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ORIGINAL ARTICLE

Synthesis, crystal structure and applications of palladium thiosalicylate complexes

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Abstract Three palladium thiosalicylate complexes $[Pd(tb)(bipy)]\cdot 3H_2O$ (**1**), $[Pd_2(tb)_2(bipy)_2]\cdot(dtdb)_2$ (**2**) and $[Pd_2(tb)_2(phen)_2]\cdot dtdb\cdot H_2O$ (**3**) (bipy = bipyridine; phen = phenanthroline) were prepared from the reaction of $PdCl_2(CH_3CN)_2$ with dithiosalicylic acid (dtdb) which underwent cleavage to form thiobenzoate anion (tb) in DMF/MeOH. Square planar geometries of the complexes with a N_2SO coordination type were proposed on the basis of single crystal X-ray structural study. The presence of trapped and uncoordinated dtdb was observed in complexes **2** and **3**. Complexes **1**–**3** were evaluated as catalysts for Heck coupling reactions of methyl acrylate with iodobenzene, and showed moderate activities at a very low catalyst loading. Complex **1** was found to inhibit the growth of bacteria and scavenge free radicals efficiently.

1. Introduction

Heck reactions are known to play significant roles in modern synthetic chemistry for C—C bond formation and involve the coupling of an aryl, vinyl halide or sulfonate with an alkene and are found to be versatile and applicable to a wide range of species [1,11,14]. Traditionally, Heck coupling reactions have been catalyzed by less stable and air sensitive phosphine based palladium complexes [8]. Hence, the study of more stable and cheaper catalysts was of due importance. Mononuclear palladium complexes of carbenes [12], benzoxazoles [5], thiosemicarbazones [7] and pyridylimines [20] have been used as catalysts in Heck coupling reactions. Palladium-based carboxylate complexes have been reported to catalyze the oxidation of glucose to gluconic acid [13] or methoxycarbonylation of iodobenzene [27], but none of them have been used in Heck reactions. Moreover, palladium carboxylate complexes are known to possess interesting biological properties [3,16]. Gao et al. [9] reported the formation of $[Pd(tb)L]\cdot mH_2O$ (**1**) (L = bipy, phen, m = 1 or 2) using a different reaction strategy and reactant which consists of stirring the co-ligands with thiosalicylic acid in the presence of $K_2[PdCl_4]$ at room temperature. In this regard, we have synthesized palladium complexes (**1**–**3**) derived from dithiosalicylic acid in the presence of bipyridine and phenanthroline that can lead to an efficient homogeneous catalyst in the conversion of aryl

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halides into Heck products at very low amounts of catalyst loading.

2. Results and discussions

2.1. Synthesis and characterization of the complexes

The palladium complexes **1** and **2** were synthesized by the slow diffusion of $PdCl_2(CH_3CN)_2$ over dtdb in DMF/MeOH in the presence of bipy (Fig. 1). Complex **2** was obtained as a residue while crystals of **1** were isolated from the filtrate after a few weeks. When phen was used as co-ligand, orange crystals of **3** were formed but no product was obtained from its filtrate even after several months. The structures of the complexes were characterized by spectral (IR, NMR) and elemental analyses data and were further confirmed by X-ray data (Table 1). The spectral and physical data of complex **1** corroborated with previous reports [9]. The carboxylate asymmetric stretching bands in complexes **2** and **3** were found to be at 1619 and 1601 cm^{-1}, confirming the deprotonation and coordination of carboxylate oxygens in these to Pd complexes [18]. Additional carboxylate stretching was observed at 1667 and 1665 cm^{-1} in IR spectra of **2** and **3**, supporting the presence of uncoordinated trapped dtdb. The S—S bonds in complexes **2** and **3** were shifted slightly to 494 cm^{-1} due to the presence of uncoordinated dtdb. Characteristic stretching bands for bipy (651 cm^{-1}) and phen (837 cm^{-1}) were found in complexes **2** and **3**, respectively. Chemical shifts arising from carbon and hydrogen atoms for the palladium complexes **2** and **3** concorded with the number and type of atoms present in their chemical environment. The aromatic protons were found to be in the range of 8.96–6.69 ppm in the ^1H NMR. The carboxylate carbons were found to be 168.4–167.6 ppm in the ^{13}C NMR spectra (see details in Section 3).

