

Short communication

Unsymmetrical cyrhetrenyl and ferrocenyl azines derived from 5-nitrofurane: Synthesis, structural characterization and electrochemistry



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ABSTRACT

A new series of unsymmetrical cyrhetrenyl and ferrocenyl azines that were monosubstituted $[(\eta^5\text{-C}_5\text{H}_4\text{-C(R)=N-N=CH(5\text{-NO}_2\text{-2-C}_4\text{H}_2\text{O}))M]$ (with $M=\text{Re}(\text{CO})_3$ and $\text{R}=\text{H}$ (**1a**) or $\text{R}=\text{Me}$ (**1b**); $M=\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ and $\text{R}=\text{H}$ (**2a**) or $\text{R}=\text{Me}$ (**2b**)) and disubstituted $[\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4\text{-C(Me)=N-N=CH(5\text{-NO}_2\text{-2-C}_4\text{H}_2\text{O}))}_2]$ (**3a**) were prepared by condensation reactions of the corresponding organometallic hydrazone $[(\eta^5\text{-C}_5\text{H}_4\text{-C(R)=N-NH}_2)]M$ with 5-nitro-2-furaldehyde. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra indicated that these compounds adopted an (*E,E*)-configuration about the $\text{C}=\text{N}$ bond and an *s-trans* conformation about the N1-N2 bond, and this result was confirmed by X-ray crystallographic analyses of **1a** and **2b**. The opposite electronic effects of the organometallic fragments correlate with the co-planarity of the $[(\eta^5\text{-C}_5\text{H}_4\text{-C(R)=N-N=CH(5\text{-NO}_2\text{-2-C}_4\text{H}_2\text{O}))]$ system, the reduction potential of the nitro group ($E_{1/2}$) and the chemical shifts of the iminic carbons.

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Azines or N–N-linked diimine ($\text{C}=\text{N}-\text{N}=\text{C}$) containing molecules are an important class of compounds that have been extensively studied for several decades due to their structural and electronic properties, numerous applications and biological activities. A detailed review of the broad chemical aspects of azine derivatives has been recently reported by Safari and Gandomi-Ravandi [1]. Most of the studies have focused on symmetrical or unsymmetrical azines that involve organic substituents [2]. However, several unsymmetrical ferrocenyl substituted azines have also received considerable attention due to their interesting electrochemical behavior as well as their potential for use as new nonlinear optical materials [3,4], ligands in coordination chemistry [5,6,7] and metal-recognition applications [8]. In addition, some ferrocenyl azines containing salicylaldimine motifs and their metal complexes have been recently explored due to their biological properties (i.e., antiparasitic or antitumor agents) [9,10].

Taking into account the promising reports that involve organometallic groups being incorporated into various anticancer, antimalarial, trypanocidal and antitubercular agents [11] along with our ongoing efforts to incorporate organometallic fragments with opposite electronic effects, which influence the electronic properties and structural parameters of new organometallic molecules [12], we report the synthesis and

characterization of new cyrhetrenyl and ferrocenyl azines based on the 5-nitrofurane pharmacophore.

The two series of organometallic derivatives were synthesized via an in situ condensation reaction between the corresponding substituted cyrhetrenyl hydrazone or ferrocenyl hydrazone, 1,1'-di-acetyl-ferrocene dihydrazone [13], and 5-nitrofurane-2-aldehyde (Scheme 1) [14].

