Of particular interest is the redox chemistry of the iron center [3,4] and the structure [5,6]. Ferrocene/ferrocenium (Fc/Fc^+) itself represents a strictly reversible one-electron redox couple. However, substituents on the ferrocene moiety would influence the redox behavior by changing energy level of the HOMO [7], so the reversibility may be significantly lowed [8]. Schiff bases are condensation products of arylamines and carbonyl compounds; these compounds are quite stable and represent versatile intermediates for preparation of a number of important compounds. Incorporation of ferrocene moiety into Schiff bases imparts the chemical and physicochemical properties which are absent or little manifested in the parent substance. Related analogues have been investigated [9,10], but we were surprised that there has been limited study of their electrochemistry character.

In this paper, we report synthesis of two Schiff base compounds bearing phenylferrocene (Scheme 1), FcL_1 [*N*-(2-hydroxybenzylidene)-3-ferrocenylaniline] and FcL_2 [*N*-(2-hydroxybenzylidene)-4-ferrocenylaniline], and these compounds were characterized by IR, ^{1}H NMR, UV–Vis, elemental analysis and cyclic voltammetry. IR spectra were measured on a Perkin–Elmer FTIR-1750 spectrometer. ^{1}H NMR spectra were recorded at room temperature on a Bruker DPX spectrometer 400 MHz, Chemical shifts are denoted in δ units (ppm) relative to Me_4Si as internal standard. UV–Vis spectra were recorded on a Unico™ UV-2102 PC spectrometer. Electrochemical experiments were performed in dry acetonitrile with CHI 650A electrochemical analyzer using a conventional three-electrode system.

The compounds 3-ferrocenylaniline and 4-ferrocenylaniline were prepared according to procedures reported in the literature [11]. 3-Ferrocenylaniline (0.277 g, 1 mmol) was dissolved in 20 ml of absolute ethyl alcohol on heating and mixed with salicylal (0.135 g, 1.1 mmol), and the mixture was refluxed until the peaks of amino disappeared according to the IR spectrum. The precipitated yellow material was filtered off after cooling down, and then the product was washed with cooled ethanol,

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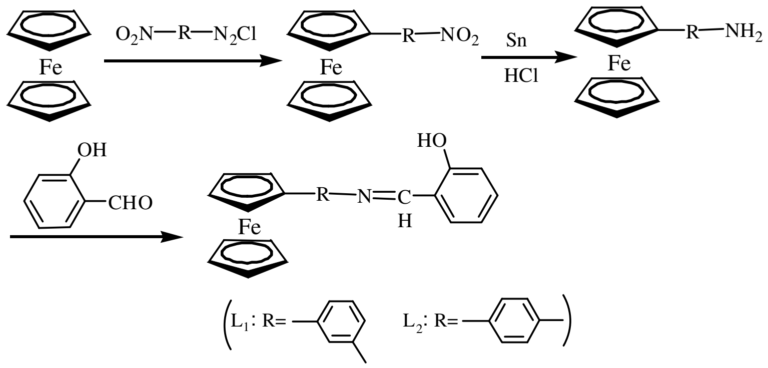

Scheme 1.

and dried on the vacuum apparatus. Yield: 81% (0.31 g); Analytical data for the compound FcL_1: Yellow solid; m.p. 144–145 °C; UV–Vis (CH_3CN) λ_{max}: 279.0 nm ($\varepsilon_{max} = 2.09 \times 10^4$ L/mol cm), 339.0 nm ($\varepsilon_{max} = 1.34 \times 10^4$ L/mol cm); IR (KBr, cm^{-1}): 3369.75 (ν-OH), 1616.78 (–C=N), 1103.92 and 999.73 (Fc), 1283.29 (ν-Ar–N);^1H NMR ($CDCl_3$, δ ppm): 4.072 (s, 5H, –Fc), 4.353 (s, 2H, –Fc), 4.687 (s, 2H, –Fc), 6.9–7.4 (m, 8H, H–Ar,), 8.617 (s, 1H, –ArOH); *Anal.* Calc. for $C_{23}H_{19}FeNO$: C, 72.44; H, 4.98; N, 3.67. Found: C, 72.63; H, 5.14; N, 3.77. Compound FcL_2 was prepared according to a similar procedure used for compound FcL_1, replacing 3-ferrocenylaniline by 4-ferrocenylaniline. Yield: 76% (0.28 g). Analytical data for the compound FcL_2: Yellow solid, m.p. 171–172 °C; UV–Vis (CH_3CN) λ_{max}: 277.4 nm ($\varepsilon_{max} = 1.60 \times 10^4$ L/mol cm), 350.0 nm ($\lambda_{max} = 1.98 \times 10^4$ L/mol cm); IR (KBr, cm^{-1}): 3445.63 (ν-OH), 1623.35 (–C=N), 1104.21 and 1000.01 (Fc), 1277.45 (ν-Ar–N);^1H NMR ($CDCl_3$, 400 MHz) ppm: 4.062 (s, 5H, –Fc), 4.354 (s, 2H, –Fc), 4.671 (s, 2H, –Fc), 6.9–7.6 (m, 8H, H–Ar), 8.687 (s, 1H, –ArOH); *Anal.* Calc. for $C_{23}H_{19}FeNO$: C, 72.44; H, 4.98; N, 3.67. Found: C, 72.53; H, 5.01; N, 3.80.

