



# A convenient route to prepare mono- and dinuclear 2-benzoylpyridine palladacycles with imidate ligands



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## ABSTRACT

New dinuclear cyclometallated palladium complexes of general formula  $[\{\text{Pd}(\mu\text{-NCO})(\text{C}^{\text{N}})\}_2]$  ( $\text{C}^{\text{N}} = 2\text{-benzoylpyridine (bzpy)}$  **I**;  $-\text{NCO}- = \text{saccharinate (sacc)}$  **a**, Phthalimidate (phthal) **b** or 4,5-dichlorophthalimidate (DiClphthal) **c** have been synthesized by a simple acid-base reaction involving the di- $\mu$ -hydroxo-precursor  $[\{\text{Pd}(\mu\text{-OH})(\text{bzpy})\}_2]$  recently reported. Analogous to **Ic**, complex **IIc** with  $\text{C}^{\text{N}} = 2\text{-phenylpyridine (phpy)}$  **II** has also been prepared, meaning the first examples reported to date of complexes including 4,5-dichlorophthalimidate as ligand coordinating a metal centre. The reaction of bridged imidato precursors against triphenylphosphine to form the mononuclear N-bonded imidato derivatives of general formula  $[\text{Pd}(\text{C}^{\text{N}})(\text{N-imidate})(\text{PPh}_3)]$  **IaP**, **IbP**, **IcP** and **IIcP** has been achieved under mild conditions. The new complexes were characterized by partial elemental analyses and spectroscopic methods. Structural characterization by X-ray diffraction of **Ib** and **IIcP**, the first crystal structure of a complex containing 4,5-diClphthal that has been deposited to date on the Cambridge Structural Database, have confirmed the proposed formulae.

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## 1. Introduction

Cyclopalladation was first described in the sixties [1], and since then several aspects of palladacycles chemistry have been specifically reviewed. Thus, their synthesis and structural characterization, their use in organometallic catalysis, their presence in medicinal chemistry or its wide use as mesogenic or luminescent agents have been extensively explored. [2] Namely, 2-benzoylpyridine cyclopalladation yielding dinuclear complexes with bridging chloride or acetate ligands was reported in 1982 [3]. To our surprise, only two articles by Ghedini and coworkers about the reactivity and interesting luminescent properties of such species, [4] and one crystal structure (refcode WOSYEI) containing this palladacyclic moiety could be found until 2015, when we described the synthesis of the hydroxo-complex  $[\{\text{Pd}(\mu\text{-OH})(\text{bzpy})\}_2]$  [5]. We also moved one step beyond, and used the basic character of this hydroxo-complex in a novel route to prepare NHC-palladacyclic

catalysts  $[\text{Pd}(\text{Bmim})(\text{X})(\text{bzpy})]$ , envisaging its synthetic potential. Indeed, the usefulness of related  $[\{\text{Pd}(\mu\text{-OH})(\text{C}^{\text{N}})\}_2]$  complexes in the preparation of new derivatives by means of an acid-base reaction has been a subject of continuous study in our group [6] and others [7]. It is worth it to highlight that in some cases the di- $\mu$ -OH precursors have even showed a differentiated performance against specific ligands, when compared to analogous di- $\mu$ -AcO precursors [5, 6b, 6e]. Regarding the plethora of applications found by new derivatives prepared from di- $\mu$ -hydroxo-complexes, we particularly succeed with those containing imidate  $-\text{CNO}-$  bridges like the ones reported here. Thus, binuclear imidate cyclometalated palladium(II) complexes and mononuclear phosphine adducts have been tested in Stille [8], Suzuki and Sonogashira cross-couplings [6a, 9], and phosphine-free anionic dinuclear imidate complexes with a palladacyclopentadiene backbone have also displayed great performance in Stille couplings [10]. Despite the relevant applications of imidato complexes also in medicinal [11] or supramolecular chemistry [12], its coordination chemistry has been scarcely investigated, being saccharinate complexes the ones that have been more extensively explored [13].

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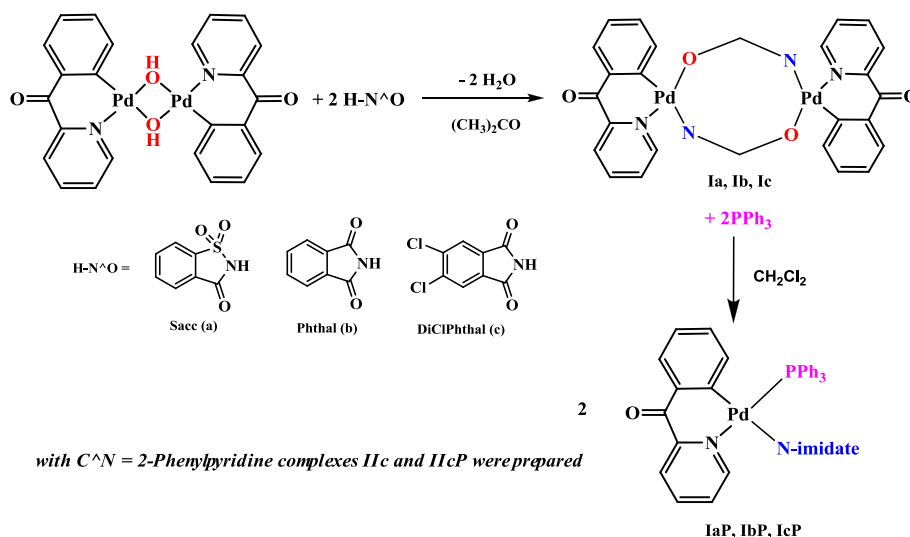
We report here the preparation of new 2-benzoylpyridine dinuclear orthometallated palladium(II) derivatives with bridging saccharinate, phthalimide or 4,5-dichlorophthalimide ligands acting in a bidentated –NCO– coordination mode. We also present the synthesis of mononuclear N-bonded imidato derivatives by reaction of the corresponding dinuclear precursor with triphenylphosphine. Spectroscopic characterization of the new compounds and the structure elucidation by X-ray diffraction analyses of both mononuclear and binuclear derivatives is also given, including the first X-ray crystal structure reported to date of a metallic complex containing 4,5-dichlorophthalimide (as searched in the CSD version 5.36 updated May 2015).

