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Homo- and heterobimetallic azines derived from ferrocene and cyrhetrene: Synthesis, structural characterization and electrochemical studies

Johana Gómez [a], Diego Sierra [b], Mauricio Fuentealba [a], Vania Artigas [a], A. Hugo Klahn [a, *]

[a] Laboratorio de Química Organometálica, Instituto de Química, Facultad de Ciencias, Pontificia Universidad Católica de Valparaíso, Av. Universidad 330, Campus Curauma, Valparaíso, Chile
[b] Laboratorio de Química Organometálica y Catálisis, Instituto de Química y Bioquímica, Facultad de Ciencias, Universidad de Valparaíso, Av. Gran Bretaña 1111, Valparaíso, Chile

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ABSTRACT

A new series of asymmetrical heterobimetallic azines [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–C(R) = N–N=C(R^1)-(η^5-C_5H_4)Re$(CO)_3$}] (**1**–**3**) and symmetrical homobimetallic cyrhetrenyl azines [{(η^5-C_5H_4)–C(R) = N}Re$(CO)_3]_2$ (**4**, **5**) have been synthesized and were spectroscopically characterized by FT-IR, NMR, EI-MS and cyclic voltammetry. The molecular structures of **1** and **4** were determined using single-crystal X-ray diffraction technique. Based on the oxidation potential of the ferrocenyl units and the high degree of planarity of the [(C_5H_4)–C(H) = N–N=C(H)-(C_5H_4)] system in complex **1**, we inferred electronic communication between the electron-withdrawing cyrhetrenyl groups through the π-conjugated azine bridge. The compounds display an (*E,E*)-configuration about the >C=N- bond, an *s-trans* conformation for the N–N bond and an *anti*-conformation for the two organometallic fragments.

1. Introduction

Azines, or bis-Schiff bases (>C=N–N=C<) [1], have been extensively studied due to their interesting structural, electronic, biologic and coordinative properties [2,3]. The synthesis of symmetrical azines is based on the condensation reaction of hydrazine with a stoichiometric amount of the respective aldehyde or ketone and has a good yield and relatively easy purification [2]. However, the preparation of asymmetrical derivatives presents several synthetic difficulties, such as low yields, long reaction times and the need for catalysts [1]. Nevertheless, a comparative study of several procedures has been reported for the synthesis of asymmetrical organic azines [2,3].

In addition to these studies, a variety of asymmetrical hybrid organic-organometallic azines have been synthesized due to their interesting physicochemical [4], pharmacological [5,6] and redox properties [7]. As far as we know, almost the totality of the reports mentioned above refers to ferrocenyl azines.

Despite these findings, and the ongoing interest in ferrocenyl azines containing electron-withdrawing and electron-donor moieties, achieving π-conjugated systems composed of two organometallic fragments directly bound by an azine bridge with either outstanding properties for non linear optics (NLO) studies [8,9] or possessing functional groups of biological relevance as antitumoral or antiparasitic agents [10] is extremely rare. According to our literature survey, only two examples of symmetrical homobimetallic azine-bridged complexes have been reported: [(η^5-C_5H_5)Fe{(C_5H_4)–C(R) = N-}$]_2$ (R = H, CH_3) [11–13] and the "*four-legged half-sandwich*" molybdenum complex [{(η^5-C_5H_4)C(Me) = N}Mo(Me)$(CO)_3]_2$, briefly described by Y.P. Wang et al. [14].

As a part of our recent interest in heterobimetallic compounds with multifunctional properties [15], herein, we describe the synthesis and characterization (including electrochemistry and X-ray crystallography) of several asymmetrical heterobimetallic aldazines and ketazines as the first examples of small molecules containing ferrocenyl and cyrhetrenyl fragments connected by azine functionality. We also describe in this work the unreported symmetrical bis-cyrhetrenyl azine [{(η^5-C_5H_4)–C(R) = N}Re$(CO)_3]_2$, R = H and Me.

* Corresponding author.
E-mail address: hugo.klahn@pucv.cl (A.H. Klahn).

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2. Experimental section

2.1. General remarks

The reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. The solvents were obtained commercially and dried and distilled under nitrogen by standard methods prior to use. Ferrocene (98%), ferrocenecarboxaldehyde (98%), acetylferrocene (95%) and an n-butyl lithium solution (1.6 M in hexanes) were obtained from Sigma Aldrich-Chile. Compounds [Re(η^5-$C_5H_4C(O)R$)$(CO)_3$] (R = H or Me) were prepared as previously described [16]. Silica gel 60 (Merck, particle size 0.063–0.200 mm) was used for both TLC and column chromatography. The infrared spectra were recorded in a CH_2Cl_2 solution using a NaCl cell on a Perkin–Elmer model 1605 FT-IR spectrophotometer. The ^1H and $^{13}C\{^1H\}$ NMR spectra as well as the $\{^1H–^{13}C\}$-HMBC, $\{^1H–^{13}C\}$–HSQC and Dept-135 experiments (Heteronuclear Multiple Bond Correlation) were recorded at 298 K on a Bruker AVANCE 400 III spectrometer (^1H NMR at 400.13 MHz and $^{13}C\{^1H\}$ NMR 100.6 MHz) using $CDCl_3$ as the solvent and $SiMe_4$ as the internal reference. The chemical shifts were referenced to the residual deuterated solvent peaks. The chemical shifts (δ) are given in ppm, and the coupling constants (J) are reported in Hz [Abbreviations for the multiplicities of the signals detected in ^1H NMR: s (singlet), d (doublet) and t (triplet)]. Electron impact (EI) mass spectra were obtained on a Shimadzu GC-MS (70 eV) at the Laboratorio de Servicios Analíticos, Pontifícia Universidad Católica de Valparaíso.