The X-ray crystal structure of FcL_1 was also presented. All measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Temperature 291(2) K, $I > 2\sigma$ reflections were 4280. The data were corrected for Lorentz and polarization effects. The crystal structure of compound FcL_1 is shown in Fig. 1. It belongs to monoclinic system $P2\ (1)/c$ space group, $a = 1.0130(2)$ nm, $\alpha = 90°$, $b = 0.77015(15)$ nm, $\delta = 93.51(3)°$, $c = 2.3386(5)$ nm, $\gamma = 90°$. The final R factor was 0.0964, $R_w = 0.2436$. Fe–C_{ring} distances range

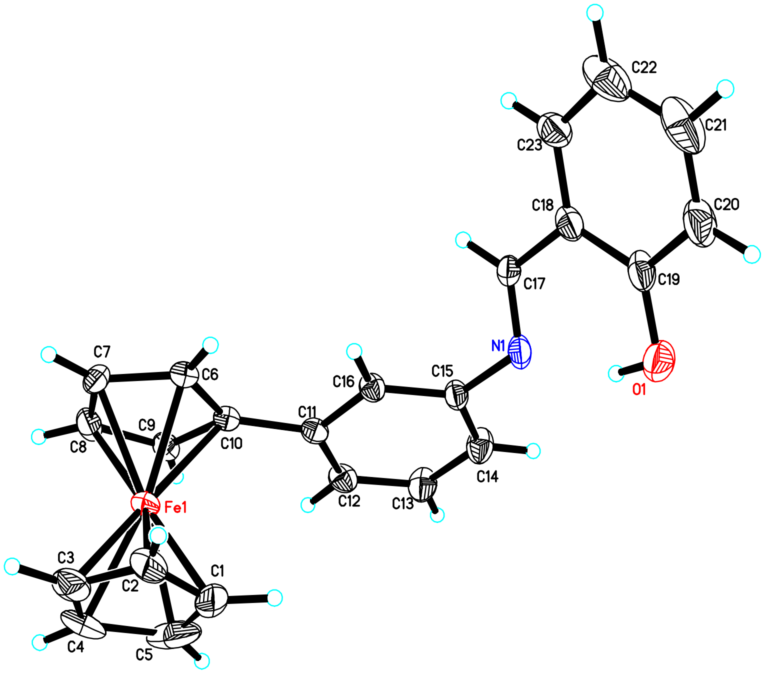

Fig. 1. The molecular structure of compound FcL_1.

from 2.004(12) to 2.048(9) Å and intracyclopentadienyl C–C bond lengths lie in the range 1.361(19)–1.45(2) Å, and C–C–C angles (average 108.03(45)°) are very similar to those reported in the literature [12]. The bond lengths and angles within the phenyl group are unexceptional. The mean deviations from planes C1 to C5 (1), C6 to C10 (2) are 0.089, 0.041 Å, respectively. The cyclopentadienyl rings in ferrocenyl fragment are planar and nearly parallel with a dihedral angle of 1.1°. It is clear from the structure that the phenyl ring is almost coplanar to the cyclopentadienyl ring plane to which it is attached; their dihedral angle (planes C11–C16 and C6–C10) is 8.5° and the dihedral angle of two phenyl rings is 49.8°. The phenyl ring is bonded with cyclopentadienyl ring at a distance of 1.473(12) Å (C10–C11). The torsion angle is 170.3(9)° for C15–N1–C17–C18. The intramolecular hydrogen bond originates from hydroxy with imine forming a six membered ring. N1···O1 = 2.606, H···N1 = 1.678 Å, N1–H1···O1 = 143.41°. Obviously, the N–H···O interactions are strong. The imine C=N distance is 1.269(13) Å.

