First Reported Aqueous Phosphoester Bond Cleavage Promoted by an Organometallic Complex

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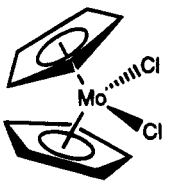
The molecule bis(η^5-cyclopentadienyl)molybdenum(IV) dichloride (Cp_2MoCl_2), **I**, is the first known organometallic compound that promotes the phosphoester bond cleavage of activated phosphodiesters and phosphomonoesters in aqueous solution. Under psuedo-first-order conditions, Cp_2MoCl_2 (110-fold excess) promotes the production of 4-nitrophenol from 4-nitrophenyl phosphate (NPP), and from bis(4-nitrophenyl) phosphate (BNPP). For both NPP and BNPP, 1 equiv of 4-nitrophenol is released, and when compared to no metal added, there are 10^5 and 10^7 enhancements in the observed rate of 4-nitrophenol production (pH 7.0, 20 °C), respectively. NMR (^{31}P) studies show that the reaction of NPP with **I** (10-fold excess) begins with Cp_2Mo coordination to form a monodentate Cp_2Mo(4-nitrophenylphosphate) complex (**II**) that undergoes intramolecular phosphoester bond cleavage to yield a mononuclear Cp_2Mo-phosphate complex(**III**).

Introduction

Phosphoester bond cleavage reactions are ubiquitous in many important biological processes and are the key transformation in the degradation of toxic organophosphorus compounds.[1] Models of this transformation[2,3] have yielded important chemical agents and mechanistic information for phosphate hydrolysis. For example, cobalt(III) polyamine complexes, which have up to a 10^8 rate enhancement in the hydrolysis of activated phosphate esters, are studied as phosphatase and ATPase models.[4] Moreover, the recent reports that lanthanide complexes promote the hydrolysis of phosphates[5] and oligonucleotides[6] bring closer the goal of designing artificial metalloenzymes that site specifically cleave nucleic acids.

While these studies have focused on organic molecules and coordination complexes,[7] little effort has been devoted to other classes of compounds such as organometallic complexes. As far as the importance of organometallic-promoted transformations are concerned,[8] there is no reported evidence that they can promote phosphoester bond cleavage in aqueous solution. Accordingly, we report that the aqueous form of bis(η^5-cyclopentadienyl) molybdenum(IV) dichloride, **I**, (Cp_2MoCl_2,



= Cp_2MoCl_2 **(I)**

where Cp = η^5-C_5H_5) is the first known organometallic complex that accelerates this particular reaction at rates comparable to the best coordination complexes. These studies further expand the repertoire of model phosphate hydrolytic systems to new compounds, and thus provide novel parameters for accelerating phosphoester bond cleavage that are unique to the physicochemistry of organometallic compounds. Moreover, this chemistry shows yet another example of aqueous phase organometallic chemistry that is relatively unexplored and can potentially rival other classes of compounds for effecting phosphate degradation.

The water soluble Cp_2MoCl_2[9] complex possesses key aqueous properties amenable for phosphate coordination chemistry which include rapid chloride hydrolysis, and a strong Cp−Mo ligation in aqueous media.[10] The aqueous chemistry of Cp_2MoCl_2 itself has been modeled[10a] as shown in Scheme 1.

That 2 equiv of base (OH^-) are consumed in the titration of $Cp_2Mo(OH_2)_2^{2+}$ suggests minimal formation of oligomers which

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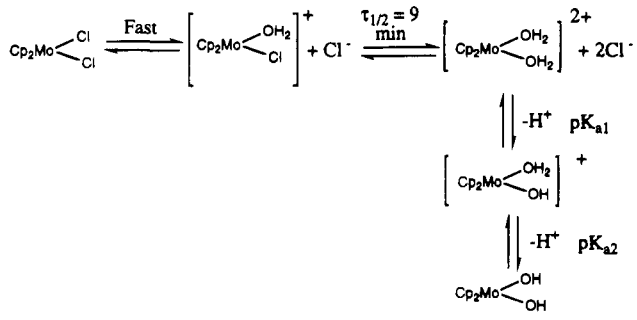
Scheme 1



may be blocked by the large cyclopentadienyl ligands. This water-stable Cp−Mo linkage minimizes metal aggregation that would inhibit phosphate hydrolysis and complicate the identification of the aquated species.[11]

With regard to the aqueous coordination chemistry of Cp_2Mo with phosphates, Prout and co-workers have crystallographically shown that the Cp_2Mo moiety can form a four-membered chelate ring with orthophosphates in the dinuclear complex, $Cp_2MoO_2PO_2MoCp_2$.[12] In addition, crystallographic and NMR studies have shown that the Cp_2Mo entity covalently binds to the phosphomonoester functionality of 2′-deoxyguanosine-5′-phosphate.[10a] Indeed, this nonlabile, monodentate coordination by the Cp_2Mo moiety could be used as a Lewis acid to activate the phosphate group.[13]

Experimental Section

All organometallic compounds were handled under prepurified argon using standard Schlenck techniques. Water was deionized (18 M Ω) and thoroughly purged with prepurified argon. D_2O as well as NaOH and HCl solutions were thoroughly saturated with argon. The complex Cp_2MoCl_2 (**I**) (Strem Chemical Co., Newburyport MA) was used as received, and its purity was checked by ^1H NMR. The sodium salts of p-nitrophenyl phosphate (NPP), and bis(*p*-nitrophenyl) phosphate (BNPP) were obtained from Sigma Chemical Co. (St. Louis MO) and used as received. Disodium phenyl phosphate and sodium diphenyl phosphate were obtained from Tokyo Kasei (Portland OR) and were also used as received. The sodium salt of bis(2,4-dinitrophenyl) phosphate (BDNPP) was synthesized and purified according to literature procedures,[14] and the purity was verified by melting point and HPLC determinations. All other chemicals were reagent grade and were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used as received.