2.1.1. X-ray crystal structure determinations

Crystals of **1** and **4** were mounted on MiTeGenMicroMounts™ in a random orientation. The diffraction data were collected at 296 K on a Bruker D8 QUEST diffractometer equipped with a bidimensional CMOS Photon100 detector using graphite monochromated Mo-Kα radiation (λ = 0.71076). The diffraction frames were integrated using the APEX2 package [17] and corrected for absorption with SADABS [18]. In both cases, non hydrogen atoms were refined using anisotropic displacement parameters, and H atoms were included in their calculated positions.

2.1.2. Electrochemical studies

Cyclic voltammetry studies of the ferrocene/ferrocenium couple (Fc/Fc^+) were carried out at room temperature using a potentiostat (ZRA SERIES G300 Electrochemical Analyzer) with a one-compartment three-electrode system comprising a platinum disk working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl (sat) reference electrode. The reported $E_{1/2}$ values (see Table 1) refer to this electrode. Each complex was dissolved in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu_4N)[PF_6] as the supporting electrolyte to give a final concentration of 10^{-3} M. Unless otherwise stated, the scan rate used was 100 mV s-1. Under these conditions, the ferrocene/ferrocenium couple was used as a reference with an $E_{1/2}$ of 0.50 V and $\Delta Ep = 110$ mV. All solutions were purged with argon, and voltammograms were recorded under a blanket of argon. The platinum working electrode was polished between runs.

2.2. Synthesis of heterobimetallic azines derived from cyrhetrene and ferrocene

The heterobimetallic compounds [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–C(R) = N–N=C(R_1)-(η^5-C_5H_4)Re$(CO)_3$}, compounds **1**–**3**] were synthesized by the reaction of ferrocenyl hydrazones [12,19] with the corresponding cyrhetrenylaldehyde or ketone.

[(η^5-C_5H_5)Fe{(η^5-C_5H_4)–C(R)=N–N=C(R_1)-(η^5-C_5H_4)Re$(CO)_3$}] with R= H, R_1= H (**1**);

R= H, R_1= Me (**2**); *or R= Me, R_1= H* (**3**)

Organometallic ferrocenyl hydrazones [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–C(R) = NNH_2)}] {R = H or Me} (1eq.) and either aldehyde- or acetyl cyrhetrene [Re{(η^5-C5H4)–C(O)-R1)}$(CO)_3$] {R_1 = H or Me} (1 eq.) was dissolved in a round-bottom flask with anhydrous methanol (25 mL) with molecular sieves and refluxed for 27 h (**1**), 36 h (**2**), or 48 h (**3**) under a nitrogen atmosphere. The solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 and filtered through Celite®, and the obtained solution was evaporated under reduced pressure until dry. The crude product was purified by chromatography on a silica gel column using CH_2Cl_2/hexane (2:1) as the eluent. The dark-red solid obtained after solvent evaporation was purified by recrystallization from $CHCl_3$/hexane (1:3) at room temperature. The complexes were isolated as a dark red solid (**1**, **3**) and a dark brown solid for **2**. [Yield: 65% **1**, 55% for **2** and 49% for **3**]. A suitable dark red crystalline solid of **1** was used for X-ray crystal structure determination.

Characterization data for **1**: IR (CH_2Cl_2, cm^{-1}): 2025 (s), ν(CO); 1932 (vs), ν(CO); 1627 (w), ν(>C=N-). ^1H NMR (400 MHz, $CDCl_3$): δ 4.23 (s, 5H, C_5H_5); 4.49 (t, J = 1.8 Hz, 2H, C_5H_4–Fe); 4.70 (t, J = 1.8 Hz, 2H, C_5H_4–Fe); 5.41 (t, J = 2.1 Hz, 2H, C_5H_4-Re); 5.92 (t, J = 2.1 Hz, 2H, C_5H_4-Re); 8.21 (s, 1H, N=*H*C-C_5H_4-Re); 8.44 (s, 1H, N=*H*C-C_5H_4–Fe). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 69.0 (C_5H_4–Fe); 69.5 (C_5H_4–Fe); 71.4 (C_5H_4–Fe); 84.6 (C_5H_4-Re; 85.8 (C_5H_4-Re); 97.4 (C_5H_4-Re); 152.1 (N=HC-C_5H_4-Re); 164.1 (N=HC-C_5H_4–Fe); 192.8 (Re–*C*O). MS (based on ^{187}Re) *m/z*: 574 $[M]^+$, 518 $[M–2CO]^+$; 490 $[M–3CO]^+$.

