



# Synthesis, characterization, crystal structures and computational studies on novel cyrhetrenyl hydrazones



Johana Gómez<sup>a</sup>, Nelson Leiva<sup>a</sup>, Rodrigo Arancibia<sup>a</sup>, Juan Oyarzo<sup>a</sup>, Gonzalo E. Buono-Core<sup>a</sup>, A. Hugo Klahn<sup>a,\*</sup>, Vania Artigas<sup>a</sup>, Mauricio Fuentealba<sup>a</sup>, Ramon Bosque<sup>b</sup>, Gabriel Aullón<sup>b</sup>, Concepción López<sup>b,\*\*</sup>, Mercè Font-Bardía<sup>c</sup>, Teresa Calvet<sup>d</sup>

<sup>a</sup> Instituto de Química, Pontificia Universidad Católica de Valparaíso, Casilla 4059, Valparaíso, Chile

<sup>b</sup> Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, E-08028 Barcelona, Spain

<sup>c</sup> Unitat de Difracció de Raigs-X, Centres Científics i Tecnològics (CCiT), Universitat de Barcelona, Solé i Sabarís 1-3, E-08028 Barcelona, Spain

<sup>d</sup> Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia, Universitat de Barcelona, Martí i Franquès s/n, E-08028 Barcelona, Spain

## ARTICLE INFO

### Article history:

Received 8 April 2016

Received in revised form

17 June 2016

Accepted 18 June 2016

Available online 25 June 2016

### Keywords:

Cyrhetrenyl hydrazones

Ferrocenyl hydrazones

Crystal structure

NMR

Computational studies

## ABSTRACT

The synthesis of novel cyrhetrenyl hydrazones of general formula  $[\text{Re}(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{R}^1) = \text{NNHR}^2](\text{CO})_3$  {with  $\text{R}^1 = \text{H}$  and  $\text{R}^2 = 4\text{-NO}_2\text{-C}_6\text{H}_4$  (**4a**),  $\text{C}_6\text{H}_5$  (**4b**) or  $\text{H}$  (**4c**) or  $\text{R}^1 = \text{Me}$  and  $\text{R}^2 = 4\text{-NO}_2\text{-C}_6\text{H}_4$  (**5a**),  $\text{C}_6\text{H}_5$  (**5b**) or  $\text{H}$  (**5c**)} is described. Compounds **4a–4c** and **5a–5c** were characterized by mass spectrometry and IR spectroscopy.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR studies revealed that **4a–4c** and **5a–5c** adopt the anti-(*E*) configuration in solution. X-ray crystal structures of compounds **4a** and **5c** confirmed the *trans*-arrangement of the cyrhetrenyl “ $\text{Re}(\eta^5\text{-C}_5\text{H}_4)(\text{CO})_3$ ” and the  $\text{-NHR}^2$  moieties and the existence of strong hydrogen bonds involving the  $\text{-NH-}$  unit. Molecular Orbital calculations at a DFT level have also been carried out in order to rationalize the influence of the nature of the substituent  $\text{R}^3$  of  $[\text{R}^3\text{CH} = \text{NNH}(4\text{-NO}_2\text{-C}_6\text{H}_4)]$  ( $\text{R}^3 = \text{ferrocenyl}$ , (**3a**), cyrhetrenyl (**4a**), phenyl (**6a**) or cymantrenyl (**7a**) on the electronic delocalization, the nucleophilicity of the imine carbon, the polarizability and hyperpolarizability of these compounds, and computational studies using time-dependent density functional (TD-DFT) calculations have also been carried out in order to assign the bands detected in their electronic spectra and to explain the effect produced by the solvent.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Sandwiches and three legged half-sandwich organometallic compounds have been studied since long ago, but nowadays constitute a very attractive area of research [1–4]. Compounds of this kind with additional  $\text{-C}(\text{R}^1) = \text{N-}$  or  $\text{-C}(\text{R}^1) = \text{NNHR}^2$  groups attached to the rings are specially relevant for different reasons. These include their utility as precursors in organic, inorganic and organometallic synthesis (especially as metallo-ligands to achieve polymeric derivatives), their interesting (chemical,

photochemical, electrochemical) properties as well as their applications in a variety of fields [1–4]. For instance, ferrocenylimines [5,6], oximes [7], azines and azoderivatives [8], thiosemicarbazones [9] or, to a lesser extent, monohydrazones  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_4\text{-C}(\text{R}^1) = \text{N-NHR}^2\}]$  ( $\text{R}^1 = \text{H}$  (**1**) or  $\text{Me}$  (**2**), Fig. 1) or the 1,1'-dihydrazones (**3**) [10,11], are valuable as ligands in coordination and organometallic chemistry (i.e. to achieve cyclometallated compounds) [5,10]. Furthermore, mono- and disubstituted ferrocenyl hydrazones (**1–3** in Fig. 1) with large non-linear optical (NLO) properties have also been reported [12].

