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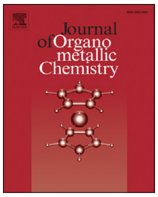

Synthesis and characterization of the P,C-palladacycles with bridging and chelating dinitrogen ligands and ONIOM calculations on the pyrazine-bridged organometallic polymers ($n = 1$ to $n = 10$)

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ABSTRACT

In this report we investigated the reaction of bromo-bridged cyclopalladated complex of tri-*o*-tolylphosphine with aromatic and aliphatic bidentate N-donor ligands (pyrazine, 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethane, 1,3-bis(4-pyridyl)propane, ethylenediamine). These reactions lead to the new P,C-palladacycles which were fully characterized by IR, NMR spectroscopies and CHN analysis. Interestingly, the linear organometallic polymer with a zig-zag manner was obtained and determined by X-ray crystallography in which the pyrazine rigid molecules act as the bridging ligands between Pd(II) centres. To understand the reason of this polymerization process, two layers ONIOM (QM:QM) calculations were performed on the organometallic polymer $[Pd(P(o\text{-tolyl})_3)(pyrazine)]_n$ ($n = 1$ to 10) in order to study the stability trend of polymer as a function of size (n). The infrared (IR) spectrum of the $[Pd(P(o\text{-tolyl})_3)(pyrazine)]_n$ was calculated for different values of n and its evolution with the size of polymer was observed. The shapes of HOMO, LUMO and the energy gap between them were also studied with increasing n.

1. Introduction

Cyclometalated complexes of a wide variety of ligands containing N, P, As, O or S as the heteroatom, have been widely described [1–5]. Cyclometalation of P-donor ligands has acquired great interest because of their application in many areas including organic synthesis, homogeneous catalysis, design of new metallomesogens and antitumoral drugs, asymmetric synthesis, resolution of racemic ligands, intermolecular aromatic C–H bond activation [6–10].

Since the first report on the synthesis of organometallic poly(-vinylferrocene) by Arimoto and Haven in 1955 [11], there is rapidly growing interest in the study, design and application of new organometallic polymers due to their potential ability to combine the properties of both organic polymers and organometallic complexes [12–17]. Main-chain organometallic polymers (MCOPs) is a special subclass related to the macromolecule that contains both organic and metallic moieties rely on the presence of metal–ligand bonds in order to exist [18]. Therefore, both the transition metal and the organic ligand have influence on the overall material to exhibit a desired property. According to the prepared structures, the organometallic polymers have been developed and applied as electronic and optoelectronic materials such as lasers, photocells, light-emitting diodes (LEDs), molecular wires, sensory materials and catalysts [19–22].

According to the ubiquitous nature of phosphine ligation in transition-metal chemistry and the significant utilities of metal P–donor interactions, we focused on the synthesis and characterization of a category of organometallic complexes deriving from tri-*o*-tolylphosphine. Cyclopalladated complexes of tri-*o*-tolylphosphine have shown considerable promise as the catalysts for organic synthesis [23]. Knowing the versatility of the dinitrogen ligands coordinated to the metal centres in different modes such as monocoordination, N^2-chelating and bridging forms [24], we decided to further explore the chemistry of Pd–P(*o*-tolyl)$_3$ with dinitrogen ligands specifically pyridine based derivatives. In this work we report the synthesis and characterization of new compounds upon the reaction of dinuclear bromo-bridged orthopalladated complex of tri-*o*-tolylphosphine with pyrazine, 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethane, 1,3-bis(4-pyridyl)propane and ethylenediamine as

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the bidentate aliphatic or aromatic N-donors. During the reaction of the orthopalladated precursor complex with the pyrazine ligand, the organometallic coordination pyrazine-bridged polymer was obtained surprisingly and structurally determined by single-crystal X-ray diffraction analysis. It consisted of 1-D polymer in which the pyrazine molecules act as the bridging ligands, joining adjacent Pd(II) ions disposed in a zig-zag fashion. To the best of our knowledge, examples of organometallic polymers starting from Pd–P(*o*-tolyl)$_3$ are rare or unknown. We believe that they could play an important role in the design of innovative materials.

The second part of our investigation concerns the theoretical calculations of the synthesized pyrazine-based polymeric compound in order to understand the reason of polymerization process. The change of the IR spectrum of [Pd(P(*o*-tolyl)$_3$)(pyrazine)]$_n$ with n was investigated to show the evolution of the spectrum of the polymer with size (n). The electronic properties of [Pd(P(*o*-tolyl)$_3$)(pyrazine)]$_n$ including the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and the energy gap between them were calculated with size. To our knowledge, there are few theoretical studies on the linear organometallic palladium polymers and clusters [25]. The Our own N-layered Integrated molecular Orbital and molecular Mechanics (ONIOM) [26] calculations, performed in this work, is the first report on the application of this method on the organometallic polymers.

2. Results and discussion

2.1. Synthesis and characterization

When palladium (II) acetate is treated with the sterically demanding tri-*o*-tolylphosphine P(*o*-tolyl)$_3$, the yellow orthopalladated acetato-bridged complex is formed in high yield from C–H activation of one *ortho*-methyl group of P(*o*-tolyl)$_3$ and concomitant elimination of acetic acid [27]. The labile acetate groups are exchanged by the halogen ligand (Br$^-$) by a metathesis reaction with tetrabutylammonium bromide. The resulting bromo-bridged complex shows inferior solubility in noncoordinating solvents. Addition of either strongly coordinating solvents (DMSO, DMF, CH_3CN, THF) or donor ligands (P-donor, N-donor) results in formation of more soluble products.