Characterization data for **2**: IR (CH_2Cl_2, cm^{-1}): 2024 (s), ν(CO); 1930 (vs), ν(CO); 1623 (w), ν(>C=N-). ^1H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H, CH_3); 4.23 (s, 5H, C_5H_5); 4.45 (t, J = 1.8 Hz, 2H, C_5H_4–Fe); 4.70 (t, J = 1.8 Hz, 2H, C_5H_4–Fe); 5.39 (t, J = 2.1 Hz, 2H, C_5H_4-Re); 5.98 (t, J = 2.1 Hz, 2H, C_5H_4-Re); 8.48 (s, 1H, N=*H*C-C_5H_4–Fe). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.4 (CH_3); 68.5 (C_5H_4–Fe); 68.7 (C_5H_4–Fe); 71.6 (C_5H_4–Fe); 84.5 (C_5H_4–Fe); 84.6 (C_5H_4-Re); 87.5 (C_5H_4-Re); 89.5 (C_5H_4-Re); 148.5 (N=HC-C_5H_4-Re); 156.5 (N=HC-C_5H_4–Fe); 192.6 (Re–*C*O). MS (based on ^{187}Re) *m/z*: 588 $[M]^+$; 560 $[M–CO]^+$; 532 $[M–2CO]^+$; 504 $[M–3CO]^+$.

Table 1
Selected bond lengths (Å), bond angles (deg.) and angles between relevant planes (deg.) of compounds **1** and **4**. Standard deviations are given in parenthesis.

	1	**4**
Bond legth		
N1 – N2	1.418(9)	1.418(7)
C7 – N2	1.250(10)	1.308(9)
N1–C6	1.282(10)	1.260(8)
C6–C1	1.463(5)	1.428(9)
C8–C7	1.470(11)	1.425(9)
Bond angles		
C1–C6–N1	122.5(7)	122.1(6)
C8–C7–N2	121.1(7)	121.4(6)
N1–N2–C7	110.2(6)	111.2(5)
C6–N1–N2	112.1(6)	114.9(6)
Angles between main planes[a]		
I and II	1.72	
II and III	4.28	
II and VI	3.27	
III and V	1.33	7.45
III and VII	2.75	5.48
II and VII	1.80	
IV and VII		12.21
IV and VI		8.39
III and IV		13.3

[a] Planes **I**: [C13–C17] and **II**: [C8–C12] formed by the atoms the Cp rings of the ferrocenyl moiety; **III**: the plane defined by [C1–C5] and **IV**: [C8–C12] of the cyrhetrenyl unit; **V**: the plane formed by [C1–C6–N1];**VI**: [N2–C7–C8]; and **VII**: [C6–N1–N2–C7].

Characterization data for **3**: IR (CH_2Cl_2, cm^{-1}): 2024 (s), ν(CO); 1931 (vs), ν(CO); 1615 (w), ν(>C=N-). ^1H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H, CH_3); 4.21 (s, 5H, C_5H_5); 4.51 (t, $J = 1.7$ Hz, 2H, C_5H_4–Fe); 4.77 (t, $J = 1.7$ Hz, 2H, C_5H_4–Fe); 5.42 (t, $J = 2.0$ Hz, 2H, C_5H_4-Re); 5.91 (t, $J = 2.0$ Hz, 2H, C_5H_4-Re); 8.16 (s, 1H, N=HC-C_5H_4-Re). $^{13}C\{^1H\}$ NMR($CDCl_3$): δ 29.7 (CH_3); 69.6 (C_5H_4–Fe); 69.9 (C_5H_4–Fe); 72.4 (C_5H_4–Fe); 84.8 (C_5H_4-Re); 85.4 (C_5H_4-Re); 86.4 (C_5H_4-Re); 146.1 (N=HC-C_5H_4-Re); 154.8 (N=HC-C_5H_4–Fe); 192.5 (Re–CO). MS (based on ^{187}Re) *m/z*: 588 $[M]^+$; 532 $[M-2CO]^+$; 504 $[M-3CO]^+$.

2.3. Synthesis of homobimetallic cyrhetrenyl azines

[{(η^5-C_5H_4)–C(R)=N}Re(CO)$_3$]$_2$ with R= H (**4**) or *R= Me* (**5**)

The symmetrical cyrhetrenyl azines were synthesized by reacting 2 equivalents of the respective cyrhetrenyl aldehyde or acetylcyrhetrene with 1 equivalent of hydrazine.

The respective cyrhetrenyl complex (100 mg) of [Re{(η^5-C_5H_4)–C(O)R}(CO)3] (0.27 mmol, R = H or 0.26 mmol, R = Me) was dissolved in anhydrous methanol (15 mL) under continuous stirring at room temperature. Subsequently, hydrazine monohydrate was added [65 μL, (1.34 mmol) and 50.0 μL, (1.03 mmol) for **4** and **5**, respectively]. The reaction times were 72 h (**4**) and 96 h (**5**). After this time, the solvent was removed under vacuum. The residue was dissolved in 10 mL of CH_2Cl_2, transferred to an extraction funnel, and treated with 30 mL of water to remove unreacted hydrazine. Finally, the organic phase was dried over anhydrous Na_2SO_4, and the solution was concentrated until dry in a rotary evaporator. Finally, the obtained solid was purified by recrystallization from CH_2Cl_2/hexane for **4** and $CHCl_3$/hexane for **5** at −18 °C, giving clear brown crystals for **4** (55% yield), suitable for X-ray analysis, and a yellow solid for **5** (66% yield).