On the other hand, the chemistry of cyrhetrene,  $[\text{Re}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$  (the typical example of a three legged half-sandwich rhenium complex), has undergone a rapid development in the last decade [13–15]. Functionalization of the ring or exchange of the CO groups by other mono or bidentate ligands have allowed to prepare a variety of new cyrhetrene derivatives. Most of them

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [hugo.klahn@pucv.cl](mailto:hugo.klahn@pucv.cl) (A.H. Klahn), [conchi.lopez@qi.ub.es](mailto:conchi.lopez@qi.ub.es) (C. López).

<sup>1</sup> Equal contribution.

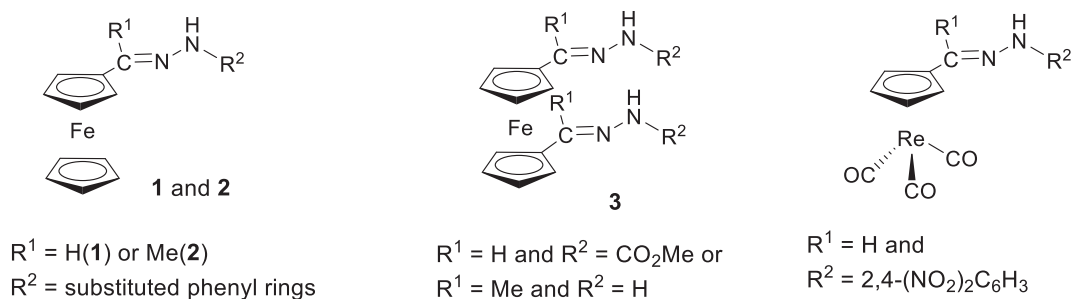


Fig. 1. Representative examples of ferrocenyl and cyrhetrenyl hydrazones described previously [10,11,17].

exhibit interesting properties, reactivity, (i.e. as metallo-ligands) and biological or catalytic activity [13–15]. Cyrhetrenylimines [6,14], amines [14a] and thiosemicarbazones [9a] have been described in the late years and their properties, applications and activities have been compared with those of their corresponding ferrocenyl analogues [6–9].

Despite the spectacular progress on the design and development of: a) organometallic compounds containing redox active centres [1–4,5a,5b] and b) new hydrazones as stimuli responsive molecules [16], cyrhetrenyl derivatives of the type  $[\text{Re}(\{\eta^5\text{-C}_5\text{H}_4\}\text{C}(\text{R}^1) = \text{NNHR}^2)(\text{CO})_3]$  are extremely scarce; as far as we know, that shown in Fig. 1, is the sole example [17]. Moreover, unsubstituted  $[\text{Re}(\{\eta^5\text{-C}_5\text{H}_4\}\text{C}(\text{R}^1) = \text{NNH}_2)(\text{CO})_3]$  compounds still remain unknown. In view of this and our interest to compare electronic effects of cyrhetrenyl and ferrocenyl moiety [5–7a,9a,10–11,14,15], here we present six new cyrhetrene derivatives of general formula  $[\text{Re}(\{\eta^5\text{-C}_5\text{H}_4\}\text{C}(\text{R}^1) = \text{NNHR}^2)(\text{CO})_3]$  with  $\text{R}^1 = \text{H}$  (**4**) or  $\text{Me}$  (**5**) and  $\text{R}^2 = 4\text{-NO}_2\text{-C}_6\text{H}_4$  (**a**),  $\text{C}_6\text{H}_5$  (**b**) or  $\text{H}$  (**c**). It should be noted that those with phenyl rings (**4a–4b** and **5a–5b**) could be visualized as derived from compounds **1** and **2**, respectively (Fig. 1) by replacement of the “ $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ ” unit by the “ $\text{Re}(\text{CO})_3$ ” moiety.

