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RATIONAL DESIGN AND CONVENIENT SYNTHESIS OF TWO NOVEL FERROCENE-BASED SULFONYL DIAMINE PRECURSORS

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ABSTRACT

In the search of new organometallic precursors, this contribution describes a convenient synthesis to obtain new ferrocene-based sulfonyl diamine derivatives. The $[(\eta^5\text{-C}_5\text{H}_4\text{SO}_2\text{NH-CH}_2\text{-CH}_2\text{-NH}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$ (**1**) and $[(\eta^5\text{-C}_5\text{H}_4\text{SO}_2\text{NH-C}_6\text{H}_4\text{-NH}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$ (**2**) compounds were prepared by the reaction between $(\eta^5\text{-C}_5\text{H}_4\text{SO}_2\text{Cl})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ and the respective diamine precursor: ethylenediamine (**1**) or *p*-phenylenediamine (**2**) in good yields (86% for **1**; 70% for **2**). Both compounds were characterized by conventional spectroscopic techniques (infrared spectroscopy, nuclear magnetic resonance spectroscopy, mass spectrometry and elemental analysis) and cyclic voltammetry. In addition, the molecular structure of **1** was determined by single-crystal X-ray diffraction.

Keywords: Cyclic voltammetry, ferrocene, organometallic, sulfonamide, X-ray.

1. INTRODUCTION

Ferrocene, the first known and archetypal metallocene, stirred up a great deal of attention immediately after its discovery in the early 1950s [1]. Based on its unique properties, ferrocene had served as a widely applicable organometallic scaffold for the preparation of functional derivatives that are finding use in very many areas. These range from mostly academic research aimed at exploring its use in the preparation of various organometallics compounds, to practically directed applications in catalysis [2], material science [3, 4] and biomedical chemistry [5].

Particularly, ferrocene derivatives have attracted considerable attention for their potential applications as nonlinear optical devices, functional materials in electrochemical sensors [6-9], and chiral catalysts [10-12]. Moreover, functionalized ferrocene derivatives are widely used in coordination chemistry as donor ligands [13-15]. Additionally, ferrocene derivatives have also attracted wide interest for their considerable biological activities [16-23]. For example, the ferroquine (FQ) is about to complete phase II clinical trials as a treatment for uncomplicated malaria [24]. On this regard, organometallic sulfonamides have also been studied as potential biological agents [25-29]. To date, Supuran and co-workers isolated ferrocenyl-1,2,3-triazoles containing sulfonamide moieties and evaluated their activity as potential carbonic anhydrase inhibitors [30]. Other ferrocenyl-sulfonamides connected by hydrazone moieties have been prepared and screened for their *in vitro* bacterial and antifungal properties[31]. Recently, Ziegler and co-workers have synthesized and characterized a new series of 1,1'-ferrocene bis(sulfonamides) derived from 1,1'-bis(sulfonylchloride)ferrocene precursor [32-34] but their biological applications have not been described. Inspired by the successful approach used by Ziegler research group, we have proposed new synthetic strategies to incorporate organometallic entities into the sulfonamide skeleton. On this regard, we have described the synthesis of new $(\eta^5\text{-C}_5\text{H}_4\text{SO}_2\text{NH-NH}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ precursor and its use to obtain new ferrocenyl Schiff bases by condensation reactions[35].

Considering the large number of studies concerning sulfonamide fragments covalently bonded to organometallic groups, in this work, we propose to combine ferrocenyl moiety with sulfonyl diamine fragments to produce $[(\eta^5\text{-C}_5\text{H}_4\text{SO}_2\text{NH-CH}_2\text{-CH}_2\text{-NH}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$ (**1**) and $[(\eta^5\text{-C}_5\text{H}_4\text{SO}_2\text{NH-C}_6\text{H}_4\text{-NH}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$ (**2**) derivatives. It is important to note that these compounds could be used as novel templates for the generation of new organometallic imines compounds with potential biological applications.

2. EXPERIMENTAL SECTION

2.1. Materials

All manipulations were conducted under a N₂ atmosphere using Schlenk techniques. The compound $(\eta^5\text{-C}_5\text{H}_4\text{SO}_2\text{Cl})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ was prepared according to published procedure [36, 37]. Ferrocene (98%), acetic anhydride (≥98.0%), chlorosulfonic acid, *p*-toluidine, oxalyl chloride (98%), ethylenediamine and

p-phenylenediamine were obtained from Sigma Aldrich and used without further purification. Solvents such as dichloromethane, chloroform, *n*-hexane, tetrahydrofuran, and acetonitrile were obtained commercially and purified using standard methods [38].