Characterization data for **4**: IR (CH_2Cl_2, cm^{-1}): 2027 (s), ν(CO); 1935 (vs), ν(CO); 1605 (w); ν(>C=N-). ^1H NMR (400 MHz, $CDCl_3$): δ 5.42 (t, $J = 2.1$ Hz, 4H, C_5H_4-Re); 5.91 (t, $J = 2.1$ Hz, 4H, C_5H_4-Re); 8.16 (s, 2H, N=HC-C_5H_4-Re). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 84.8 (C_5H_4-Re); 85.6 (C_5H_4-Re); 86.4 (C_5H_4-Re); 154.8 (N=HC-C_5H_4-Re); 192.5 (Re–CO). MS (based on ^{187}Re) *m/z*: 724 $[M]^+$; 696 $[M-CO]^+$; 668 $[M-2CO]^+$; 612 $[M-4CO]^+$.

Characterization data for **5**: IR (CH_2Cl_2, cm^{-1}): 2028 (s), ν(CO); 1936 (vs), ν(CO); 1610 (w), ν(>C=N-). ^1H NMR (400 MHz, $CDCl_3$): δ 2.02 (s, 6H, CH_3); 5.37 (t, $J = 2.1$ Hz, 4H, C_5H_4-Re); 5.92 (t, $J = 2.1$ Hz, 4H, C_5H_4-Re).$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.4 (CH_3); 84.7 (C_5H_4-Re); 86.1 (C_5H_4-Re); 86.4 (C_5H_4-Re); 154.8 (N=(CH_3)C–C_5H_4-Re); 193.5 (Re–CO). MS (based on ^{187}Re) *m/z*: 752 $[M]^+$; 724 $[M-CO]^+$; 696 $[M-2CO]^+$; 640 $[M-4CO]^+$.

3. Results and discussion

3.1. Synthesis and characterization of the compounds

The new hetero- and homobimetallic azines **1**–**5** (Scheme 1) were synthesized by adapting procedures previously reported for ferrocenyl azines [12,13,20]. For the asymmetrical heterobimetallic derivatives **1**–**3**, the synthesis is based on an *in situ* condensation reaction between previously reported ferrocenyl hydrazones [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–C(R) = N–NH_2)}] [12,21] and either cyrhetrenecarboxaldehyde or acetyl cyrhetrene. For the symmetrical homobimetallic cyrhetrenyl azines **4** and **5**, the synthesis was performed by a direct reaction between the cyrhetrenyl carbonyl precursor [Re{(η^5-C_5H_4)–C(O)R)}(CO)$_3$] {R = H, Me} and monohydrated hydrazine (yields 55 and 66%, respectively) (Scheme 1).

All these new complexes are air and thermally stable in the solid-state and are soluble in most polar organic solvents but only slightly soluble in non polar solvents.

The identification of the new complexes was inferred by spectroscopic techniques (FT-IR, ^1H and ^{13}C NMR) and mass spectrometry. Additionally, the molecular structures of **1** and **4** were determined by X-ray diffraction.

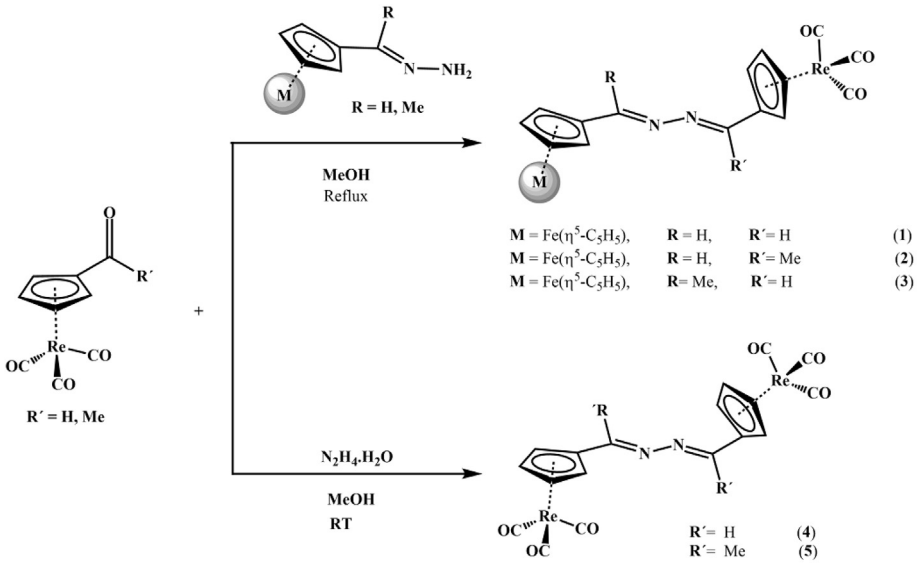
The FT-IR spectra of these new compounds in CH_2Cl_2 solution show the typical absorption band pattern for tricarbonyl complexes (νCO) from 2028 to 1931 cm^{-1} for the symmetrical and asymmetrical stretching of the CO ligands coordinated to the rhenium atom. These bands are shifted to higher wavenumber compared to that for a cyrhetrenyl hydrazones of general formula [Re{(η^5-C_5H_4)–C(R) = N–NH_2}(CO)$_3$, R = H, CH_3, (νCO 2024 – 1920 cm^{-1})] [21]; this behavior is probably due to the increase of electronic delocalization through the >C=N–N=C< bridge. Additionally, these spectra show the band assigned to the stretching vibrations of the >C=N- groups from 1610 to 1627 cm^{-1}, which is in good agreement with the frequencies of ferrocenyl azine analogs [22] and cyrhetrenyl azines reported by our laboratory [23].