## 2. Results and discussion

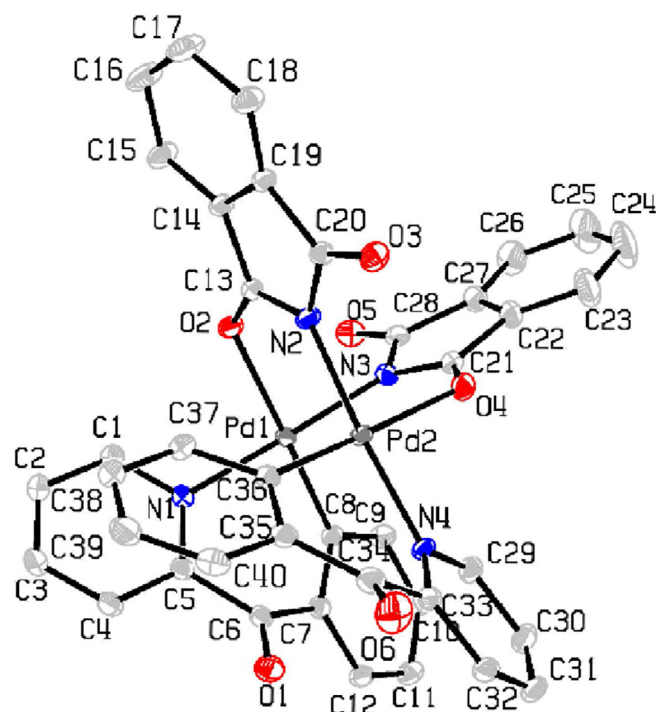
As presented in Scheme 1, the precursor  $[\{\text{Pd}(\mu\text{-OH})(\text{bzpy})\}_2]$  reacted with imidate-type ligands to give the dinuclear complexes **Ia**, **Ib** and **Ic** in which the imidato ligands displayed a bridging –NCO– coordination mode. The detailed mild conditions used to obtain these and analogous complex **Ic** with C^N = 2-phenylpyridine are described in the experimental section.

The formation of new dinuclear complexes **Ia**, **Ib** and **Ic** can be easily followed through its IR spectra, characterized by the disappearance of typical –OH stretching absorption at  $3433\text{ cm}^{-1}$  and important changes in the carbonyl region when compared to the spectrum of the precursor. Thus, together with the carbonyl absorption of orthometallated benzoylpyridine, two strong bands attributed to imidato-carbonyl stretching in the range  $1739\text{--}1715$  and  $1626\text{--}1619\text{ cm}^{-1}$ , were detected. According to previously reported data [14] the appearance of two bands in this region suggests coordination of one carbonyl group to the metal as a part of an –NCO– bridging unit. Again, the  $^1\text{H}$  NMR spectrum of the precursor showed a high field resonance ( $-1.60\text{ ppm}$ ) typical of palladium hydroxo-complexes [6d, 15] that is not found in the new derivatives. In addition, new aromatic resonances accounting the coordination of the imidate ligands were observed. Being this the first report of a metallic complex containing 4,5-dichlorophthalimide as ligand, we expanded the scope with well-known 2-phenylpyridine, preparing analogous dinuclear **Ic**.

Mass spectrometry (HPLC/MS TOF) was useful for the characterization of the new derivatives, displaying a common fragment at  $\text{M}^+$ -imidate, among others collected in the experimental section.



**Scheme 1.** Two reaction steps proposed for the synthesis of the new mono- and dinuclear derivatives.



**Fig. 1.** ORTEP drawing of  $[\{\text{Pd}(\mu\text{-phthal})(\text{bzpy})\}_2]$  (**Ib**), showing all non-hydrogen atoms and the atom numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

The abundances of the signals around the pattern ion are consistent with the natural isotopic ones.

We were able to obtain single crystals of complex **Ib** suitable for X-ray diffraction analysis, that unambiguously confirmed the proposed molecular structure. This is presented in Fig. 1, and Table 1 collects selected bond distances and angles.

As mentioned in the introduction, C^N-coordination is still rare for 2-benzoylpyridine. A search in the CSD version 5.36 (updates Nov. 2014, feb. 2015 and may 2015) reveals that most examples to date report this ligand acting in a N^O bidentated mode. In **Ib** the two orthometallated ligands appear superimposed in a *transoid* disposition, with the two carbonyl groups pointing up in *ca.*  $30^\circ$

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