The electrochemical parameters for two compounds and related compounds obtained from the CV are summarized in Table 1. The cyclic voltammetric behavior of these compounds show one pair of well-defined and stable redox waves in the potential range of 0.0–1.0 V at the GC electrode, which is attributed to the Fc/Fc$^+$ redox process. It is interesting to find that the formal potential (E^0), taken as the average of E_{pa} and E_{pc}, of these compounds show a gradual increase in the order 3-ferrocenylaniline ≈ 4-ferrocenylaniline < ferrocene < FcL_2 ≈ FcL_1, suggesting that the electron withdrawing imine group substantially in FcL_1 and FcL_2 significantly influence the redox potential of the iron center. At the same time, the formal potential of FcL_1 and FcL_2, 3-ferrocenylaniline and 4-ferrocenylaniline are very close, which indicate ferrocene subunit in both case are in the equivalent environment. For two novel ferrocene derivatives and related compounds, the values of the diffusion coefficient (D) obtained confirm this concept that the D values decreases as an increase in the molecular weight of the compound and the size of the molecules. According to Nicholson formula [13], the standard rate constant of the electrode reaction (k_s) values of compounds are also calculated, shown in Table 1.

Moreover, though not seen in Table 1, FcL_1 and FcL_2 also exhibit an irreversible anodic process at higher potential values, which is obviously assigned to the oxidation of hydroxybenzylidene. The important feature of CVs was the pronounced shape change between the first and second scans (Fig. 2(A)). The currents for the second scan in Fig. 2(A) were much

Table 1
Electrochemical data of FcL_1, FcL_2 and related compounds

Compound	CV data				Kinetics data		
	E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)	E^0 (V)	$D_0 \times 10^5$ (cm^2/s)		$k_s \times 10^2$ (cm/s)
					CV	CA	
Ferrocene	0.473	0.400	73	0.437	2.38	2.40	2.35
3-Ferrocenylaniline	0.405	0.334	71	0.370	1.42	1.45	1.82
4-Ferrocenylaniline	0.409	0.337	72	0.373	1.51	1.47	1.85
FcL_1	0.522	0.450	72	0.485	1.02	1.10	1.56
FcL_2	0.528	0.455	73	0.492	1.10	1.18	1.62

(a) All potentials are referred to the saturated calomel electrode (SCE) in CH_3CN solution, v = 100 mV/s.
(b) $\Delta E_p = (E_{pa} - E_{pc})$, $E^0 = (E_{pa} + E_{pc})/2$.
(c) CV:D was computed from normalized peak currents data using CV relationships; CA:D was computed from i–t data using Cottrell relationships.

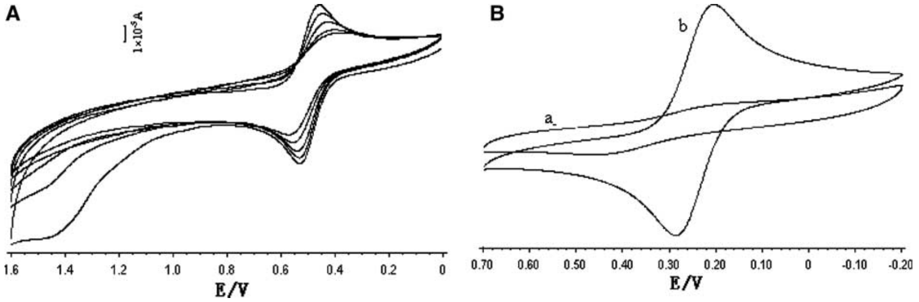

Fig. 2. (A) Consecutive CVs of 5×10^{-4} mol/L FcL_1 at a GC electrode in 0.1 M TBAP acetonitrile from 0.0 to 1.6 V. (B) CVs of 5×10^{-3} mol/L ferricyanide in aqueous KCl (0.1 mol/L) at the GC electrode: (a) following five cycles through the oxidation process of FcL1, and at a clean GC electrode; (b) v = 100 mV/s.

lower than those of the first scans. The disappearance of the irreversible peak and the decrease of electrochemical reversibility for Fc/Fc$^+$ after the first scan suggested a rapid and efficient passivation of the GC surface similar to that following the electrochemical oxidation of phenol [14,15]. As with phenol, the oxidized product of the electrode reaction at higher potential undergoes a following chemical reaction to produce a passivating, non-conducting film on the electrode surface. It is clear also from the magnitude of the currents on the second and subsequent potential cycles that complete passivation of the electrode surface has not occurred. Electrode surface passivation was also tested by probing the electrochemistry of the ferri/ferrocyanide couple on electrodes that has been repeatedly cycled through the oxidation of compounds FcL_1 and FcL_2. Fig. 2(B) shows CVs of ferricyanide at clean GC electrodes as well as at those which had been used for repetitive oxidative cycling of the target compounds. In both cases there is severe attenuation of the electrochemical detection of the probe redox ion, indicating deposition of an electropolymerized layer.

Electrochemical studies reveal that the electron withdrawing imine group substantially influences the redox potential of the iron center and oxidation of the substituents on the ferrocene moiety leads to an electrode passivation process. For two novel ferrocene derivatives, further studies on other properties are underway and will be reported in due course.

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