The ^1H NMR shows the signal assigned to the iminic hydrogen having a chemical shift in the range of $8.01 < \delta < 8.64$ (see Supplementary information, Figs. 1S–5S). The position of these signals agrees with that reported for organometallic azines [23]. For complexes **2**, **3** and **5**, the spectra exhibit a singlet from 2.02 to 2.40 ppm, which was assigned to the iminic methyl group, in agreement with other reported ferrocenyl and cyrhetrenyl ketazines. It should be noted that the correct assignment of the signals was performed using ^1H–^{13}C HSQC and DEPT-135 experiments.

Additionally, chemical shifts of the iminic carbons in the ^{13}C NMR of complexes **1**–**3** (see Supplementary information, Table 1S and Figs. 1S–5S), show a dependence on the electronic nature of the organometallic fragments. In all compounds, the iminic carbon attached to the cyrhetrenyl moiety (152.1 for **1**, 148.5 for **2**, 146.1 ppm for **3**) has a chemical shift displaced upfield with respect to the signal assigned to the carbon atom bonded to the ferrocenyl fragment (164.1 for **1**, 156.5 for **2**, 154.8 ppm for **3**). The position of these resonances suggests a significant change in the electronic density of the ˃C=N- units of the azine bridge, produced by the electron-withdrawing and electron-donor of the cyrhetrenyl and ferrocenyl fragments, respectively. We have observed similar trend in hybrid cyrhetrenyl and ferrocenyl azines containing 5-nitrofurane or 5-nitrothiophene {[(η^5–C_5H_4)–C(R) = N–N=CH-(5-NO_2-2-C_4H_2X)]M, M = Re(CO)$_3$, Fe(η^5–C_5H_5), X = O, S} [10,23] and in the bimetallic cyrhetreny-ferrocenyl imines [15].

It is well known that the azine bridges of asymmetrical and symmetrical complexes may adopt either four or three conformational isomers, respectively; however, the (*E,E*)-configuration should be favored due to steric effects of the two bulky organometallic fragments [2]. For all compounds, this assumption was partially supported by the ^1H and ^{13}C NMR spectra (Supplementary information, Figs. 1S–5S), in which one signal assigned to the iminic hydrogen and the methyl group confirms the presence of only one species. The final confirmation was obtained from the molecular structure of complexes **1** and **4**, which clearly showed the (*E,E*) isomer in both molecules. This indicated that azines **1** and **4** retained the (*EE*) form in the solid state and also in $CDCl_3$ solution. This behavior is consistent with previous reports for ferrocenyl and cyrhetrenyl azines [23].

The electron-impact mass spectra of the complexes further confirm the integrity of the dinuclear complexes. All compounds exhibited peaks, with the expected isotopic pattern, for the molecular ions and fragments formed by the loss of CO ligands (Supplementary information, Figs. 6S–7S).



Scheme 1. Synthesis of the asymmetrical heterobimetallic azines (**1**–**3**) and the symmetrical homobimetallic cyrhetrenyl azines (**4**–**5**).

3.2. X-ray crystallography

In addition to the spectroscopic data, the molecular structure of heterobimetallic azine **1** and homobimetallic cyrhetrenyl azine **4** were determined by single-crystal X-ray diffraction analysis. The ORTEP plots of the complexes are presented in Figs. 1 and 2, and the thermal ellipsoids are drawn at a 50% probability level. The details about the data collection, crystallographic data and structure refinement parameters for the complexes are summarized in the Supplementary information (Tables 2S–4S). Selected bond lengths, bond angles, and the angles between relevant planes are listed in Table 1.

For both complexes, most of the parameters are quite similar and routine, in agreement with those reported for other octahedral sandwich and half-sandwich *"three-legged piano stool"* complexes [24]. In complex **1**, the ferrocenyl fragment has an eclipsed conformation similar to that found in other monosubstituted ferrocenyl derivatives [25,26].

The environment of the azine bridge in both compounds (**1**, **4**) is represented by the trigonal planar geometry of both iminic carbons, >C═N–, which is slightly distorted from 120° with angles ranging from 121.1° to 122.5°. Additionally, the two nitrogen atoms have a bent geometry, with >C═N–N– angles of 110.2(6)° and 112.1(6)° for **1** and 111.2(5)° and 114.9(6)° for complex **4**, which is in good agreement with the values reported for ferrocenyl and cyrhetrenyl azines [23].