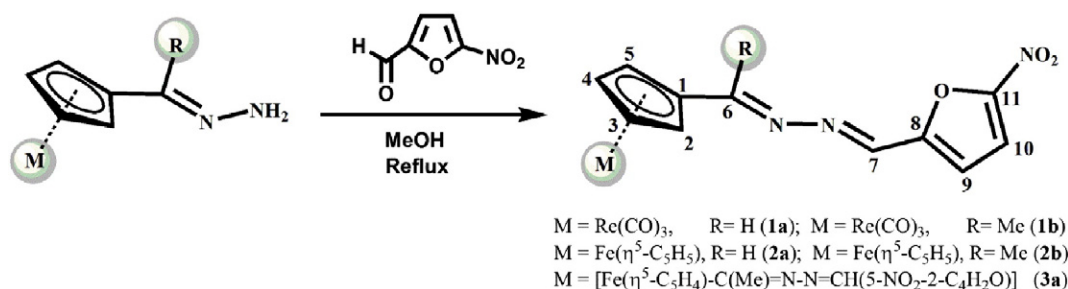
The resulting compounds were isolated as pure material (by NMR) after purification by column chromatography and crystallization. All the compounds were thermally stable, soluble in polar organic solvents and insoluble in hexane and benzene [14].

The IR spectra of these compounds exhibited the expected absorption band for the $\nu(\text{C}=\text{N})$ stretch in the range of $1603\text{--}1608\text{ cm}^{-1}$ in a CH_2Cl_2 solution. Similar $\nu(\text{C}=\text{N})$ frequency values have been reported for ferrocenyl azine $[\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4\text{-C(Me)=N-N=C(H)(C}_6\text{H}_3\text{-2,6-R)}\}_2]$ [5]. However, this band is shifted to lower wavenumber compared to that for a single organometallic imine derived from 5-nitrofurane $\{[(\eta^5\text{-C}_5\text{H}_4\text{-N=CH(5\text{-NO}_2\text{-2-C}_4\text{H}_2\text{O}))M]$, $M=\text{Re}(\text{CO})_3$, $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ ($1610\text{--}1630\text{ cm}^{-1}$) [12a]. This result can be interpreted as a large electronic delocalization between the metal fragment and the nitrofurane ring through the azine bridge. Additionally, the shift of the asymmetric (ν_{as}) and symmetric (ν_{s}) stretching of the $\nu(\text{CO})$ absorption bands of **1a** and **1b** to higher energy compared to those measured for the hydrazone precursors $[\text{Re}\{(\eta^5\text{-C}_5\text{H}_4\text{-C(R)=N-NH}_2)\}(\text{CO})_3]$ [13a] further confirms that the electronic delocalization increased due to the $\text{C}=\text{N}-\text{N}=\text{C}$ moiety.

For all the complexes, the ^1H NMR spectra indicated the presence of a single compound, as expected for these types of molecules. In most of

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Scheme 1. Synthesis of compounds **1a**, **1b**, **2a**, **2b**, and **3a**, and atom numbering system for the NMR data.

the cases, this compound adopted an (*E,E*)-configuration [15]. In addition to the hydrogen resonance characteristics of the cyrhetrenyl and ferrocenyl fragments, complexes **1b**, **2b** and **3a** exhibited singlets at approximately 2.30–2.42 ppm and 8.14–8.30 ppm, which were unequivocally assigned to the Me and –NC(H)– groups, respectively. The proton resonances of the two imine protons (H⁶, H⁷) in **1a** and **2a** are represented by singlets in the δ 8.38–8.65 range. For all the cases, two doublets observed at approximately δ 7.05–7.40 were assigned to protons on the furfuryl ring (H⁹, H¹⁰). The correct assignments of these resonances were determined by 2D heteronuclear correlation NMR {¹H–¹³C}–HMBC, {¹H–¹³C}–HSQC and Dept-135 [14].

