Chinese Chemical Letters Vol. 13, No. 12, pp 1170 – 1173, 2002
http://www.imm.ac.cn/journal/ccl.html

Highly Efficient Degradation of Thiophosphate Pesticides Catalyzed by Cyclopalladated Ferrocenylketimines

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Abstract: In this paper, four functional substituted derivatives of cyclopalladated ferrocenylketimines **1~4**, which were as mimetics of metal-dependent esterases for catalyzing the hydrolysis of thiophosphoric acid esters pesticides, were synthesized and characterized. All the four cyclopalladated complexes can efficiently catalyze the degradation of thiophosphoric acid pesticides, such as methyl parathion. The Pd catalyst with coordinated oxime is more active and exhibits an increased selectivity towards sulfur containing pesticides.

Key words: Ferrocenylketimine, cyclopalladation, thiophosphate, catalysis.

Thiophosphoric acid esters pesticides such as parathion, methyl parathion, with an annual world production of hundred thousands of tons, are powerful pollution sources and their remains in the environment is a recognized ecological threat[1]. Creation of "green'' catalytic processes for degradation of thiophosphoric acid esters is therefore an urgent task of contemporary chemical technology and biotechnology. Significant progress has been made by the use of organophosphate hydrolases (OPH), a class of metal-dependent enzymes whose vital virtue is in the detoxification of organophosphoric species[2] and orthometalated complexes of Pd^{II} and Pt^{II} as mimetics of metal-dependent esterases have been developed[3]. The catalysts display regio- and stereo-selectivity as well as reasonable rate accelerations at neutral pH values[4].

In order to purify ecological environment and improve the level of human health, designing and synthesizing chemical catalysts with efficient catalytic specificity and activity and with the features of enzyme active sites is believed to be particularly promising[5~7]. We introduced several functional substituted derivatives of cyclopalladated ferrocenylketimines **1~4** as mimetics of metal-dependent esterases for the hydrolysis of thiophosphoric acid esters pesticides, such as methyl parathion.

Experimental

The ligands ferrocenylketimines **1~4** were prepared by condensing acylferrocene with hydroxylamine hydrochloride, ethanolamine, *o*-anisidine and *m*-anisidine, respectively. The cyclopalladation of the ferrocenylketimine were performed by the literature′s procedure[8]. A solution of lithium tetrachloropalladate in methanol (containing a small

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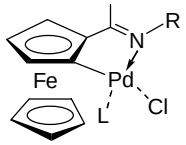
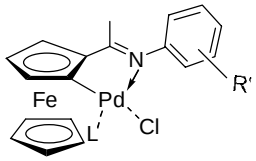


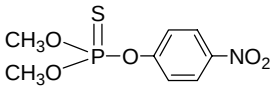
1. R = -OH; L = DMSO

2. R = -CH_2CH_2OH; L = DMSO



3. R' = o-OCH_3; L = DMSO

4. R' = m-OCH_3; L = DMSO



methyl parathion

amount of dimethyl sulfoxide), was added under stirring to a solution of equimolar NaOAc and ferrocenylketimines in methanol. The resulting red solution was stirred at room temperature for 20 h and then filtered. The solid obtained was purified by recrystallization or through a rapid chromatographic process on silica gel to produce the cyclopalladated compounds **1~4**. All the ferrocenylketimines and the cyclopalladated compounds were characterized by EA, IR, UV, and NMR, respectively. The results obtained were in accordance with the structures and compositions of the new compounds.

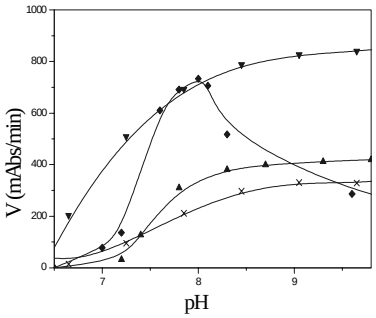
Kinetics UV method

In order to compare the reactivity of **1~4** in catalyzing thiophosphodiester hydrolysis, a series of reactions were performed with varied the catalysts and the thiophosphate concentrations (**Figure 2**). The hydrolysis of methyl parathion was monitored on UV at the absorbance of 400 nm due to the release of 4-nitrophenolate [Shimadzu 2100 UV-vis Spectrophotometer, kinetics soft package (P/N 206-16813)]. The reaction rate was calculated by using the regression line method. The hydrolysis of methyl parathion was initiated by adding 1.0 mL of the freshly prepared solution of cyclopalladated compound (2×10^{-4} mol/L) in DMF to 1.0 mL of the methyl parathion stock solution (10^{-4} mol/L), mixed with 0.025 mol/L phosphate and 0.01 mol/L $NaClO_4$ in water). The pH of the reaction mixture was adjusted by saturated aq. solution of NaOH.