The compounds display an (*E*,*E*)-configuration about the iminic bond, >C(R) = N–, and an *s-trans* conformation is observed about the N1–N2 single bond, which is reflected by the torsion angles defined by the atoms C6–N1–N2–C7 [**1**, 176.3(13)° and **4**, -170.4(3)°]. This stereochemistry is consistent with that previously reported for symmetrical and asymmetrical aromatic azines [27]. Additionally, both structures exhibited an *anti*-arrangement of the organometallic fragments, which are located on opposite sides with

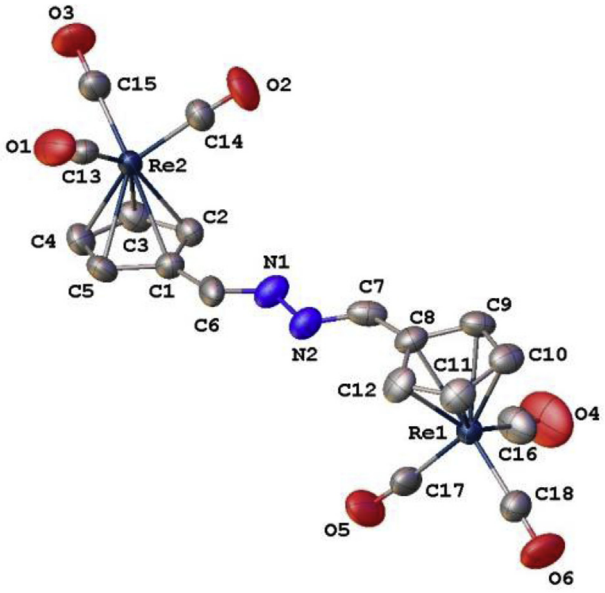


Fig. 2. ORTEP diagram for homobimetallic cyrhetrenyl azine [{(η5-C5H4)–C(H) = N} Re(CO)3]2 (**4**).

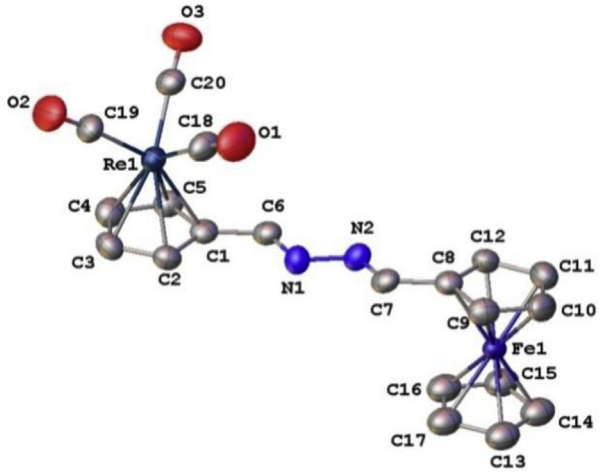


Fig. 1. ORTEP diagram for heterobimetallic azine, [(η5-C5H5)Fe{(η5-C5H4)–C(H) = N-N═C(H)-(η5-C5H4)Re(CO)3}], (**1**).

respect to the plane [(C_5H_4)–C(R) = N–N=C(R')-(C_5H_4)], in a similar fashion to those found in symmetrical ferrocenyl and molybdenum azines previously published [12,14]. Finally, another important issue related to the structure of complex **1** is the coplanarity of the two cyclopentadienyl rings when compared with those measured in **4** (the angles between their main planes are 4.28° and 13.3°, respectively). This finding is relevant because it is well known that deviations from coplanarity between cyclopentadienyl rings are commonly associated with a decrease in electronic delocalization (Table 1) [15].

With the aim of obtaining more insight into the electronic communication between the organometallic groups through the azine bridge, the dihedral angles constituted by the [N1–C6–C1–C2–C3–C4–C5] and [N2–C7–C8–C9–C10–C11–C12] planes were calculated. Heterobimetallic azine **1** showed a high degree of planarity with a dihedral angle value of 3.16(11)°, whereas **4** showed a distortion of planarity with a dihedral angle of 13.03(5)°. These findings indicate that the electronic communication between the electron-donating ferrocenyl group and the electron-withdrawing cyrhetrenyl fragment is more efficient in complex **1.** Similar results were observed in other hybrid organometallic-organic azines containing the electron-donating ferrocenyl fragment and electron-withdrawing moieties, such as 5-nitrofurane [23], 5-nitrothiophene [10] and 4-nitrophenyl groups [26].

On the other hand, the lack of coplanarity of homobimetallic cyrhetrenyl azine **4** [the angles between the main planes Cp(Re) and [C6–N1–N2–C7] are 5.48° and 12.21°, respectively] is not unexpected because similar deviations have been reported for the complex [{(η^5- C_5H_4)C(Me) = N}Mo(Me)$(CO)_3$]$_2$ [14].

Additionally, crystal packing of molecular structures **1** and **4** (Supplementary information, Figure 8S) was observed to be stabilized by a network of intermolecular C–H·····O (2.690 and 2.629 Å, respectively) interactions between the cyclopentadienyl ring of the cyrhetrene fragment and the oxygen atom of the other CO ligand of the cyrhetrene unit, extending the assembly of the molecules in the crystal. This interaction could be favored by an *anti*-arrangement of "Re$(CO)_3$" and "Fe(η^5-C_5H_5)", as observed in ferrocenyl/cyrhetrenyl aldimines [15], symmetrical ferrocenyl azines [12] and CpMo(-$CO)_3$Me azine [14].