The most interesting features of the ¹³C{¹H} NMR spectra of these complexes are the resonances corresponding to the carbons contained in the azine bridge. Due to the established coplanarity of the conjugated –C(R)=N=N=C(H)– system in the solid state (see below), the ¹³C-chemical shift values (δ) of the iminyl carbons are significant and exhibit a dependence on the electronic effects of the organometallic fragments. First, in all cases, the iminyl carbon bound to the 5-nitrofuran group (C⁷) is shielded with respect to the organometallic iminyl carbons (C⁶). Second, compared to the δ values of the iminyl carbons (C⁷), these atoms are deshielded when the cyrhetrenyl moiety is connected to the furfuryl ring (149.3, 148.1 ppm for **1a** and **1b**, respectively), and for the ferrocenyl fragment (146.9 for **2a**, 144.6 for **2b** and 145.1 ppm for **3a**), a similar behavior was observed in cyrhetrenyl and ferrocenyl imine complexes of the form {[η^5 -C₅H₄)-N=CH-(5-NO₂-2-C₄H₂O)]M, M=Re(CO)₃, Fe(η^5 -C₅H₅)} [12a]. Third, the low-field shift of the resonance of the iminyl carbon bound to the ferrocenyl fragment compared to the cyrhetrenyl analogs ($\Delta\delta$ = 10.2 ppm in **1a**, **2a** and $\Delta\delta$ = 16.8 ppm in **1b**, **2b**) is similar to that observed for a series of ferrocenyl- and cyrhetrenyl-thiosemicarbazones that was recently reported by our group [16]. Therefore, these results further confirm that the nature of the organometallic framework modifies the degree of electronic delocalization on the –C(R)=N=N=C(H)– unit.

The results from electron impact mass spectrometry confirmed the integrity of the cyrhetrenyl and ferrocenyl azines. All the complexes exhibited a peak with an *m/z* value that corresponded to their molecular weight. In addition, the successive loss of three CO ligands results in the most relevant fragments observed in the spectra of **1a** and **1b**.

To gain additional insight into the electronic effects of the organometallic groups in this type of compound, a preliminary electrochemical study was performed. The reduction potential ($E_{1/2}$) in a range from –0.51 to –1.4 V, which corresponds to the reduction of the nitro group bound to a furane moiety, was measured. As expected, the cyclic voltammograms exhibit two successive reduction waves in the DMSO solution. As reported in previous studies [17], the first reduction wave, which occurred in the potential range of –0.61 to –0.75 V, was correlated to a reversible one-electron transfer due to the reduction of Ar–NO₂ to the stable anion radical (i.e., Ar–NO₂^{•–}). The second reduction wave (–1.07 to –1.37 V) is most likely due to the production of the hydroxylamine derivative (i.e., Ar–NHOH) (see supplementary materials, Fig. 1S). Similar behaviors have been observed for organometallic Schiff bases derived from 5-nitrofuran and 5-nitrothiophene [12].

Taking into account the $E_{1/2}$ of the first reduction wave of analogous compounds, the $E_{1/2}$ values correlated with the electronic nature of the substituent attached to the azine bridge in the two series of compounds. Therefore, the reduction potentials of Ar–NO₂ exhibited a cathodic shift for ferrocenyl azines ($E_{1/2}$: –0.69 V for **2a**, –0.71 V for **2b** and –0.71 V for **3a**) due to the electron donor ability of ferrocene. However, with the electron withdrawing cyrhetrenyl fragment, anodic peak potentials were observed ($E_{1/2}$: –0.64 V for **1a**, –0.65 V for **1b**). These results confirm our previous observations concerning the close relationship between the electronic nature of the substituent and the ability of the nitro group to be reduced in these types of compounds and suggest that electronic communication may exist between the two substituents on the azine scaffold.

Single crystal X-ray diffraction studies have been successfully carried out for **1a** and **2b**. The crystal data, data collection and refinement parameters are provided in the supplementary materials (Table S1). The ORTEP drawings with the corresponding atom-labeling scheme are shown in Fig. 1 for **1a** and Fig. 2 for **2b**.

In **1a**, the cyrhetrenyl group exhibited a typical three-legged piano stool type of structure, which is commonly observed for other half sandwich rhenium (I) complexes [12,18]. The asymmetric unit of the orthorhombic lattice contains two molecules ($Z' = 2$), but only one of these molecules is shown in Fig. 1. In **2b** (Fig. 2), the ferrocenyl fragment has an eclipsed conformation similar to that found in other monosubstituted ferrocenyl derivatives [4a,5,9].