Infrared spectra were recorded in solid state (KBr pellet) on a Jasco FT-IR 4600 spectrophotometer. NMR spectra were measured on a Bruker spectrometer model ASCEND TM 400 MHz. All NMR spectra are reported in parts per million (ppm, δ) relative to tetramethylsilane (Me₄Si), with the residual solvent proton resonances used as internal standards. Coupling constants (J) are reported in Hertz (Hz), and integrations are reported as number of protons. The following abbreviations were used to describe the peak patterns: s = singlet, d = doublet, t = triplet, and m = multiplet. Mass spectra were obtained at the Laboratorio de Servicios Analíticos, Universidad Católica de Valparaíso on a Shimadzu GC-MSA. Elemental analyses were measured on a Perkin Elmer CHN Analyzer 2400.

2.2. Synthesis

2.2.1. Synthesis of $[(\eta^5\text{-C}_5\text{H}_4\text{SO}_2\text{NH-CH}_2\text{-CH}_2\text{-NH}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$ (**1**)

A Schlenk tube was charged with a magnetic stir bar, ethylenediamine (0.60 mL, 8.64 mmol), triethylamine (3.60 mL, 25.6 mmol) and anhydrous CH₂Cl₂ (20.0 mL). The resulting mixture was cooled to -10°C and a solution of $(\eta^5\text{-C}_5\text{H}_4\text{SO}_2\text{Cl})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ (1.23 g, 4.32 mmol) in anhydrous CH₂Cl₂ (10.0 mL) was added dropwise. The reaction mixture was stirred for 24 h at room temperature. After this time, the solvent was removed under reduced pressure. The solid obtained was dissolved in chloroform, washed with 10% sodium carbonate (20.0 mL) and deionized water (20.0 mL). The organic layer was dried with anhydrous Na₂SO₄ and the solvent was removed by evaporation under reduced pressure to give a yellow solid. Compound **1** was isolated as yellow crystals after purification from CHCl₃/hexane mixture (1:4) at -18°C (Yield: 1.13 g, 3.68 mmol, 85%). FT-IR (KBr, cm⁻¹): 3362 (νN-H₂), 3106 (νN-H), 1307 (νS-O), 1189 (νS-O). ¹H NMR (DMSO-*d*₆): δ 4.57 (s, 2H, C₅H₄); 4.44 (s, 2H, C₅H₄); 4.35 (s, 5H, C₅H₅); 2.71 (t, *J* = 6.3 Hz, 2H, CH₂). ¹³C NMR (DMSO-*d*₆): δ 88.8 (C₅H₄-*ipso*); 70.1 (C₅H₅); 70.0 (C₅H₄); 68.1 (C₅H₄); 46.8 (CH₂); 41.7 (CH₂). Mass spectrum (*m/z*): 308 [M⁺]. Anal. (%) Calc. for C₁₂H₁₆FeN₂O₂S: C, 46.77; H, 5.23 and N, 9.09; found: C, 46.84; H, 5.24 and N, 9.08.

2.2.2. Synthesis of $[(\eta^5\text{-C}_5\text{H}_4\text{SO}_2\text{NH-C}_6\text{H}_4\text{-NH}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$ (**2**)

A Schlenk tube was charged with a magnetic stir bar, $(\eta^5\text{-C}_5\text{H}_4\text{SO}_2\text{Cl})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ (1.04 g, 3.67 mmol) and anhydrous THF (20.0 mL). Subsequently, triethylamine (1.0 mL, 7.33 mmol) was added dropwise under stirring. After a few minutes, a solution of *p*-phenylenediamine (0.31 g, 3.67 mmol) in anhydrous THF (20.0 mL) was slowly added. The reaction mixture was stirred for 24 h at room temperature. After that time, the solution was filtered, and the solvent was removed under reduced pressure. (Yield: 0.91 g, 2.56 mmol, 70%). FT-IR (KBr, cm⁻¹): 3445 (νN-H₂), 3228(νN-H), 1307 (νS-O), 1186 (νS-O). ¹H NMR (DMSO-

