

Synthesis and properties of new trinuclear Mo(II) complexes containing imidazole and benzimidazole ferrocene units

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Dedicated to Piero Zanello.

Abstract

The reaction of FcCOCl ($\text{Fc} = (\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)$) with benzimidazole or imidazole in 1:1 ratio gives the ferrocenyl derivatives $\text{FcCO}(\text{benzim})$ (**L1**) or $\text{FcCO}(\text{im})$ (**L2**), respectively. Two molecules of **L1** or **L2** can replace two nitrile ligands in $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{CH}_3\text{CN})_2\text{Br}]$ or $[\text{Mo}(\eta^3\text{-C}_5\text{H}_5\text{O})(\text{CO})_2(\text{CH}_3\text{CN})_2\text{Br}]$ leading to the new trinuclear complexes $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{L})_2\text{Br}]$ (**C1** for $\text{L} = \text{L1}$; **C3** for $\text{L} = \text{L2}$) and $[\text{Mo}(\eta^3\text{-C}_5\text{H}_5\text{O})(\text{CO})_2(\text{L})_2\text{Br}]$ (**C2** for $\text{L} = \text{L1}$; **C4** for $\text{L} = \text{L2}$) with **L1** and **L2** acting as *N*-monodentate ligands. **L1**, **L2** and **C2** were characterized by X-ray diffraction studies. $[\text{Mo}(\eta^3\text{-C}_5\text{H}_5\text{O})(\text{CO})_2(\text{L1})_2\text{Br}]$ was shown to be a trinuclear species, with the two **L1** molecules occupying one equatorial and one axial position in the coordination sphere of Mo(II). Cyclic voltammetric studies were performed for the two ligands **L1** and **L2**, as well as for their molybdenum complexes, and kinetic and thermodynamic data for the corresponding redox processes obtained. In agreement with the nature of the frontier orbitals obtained from DFT calculations, **L1** and **L2** exhibit one oxidation process at the Fe(II) center, while **C1**, **C3**, and **C4** display another oxidation wave at lower potentials, associated with the oxidation of Mo(II).

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1. Introduction

The large amount of applications of ferrocene derivatives in fields ranging from non-linear optical materials, electrochemical sensors, liquid crystals, catalysis and nanoparticles, has contributed to a high interest in their chemistry [1,2]. In addition, the introduction of groups with coordinating capabilities further allows the ferrocenyl moiety to become an organometallic ligand, which can bind with other metal centers in order to enhance their properties. Some antitumor activity has been detected in the ferr-

ocenium ion, and although the results were not outstanding, they were promising enough to be extended to specially designed systems [3]. As a matter of fact, when ferrocene was introduced in certain molecules, their cytotoxic activity was enhanced [4]. The versatility of the ferrocenyl unit, allowing for relatively easy functionalization of one or two rings, as well as the redox capability of the iron center, explains this success, making possible the tuning of the same basic unit to different challenges. The chemistry of ferrocenyl amides containing aminoacids and peptides has been developed to include the introduction of groups able to bind to biological targets in attempts to improve biological applications [5]. The synthesis of ferrocene labeled aminoacids has been carried out [6] and the ligand capability of new ferrocenyl moieties toward several

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metal fragments analyzed [7]. New species and their properties [8] have been studied in detail, namely as sensors [9].

We have been interested in the chemistry of Mo(II) allyl complexes [10], and their association with iron in polynuclear species, a combination well known in biological systems, such as nitrogenases [11]. The Mo(allyl) complexes of this family have proved to be rather versatile, acting as catalysts in several reactions [12,13] and exhibiting some antitumoral activity *in vitro* [14].

In this work, we describe the syntheses and characterization of two ferrocenyl derivatives containing imidazole and benzimidazole attached to one ring and their complexes with the Mo(η^3 -allyl)(CO)Br fragment, leading to trinuclear compounds linked by those units. The structures of the two ferrocenes and one complex were determined by single-crystal X-ray diffraction. Electrochemical studies were performed to study the redox properties of the new species and the role of the metal–metal interaction, and DFT calculations [15] were used to rationalize the experimental data. The biological activity of some complexes was studied on two cancer cell lines and compared to a reference compound.

2. Results and discussion

2.1. Chemical and structural studies

The new ferrocenyl benzimidazole **L1** and the related ferrocenyl imidazole **L2** [16] ligands (Fig. 1) were obtained from the coupling reaction between FcCOCl [Fc = (η^5 -C₅H₅)Fe(η^5 -C₅H₄)] and benzimidazole or imidazole, respectively, in a 1:1 ratio, in dichloromethane and in the presence of NEt₃.