2.2. Structures of $[Pd(tb)(bipy)]\cdot 3H_2O$ (*1*) and $[Pd_2(tb)_2(bipy)_2]\cdot(dtdb)_2$ (*2*)

The molecular structures of **1** and **2** are shown in Figs. 2 and 3, respectively, with selected bond lengths and bond angles tabulated in Table 2. Complex **1** crystallizes in an orthorhombic system, in which dtdb underwent reductive cleavage at the S—S bond, resulting in an OS donor chelate. The coordination geometry around the Pd atom in **1** is found to be square planar, coordinated to two nitrogens of bipyridine, sulfur and one oxygen of the carboxylic acid in a monodentate fashion, resulting in a PdN_2OS type of complex.

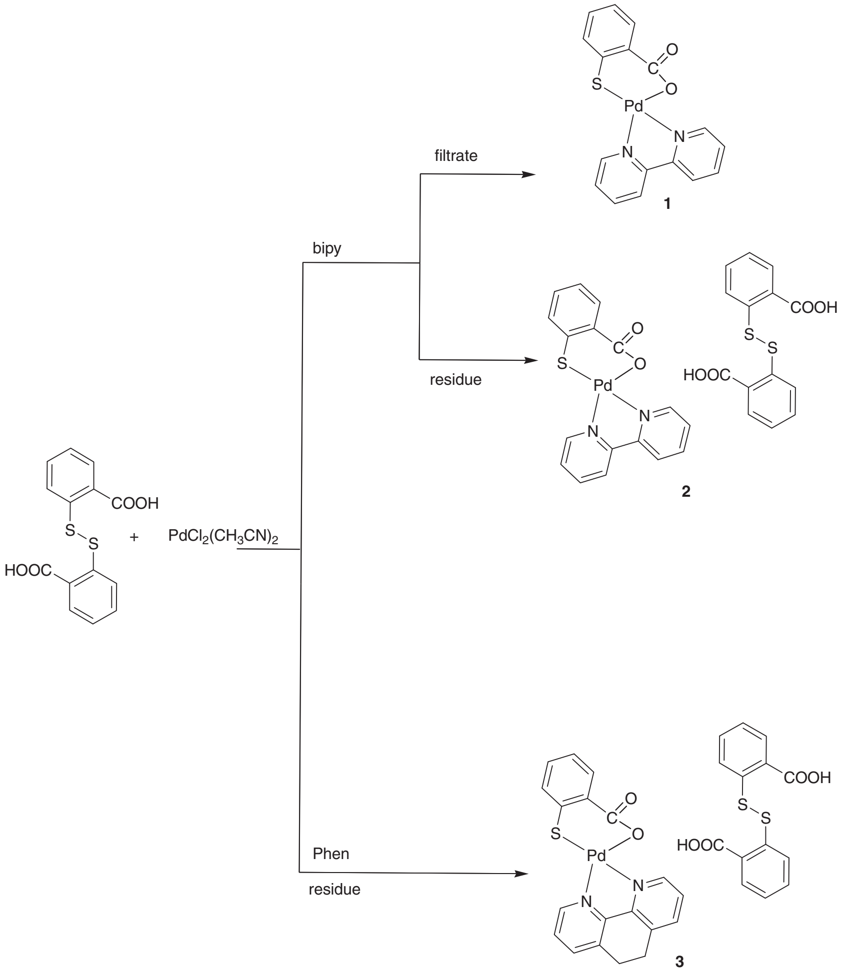

Figure 1 Synthesis of palladium complexes **1**–**3**.