



Preparation, separation and characterisation of two regioisomers of a *N*-hydroxyalkylpyridylpyrazole ligand: A structural investigation of their coordination to Pd(II), Pt(II) and Zn(II) centres

Carlos Luque^a, Josefina Pons^{a,*}, Teresa Calvet^b, Mercè Font-Bardia^{b,c}, Jordi García-Antón^a, Josep Ros^a

^a Departament de Química, Unitat de Química Inorgànica, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

^b Cristal·lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, 08028 Barcelona, Spain

^c Unitat de Difracció de RX, Serveis Científic-Tècnics, Universitat de Barcelona, Solé i Sabarís 1-3, 08028 Barcelona, Spain

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ABSTRACT

The reaction of the β -diketone 1-phenyl-3-(pyridin-2-yl)propane-1,3-dione, and the monosubstituted hydrazine 2-hydroxyethylhydrazine has been investigated. Two regioisomers were identified, 2-(3-phenyl-5-(pyridin-2-yl)-1*H*-pyrazol-1-yl)ethanol (pzol.1) and 2-(5-phenyl-3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)ethanol (pzol.2) in 57:43 ratio. The separation of the regioisomers was done by silica column chromatography using ethyl acetate as eluent.

Palladium(II) and platinum(II), [MCl₂(pzol.1)₂], [MCl₂(pzol.2)], and zinc(II), [ZnCl₂(pzol.1)], [ZnCl₂(pzol.2)] complexes were synthesised and characterised. The crystals and molecular structures of [PdCl₂(pzol.2)]·H₂O and [ZnCl₂(pzol.2)] were solved by X-ray diffraction, and consist of mononuclear complexes. In complex [PdCl₂(pzol.2)]·H₂O, the Pd(II) centre has a typical square planar geometry, with a slight tetrahedral distortion. The tetra-coordinated atom is bonded to one pyridinic nitrogen, one pyrazolic nitrogen and two chlorine atoms in *cis* disposition. The pzol.2 ligand acts as a bidentate chelate forming a five-membered metallocycle ring. In complex [ZnCl₂(pzol.2)], the Zn(II) is five-coordinated with two Zn–N bonds (Zn–N_{pz} and Zn–N_{py}), one Zn–OH bond and two Zn–Cl bonds. The coordination geometry is intermediate between a trigonal bipyramid and a square pyramid. In this complex, the ligand pzol.2 is tridentate and forms two metallocycle rings.

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1. Introduction

The coordination chemistry of the pyrazole-derived ligands has been extensively studied in recent years [1]. In particular, the chemistry of *N*-hydroxyalkylpyrazole and *N*-hydroxyalkyl-3,5-dimethylpyrazole compounds has been studied by Driessen et al. They have described the synthesis and characterisation of some of these ligands with Ni(II), Cu(II), and Co(II) [2]. Moreover, the [SnMe₂Cl₂(HL)] (HL = 1-hydroxymethylpyrazole) has also been studied [3].

In our group, we have continued the study of the *N*-hydroxyalkylpyrazole and *N*-hydroxyalkyl-3,5-dimethylpyrazole ligands. In particular, we have described the reaction of the ligands that contain hydroxymethyl, hydroxyethyl or hydroxypropyl moieties with Pd(II) and Pt(II), obtaining complexes with stoichiometry [MCl₂(L')₂]. In all these complexes, the ligand L' acts as monodentate via *N*-pyrazole [4].

The pyrazole ring is present in many pharmacologically important compounds. Although many methods are known for the construction of this ring system, the search for novel synthetic methodology addressing the necessity for a particular regioisomer is always desirable [5].

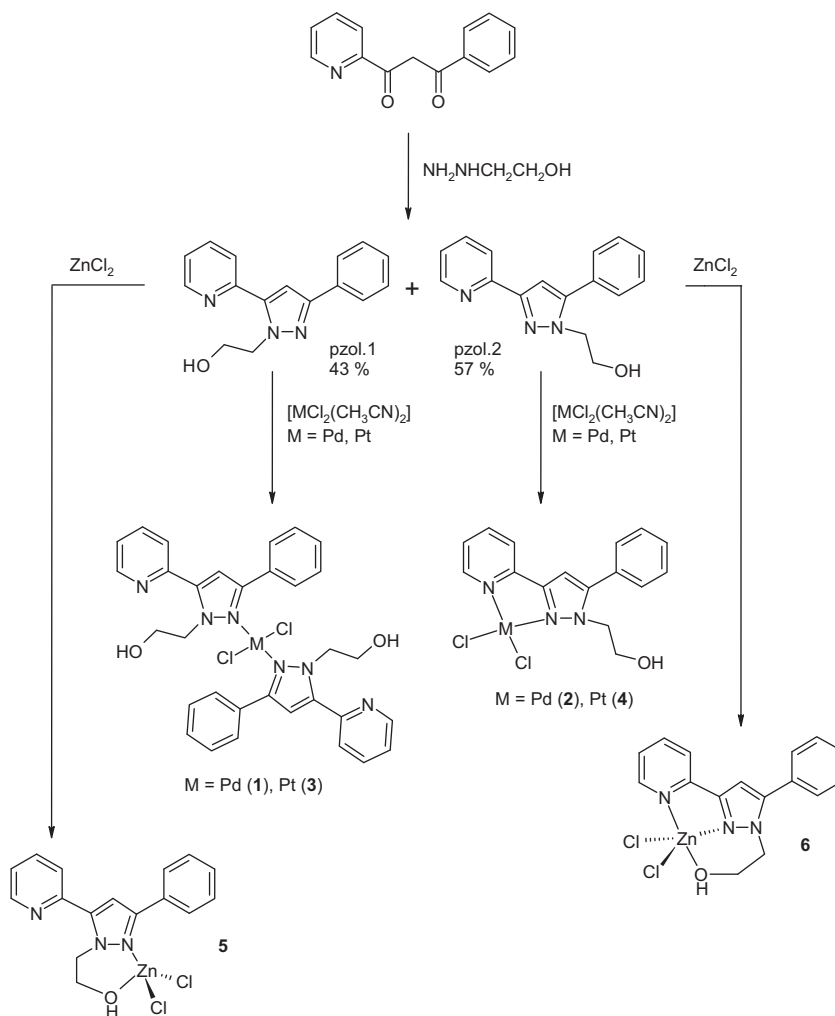
In recent years, we have developed general synthesis of 1,3,5-substituted pyrazole derived ligands, and focussed the research on the development of methods for regioselective synthesis [6].

