

Novel cyclometallated Pd(II) and Pt(II) complexes with indole derivatives and their use as catalysts in Heck reaction

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Abstract

Several palladacycle and platinacycle complexes have been prepared from easily available or naturally occurring indole derivatives, such as gramine and related compounds. Dimeric complexes were obtained with Pd(OAc)₂, while Pt(DMSO)₂Cl₂ mainly afforded monomeric structures. A notable feature of these reactions was the formation of new M–C bonds between Pd or Pt and C-2 and C-3 of the indole ring. With ligands like 2-(2'-pyridyl)-1*H*-indoles, N–N metallacycles were generated instead: in fact new C–M bonds with the C-3 position could only form if *N*-substituted indoles were used. The reactivity of Pd dimeric complexes with PPh₃, *sym*-collidine and DMAP was explored to obtain monomeric complexes. Three such compounds were prepared, one of which was characterized by X-ray diffraction. Metathetical reactions were carried out to effect a ligand exchange replacing OAc with halide ions, with the aim to synthesize μ-Cl and μ-Br bridged structures. Turning to the synthesis of hetaryl complexes, functionalization of the C-2 position on the indole ring was achieved. These complexes were prepared by substitution reactions starting from gramine and/or its alkylammonium salts.

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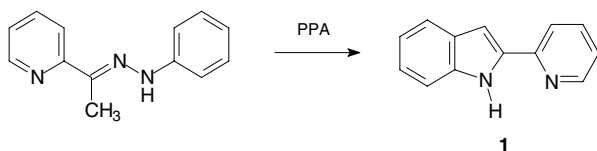
1. Introduction

Intramolecular activation of C–H bonds through the agency of transition metal ions (cyclometallation), first described by Kleiman and Dubeck [1], has attracted much interest in the last two decades. Many useful applications of cyclometallated compounds in organic chemistry are well established, e.g., to the synthesis of heterocycles and of enantiomerically enriched molecules, to prepare liquid crystals (metallomesogens) [2], to the resolution of racemates and to the evaluation of

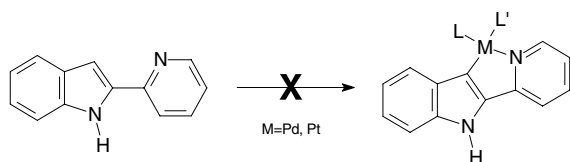
optical purity [3]. Finally, they have proved useful in the design of molecules with promising photochemical [4] and anticancer properties [5]. Cyclometallated compounds are organometallic complexes embodying an E–M–C connectivity of σ-bonds, where E is a heterodonor atom of the 15- or 16-group, M a metallic atom and C a carbon donor. They are usually classified according to the metal, the donor atom(s) or chelate ring size. Cyclopalladated compounds with a variety of N-donor ligands (e.g., amines, azobenzenes, imines [6], hydrazones [7], oximes and N-centered hetarenes) have been extensively investigated. Whereas heteroatom-directed cyclometallation of benzenoids and hetarenes is well known, the chemistry of the analogous indole derivatives remains partially unexplored [6–11]. In this

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Scheme 1.



Scheme 2.

context we are currently studying the structures and physico-chemical properties of 5- and 6-membered metallacycles containing an indole subunit with a tethered N-donor group [8–11]. In particular we have focused our interest on complexes of Pt(II) and Pd(II) with variously substituted bidentate [C, N] amines and imines as well as tridentate [C, N, O] hydrazones. The present work examined the formation of Pd(II) and Pt(II) complexes with 2-(2-pyridyl)-1H-indole (HL^1) **1** and their performance as precatalysts in the Heck reaction between iodobenzene and *tert*-butylacrylate. **1** was prepared in excellent yield by Fischer indolization [12] of 2-acetylpyridine with phenylhydrazine in polyphosphoric acid (PPA) at 150 °C (Scheme 1).

The juxtaposition of a pyridine and an indole system, presenting two potential donor sets (i.e., N,N or C,N) in a 1,4-relationship is particularly interesting. Pyridine behaves as a π -deficient system with Lewis basicity while indole is a π -excessive system $10e^-$ system with a good H-bond donor atom. When we used **1** as ligand for the synthesis of cyclometallated compounds with the aim to generate a new C–M bond, we found that **1** behaves exclusively as a nitrogen chelating agent, forming a N–M–N coordination compound.