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d_{δ}): δ 8.93 (s, 1H, NH); 6.65 (d, 2H, $J = 8.5$ Hz, C_6H_4); 6.38 (d, 2H, $J = 8.6$ Hz, C_6H_4); 5.29 (s, 2H, NH_2); 4.35 (s, 4H, C_5H_4); 4.30 (s, 5H, C_5H_5). ^{13}C NMR (DMSO- d_6): δ 146.7 (C_6H_4); 126.6 (C_6H_4); 124.9 (C_6H_4); 117.5 (C_6H_4); 114.4 (C_6H_4); 88.8 (C_5H_4 -ipso); 70.6 (C_5H_5); 70.3 (C_5H_4); 68.7 (C_5H_4). Mass spectrum (m/z): 356 [M^+]. Anal. (%) Calc. for $C_{16}H_{16}FeN_2O_2S$: C, 53.95; H, 4.53 and N, 7.86; found: C, 53.89; H, 4.54 and N, 7.85.

2.3. X-ray crystal structure determinations

Single crystal of compound **1** suitable for X-ray diffraction was obtained as described above. The crystal was carefully chosen using a stereo zoom microscope supported by a rotatable polarizing stage. The data were collected at room temperature on a Bruker APEX II CCD Quazar equipped with a Silver Incoatec microsource (0.56086 Å). The crystal was glued to a thin glass fibre using inert oil and mounted on the diffractometer. The intensity data were processed using a Bruker suite of data processing programs (Bruker Analytical X-ray Systems, Inc., 2016. Apex3, Version 1 User Manual, M86-EXX229, Madison, WI), and absorption corrections were applied using SADABS Bruker Analytical X-ray Systems, Inc., 2016). The crystal structure was solved by the charge flipping method using SUPERFLIP[39] and the data were refined by full matrix least-squares refinement on I with anisotropic displacement parameters for non-H atoms using XL refinement package, as implemented in Olex2 suite [40].

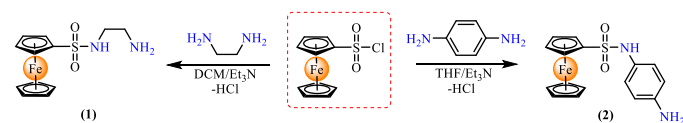
2.4. Electrochemical studies

Cyclic voltammetry (CV) studies were carried out at room temperature using a CHI620E potentiostat and a three-electrode cell. Each compound was dissolved in anhydrous CH_3CN containing 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (Bu_4N)[PF_6] as a supporting electrolyte to give a final concentration of $10^{-3} \text{ mol L}^{-1}$. Glassy carbon was used as working electrode, and a platinum wire as the auxiliary electrode. The reference electrode contained a silver wire with 10 mM silver nitrate in (Bu_4N)[PF_6] electrolyte solution. All electrolyte solutions were thoroughly prepurged using purified nitrogen gas before use. The measurements were carried out at a scan rate of 50, 100, 150 and 200 $mV s^{-1}$, and ferrocene was used as an internal reference.

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization of new ferrocenylsulfonyl diamine precursors

The new ferrocenylsulfonyl diamine precursors (**1** and **2**) were prepared by the reaction between $(\eta^5-C_5H_4SO_2Cl)Fe(\eta^5-C_5H_5)$ and the respective diamine precursor: ethylenediamine (**1**) or *p*-phenylenediamine (**2**) (Scheme 1). The new compounds were isolated as solid samples in good yields (85% for **1**; 70% for **2**). The new compounds are air-stable and slightly soluble in most polar organic solvents (e.g. $CHCl_3$, DMSO and CH_3CN). Both compounds were characterized by conventional spectroscopic techniques and cyclic voltammetry.



Scheme 1. Synthesis of compounds **1** and **2**.

The FT-IR spectra (KBr disk) of all compounds (Figures S1-S2†) showed the expected absorption bands for the ν_{N-H} and ν_{SO_2} stretches in the ranges of 3445–3228 cm^{-1} and 1307–1186 cm^{-1} , respectively. Similar frequency values have been reported for others organic and organometallic sulfonamide analogues [41–43]. A strong molecular ion was shown in the mass spectrum of each ferrocenylsulfonyl diamine precursors (Figures S13-S14†). The elemental analysis data determined for all compounds agrees with their proposed formulas.