3.3. Electrochemical studies

To provide more evidence of the electronic communication in these compounds, the electrochemical behavior of compounds **1**–**3** was determined by cyclic voltammetry of freshly prepared solutions in dichloromethane with (Bu_4N)[PF_6] as the background electrolyte. Analyses of oxidation potential values were carried out at a scan rate of 100 mVs^{-1} in a range of $-0.25\,V < E < 1.5\,V$. A comparison of the relevant electrochemical data for the compounds under study is presented in Table 2.

Cyclic voltammetry of heterobimetallic ferrocenyl azines **1**–**3** exhibits the typical behavior of ferrocenyl compounds, showing a reversible process corresponding to the mono-electronic oxidation of the ferrocene, with a half-wave potential ($E_{1/2}$) in the range of 0.62–0.67 V for the couple [Fe/Fe^+] and with anodic and cathodic peak differences (ΔEp) between 70 and 110 mV. Peak current ratios [I_{pa}/I_{pc}] around the unit suggest a reversible single electron transfer process. These findings agree with those expected for a simple reversible one electron-process [28].

Previous electrochemical studies on monosubstituted ferrocene derivatives have demonstrated that the presence of electron-donating groups increases the proclivity of the ferrocenyl unit towards oxidation and that the presence of electron-withdrawing groups reduces the capacity of this fragment to be oxidized [29]. For all heterobimetallic azines containing ferrocenyl fragments, the anodic peaks appeared at higher potentials with respect to ferrocene (0.5 V) (Table 2).

These findings agree with the anodic potentials measured in ferrocenyl azines attached to a 5-nitroheterocycle group under identical experimental conditions [10]. The presence of an electron-withdrawing group, [Re(η^5-C_5H_4)$(CO)_3$], affected the redox properties of the ferrocenyl fragment, indicating effective electronic communication between two organometallic fragments connected by a conjugated azine bridge (Table 2). Finally, other interesting features related to the electrochemistry of these compounds are as follows: *i)* the substitution of the iminic hydrogen for the electron-donating methyl group has a slight effect on the oxidation potentials ($0.62\,V < E_{1/2} < 0.67\,V$) of the ferrocenyl backbone. This electrochemical behavior is consistent with different ferrocenyl substituted azines, and the oxidation properties are governed by the nature of the aryl substituent [30]; *ii)* for all heterobimetallic azines, the anodic peaks appeared at lower oxidation potential ($E_{1/2}$) than those measured for ferrocenyl azines derived of 5-nitroheterocycles ($0.69\,V < E_{1/2} < 0.75\,V$) previously published by our laboratory [10], which means that the electronic communication between the two metallic centers joined by the azine core is less efficient probably due to lower electron-withdrawing effect of the cyrhetrenyl group compared to the 5-nitroheterocyclic; and *iii)* in all cases, the cyrhetrenyl group did not show a voltammetric response under the experimental conditions analyzed. Similar behavior was also observed for asymmetric cyrhetrenyl azines derived from 5-nitroheterocycles [10].

Table 2
Half-wave potentials for the reversible couple Fc/Fc^+ for complexes **1**–**3**.

Compound	R	R′	E_{pa}(V)	E_{pc}(V)	$E_{1/2}$(V)[a]	Δ_{ep}(mV)[b]
Ferrocene			0.55	0.44	0.5	110
1	H	H	0.67	0.56	0.62	110
2	H	Me	0.69	0.61	0.65	80
3	Me	H	0.7	0.63	0.67	70

[a] $E_{1/2} = (E_{pa} + E_{pc})/2$.
[b] $\Delta E\,p = E_{pa} - E_{pc}$.

4. Conclusion

Asymmetrical heterobimetallic azines (**1**–**3**) were successfully synthesized through condensation reactions of the corresponding ferrocenyl hydrazones with either acetylcyrhetrene or cyrhetrenecarboxaldehyde, whereas the symmetrical homobimetallic cyrhetrenyl azines (**4**–**5**) were obtained by direct reaction of the appropriated substituted cyrhetrene (acetyl or aldehyde) with $N_2H_2{\cdot}H_2O$. These new derivatives were characterized by standard spectroscopic, crystallographic and electrochemical techniques.

The shift of the $E_{1/2}$ of the ferrocenyl units to more anodic potentials indicates that the presence of the electron-withdrawing cyrhetrenyl group is electronically communicated with the ferrocenyl group through the π-conjugated azine bridge. The high degree of planarity in the [(C_5H_4)–C(H) = N–N=C(H)-(C_5H_4)] system of complex **1** confirms the above conclusion.

Furthermore, crystallographic studies of complexes **1** and **4** indicated that both compounds exhibit the less sterically hindered (*E,E*) isomer, an *s-trans* conformation of the N–N bond and the *anti*-conformation of the two organometallic fragments. Finally, we believe that these heterobimetallic azines will be of interest as building blocks for and especially as ligands to other transition metals to achieve heteropolymetallic compounds that are attractive for the preparation of new materials with applications in catalysis and material science.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2018.12.006.

