



1-Methyl-4-ferrocenylmethyl-3,5-diphenylpyrazole: A versatile ligand for palladium(II) and platinum(II)

Pradipta Kumar Basu^a, Asensio González^a, Concepción López^{b,*}, Mercè Font-Bardía^c, Teresa Calvet^c

^a Laboratori de Química Orgànica, Facultat de Farmàcia, Universitat de Barcelona, Pl. Pius XII s/n, E-08028-Barcelona, Spain

^b Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, E-08028-Barcelona, Spain

^c Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia, Universitat de Barcelona, Martí i Franquès s/n, E-08028-Barcelona, Spain

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ABSTRACT

The syntheses and characterization of two novel ferrocene derivatives containing 3,5-diphenylpyrazole units of general formula [1-R-3,5-Ph₂-(C₃N₂)-CH₂-Fc] {Fc = (η⁵-C₅H₅)Fe(η⁵-C₅H₄) and R = H (**2**) or Me (**3**)} together with a study of their reactivity with palladium(II) and platinum(II) salts or complexes under different experimental conditions is described. These studies have allowed us to isolate and characterize *trans*-[Pd{1-Me-3,5-Ph₂-(C₃N₂)-CH₂-Fc}]₂Cl₂ (**4a**) and three different types of heterodimetallic complexes: *cis*-[M{1-Me-3,5-Ph₂-(C₃N₂)-CH₂-Fc}]Cl₂(dmsO) {M = Pd (**5a**) or Pt (**5b**)}, the cyclometallated products [M{κ²-C,N-[3-(C₆H₄)-1-Me-5-Ph-(C₃N₂)]-CH₂-Fc}Cl(L)] with L = PPh₃ and M = Pd (**6a**) or Pt (**6b**) or L = dmsO and M = Pt (**8b**) and the *trans*-isomer of [Pt{1-Me-3,5-Ph₂-(C₃N₂)-CH₂-Fc}]Cl₂(dmsO) (**7b**). In compounds **4a**, **5a**, **5b** and **7b**, the ligand behaves as a neutral N-donor group; while in **6a**, **6b** and **8b** it acts as a bidentate [C(sp²,phenyl),N(pyrazole)][−] group. A comparative study of the spectroscopic properties of the compounds, based on NMR, IR and UV–Visible experiments, is also reported.

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1. Introduction

The synthesis and design of ferrocene derivatives containing heterocyclic systems have attracted great interest in recent years [1–3] because of their physical or chemical properties as well as for their applications in a wide variety of areas including homogeneous catalysis [1,2d,3c] and Biomedicine [2e]. In this sort of compounds, the presence of heterocycles with one or more atoms with good donor abilities is especially interesting in view of their use as ligands for transition metals to give heteropolymetallic complexes [1,2d,4] in which the existence of two or more proximal metal ions may induce a co-operative effect [4].

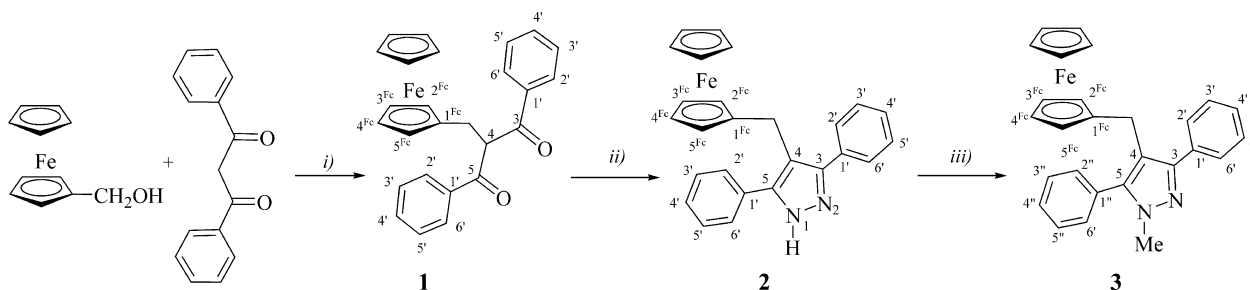
On the other hand, palladium(II) and platinum(II) complexes with heterocyclic ligands with two potentially donor atoms is one of the research areas that has undergone a fast development during the last years [5–17]. Among all the examples reported so far those containing pyrazole backbones are specially attractive [6–8]. Compounds of this kind exhibiting greater antitumoral activity and lower toxicity than *cis*-[PtCl₂(NH₃)₂] or antibacterial activity have been reported [6c,7h]. Furthermore, some examples of their utility in Macromolecular Chemistry [7a,i–k] or in homogeneous catalysis [8a] have also been published.