The 1H NMR spectra for complexes **1** and **2** indicate the presence of a single compound (Figures S3-S5†). For both complexes, the resonances assigned to the protons of unsubstituted cyclopentadienyl appeared as a singlet in the region δ 4.40 – 4.30. The two signals observed at δ 4.57 – 4.44 (**1**) and δ 4.35 – 4.30 (**2**) are assigned to the hydrogen nuclei of the substituted ring. These results agree with the values reported for several ferrocenyl complexes [37, 44, 45]. For compound **1**, additional signals were observed at δ 2.94 and δ 2.75 (Figure S4†),

and they were attributed to the presence of the $-CH_2CH_2-$ group. It is important to mention that this assignment was confirmed by DEPT 135 experiment (Figure S9–10†). In the case of **2** (Figure S5†), the multiplets observed between δ 6.65 and δ 6.38 were attributed to the hydrogen atoms of the $-C_6H_4-$ ring. Moreover, two singlets are observed at δ 8.92 and δ 5.29 corresponding to $-NH-$ and $-NH_2$ moieties, respectively. Similar δ have been reported for other organometallic tosyl hydrazones[35, 41]. Unfortunately, these signals were not observed for compound **1**.

The ^{13}C NMR data were also in agreement with the proposed structures (Figures S6-S8†), both compounds showed the characteristic carbon nuclei of the organometallic fragments between δ 89.0–68.0. As expected for compound **2**, the resonances for the carbon atoms of the phenyl rings were observed at low field (δ 150–115) and did not show any noticeable differences from those reported for the organic or organometallic analogues mentioned above [30, 46, 47]. For other hand, compound **1** exhibited two resonances at δ 41.7 and δ 46.8, which were assigned to the $-CH_2CH_2-$ entity.

3.2. X-ray crystallography

To compare the structural parameters of the organometallic sulfonamides with data reported for related compounds, we performed crystallographic studies of **1**. Single crystal of **1** was obtained by slow diffusion from $CHCl_3$ /hexane solvent mixture. Figure 1 show the ORTEP view of the structure of **1**, including selected bond distances and angles. A full description of the crystal data, data collection and refinement parameters are given in the Table S1†.

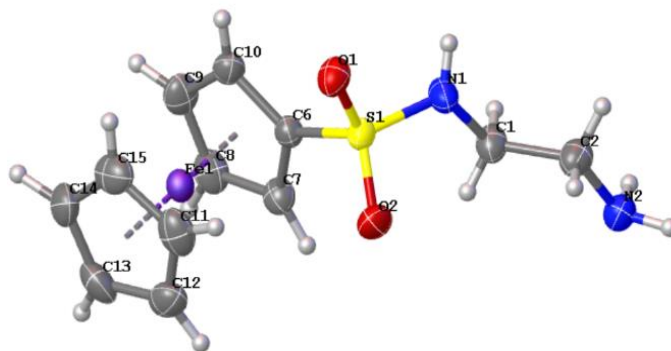


Figure 1. ORTEP of the molecular structure of the compound $[(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4SO_2NH-CH_2-CH_2-NH_2)]$. Bond distances (Å) selected: C_5H_4 (centroid)-Fe 1.651(4); Fe- C_5H_5 (centroid) 1.656(4); S(1)-N(1) 1.597(3); S(1)-O(1) 1.438(2); S(1)-O(2) 1.436(2); S(1)-C(6) 1.757(3); N(1)-C(1) 1.468(6); N(2)-C(2) 1.468(5); C(2)-C(1) 1.507(5). Angles ($^\circ$) selected: N(1)-S(1)-O(1) 106.8(1); N(1)-S(1)-O(2) 108.2(1); N(1)-S(1)-C(6) 108.6(2); O(1)-S(1)-O(2) 119.5(1); O(1)-S(1)-C(6) 106.8(1); O(2)-S(1)-C(6) 106.5(1); S(1)-N(1)-C(1) 120.4(3).

The compound **1** crystallizes in a monoclinic crystal system in the centrosymmetric space group $P2(1)/c$. For compound **1** the bond lengths of S(1)-O(1) (~1.438 Å), S(1)-O(2) (~1.436 Å), and S(1)-N(1) (~1.597 Å) and the angles N(1)-S(1)-O(1) 106.8 $^\circ$; N(1)-S(1)-O(2) 108.2 $^\circ$; N(1)-S(1)-C(6) 108.6 $^\circ$ and O(1)-S(1)-O(2) 119.5 $^\circ$. Furthermore, the geometry around the S(1) atom deviates from the distorted tetrahedral, and the maximum and minimum angles around S(1) are ~106.2 $^\circ$ and ~119.5 $^\circ$; this is similar to those reported for other organic sulfonamides[48, 49] and organometallic sulfonamides with ferrocenyl group [29, 41]. Finally, the substituted and unsubstituted Cp unit contained in the ferrocenyl moiety are nearly eclipsed, like other monosubstituted ferrocenyl derivatives [50].