References

[1] K.M. Khan, W. Jamil, N. Ambreen, M. Taha, S. Perveen, G.A. Morales, Ultrason. Sonochem. 21 (2014) 1200–1205.
[2] J. Safari, S. Gandomi-Ravandi, RSC Adv. 4 (2014) 46224–46249.
[3] J. Grzegorzek, Z. Mielke, A. Filarowski, J. Mol. Struct. 976 (2010) 371–376.
[4] Caballero R. Martínez, V. Lloveras, I. Ratera, J. Vidal-Gancedo, K. Wurst, A. Tárraga, P. Molina, J. Veciana, J. Am. Chem. Soc. 127 (2005) 15666–15667.
[5] M.M. Abd-Elzaher, W.H. Hegazy, A. El-Din, M. Gaafar, Appl. Organomet. Chem. 19 (2005) 911–916.
[6] T. Stringer, H. Guzgay, J.M. Combrinck, M. Hopper, D.T. Hendricks, P.J. Smith, K.M. Land, T.J. Egan, G.S. Smith, J. Organomet. Chem. 788 (2015) 1–8.
[7] R. Martínez, I. Ratera, A. Tárraga, P. Molina, J. Veciana, Chem. Commun. (2006) 3809–3811.
[8] A. Houlton, N. Jasim, R. Roberts, J. Silver, D. Cunningham, P. McArdle, Tim Higgins, J. Chem. Soc. Dalton Trans. (1992) 2235–2241.
[9] H.K. Sharma, K.H. Pannell, I. Ledoux, J. Zyss, A. Ceccanti, P. Zanello, Organometallics 19 (2000) 770–774.
[10] J. Gómez, A.H. Klahn, M. Fuentealba, D. Sierra, C. Olea-Azar, J.D. Maya, M.E. Medina, J. Organomet. Chem. 839 (2017) 108–115.
[11] G.S. Goldin, T.A. Balabina, T.V. Tynkina, A.N. Ushakova, J. Gen. Chem. USSR. 43 (1971) 1262–1265.
[12] A.G. Osborne, M.W. Silva, M.B. Hursthouse, K.M.A. Malik, G. Opromolla, P. Zanello, J. Organomet. Chem. 516 (1996) 167–176.
[13] R.M.T. Casey, P. Guinan, A. Canavan, M. McCann, Polyhedron 10 (1991) 483–489.
[14] Y.P. Wang, W.D. Tang, H.Y. Cheng, T.S. Lin, J. Organomet. Chem. 729 (2013) 68–80.
[15] J. Oyarzo, A. Acuña, H. Klahn, R. Arancibia, C.P. Silva, R. Bosque, C. López, M. Font-Bardía, C. Calvis, R. Messeguer, Dalton Trans. 47 (2018) 1635–1649.
[16] (a) J. Heldt, N. Fischer-Durand, M. Salmain, A. Vessières, G. Jaouen, J. Organomet. Chem. 689 (2004) 4775–4782;
(b) S. Jones, M. Rausch, P. Bitterwolf, J. Organomet. Chem. 396 (1990) 279–287.
[17] Bruker, APEX2, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.
[18] Bruker, SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
[19] K. Chanawanno, H.M. Rhoda, A. Hasheminasab, L.A. Crandall, A.J. King, R.S. Herrick, V.N. Nemykin, C.J. Ziegler, J. Organomet. Chem. 818 (2016) 145–153.
[20] R. Bosque, C. López, J. Sales, X. Solans, J. Silver, J. Chem. Soc. Dalton Trans. (1996) 3195–3200.
[21] J. Gómez, N. Leiva, R. Arancibia, J. Oyarzo, G.E. Buono-Core, A.H. Klahn, V. Artigas, M. Fuentealba, R. Bosque, G. Aullón, C. López, M. Font-Bardía, T. Calvet, J. Organomet. Chem. 819 (2016) 129–137.
[22] C. López, R. Bosque, J. Arias, E. Evangelio, X. Solans, M. Font-Bardía, J. Organomet. Chem. 672 (2003) 34–42.
[23] J. Gómez, A.H. Klahn, M. Fuentealba, D. Sierra, C. Olea-Azar, M.E. Medina, Inorg. Chem. Commun. 61 (2015) 204–206.
[24] D. Sierra, N. Bhuvanesh, J.H. Reibenspies, J.A. Gladysz, A.H. Klahn, J. Organomet. Chem. 749 (2014) 416–420.
[25] W. Nkoana, D. Nyoni, P. Chellan, T. Stringera, D. Taylor, P.J. Smith, A.T. Hutton, G.S. Smith, J. Organomet. Chem. 752 (2014) 67–75.
[26] A. Houlton, N. Jasim, R. Roberts, J. Silver, D. Cunningham, P. McArdle, T. Higgins, J. Chem. Soc. Dalton Trans. (1992) 2235–2241.
[27] (a) R. Karmakar, C.R. Choudhury, S.R. Batten, S. Mitra, J. Mol. Struct. 826 (2007) 75–81;
(b) J. Grzegorzek, Z. Mielke, A. Filarowski, J. Mol. Struct. 976 (2010) 371–376.
[28] C. López, R. Bosque, S. Perez, A. Raig, E. Molins, X. Solans, M. Font-Bardia, J. Organomet. Chem. 691 (2006) 475–484.
[29] (a) P.E. Kleyi, C.W. McCleland, T.I.A. Gerber, Polyhedron 29 (2010) 1095–1101;
(b) S.R. Gupta, P. Mourya, M.M. Singh, V.P. Singh, J. Organomet. Chem. 767 (2014) 136–143.
[30] V.A. Sauro, Mark S. Workentin, Can. J. Chem. 80 (2002) 250–262.