

Synthesis and immobilization of oxime-derived palladacycles as effective and reusable catalysts for the degradation of phosphorothionate pesticides



Fu-Hua Lu^a, Pan Yue^a, Xue-Rui Wang^a, Zhong-Lin Lu^{a,b,*}

^a College of Chemistry, Beijing Normal University, Beijing 100875, China

^b State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

ARTICLE INFO

Article history:

Received 3 April 2013

Accepted 27 April 2013

Available online 4 May 2013

Keywords:

Palladacycle

Immobilization

Methanolysis

Phosphorothionates

Pesticides

ABSTRACT

New oxime-derived palladacycles were prepared, spectral characterized, and immobilized on silica gel. Homogeneous catalysis indicates that pyridine coordinated oxime-derived palladacycles **1** and **2** were very effective in the methanolysis of fenitrothion, but suffered from the formation of the inactive dimer at higher concentration. Immobilization of oxime-derived chloro-coordinated mononuclear and chloro-bridged dinuclear palladacycles afforded the high efficient and recoverable heterogeneous catalysts Si-Pd1 and Si-Pd2, both solid catalysts proved to be reusable in 10 runs and fascinated the degradation of a series of phosphorothionate pesticides up to 4.9×10^8 folds at pH 8.8 and 25 °C.

© 2013 Elsevier B.V. All rights reserved.

Phosphorothionates 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 [1,2]. Due to their widespread use and their persistence, the environmental accumulation of these toxic chemicals presents a serious ecological and health threat. Many efforts have been directed to the catalytic or enzymatic hydrolysis and oxidation of these organophosphates [3,4]. Metallocycles of palladium and platinum, especially oxime-derived palladacycles, were reported to be remarkably good catalysts for the hydrolysis of sulfur-containing organophosphates such as fenitrothion, diazinon and methyl parathion [5–7]. The problems related to the catalytic hydrolysis of phosphorothionates come from poor catalyst solubility and dimerization under basic condition, as well as product inhibition to the catalysts in their anionic forms. Recently, alternative methodologies, i.e. metal-ion catalyzed alcoholysis, for the rapid decomposition of organic phosphates were presented [8,9]. Our recent studies have shown that some palladacycles can greatly promote the methanolysis of phosphorothionates [10–12]. However, the high cost of palladacycles limited their practical applications. In fact, many examples of immobilized palladacycle catalysts for diverse processes exist, most of them have been applied to the catalysis of C–C bond formations and related cross-coupling reactions [13–16]. Thus, it is very desirable to combine both the advantages of methanolysis and heterogeneous catalysts for the development of efficient and environmental benign method for the degradation of phosphorothionates.

In this communication, we reported on the synthesis of some new oxime-derived palladacycles and their immobilization as the high efficient and reusable catalysts for the decomposition of toxic P = S pesticides.

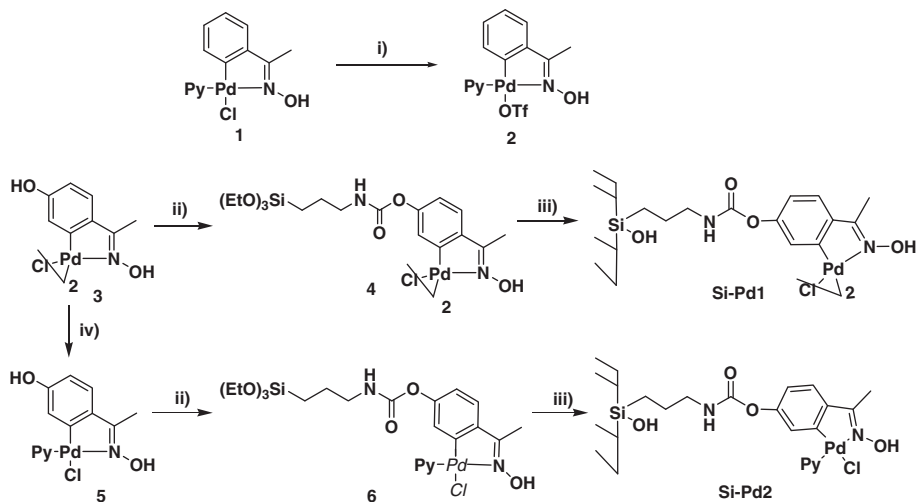
Synthesis of oxime-derived palladacycles and their heterogenization are shown in Scheme 1.

Palladacycle **2** was obtained from its corresponding chloride **1**, which was prepared according to the literature [17], by the reaction with silver triflate (AgOTf) in dichloromethane. For the heterogenization of oxime palladacycle, the following procedure was processed. The dimeric palladacycle **3** was prepared according to the literature method with high yields and characterized [18]. The corresponding monomeric palladacycle **5** was afforded from the reaction of **3** with pyridine in benzene solution. Both palladacycles **3** and **5** were further modified with (3-isocyanatopropyl)-triethoxysilane in acetone to produce palladacycles **4** and **6**. The immobilized palladacycles Si-Pd1 and Si-Pd2 were obtained by the reactions of **4** and **6** with commercially available silica gel in toluene.