The infrared spectra of these ferrocenes exhibit the expected bands, the most characteristic ones being the C=O stretching observed at 1674 cm⁻¹ for **L1** and at 1680 cm⁻¹ for **L2**. This last value differs significantly from the one reported in [16], and may originate from the different synthetic procedure adopted which may have produced another polymorph. For **L1**, the most important frequencies for the ferrocene moiety are found at 3113 (ν_{C-H}), 1441 (ν_{C-C}), 1105 (asymmetric ring breathing), 999 (δ_{C-H}), 821 (π_{C-H}), 502 (δ_{Fe-Cp})_a and 450 cm⁻¹ (ν_{Fe-Cp}) [17].

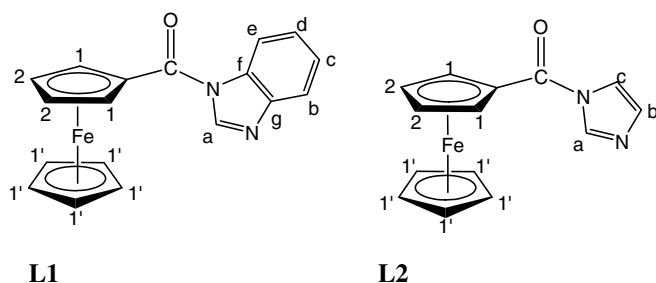


Fig. 1. Schematic representation of the two ligands **L1** and **L2** with the numbering scheme adopted.

The ¹H NMR spectrum of **L1** in CDCl₃ shows the signals of the benzimidazole ring protons as a singlet at 8.81 ppm (Ha), two doublets at 8.24 and 7.85 ppm (Hb and He), and one multiplet at 7.43 ppm (Hc and Hd). The resonance of the Cp ring H1' protons is observed as a singlet at 4.32 ppm, and those of H1 and H2 of the substituted Cp ring as multiplets at 4.98 and 4.67 ppm. These chemical shifts are very close to those of the **L2** ligand [16], the only relevant change being the shift of Ha from 8.41 to 8.81 ppm upon introduction of the benzene ring.

The ¹³C NMR spectrum of the two ligands is also very similar, the chemical shifts being essentially the same for the ferrocenyl carbon atoms (C1' 70.63, 70.66; C1 71.67, 71.65; C2 72.60, 72.92, for **L1** and **L2**, respectively). Large shifts are observed for the imidazole carbon atoms, specially those where H is replaced by carbon (Cc,b in **L1** and Cf,g in **L2**).

The **L2** and **L1** ligands were also structurally characterized by single crystal X-ray diffraction. The molecular structures of **L1** and **L2** together with the labelling scheme adopted are presented in Figs. 2 and 3, respectively. In **L2**, the imidazole moiety adopts a *cis* configuration relative to the carbonyl from the amide group leading to a C(3)–N(2)–C(1)–O(11) torsion angle of –17.6° and a C3–H···O(11) intramolecular distance of 2.591 Å. By contrast in **L1**, the

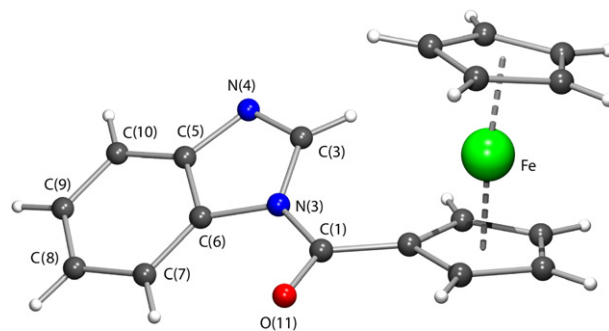


Fig. 2. Molecular structure of [(η^5 -C₅H₅)Fe(η^5 -C₅H₄CON₂C₇H₅)] (**L1**). The atomic notation scheme used for Cp rings is omitted for clarity.

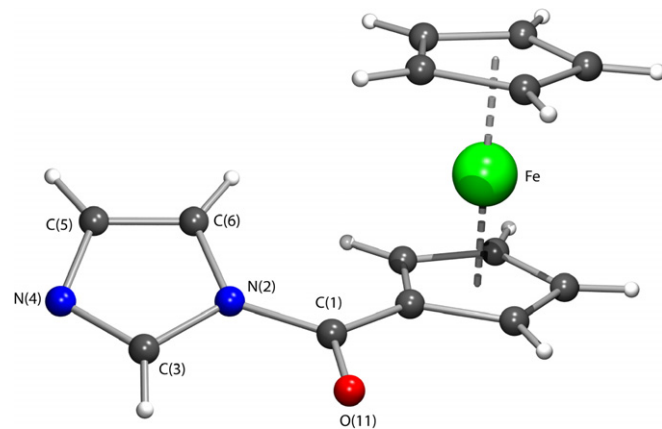


Fig. 3. Molecular structure of [(η^5 -C₅H₅)Fe(η^5 -C₅H₄CON₂C₃H₃)] (**L2**). The atomic notation scheme used for Cp rings is omitted for clarity.

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