



Palladacycles with C,N-bidentate and N,C,N'-tridentate ligands: Structures, spectral study and catalytic methanolysis of P=S pesticides

Zhong-Lin Lu^{a,*}, Xue-Rui Wang^a, Bian-Bian Liu^a, Rui-Yao Wang^b

^aThe College of Chemistry, Beijing Normal University, Xijiekouwai Street 19, Beijing 100875, China

^bDepartment of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

ARTICLE INFO

Article history:

Received 25 February 2010

Received in revised form

28 May 2010

Accepted 3 June 2010

Available online 15 June 2010

Keywords:

Palladacycle
Crystal structure
Methanolysis
Pesticides
Kinetics

ABSTRACT

Palladacycles **2–4** with C,N-bidentate and N,C,N'-tridentate ligands were prepared and characterized. The X-ray crystal structures of [2,6-bis(*N,N*-dimethylaminomethyl)phenyl-N,C¹,N'-](aqua)palladium(II) triflate (**2**), (*N,N*-dimethylaminobenzyl-C¹,N)(4-trifluoromethylpyridine)(aqua)palladium(II) triflate (**3**), and (*N,N*-dimethylaminobenzyl-C¹,N)(4-*N,N*-dimethylaminopyridine)(aqua)palladium(II) triflate (**4**), were determined. While **2** is much less active, **3** and **4** effectively catalyze the methanolysis of the P=S pesticides. The catalytic activities were higher with the trifluoromethylpyridine co-ligand as compared to palladacycles containing 4-*N,N*-dimethylaminopyridine and pyridine co-ligands. ¹H NMR spectra and the catalytic kinetic dependences on concentration and pH revealed that the active species was a palladacycle containing one methoxide and one pyridine in the coordination sphere. A plot of the catalytic activity vs. free [pyridine] indicated the participation of a common species. The proposed catalytic mechanism involves a pre-equilibrium binding of the P=S pesticide to palladium(II) center followed by dissociation of the pyridine and subsequent cleavage of the P–OAr unit through the intramolecular displacement on phosphorus by the adjacent Pd-coordinated methoxide.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Phosphorothionate esters are widely used as agricultural pesticides because of their high insecticidal and acaricidal properties and much lower mammalian toxicity than the analogous P=O counterparts [1]. Some chemically related neutral P=O containing organophosphates (OP) are also used as neurotoxins and chemical warfare (CW) agents [2]. Due to their toxicity, lingering effects on the environment, dangers emerging from aging stockpiles and the requirements of the 1992 Chemical Weapons Convention Treaty [3] that signatory nations destroy scheduled CW agents by 2012, the development of efficient methods for the controlled decomposition of these OP materials is of on-going interest.

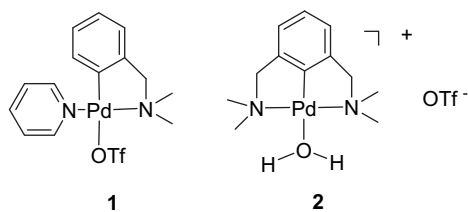
Many efforts have been directed to the catalytic or enzymatic hydrolysis and oxidation of these organophosphates, but their efficiency and safety still need to be improved [4]. Recently, alternative methodologies, i.e. metal-ion catalyzed alcoholysis, for the rapid decomposition of neutral OP compounds including phosphate triesters, phosphonates, phosphorothionates and

phosphonothionates were presented [5]. The advantages of a catalytic alcoholysis method over hydrolysis include greater substrate solubility in the alcohol medium, greatly increased reaction rates probably attributable to a less polar medium that also gives enhanced M^{x+}:substrate pre-equilibrium complexation [5g], and the fact that the products are also neutral OP compounds that are non-inhibitory since they bind to the metal catalyst with a similar strength as the starting OP materials. Lanthanides such as La³⁺, being “hard” metal ions in the Pearson “hard/soft” sense, can accelerate the methanolysis of P=O esters like paraoxon (*O,O*-diethyl *O-p*-nitrophenyl phosphate) by ~10⁹-fold [5f], and a 1,5,9-triazacyclononane complex of Cu(II), a “soft” metal ion, was shown to be very efficient for promoting the decomposition of P=S esters like fenitrothion for which La³⁺ is ineffective [5c,h].

It is reported that cyclometalated palladium and platinum complexes effectively catalyze the hydrolysis of phosphorothionates [4d,6]. Our studies [5a] have shown that a palladacycle with coordinated [(*N,N*-dimethylamino)methyl]phenyl, and pyridine ligands, namely Pd(dmba)(py)(OTf), **1**, also promotes the methanolysis of phosphorothionates and shows greater catalytic efficacy and specificity for these P=S derivatives than do any of the Cu(II) complexes that have been investigated [5a]. At higher ³pH, the coordinated pyridine in **1** partly dissociated from the Pd and,

* Corresponding author. Fax: +86 10 58801804.

E-mail address: luzl@bnu.edu.cn (Z.-L. Lu).



Scheme 1.

according to the ξ pH/rate profile data, the catalytically active species has a bound methoxide generated with an apparent ξ pK_a of 10.8. However, whether the catalytically active complex contains a coordinated pyridine or another ligand such as a methanol in addition to the essential coordinated methoxide, was not made clear in that study. Furthermore, the effect of the basicity of the co-ligand pyridine and the reactivity of the widely used pincer palladacycles on the methanolysis needs to be evaluated.