## 2. Results and discussion

### 2.1. Synthesis and solution studies

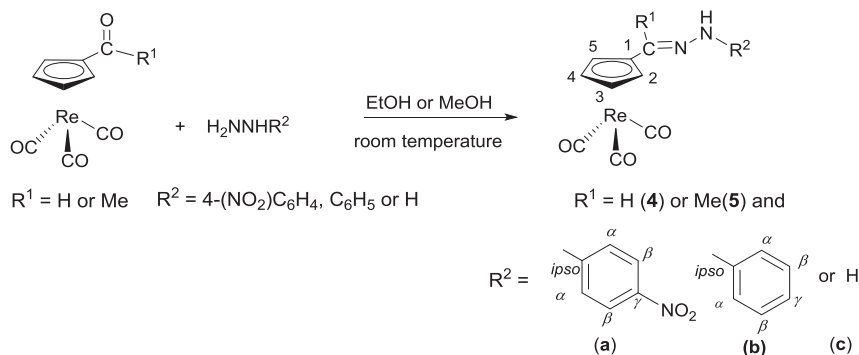
The new cyrhetrenyl hydrazones  $[\text{Re}(\{\eta^5\text{-C}_5\text{H}_4\}\text{C}(\text{R}^1) = \text{N-NHR}^2)(\text{CO})_3]$  (**4a**, **4b**, **5a** and **5b**) were prepared by adaptation of the procedures reported for their ferrocenyl analogues (**1** or **2** in Fig. 1) [12a]; while compounds **4c** and **5c** (with  $\text{R}^2 = \text{H}$ ) were obtained following the method described for 1,1'-diacetylferrocene dihydrazone [10c]. In all cases, the processes are based on condensation reactions between formyl- (for **4a–4c**) or acetyl- (for **5a–5c**) cyrhetrene and the corresponding hydrazine in anhydrous methanol (Scheme 1). The new compounds, that were

isolated as yellow (**4a–4c**, **5a** and **5c**) or red (**5b**) crystalline solids after crystallization from  $\text{CH}_2\text{Cl}_2$ /hexane mixtures, exhibit high solubility in  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ , and they are practically insoluble in hexane. It should be noted that **4c** is less stable (in solution as well as in the solid state) than **4a**, **4b** and **5a–5c** and it was characterized immediately after its isolation.

Compounds **4a–4c** and **5a–5c** were characterized by electron impact (EI) mass spectrometry, infrared spectroscopy and NMR studies. Their MS spectra showed peaks due to the molecular cations  $[\text{M}]^+$  and those arising from the successive dissociation of the remaining CO ligands. IR spectra of **4a–4c** and **5a–5c** in  $\text{CH}_2\text{Cl}_2$  showed the following common features: a) two intense bands at 2023 and 1929  $\text{cm}^{-1}$ , that are characteristic of the asymmetric ( $\nu_{\text{as}}$ ) and symmetric ( $\nu_{\text{s}}$ ) stretchings of the terminal CO ligands of cyrhetrene derivatives [9a,14,15], and b) an intense and sharp absorption (at around 1600  $\text{cm}^{-1}$ ) in the same range as observed for ferrocenyl hydrazones  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\{\eta^5\text{-C}_5\text{H}_4\}\text{C}(\text{R}^1) = \text{N-NHR}^2)]$  with  $\text{R}^1 = \text{H}$  (**1**) or  $\text{Me}$  (**2**) [10–12], that has been assigned to the stretching of the functional  $>\text{C}=\text{N}-$ .

It is well-known that hydrazones may adopt two different forms (*E*- or *Z*-) [6,18] in the solid state and also in solution.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **4a–4c** and **5a–5c** showed only one set of resonances, thus suggesting that only one of the two isomers was present in  $\text{CDCl}_3$  solution at room temperature (we will return to this point later on).

Proton-NMR spectra of **4a–4c** and **5a–5c** showed two triplets of identical intensities assigned to the pairs of protons ( $\text{H}^2$ ,  $\text{H}^5$ ) and ( $\text{H}^3$ ,  $\text{H}^4$ ) of the “ $\text{Re}(\eta^5\text{-C}_5\text{H}_4)$ ” moiety and an additional singlet, in the range  $7.3 < \delta < 8.0$  ppm for **4a–4c**, or at around 1.9 ppm (for **5a–5c**), due to the  $^1\text{H}$  nuclei of the  $\text{R}^1$  units (H and Me, respectively). The resonance of the  $-\text{NH}-$  proton appeared as a broad singlet for **4c** and **5c** (at 5.26 and 5.48 ppm); while for **4a**, **4b**, **5a** and **5b** this signal was much narrower and low-field shifted. Additional resonances due to the aromatic protons of the phenyl rings of **4a–b** and **5a–b** were also observed.



Scheme 1. Synthesis of compounds  $[\text{Re}(\{\eta^5\text{-C}_5\text{H}_4\}\text{C}(\text{R}^1) = \text{N-NHR}^2)(\text{CO})_3]$  with  $\text{R}^1 = \text{H}$  (**4**) or  $\text{Me}$  (**5**) and atom numbering system for NMR data.

Download English Version:

<https://daneshyari.com/en/article/1324459>

Download Persian Version:

<https://daneshyari.com/article/1324459>

[Daneshyari.com](https://daneshyari.com)