Results and Discussion

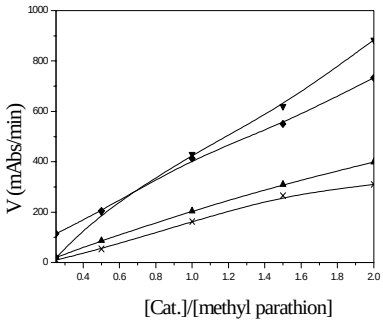
Kinetic data were obtained for all the cyclopalladated complexes **1~4** in combination with methyl parathion. The hydrolysis of methyl parathion was very slow at even pH 10.5 in the absence of catalyst. Addition of a catalytic amount of the cyclopalladated compound strikingly enhanced the hydrolysis rate as shown in **Figure 1**. The curves represented the reactions catalyzed by the different palladated complexes at various pH values. The rate of hydrolysis of methyl parathion initially increases linearly with the increase of the pH value, then gradually deviates down and tends to equilibrate (for catalysts **1**, **3** and **4**). To our surprise, the rate of hydrolysis of methyl parathion was also catalyzed by **2** but the reaction rate increased sharply in the pH 7.0 to 8.0, then decreased with the increase of the pH (8.0 to 10.0). The result makes us infer that there may be an ethoxyl anion formed at the high pH value. The anionic group attacked at the Pd atom more easily than at the P atom and formed a five-membered ring complex, which was stable enough and enormously blocked the coordination attack of the S atom

Figure 1 Plot of the hydrolysis rate of methyl parathion (5×10^{-5} mol/L) with catalysts **1-4** at pH 6-10



1 (▼), **2**( ), **3**( ), **4**( ), T=30 , in 0.025 mol/L CHES buffer and 0.01 mol/L $NaClO_4$

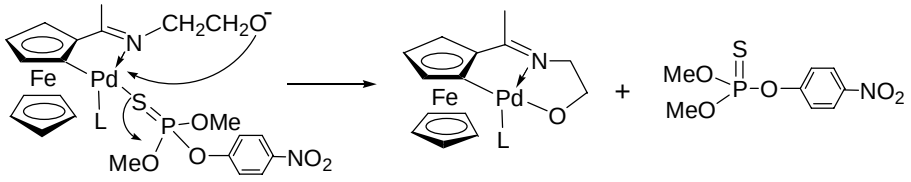
Figure 2 The dependance of the hydrolysis rate of methyl parathion with catalysts **1-4** on the ratio of [Cat.]/ [phosphate]



1(▼), **2**( ), **3**( ), **4**( ), T=30 , pH=8.5, in 0.025 mol/L CHES buffer and 0.01 mol/L $NaClO_4$

in methyl parathion as shown in **Scheme 1**. Furthermore, at high pH value the reaction mixture showed bicyclic fragment (*m/z* 411) in the MS. This result supported our inferences. It is interesting to note that the structures of the ferrocenyl ketimine ligands have significant effects on the rate of hydrolysis of the methyl parathion. From **Figure 1** and **2** we can see that the cyclopalladated ferrocenylketimines with hydroxyl or hydroxyethyl (compound **1** and **2**) were much effect than those with *o*-anisidine or *m*-anisidine groups (compound **3** and **4**). With increase of the ratio of the catalyst and methyl parathion, the hydrolysis rate increased as shown in **figure 2**.

Scheme 1

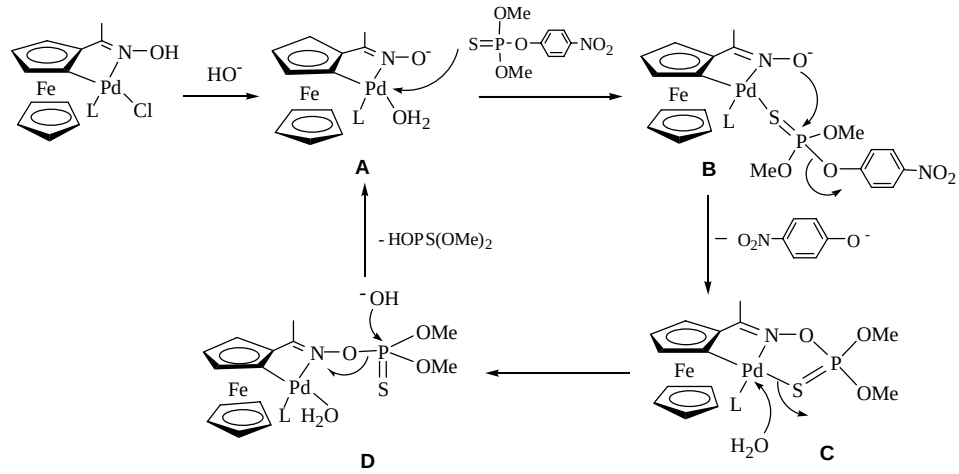


To take **1** as an example**,** the catalysis mechanism of the cyclopalladated compounds was proposed as shown in **Scheme 2**. The S atom of methyl parathion attacked the metal center of the cyclopalladated compounds and formed the Pd-S bonded intermediate **B**. The positive charge at P was increased in **B**, due to the coordination with the catalyst, and thus facilitated the intramolecular neucleophilic attack by the oximate. With the departure of the phenolate ion, the second five membered ring was formed to generate unstable intermediate **C**. Water attacked at Pd caused the Pd-S bond cleavage to form **D**. The catalytic cycle was then completed after releasing of the thiophosphate.

In conclusion, cyclopalladated ferrocenylketimines efficiently catalyze the degradation of thiophosphoric acid pesticides, such as methyl parathion. Comparison with the cyclopalladated complexes formed from different substituted ligands indicated that the Pd catalyst with coordinated oxime is more active and exhibits an increased

selectivity towards sulfur containing pesticides. Cyclopalladated compounds with coordinated oxime could be used to create even more specific and reactive catalysts.

Scheme 2 Plausible reaction mechanism for the hydrolysis of methyl parathion catalyzed by cyclopalladated ferrocenylketimine



Acknowledgment

We are grateful to the National Natural Science Foundation of China (29872034) and the Natural Science Foundation of Henan Province for the financial support .

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Received 8 March, 2002