

Use of Organomolybdenum Compounds for Promoted Hydrolysis of Phosphoester Bonds in Aqueous Media

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Organophosphate pesticides are one of the most significant causes of severe toxicity and death from acute poisoning worldwide, being responsible for more than 200000 deaths each year in developing countries.[1] Moreover, their accumulation in the environment is a recognized ecological threat, as they have harmful effects on mammalian species owing to long-term exposure to sublethal doses.[2]

Hydrolysis is considered to be a possible strategy to eliminate organophosphate pesticides (since the hydrolysis products have a substantially lower toxicity), but in the absence of a catalyst or enzyme, phosphoester hydrolysis is extremely slow. For this reason, a growing interest in the metal promoted hydrolysis of phosphoesters has arisen.

As part of our work to explore molybdenum compounds for the promoted hydrolysis of phosphoesters [3,4], in the present work [5] we have studied the performance of the dimeric chloride complex $[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2(\mu\text{-Cl})_2]$ (**1**; Ind = indenyl) as a hydrolysis promoting agent of *para*-nitrophenylphosphate (*p*NPP) to give *para*-nitrophenol (*p*NPh) and inorganic phosphate (Scheme 1).

In this study, we further report that the dissolution of **1** in *N,N*-dimethylformamide (DMF) gives the ring-slipped complex $[(\eta^3\text{-Ind})\text{Mo}(\text{CO})_2\text{Cl}(\text{DMF})_2]$ (**2**), which subsequently can undergo aerial oxidation to give the dinuclear oxomolybdenum(V) chloride $[\text{Mo}_2\text{O}_2(\text{DMF})_4(\mu\text{-O})_2\text{Cl}_2]$ (**3**) (Scheme 2). The structures of **2** and **3**·DMF have been determined by single-crystal X-ray diffraction.

Compound **3** was also examined as a hydrolysis-promoting agent and the results are compared with those obtained for $\text{Mo}(\text{CO})_6$ and $[\text{MoO}_2\text{Cl}_2(\text{DMF})_2]$. [3,4] For assays performed with 30–100 mol-% of **1** or **3** relative to *p*NPP in aqueous media, both compounds promote the production of *p*NPh from *p*NPP, compound **3** being very efficient with $t_{1/2} < 80$ min.

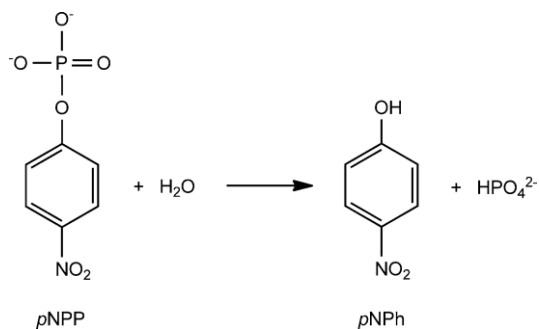
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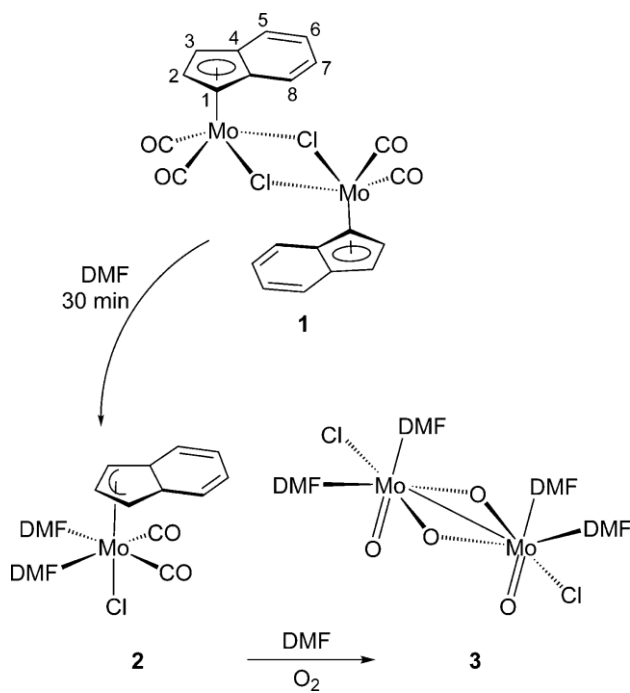
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Scheme 1. Hydrolysis of *para*-nitrophenylphosphate (*p*NPP) to give *para*-nitrophenol (*p*NPh)



Scheme 2. Synthesis of **2** and **3** from **1**