In a recent paper, we presented the synthesis and characterisation of a new 1,3,5-substituted pyrazole derived ligand, containing an alcohol functionality: namely, 2-(3-(pyridin-2-yl)-5-trifluoromethyl-1*H*-pyrazol-1-yl)ethanol (L') and its reactivity toward Pd(II). These reactions yield *cis*-[PdCl₂(L')], [Pd(L')₂](BF₄)₂ and [PdCl(L')](BF₄). In complexes *cis*-[PdCl₂(L')] and [Pd(L')₂](BF₄)₂, the ligand L' acts as bidentate via *N*-pyrazole and *N*-pyridine. However, for complex [PdCl(L')](BF₄), the ligand L' acts as tridentate via *N*-pyrazole, *N*-pyridine and the oxygen atom of the alcohol group [7].

As an extension to these results, in the present paper we describe the preparation, separation and characterisation of two regioisomers of a 1,3,5-substituted pyrazole derived ligand,

* Corresponding author. Fax: +34 93 581 31 01.

E-mail addresses: josefina.pons@uab.es, josefina.pons@uab.cat (J. Pons).



Scheme 1.

2-(3-phenyl-5-(pyridin-2-yl)-1*H*-pyrazol-1-yl)ethanol (pzol.1) and 2-(5-phenyl-3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)ethanol (pzol.2) (Scheme 1). It is important to note that ligand pzol.2 has been previously reported by some of the authors of the present manuscript. The reactivity of pzol.2 towards Pd(II) has also been previously assayed, yielding [PdCl₂(pzol.2)]. This complex was used in Heck reaction catalysis [8]. In the present manuscript, the reactivity of both pzol.1 and pzol.2 with [MCl₂(CH₃CN)₂] (M = Pd(II), Pt(II)) and ZnCl₂ was studied.

2. Results and discussion

2.1. Synthesis of the ligands

The 1-phenyl-3-(pyridin-2-yl)propane-1,3-dione was prepared by Claisen condensation of methyl-2-pyridinecarboxylate and acetophenone, using NaOEt as base and dry toluene as solvent [9]. Treatment of 1-phenyl-3-(pyridin-2-yl)propane-1,3-dione with 2-hydroxyethylhydrazine in ethanol at room temperature produced two regioisomers, 2-(3-phenyl-5-(pyridin-2-yl)-1*H*-pyrazol-1-yl)ethanol (pzol.1) and 2-(5-phenyl-3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)ethanol (pzol.2) in 93% yield. The separation of the regioisomers was carried out by silica column chromatography using ethyl acetate as eluent. The ratio of the regioisomers has been calculated through ¹H NMR experiments, especially

from the integration of the pyrazolic proton (43 pzol.1: 57 pzol.2) (Scheme 1). Fig. 1 shows the ¹H NMR spectra of the ethylenic and pyrazolic hydrogens for the mixture of regioisomers (pzol.1 + pzol.2) and for each regioisomers after separation.

The assignment of each one of the regioisomers was confirmed by NOESY experiments. The regioisomer pzol.1 presents NOE-interactions between the protons of the hydroxyalkyl chain and the pyridyl group. For pzol.2, no NOE-interactions between these groups were observed.

Both regioisomers were characterised by elemental analysis, infrared, ¹H and ¹³C{¹H} NMR spectroscopy, and electrospray mass spectrometry (ESI(+)-MS). For the assignment of the ¹³C{¹H} NMR spectra, we have employed HSQC techniques. The ¹H NMR spectra display the *ortho*-pyridinic hydrogen (Scheme 1) at $\delta = 8.72$ ppm (²*J* = 4.8 Hz) (pzol.1), and $\delta = 8.64$ ppm (²*J* = 4.5 Hz) (pzol.2) as doublets. The pyrazolic hydrogen was observed at $\delta = 6.87$ ppm (pzol.1), and 6.99 ppm (pzol.2). The ¹³C{¹H} NMR spectra contained the signals at $\delta = 104.3$ ppm (pzol.1), and 105.2 ppm (pzol.2), attributable to the CH of the pyrazole [10]. In the mass spectra (ESI(+)-MS) of pzol.1 and pzol.2 ligands, one signal is observed at 266 (100%), attributable to [L + Na]⁺ (L = pzol.1, pzol.2).

2.2. Synthesis and general characterisation of complexes

The reaction of the ligands (pzol.1, pzol.2) with [MCl₂(CH₃CN)₂] (M = Pd(II) [11] or Pt(II) [12]), in CH₂Cl₂ for Pd(II) complexes and in

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