Ligand **1** could, in principle, behave as an ambident nucleophile (N-1 vs. C-3) although normally indoles prefer electrophilic substitution (e.g., cyclometallation) at C-3, the 1-position being clearly less reactive. The reaction in degassed EtOH of **1** with $Li_2[PdCl_4]$ in the presence of NaOAc as a proton scavenger (room temperature, 2 h) afforded the orange $[(L^1-N,N) Pd(\mu-Cl)]_2$ complex **2** exhibiting N,N ligation, whose structure was supported by elemental analysis and IR spectroscopy. The absence of the two bands at 3100 and 3010 cm^{-1} attributed to the $\nu_{(N-H)}$ mode of the ligand indicated that **1** had been deprotonated and coordinated in the amido (indolato) form (Scheme 2).

Complex **2** was uneventfully converted to the bromo-bridged analogue, $[(L^1-N,N) Pd(\mu-Br)]_2$ **3** by metathetical reaction with LiBr in MeOH at room temperature.

On the other hand, the reaction of **1** with equivalent amounts of $Pd(OAc)_2$ in dichloromethane at room temperature (1 h) produced the dimeric acetate complex $[(L^1-N,N) Pd(\mu-OAc)]_2$ **4** (Scheme 3). Strong bands were observed at 1572, 1412 cm^{-1} due to $\nu_{as}(COO)$ and $\nu_s(COO)$, values consistent with a bridged acetate ligand; in 1H NMR spectra the singlet resonance at 2.35 ppm (6H) was assigned to the magnetically equivalent Me acetate groups, in accord with a *trans* geometry of the $[N^{\wedge}N]$ cyclometallated compound **4**.

Complex **5** $[(L^1-N,N) Pd(DMAP)(OAc)]$ was isolated after the addition to complex **4** of 4-dimethylaminopyridine (DMAP) in CH_2Cl_2 . The 1H NMR spectrum of **5** was unexceptional. Pale yellow crystals suitable for single-crystal X-ray structure determination were obtained by vapour diffusion of Et_2O into a CH_2Cl_2 solution of the crude product. **5** was then fully characterized by X-ray diffraction. Likewise complex **4** could be reacted with the appropriate ligating species to give **6** and **7**. A sample of **4** placed in an NMR tube was treated at room temperature in $CDCl_3$ with 1 equiv. of triphenylphosphine or 2,4,6-trimethylpyridine (*sym*-collidine), whereupon an instantaneous reaction took place to give the corresponding $[(L^1-N,N) Pd L(OAc)]$ complexes **6** and **7**, respectively (Scheme 4). These complexes were isolated in essentially quantitative yields by simply removing the solvent. The 1H NMR spectrum of **7** as well as 1H NMR and ^{31}P NMR spectra of the complex **6** showed only one set of signals, suggesting that only one isomer was obtained. The crystal structure of **5** evidenced an *anti* disposition of the pyridine and DMAP moieties. By analogy we propose the same geometry for **6** and **7** [13], as attempts to obtain single crystals of these compounds for X-ray diffraction studies were unsuccessful.

Metathetical reactions also occurred when complex **4** was treated with LiX (Scheme 5).

When $[Pt(DMSO)_2Cl_2]$ (DMSO = dimethylsulfoxide) was refluxed in ethanol with compound **1**, the monomeric platinum derivative **8** was obtained (Scheme 6).

The observation of a single SME resonance at 3.61 ppm with ^{195}Pt satellites ($^3J_{Pt-H} = 25$ Hz) as well as the finding in the IR spectrum of ν_{S-O} at 1122 cm^{-1} indicated an S-bonded DMSO configuration. Compound **8** was also fully characterized by X-ray diffraction.

Following with our aim to obtain new $[N-C-M]$ systems we turned to N-protected indoles, expecting cyclometallation at C-3 to emerge. This strategy led us to synthesize cyclometallated complexes with a new metal-nitrogen bond and a new C–M bond with C-3 of the indole derivative. In fact 1-methyl-2-(2'-pyridinyl)-1H-indole (L^2) formed almost quantitatively Pd and Pt complexes in accordance to our expectation (Scheme 7).

The substituent at the nitrogen atom should protect it from chelation, but should not deactivate the indole nucleus towards the electrophilic attack by the metal.

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