Under the above consideration and with the aim to develop more efficient catalysts, we have prepared some new palladacycles; one with the NCN pincer ligand (**2** in Scheme 1) which provides some additional rigidity to the metal carbon bond by virtue of the two chelating arms and two variants of **1** where pyridine is replaced by two other substituted pyridine ligands (**3** and **4** in Scheme 2) in order to probe the effect of pyridine basicity on the kinetic reactivity. We report here the syntheses, structural characterizations and the kinetic studies of their catalytic methanolysis of fenitrothion (**5**) and turnover experiments for the **3**-promoted methanolysis of some other P=S esters shown in Scheme 3.

2. Results and discussion

2.1. Syntheses of the complexes 2–4

Syntheses of the above palladacycles were straightforward from their corresponding chlorides (see experiment part), the exchange of the counter ion from chloride to triflate with silver triflate with 2 h at room temperature gave good yields of the desired compounds, the structures of which were confirmed by ¹H NMR, mass spectra, elemental analysis, and X-ray single crystal characterization. The water molecules that are coordinated to the Pd in the crystal structures in Figs. 1–3 most likely arise from adventitious water in the solvents during preparation and purification. We note that such water molecules often appear in the crystals of many palladacycles containing triflate, despite the crystals being grown from dry solvent. This may suggest energetically favorable interactions with the closely packed triflate counterions in the solid forms. In methanol, where the triflate ions are dissociated from the complex and the [MeOH] greatly exceeds that of adventitious water, there is no reason to expect that water will preferentially bind to the metal ion, which is consistent with the observations that the products of the reaction are derived from methanolysis and not hydrolysis.

2.2. Description of crystal structures of complexes 2–4

The palladium in complex **2** (Fig. 1) is bound to two mutually *trans* NMe₂ moieties, the phenyl carbon (via C(1)) and the oxygen atoms from a water molecule. The geometry around the metal center is a slightly distorted square-planar coordination sphere with C(1)–Pd–O(1) and N(1)–Pd–N(2) angles being 177.04(8)° and 163.73(7)°, respectively. The five-membered metallacycles are puckered in the same direction, with Pd–N1–C7–C2 and Pd–N2–C10–C6 torsion angles of –32.72° and –61.72°,

respectively. The bond lengths and angles (see Table 1) are in good agreement with those in [Pd(NCN)(OH₂)]BF₄ [7].

For complexes **3** and **4**, the palladium atom displays the expected nearly square planar coordination with the two coordinated nitrogen atoms positioned *trans* to one another. For complex **4**, there are two kinds of molecules in the unit cell with slight differences in bond distances and bond angles. The dihedral angles between the pyridine ring and palladacycle ring are 68.9 and 60.66/61.57° in complexes **3** and **4**, respectively. The dihedral angle between the planes {C1PdN1} and {N2PdO1} in complex **3** is 0.98°, while that in the two molecules of complex **4** equals to 2.19° and 2.45°, respectively, indicating that the square planar coordination geometry is more distorted in **4** than in **3**.

The Pd–C, Pd–N, and Pd–O bond lengths in complexes **3** and **4** (see Table 1) fall within the range of the values reported for other cyclopalladated derivatives of (*N,N*-dimethylamino)methylbenzene [5a]. The longer Pd–O (water) bond length of 2.17 Å is attributed to the *trans* effect from the strong σ -donor of the phenyl carbon atom. Surprisingly, the Pd–N (pyridines) bond lengths in complexes **3** and **4** are in good agreement with that in complex **1** (2.035(2) Å), and not effected by the *para* substituent groups on the pyridine ring, no matter whether it is an electron-donating substituent (*N,N*-dimethylamino) or electron-withdrawing substituent (trifluoromethyl). The Pd–C and Pd–N (amine) bond lengths are also not affected.

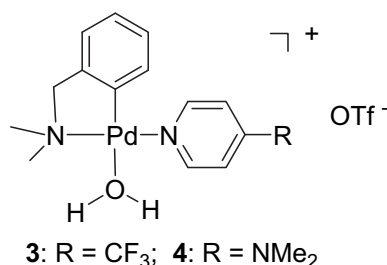
It can clearly be seen that the Pd–C bonds in complexes **3** (1.967(3) Å) and **4** (1.965(3)/1.973(3) Å) are somewhat longer than that in complex **2** (1.906(2) Å), while the Pd–N (amine) bonds in **3** (2.071(3) Å) and **4** (2.072(2)/2.066(2) Å) are shorter than that in **2** (2.1003(18) Å), which can be attributed to the NCN pincer chelate effect and *trans* effect (pyridine versus amine groups).

In the crystals of compounds **2**, **3** and **4**, each triflate anion is hydrogen-bonded to two water molecules in the coordination sphere, and each water molecule to two triflate anions (see Fig. 4). Palladacycles **2** and **3** are dimerized through H-bonding, while the arrangement in **4** actually gives a contiguous chain. Such intermolecular hydrogen-bonding exists in the crystal lattice of each complex, and plays an important role in stabilizing the ionic structure [7].

2.3. Solution NMR studies of palladacycles 1, 3 and 4 (5×10^{-3} M) in methanol

To obtain information about the speciation of palladacycles in methanol solution as a function of pH, the ¹H NMR spectra of **1**, **3** and **4** were studied under different conditions. Since the phenyl-H⁶ of the palladacycles, as well as the benzylic CH₂ and NCH₃ protons, are sensitive to changes in the Pd-coordination sphere, their chemical shifts and integrals were studied in more detail.

In methanol-d₄, the ¹H NMR spectra of **1**, **3**, and **4** (5×10^{-3} M) are consistent with a single observable material that we assign as palladacycle **11** (see Scheme 4 and Supporting material Figs. S1–S3)



Scheme 2.

Download English Version:

<https://daneshyari.com/en/article/1324055>

Download Persian Version:

<https://daneshyari.com/article/1324055>

[Daneshyari.com](https://daneshyari.com)