As clearly shown in Scheme 1, the reaction of a dimeric bromo-bridged complex with AgOTf (1:2) in THF, resulted in the precipitation of AgBr as a white solid and the soluble orthopalladated intermediate containing coordinated THF solvent molecules and OTf molecule as a counter ion. After filtration, the solution was treated with 1 equiv of bidentate N-donors (pyrazine, 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethane, 1,3-bis(4-pyridyl)propane or ethylenediamine) to afford new complexes **1**–**5**, respectively. CH_2Cl_2 and n-hexane were used for recrystallization and purification of the products.

The FT-IR spectra of complexes **1**–**5** show a strong peak at 470–520 cm^{-1} due to the P–C stretching vibrations [4,9]. The IR spectra of complexes **1**–**4** show the absorption in the range of 1615–1631 cm^{-1}, which is diagnostic of the C=N stretching vibrations [9]. In the FT-IR spectrum of complex **5**, the characteristic absorptions at 3254 and 3306 cm^{-1} are related to the NH stretching vibrations of ethylenediamine. With respect to the literature [28], the presence of characteristic peaks at about 1181 and 1206 cm^{-1} in the IR spectra related to the stretching vibration of SO_3 and CF_3, respectively, confirming the presence of OTf in all of the complexes. The CHNS results of the prepared compounds with proposed structures were in good agreement with the calculated values.

Surprisingly, the structure determination and spectroscopic characterization of **1** revealed polymeric cyclopalladated compound with general unit formula [Pd(P(*o*-tolyl)$_3$)(μ-pyrazine)]$_2$.2OTf. The rigid pyrazine molecules act as the bridging ligands between each two Pd centres as a result of the substitution reactions.

In the ^{1}H NMR spectrum, the signals due to the CH_3 and CH_2 protons of tri-*o*-tolylphosphine are indicated by broad signals at 2.51 and 3.55 ppm. The ^{31}P-{^{1}H} NMR spectrum of **1** shows one singlet at about 36.95 ppm that is attributed to the PdP.

Single crystal of polymer **1** was grown in a concentrated dichloromethane solution of **1** by slow diffusion of n-hexane. The structure was confirmed by single crystal X-ray analysis (Figs. 1–3). As clearly shown in Fig. 1, each palladium atom is located in a slightly distorted square planar environment, surrounded by carbon atom of the orthometallated tolyl ring, the phosphorus atom and two nitrogen atoms belonging to the bridging pyrazine molecules, confirming the metallation of tri-*o*-tolylphosphine. Complex **1** has been crystallized in the triclinic space group *P*-1. The summation of the bond angles around the palladium is almost ideally 360°. Although the orthometallated ligand is remarkably warped, the environment around the Pd is planar. Pyrazine molecules act as the spacer units between the orthometallated moieties to form the polymeric structure. Single crystal X-ray analysis confirmed the presence of two OTf molecules as the counter ions. The solid state structure of complex **1** consists of the dimeric units of formula [Pd(P(*o*-tolyl)$_3$)(μ-pyrazine)]$_2$.2OTf. As already mentioned, there are many examples of transition metal polymeric compounds in the literature but as far as we know, none of them show this arrangement, in which the pyrazine molecule acts as a bridging ligand, joining adjacent orthopalladated centres disposed in a zig-zag fashion in addition to the presence of two surrounding OTf counter ions. All of the distances are in accordance with the other cyclopalladated compounds (Fig. 1) [9]. As a consequence of the different trans influences [9], the Pd–N bonds having phosphorus atoms in their trans position [Pd2–N4: 2.141(14) Å] are shorter than those having a trans relationship with respect to the aliphatic tolyl carbon [Pd2–N2: 2.158(15) Å]. The angles between adjacent zig-zag fashion polymeric units as N–Pd–N lie in 89.6(5)° [N3–Pd1–N1] and 81.00(11)° [N2–Pd2–N4].

The ORTEP view, crystal data and structural refinement parameters of complex **1** are shown in Fig. 1 and Table 1, respectively. Moreover, Fig. 1 contains some selected bond lengths (Å) and angles (°) obtained experimentally from solid state crystallography of polymer **1**.

Concerning the X-ray crystal structure, complex **1** has a pyrazine-based polymeric structure (Figs. 2 and 3). The crystal packing of complex **1** with Z = 2 is clearly shown in Fig. 3.

Dinuclear cyclopalladated complexes **2**, **3** and **4** with dipyridyl bridges were synthesized by the reaction of the bromo-bridged precursor complex with 2 equiv of AgOTf in THF for 2 h, followed by the addition of 1 equiv of dipyridyl derivatives (4,4'-bipyridine, 1,2-bis(4-pyridyl)ethane, 1,3-bis(4-pyridyl)propane) (Scheme 1). The ^{1}H NMR spectra of **2**–**4** show the expected resonances for all of the groups present in these molecules and don't show any unusual features. In each ^{1}H NMR spectrum, the signals due to the CH_3 and CH_2 protons of tri-*o*-tolylphosphine are indicated as broad signals in the range 2.05–3.90 ppm. *Ortho* protons of dipyridyl bridges are located in the range 7.90–8.78 ppm. The ^{31}P-{^{1}H} NMR spectra show a singlet at 36.60 and 34.18 ppm for PdP in complex **2** and **3** containing rigid 4,4'-bipyridine and 1,2-bis(4-pyridyl)ethane as the bridging ligands, respectively. Complex **4** with 1,3-bis(4-pyridyl) propane as a flexible bridge ligand revealed two set of signals at 34.14 and 39.69 ppm in the ^{31}P-{^{1}H} NMR spectrum corresponding to the presence of *trans*/*cis*-type geometrical isomers.

According to the spectroscopic characterization, complex **5** is a mononuclear cyclopalladated complex containing a metallated tri-