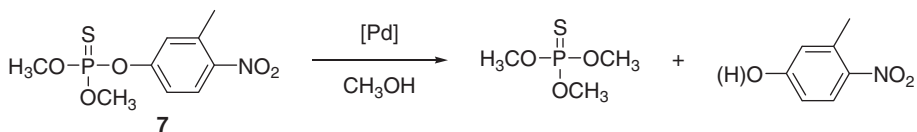
New palladacycles **2**, **4**, **5** and **6** were fully characterized by ¹H NMR, ¹³C NMR, MS, and IR spectra (see Supplementary material). From the ¹H NMR spectra of **2**, **5** and **6**, the typical features of the *N,N*-trans conformation in the palladacycles were confirmed in solution, which is common for the pyridine coordinated monomeric palladacycles. For the immobilized palladacycles, the respective palladium and nitrogen contents were determined by inductively coupled plasma-optical emission spectroscopy and microanalysis, respectively. The analyzed data for Si-Pd1 are 0.159 mmol N and 0.096 mmol Pd per each gram of silica; while those for Si-Pd2 are 0.88 mmol N and 0.036 mmol Pd per each gram of silica. The analyzed loadings are comparable to those

* Corresponding author at: College of Chemistry, Beijing Normal University, Beijing 100875, China. Tel./fax: +86 10 58801804.

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



Scheme 1. Synthesis of oxime palladacycles and their immobilization on silica gel: i) AgOTf; ii) (3-isocyanato-propyl)triethoxysilane, acetone; iii) silica gel; and iv) pyridine (Py).



Scheme 2. Methanolysis of fenitrothion in the presence of palladacycles.

previously reported for grafting of oxime carbpalladacycle complexes on silica gel [16,18,19].

To explore the catalytic activities of the oxime-derived palladacycles prepared in this work, compounds **1** and **2** were applied in the methanolysis of fenitrothion (Scheme 2). In the preliminary experiments, it was found that the methanol stock solutions of **1** and **2** are stable at least for 1 week since their fresh stock solutions and the stored ones give almost the same rate constants in the reaction. We also noticed that the free ligand oxime and palladium chloride showed very poor performance in the catalysis. The concentration dependences of the reaction rates were measured at $\text{pH } 8.8 \pm 0.1$ and room temperature (see Fig. 1). It can be seen that along the increase of the concentration of **1** and **2**, the reaction rates were greatly increased at lower concentration range but then saturated and even decreased at higher concentration range, which was resulted from the formation of the inactive dimer of **1** and **2** in methanol solutions. From the data, the catalytic activity of **1** and **2** is very close, indicating that the effects of the counter anions are not obvious in the present experimental condition. As a comparison, the $t_{1/2}$ values of the methanolysis of fenitrothion in

the presence of 0.01 mmol L^{-1} of **1** and **2** are calculated to be 264 and 222 s, while that of the background reaction is $4.2 \times 10^{10} \text{ s}$ at $\text{pH } 8.8 \pm 0.1$ and room temperature [20]. Therefore, **1** and **2** afforded an acceleration of 1.6×10^8 and 1.9×10^8 folds. The pH dependence of the reaction rates with palladacycle **2** is shown in Fig. 2, the appearance of the plot suggests a catalytic process where a basic form of **2** is active, the kinetic pK_a of **2** can be fitted to be 8.8 ± 0.1 , which is much lower than that of ortho-palladated dimethylbenzylamine compound ($\text{pK}_a = 10.8$) [11]. As a short summary, the homogeneous catalysis indicates that oxime-derived palladacycles **1** and **2** are very effective in the catalytic methanolysis of fenitrothion. However, the formation of the inactive dimer at higher concentration seriously limited to further improve their catalytic activity and application.

The catalytic activities of the immobilized palladacycles were then evaluated at $\text{pH } 8.8 \pm 0.1$ and room temperature. Firstly, the kinetics of the methanolysis of fenitrothion catalyzed by different amounts of Si-Pd1 (10.0, 20.0 mg) and Si-Pd2 (20.0 mg) were monitored by UV/Vis spectrophotometry following a pH-jump procedure (the detail seen in the Supplementary material). The results were shown in Fig. 3.

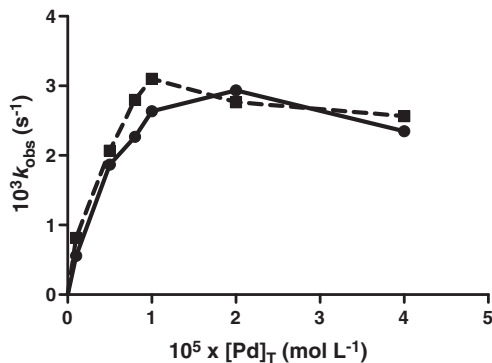


Fig. 1. A plot of k_{obs} vs. $[\text{Pd}]$ of **1** (●) and **2** (■) for the methanolysis of **7** ($2.0 \times 10^{-5} \text{ mol L}^{-1}$) at $\text{pH } 8.8 \pm 0.1$, *N*-isopropylmorpholine buffer (2.0 mmol L^{-1}), $25 \pm 0.1^\circ \text{C}$.

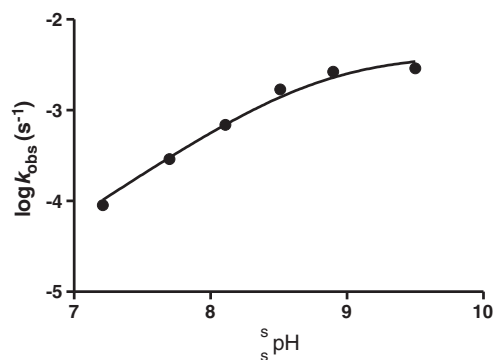


Fig. 2. Plot of $\log k_{\text{obs}}$ vs. pH for the methanolysis of **7** ($2.0 \times 10^{-5} \text{ mol L}^{-1}$) catalyzed by $1.0 \times 10^{-5} \text{ mol L}^{-1}$ of **2** at $25 \pm 0.1^\circ \text{C}$.

Download English Version:

<https://daneshyari.com/en/article/7749709>

Download Persian Version:

<https://daneshyari.com/article/7749709>

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