The most interesting features of structures **1a** and **2b** can be summarized as follows: *i*) in the solid state, both compounds adopted an (*E,E*)-configuration for the –C(R)=N– moiety, and an *s-trans* conformation was observed about the N1–N2 bond, which is reflected by the torsion angles defined by the atoms C6–N1–N2–C7 (**1a**, 175.5(5)^o and **2b** – 170.6(9)^o). This stereochemistry is consistent with that previously reported for symmetrical and unsymmetrical aromatic azines [15, 19]. *ii*) Both structures possessed a high degree of planarity along the C₅H₄C(R)NNC(H)C₄H₂O–5NO₂ fragment (i.e., the dihedral angle between the [C₅H₄C(R)N] and [NC(H)C₄H₂O–5NO₂] least-square planes is only 6.99(16)^o for **1a** and 0.60(2)^o for **2b**). A similar degree of coplanarity has been previously reported for other substituted

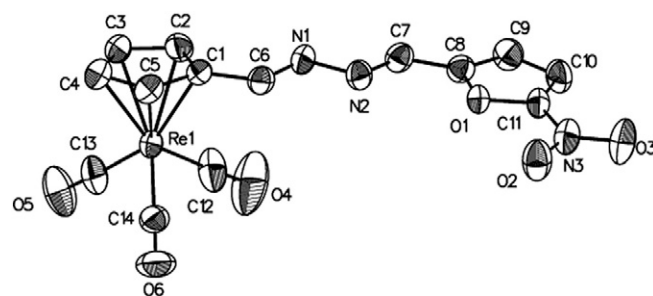


Fig. 1. ORTEP drawing of the molecular structure of [Re(η^5 -C₅H₄)-CH=N=N=CH(5-NO₂-2-C₄H₂O)](CO)₃ (**1a**) with the numbering scheme (thermal ellipsoids with 50% probability). Selected bond lengths (Å): C1–C6, 1.461(7); C6–N1, 1.279(7); N1–N2, 1.406(5); N2–C7, 1.257(8); C7–C8, 1.436(7).

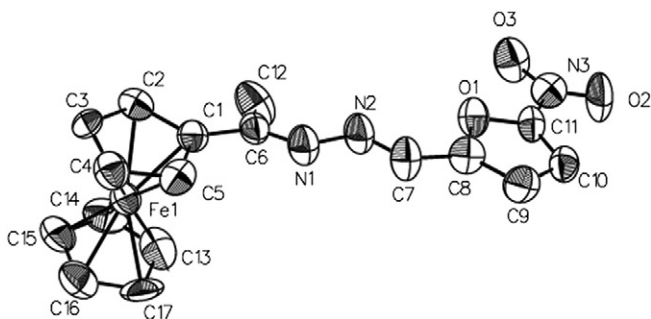


Fig. 2. ORTEP drawing of the molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-C}(\text{CH}_3)=\text{N}-\text{N}=\text{CH}(5\text{-NO}_2\text{-2-C}_4\text{H}_2\text{O}))]$ (**2b**) with the numbering scheme (thermal ellipsoids with 50% probability). Selected bond lengths (Å): C1–C6, 1.485(12); C6–N1, 1.283(10); N1–N2, 1.427(10); N2–C7, 1.252(11); C7–C8, 1.463(12).

ferrocenyl azines. [3,4a]. *iii*) The bond distances of the azine bridge in both structures are consistent with the N–N single bond and C=N double bond that have been previously reported for other organic and ferrocenyl azines [13b,20]. This result may impede fluid electronic communication between the organometallic fragment and the 5-nitrofurane ring through an extensive π -conjugated backbone [2,4a]. *iv*) The bond lengths of the 5-nitrofurane group (O1–C8, C8–C9, C10–C11, C11–N3) are much shorter in **2b** than that in **1a**. These parameters may suggest conjugative effects of the attached azine, which push the electron density from the heterocyclic ring, resulting in shortening of the bond lengths (see supplementary material, Tables S2 and S3).