In addition, when the pyrazole contains substituents in which there is a σ(C–H) bond with the proper orientation, cyclopallada-

[9] or platinumated [10] complexes can also be isolated. The interest on metallacycles with a σ(M–C) (M = Pd or Pt) bond has increased exponentially due to their properties and applications in different areas [11–17]. Metallomesogens [11], precursors for homogeneous catalysis [13], antitumor drugs [14] and “building blocks” for Supramolecular Chemistry [15] containing pallada- and platinacycles have been reported. In addition, the high reactivity of the σ(M–C) bond in this sort of compounds makes them valuable precursors in organic synthesis [11a,12b,c,16] including the total synthesis of natural products [12b,16]. However, and despite the increasing interest on palladium(II) and platinum(II) complexes with ligands containing simultaneously a ferrocenyl unit and a (N,O) or a (N,S) heterocycle [3,4], parallel studies on related compounds with pyrazole rings are scarce [4c,18,19]. A few palladium(II) complexes containing this type of ligands are known and most of them contain additional allylic ligands [3c,19]. Only one example of a cyclopalladated complex having simultaneously the ferrocenyl and the pyrazolyl units has been described so far [4c], but platinum(II) derivatives are still unknown. In view of these facts, and as a part of a project centred on the synthesis of heterodimetallic complexes with heterocycles having ferrocenyl moieties [3c,d,4,12d], we focused our attention on: (a) the synthesis of novel pyrazolyl containing ferrocene derivatives and (b) the study of their reactivity towards palladium(II) and platinum(II) salts or complexes. In this work, we present the syntheses and characterization of [1-R-3,5-Ph₂-(C₃N₂)-CH₂-Fc] {Fc = (η⁵-C₅H₅)Fe(η⁵-C₅H₄) and R = H (**2**) or Me (**3**)} (Scheme 1) that contain the

* Corresponding author. Tel.: +34 93 403 91 34; fax: +34 490 77 25.

E-mail address: conchi.lopez@qi.ub.es (C. López).



Scheme 1. (i) HBF_4 (40%)/ CH_2Cl_2 . (ii) N_2H_4 , EtOH under reflux. (iii) NaOH (40%), CH_2Cl_2 and MeI.

3,5-diphenylpyrazolyl group in the pendant arm of the ferrocene as well as a variety of palladium(II) and platinum(II) complexes derived from these ligands.

2. Results and discussion

2.1. The ligands

The preparation of the new ferrocenyl ligands [1-R-3,5- Ph_2 -(C_3N_2)- CH_2 -Fc] (R = H or Me) was achieved following the sequence of reactions presented in Scheme 1. First, 3-ferrocenylmethyl dibenzoylmethane (**1**) was obtained by electrophilic coupling on position 3 of the diketone using ferrocenylmethanol (Fc- CH_2OH) [20] in a two-phase CH_2Cl_2 /40% aqueous HBF_4 mixture (Scheme 1, step (i)) [21]. Subsequent treatment with hydrazine in ethanol at reflux temperature (Scheme 1, step (ii)) [4c] followed by purification of the crude product of the reaction by column chromatography gave [1-R-3,5- Ph_2 -(C_3N_2)- CH_2 -Fc] with R = H (**2**). The subsequent alkylation with methyl iodide (Scheme 1, step (iii)) using the same procedure as described before for indigo [22], gave [1-Me-3,5- Ph_2 -(C_3N_2)- CH_2 -Fc] (**3**) in good yield (98%).

Compounds **1–3** were characterized by elemental analyses, mass spectrometry, infrared spectra and mono- and two-dimensional NMR experiments. The elemental analyses (Section 3) were consistent with the proposed formulae and their mass spectra showed a peak at $m/z = 422.1$ (for **1**), 419.1 (for **2**) and 433.1 (for **3**) that agree with the values expected for the $\{[\text{M}+\text{H}]^+\}$ cations.

Proton NMR spectra of **1–3** showed the typical patterns of monosubstituted ferrocene derivatives [1,23] and the resonances due to the $-\text{CH}_2-$ protons appeared as a doublet (in **1**) or as a singlet (in **2** and **3**) in the range 3.10–4.00 ppm. The signals observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1–3** were assigned with the aid of two-dimensional $\{^1\text{H}-^{13}\text{C}\}$ HSQC and HMBC experiments. The resonances due to the quaternary carbon nuclei of **1–3** were easily identified by comparison of the signals detected in the $^{13}\text{C}\{^1\text{H}\}$ and in the $\{^1\text{H}-^{13}\text{C}\}$ HSQC, and the analyses of the cross peaks between the $-\text{CH}_2-$ protons allowed to assign the resonances of the *ipso* carbon of the ferrocenyl unit ($\text{C}^{1\text{Fc}}$) and of the C^3-C^5 nuclei.