3.3. Electrochemical studies

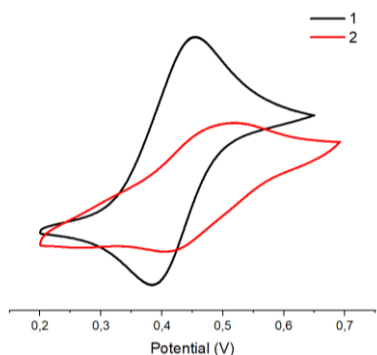
With the aim of comparing the effect of the substitution in one of the cyclopentadienyl rings on the redox potential of the iron(II) present in the ferrocenyl group, electrochemical experiments were carried out. The redox behavior of the new ferrocenylsulfonyl diamine precursors **1** and **2** in CH_3CN was studied using cyclic voltammetry according to the conditions described in the Experimental section. All the potentials are referenced to the Ag/Ag^+ electrode (non-aqueous) and the results are summarized in Table 1.

Table 1. Values of potentials for the ferrocenyl group in precursors synthesized **1** and **2**, compared to ferrocene under the same conditions.

Compound	Epc (V)	Epa (V)	E _{1/2} (V)	ΔE (V)
Fc	0.057	0.12	+ 0.09	0.06
1	0.39	0.45	+ 0.42	0.06
2	0.45	0.50	+ 0.45	0.05

The separation between the oxidation and reduction peaks $\Delta E = (E_{pc} - E_{pa})$ agrees with those expected for a simple reversible one electron-process[51]. Therefore, the cyclic voltammograms of **1** and **2** (Figure 2) each displayed a fully reversible one-electron transfer process corresponding to the Fc/Fc⁺ couple.

In comparison with ferrocene ($E_{1/2} = +0.09$ V), the values corresponding **1** and **2** compounds increased (+ 0.42 V for **1** and + 0.45 for **2**). This is due to the electron acceptor effect of the sulfonyl group, which indicates that iron oxidizes with greater difficulty. It is important to mention that the structural difference between compounds **1** and **2** is the change in the bonding bridge between the sulfonamide and terminal amine. This when correlated with the value of the $E_{1/2}$, it is observed that it increases slightly. Which indicates a possible effect of the aromatic bridge compared to the aliphatic, where the iron(II) in compound **2** was oxidized with greater difficulty.

**Figure 2.** Voltammogram of **1** and **2** at 100 mVs⁻¹ in acetonitrile and 0.1 molL⁻¹ Bu₄NPF₆ on glassy carbon electrode and non-aqueous electrode Ag/Ag⁺ as reference.

CONCLUSIONS

This work describes the synthesis of $[(\eta^5\text{-C}_5\text{H}_4\text{SO}_2\text{NH-CH}_2\text{-CH}_2\text{-NH}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$ (**1**) and $[(\eta^5\text{-C}_5\text{H}_4\text{SO}_2\text{NH-C}_6\text{H}_4\text{-NH}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$ (**2**) derivatives by the reaction between $(\eta^5\text{-C}_5\text{H}_4\text{SO}_2\text{Cl})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ and ethylenediamine or *p*-phenylenediamine, respectively. The structures of the two complexes were inferred using conventional spectroscopic and analytical techniques (infrared, ¹H and ¹³C NMR, and elemental analysis). The molecular structure of **1** was confirmed by single-crystal X-ray analysis, confirming that the ferrocenyl moiety was incorporated into sulfonyl ethylenediamine skeleton. In addition, cyclic voltammetry experiments correlated the relationship between $E_{1/2}$ and the nature of aliphatic (**1**) or aromatic (**2**) bridge in these compounds. It is important to note that these compounds could be used as novel templates for the generation of new organometallic imines compounds with potential biological applications.

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APPENDIX A. SUPPLEMENTARY MATERIAL

Electronic Supplementary Information (ESI) available: Characterization data and X-ray crystal structure determinations. CIF files containing tables of crystallographic parameters, bond distances, bond angles, as well as a list of structure factors have been deposited in the Cambridge Crystallographic Data Centre (CCDC 2236934 for **1**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/contents/retrieving.html; from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or via e-mail: deposit@ccdc.cam.ac.uk.

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