In summary, a new series of unsymmetrical cyrhetrenyl and ferrocenyl azines complexes (**1a**, **1b**, **2a**, **2b**, **3a**) containing 5-nitro-2-furaldehyde were successfully synthesized and characterized using standard spectroscopic techniques and X-ray crystallography. Based on the co-planarity of the $[(\eta^5\text{-C}_5\text{H}_4\text{-C}(\text{R})=\text{N}-\text{N}=\text{CH}(5\text{-NO}_2\text{-2-C}_4\text{H}_2\text{O}))]$ system, which adopted an (*E,E*)-configuration and an *s-trans* conformation, the reduction potential of the nitro group ($E_{1/2}$) and the chemical shifts of the iminic carbons (C^6 , C^7), extensive π -conjugation of the azine bridge were observed along with a correlation between the opposite electronic effects of the cyrhetrenyl and ferrocenyl fragments.

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Appendix A. Supplementary material

CCDC 1415028 and 1415029 contain the supplementary crystallographic data for **1a** and **2b**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found in the online version, at: <http://dx.doi.org/10.1016/j.inoche.2015.10.007>

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- [14] Cyrhetrenyl and ferrocenyl azines were synthesized according to previously published procedures [4]. Hydrazones $[(\eta^5\text{-C}_5\text{H}_4\text{-C}(\text{R})=\text{N}-\text{NH}_2)]\text{M}$ [$\text{M}=\text{Re}(\text{CO})_3$, $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$; $\text{R}=\text{H}$, CH_3] (1 eq.) and 5-nitro-2-furaldehyde (2 eq.) were dissolved in anhydrous methanol (30 mL) and refluxed for 3 h under a nitrogen atmosphere in the presence of molecular sieves. Then, the solvent was removed under vacuum. The residue that was dissolved in CH_2Cl_2 was filtered through Celite, and the solution was evaporated under reduced pressure. Column chromatography on silica gel using hexane/ CH_2Cl_2 (2:1) as the eluent moved a colored band that contained the product. Finally, the solid obtained after solvent evaporation was purified by crystallization from CH_2Cl_2 /hexane (1:3) at -18°C . **1a**: Yellow crystalline solid, yield: 41%. A suitable crystal of this crop was used for X-ray crystal structure determination. IR (CH_2Cl_2 , cm^{-1}): 2028 (s), (νCO); 1936 (vs), (νCO); 1603 (w), ($\nu\text{C}=\text{N}$). ^1H NMR (400 MHz, CDCl_3): δ 5.46 (t, 2H, H^3 and H^4); 5.99 (t, 2H, H^2 and H^5); 7.10 (d, 1H, $J = 3.9$, H^9); 7.40 (d, 1H, $J = 3.8$, H^{10}); 8.36 (H^9); 8.38 (s, 1H, H^7). ^{13}C NMR (CDCl_3): δ 85.0 (C_5H_4); 87.0 (C_5H_4); 94.5 (C^1); 112.7 ($\text{C}_4\text{H}_2\text{O}$); 115.3 ($\text{C}_4\text{H}_2\text{O}$); 149.3 (C^7); 151.2 (C^8); 157.6 (C^6); 192.3 ($\text{Re}-\text{CO}$). MS (based on ^{187}Re) m/z : 501 [M^+]; 473 [$\text{M}-\text{CO}$] $^+$; 445 [$\text{M}-2\text{CO}$] $^+$; 417 [$\text{M}-3\text{CO}$] $^+$. **1b**: Dark yellow crystalline solid, yield: 37%. IR (CH_2Cl_2 , cm^{-1}): 2030 (s), (νCO); 1939 (s), (νCO); 1608 (w), ($\nu\text{C}=\text{N}$). ^1H NMR (400 MHz, CDCl_3): δ 2.30 (s, 3H, CH_3); 5.51 (t, 2H, H^3 and H^4); 6.14 (t, 2H, H^2 and H^5); 7.05 (d, 1H, $J = 3.8$, H^9); 7.40 (d, 1H, $J = 3.9$, H^{10}); 8.14 (s, 1H, H^7). ^{13}C NMR (CDCl_3): δ 22.6 (CH_3); 85.1 (C_5H_4); 85.9 (C_5H_4); 86.7 (C^1); 113.5 ($\text{C}_4\text{H}_2\text{O}$); 114.4 ($\text{C}_4\text{H}_2\text{O}$); 148.1 (C^7); 154.8 (C^6); 192.9 ($\text{Re}-\text{CO}$). MS (based on ^{187}Re) m/z : 515 [M^+]; 487 [$\text{M}-\text{CO}$] $^+$; 459 [$\text{M}-2\text{CO}$] $^+$; 431 [$\text{M}-3\text{CO}$] $^+$. **2a**: Dark violet solid, yield: 33%. IR (CH_2Cl_2 , cm^{-1}): 1605 (w), ($\nu\text{C}=\text{N}$). ^1H NMR (400 MHz, CDCl_3): δ 4.25 (s, 5H, C_5H_5); 4.57 (t, 2H, H^3 and H^4); 4.76 (t, 2H, H^2 and H^5); 7.06 (d, 1H, $J = 3.8$, H^9); 7.40 (d, 1H, $J = 3.8$, H^{10}); 8.44 (s, 1H, H^7); 8.65 (s, 1H, H^6). ^{13}C NMR (CDCl_3): δ 69.5 (C_5H_4); 69.7 (C_5H_5); 72.1 (C_5H_4); 76.0 (C^1); 113.0 (C^8); 114.3 ($\text{C}_4\text{H}_2\text{O}$); 114.6 ($\text{C}_4\text{H}_2\text{O}$); 146.9 (C^7); 167.8 (C^6); 152.2 (C^{11}). MS (m/z): 351 [M^+]. **2b**: Dark purple crystalline solid, yield: 52%. A crystal was selected for X-ray crystallography. IR (CH_2Cl_2 , cm^{-1}): 1603 (w), ($\nu\text{C}=\text{N}$). ^1H NMR (400 MHz, CDCl_3): δ 2.42 (s, 3H, CH_3); 4.21 (s, 5H, C_5H_5); 4.49 (t, 2H, H^3 and H^4); 4.79 (t, 2H, H^2 and H^5); 7.06 (d, 1H, $J = 3.8$, H^9); 7.40 (d, 1H, $J = 3.8$, H^{10}); 8.27 (s, 1H, H^7). ^{13}C NMR (CDCl_3): δ 16.2 (CH_3); 68.3 (C_5H_4); 69.8 (C_5H_5); 71.3 (C_5H_4); 81.5 (C^1); 113.1 ($\text{C}_4\text{H}_2\text{O}$); 113.5 ($\text{C}_4\text{H}_2\text{O}$); 144.6 (C^7); 171.6 (C^6); 152.9 (C^{11}). MS (m/z): 365 [M^+]. **3a** was synthesized similarly to **2a** and **2b**, but 1,1'-di-acetyl-ferrocene dihydrazone was used instead of acetylferrocenyl hydrazone. Crystallization from the CH_2Cl_2 /hexane mixture (1:4) at -18°C afforded a dark red solid, yield: 34%. IR (CH_2Cl_2 , cm^{-1}): 1603 (w), ($\nu\text{C}=\text{N}$). ^1H NMR (400 MHz, CDCl_3): δ 2.37 (s, 3H, CH_3); 4.51 (t, 2H, H^3 and H^4); 4.84 (t, 2H, H^2 and H^5); 7.03 (d, 1H, $J = 3.6$, H^9); 7.36 (d, 1H, $J = 3.6$, H^{10}); 8.27 (H^7). ^{13}C NMR (CDCl_3): δ 16.2 (CH_3); 69.7 (C_5H_4); 72.4 (C_5H_4); 82.9 (C^1); 113.1 ($\text{C}_4\text{H}_2\text{O}$); 113.7 ($\text{C}_4\text{H}_2\text{O}$); 145.1 (C^7); 170.4 (C^6); 152.6 (C^{11}). MS (m/z): 544 [M^+].
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