2.2. Palladium(II) complexes

Treatment of [1-Me-3,5- Ph_2 -(C_3N_2)- CH_2 -Fc] (**3**) with $[\text{PdCl}_2(\text{dmsO})_2]$ [24] (in a 2:1 molar ratio) in refluxing methanol for 3.5 h under reflux produced a pale yellow solid that was identified as the heterotrimetallic complex $[\text{Pd}\{1\text{-Me-3,5-Ph}_2\text{-(C}_3\text{N}_2\text{)-CH}_2\text{-Fc}\}_2\text{Cl}_2]$ (**4a**) (Scheme 2, step (i)). It is well-known that in palladium(II) complexes of the type $[\text{Pd}(\text{L})_2\text{Cl}_2]$ (with L = planar N-donor ligand) the “ PdCl_2 ” is nearly orthogonal to the main plane of the N-donor ligand [25,26]. For this arrangement of groups, the use of molecular models reveals that in *cis*- $[\text{Pd}\{1\text{-Me-3,5-Ph}_2\text{-(C}_3\text{N}_2\text{)-CH}_2\text{-Fc}\}_2\text{Cl}_2]$, the steric hindrance is greater than in the

trans-isomer (**4a**). In addition, the IR spectrum of **4a** in the range of metal–ligand vibrations showed two bands at $\nu = 498$ and 334 cm^{-1} . According to Ref. [27] these absorptions are due to the Pd–N and Pd–Cl stretching vibrations of *trans*- $[\text{Pd}(\text{N-donor})_2\text{Cl}_2]$ complexes. In view of these findings we assume that **4a** is the *trans*-isomer of $[\text{Pd}\{1\text{-Me-3,5-Ph}_2\text{-(C}_3\text{N}_2\text{)-CH}_2\text{-Fc}\}_2\text{Cl}_2]$.

In contrast with these results, when the reaction was carried out using equimolar amounts of **3** and $[\text{PdCl}_2(\text{dmsO})_2]$ [24] a different product was obtained. Elemental analyses were consistent with those expected for $[\text{Pd}\{1\text{-Me-3,5-Ph}_2\text{-(C}_3\text{N}_2\text{)-CH}_2\text{-Fc}\}(\text{dmsO})_2\text{Cl}_2]$ (**5a**) (Scheme 2, step (ii)) and its ^1H NMR spectrum in CDCl_3 at 298 K showed an intense singlet at 3.25 ppm assigned to the protons of the dmsO ligand; however, no evidence of the existence of NOE peaks between these protons and any of the coordinated ligand **3** were detected in the $\{^1\text{H}-^1\text{H}\}$ NOESY spectrum. The far IR spectrum of **5a** showed two absorption bands of the Pd–Cl stretching vibrations at 298 and 320 cm^{-1} . Their position is similar to those reported for $[\text{PdCl}_2(\text{dmsO})(\text{L})]$ with L = 5,7-*di*-*tert*-butyl-1,2,4-triazolo[1,5-*a*]pyrimidine, for which: (a) the crystal structure confirmed a *cis*-arrangement of the two Cl^- ligands and (b) only one singlet due to the protons of the dmsO ligand was also observed in the ^1H NMR spectrum [28]. On these bases, we tentatively postulate that in **5a**, the Cl^- ligands are in a *cis*-disposition.

It is well-known that for N-donor ligands (L), the formation of the palladacycle usually takes place in two steps, first the coordination of two (or one) units of the ligand to give *trans*- $[\text{Pd}(\text{L})_2\text{X}_2]$ [or $[\text{Pd}(\text{L})\text{X}_3]^-$] species, followed by the subsequent electrophilic attack of the palladium(II) species formed to the carbon atom [11a,29]. Despite the arrangement of ligands in **4a** is identical to those of the *trans*- $[\text{Pd}(\text{L})_2\text{X}_2]$ species formed in the first step of the cyclopalladation process, no evidence of the formation of any palladacycle were detected by ^1H NMR when **4a** was refluxed in toluene for long periods (up to 12 h). In view of these results and since it is well-known that $\text{Pd}(\text{OAc})_2$ is a better metallating agent than $[\text{PdCl}_2(\text{dmsO})_2]$ [11a,29] we also studied the reactivity of **3** with this salt.

When ligand **3** was treated with $\text{Pd}(\text{OAc})_2$ in toluene under reflux for 3.5 h followed by: (a) the addition of PPh_3 first and LiCl later on and (b) a column chromatography on silica gel, the cyclopalladated complex $[\text{Pd}\{\kappa^2\text{-C,N-[3-(C}_6\text{H}_4\text{)-1-Me-5-Ph-(C}_3\text{N}_2\text{)]-CH}_2\text{-Fc}\}\text{Cl}(\text{PPh}_3)]$ (**6a**) (Scheme 2, step (iii)) was isolated in fairly good yield (74%). In this product, the ligand acts as a bidentate $[\text{C}(\text{sp}^2, \text{phenyl}), \text{N}(\text{pyrazole})]^-$ group and the phosphine is in a *cis*-arrangement in relation to the metallated carbon atom, in good agreement with the so-called *transphobia effect* [30].

It should be noted that when any of the reactions depicted in Scheme 1, steps (i) and (ii) were performed under identical conditions but using [1-R-(3,5- Ph_2 -(C_3N_2)- CH_2 -Fc] with R = H (**2**), instead of ligand **3**, the starting materials were recovered unchanged and no evidence of the formation of any palladium(II) complex was detected by NMR. The well-known tautomeric process involving the proton transfer between the two nitrogen atoms

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