Physical and Analytical Measurements. Proton and phosphorus NMR spectra were recorded on a Bruker QE-300 (FT, 300 and 121 MHz). Proton chemical shifts are referenced to Me_4Si (TMS) and phosphorus chemical shifts to 85% H_3PO_4. Kinetic studies were carried out with UV/visible measurements using a Hewlett-Packard 8452A diode array spectrophotometer equipped with a Fisher Scientific Model 9000 theromstat.

Kinetics. UV Methods. The hydrolysis of NPP, BNPP, and BDNPP was monitored by following the production of the *p*-nitrophenolate anion at 400 nm in H_2O (Supplemental Figure 1). All measurements were done in a 1 mL cuvette sealed under an argon atmosphere. Blank runs of aqueous **I** at the desired pH were run prior to the addition of the phosphate esters to ensure no changes at 400 nm.

All rate determinations were done with at least 110-fold molar excess of **I** over the phosphate esters to ensure pseudo-first-order conditions.

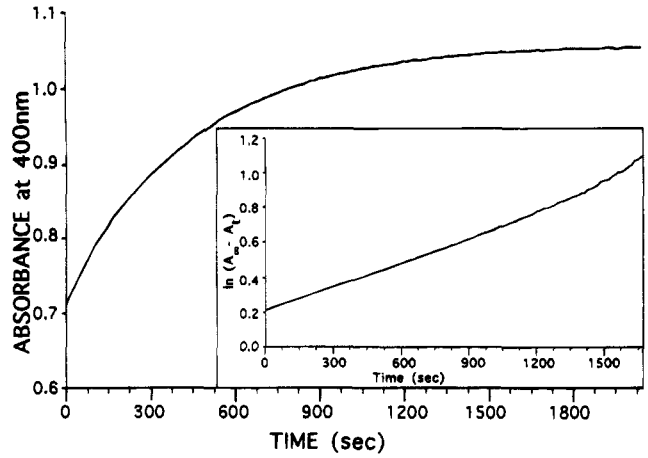


Figure 1. Absorbance at 400 nm vs time for the reaction of NPP (45 uM) and **I** (5 mM) at 30 °C in H_2O (pH 7.7). Inset is the plot of of $\ln(A_\infty - A_t)$ vs time, where A_∞ and A_t are the experimentally determined absorbance values at long reaction times and times t, respectively.

Observed first-order rate constants (k_{obsd}) were calculated according to eq 1, where A_∞, A_0, and A_t are experimentally determined absorbance

$$\ln[(A_\infty - A_t)/(A_\infty - A_0)] = -k_{obsd}t \qquad (1)$$

values at long reaction time, at time zero, and time t, respectively. The rate constants were obtained by fitting the first three half-lives of the kinetic data to the first-order kinetics equation where the correlation coefficient was > 0.99 (Figure 1). In a typical kinetics experiment, a 5 mM aqueous solution of **I** was freshly prepared under an argon atmosphere and the pH was adjusted with NaOH and HCl. After 20 min, 1 mL of the **I** solution was syringed into an argon-purged 1.0 mL cuvette capped with a rubber septa and allowed to thermally equilibrate (30 °C) in the spectrophotometer. The hydrolysis of the phosphate ester was initiated with the addition of 10 μL of a freshly prepared solution of the phosphate salt (4.5 mM) that was purged with argon. NaCl (10 mM) had no appreciable effect on the rate of hydrolysis, and there were no major changes in k_{obsd} when the reactions were run in D_2O.

NMR Studies. In the ^1H and ^{31}P NMR experiments, the hydrolysis of NPP (10 mM) in aquated **I**(100 mM) was done in 2 mL of D_2O under an Ar atmosphere (pD 7.7, 20 °C). For ^1H NMR studies, the hydrolysis was followed by observing the signals for free 4-nitrophenol (6.97 ppm, d; 8.37 ppm, d) and NPP (7.52 ppm, d; 8.44 ppm, d). ^{31}P NMR measurements were done with a 10 μs pulse length and a 1 s pulse delay, and the hydrolysis was observed by monitoring the signals at 2 (starting NPP), 33, and 44 ppm.

Results and Discussion

We find our phosphoester cleavage results to be remarkable given the intractable aqueous chemistry of most organometallic compounds and the paucity of well behaved organometallic transformations in aqueous solvents.[15] Furthermore, the *p*-nitrophenolate production rates by aquated Cp_2MoCl_2 are comparable to the best coordination compounds which underscores the novelty of this finding. We therefore set out to investigate the fundamental steps involved in the Cp_2MoCl_2-(aq)-promoted phosphate ester bond cleavage. From a structural perspective of the metal−chloride geometry, **I** bears a resemblance to Co(III) complexes such as $[Co(trpn)Cl_2]^+$ (trpn = tris(aminopropyl) amine) and $[Co(cyclen)Cl_2]^+$ (cyclen = 1,4,7,-10-tetraazacyclododecane) which are known to liberate *p*-

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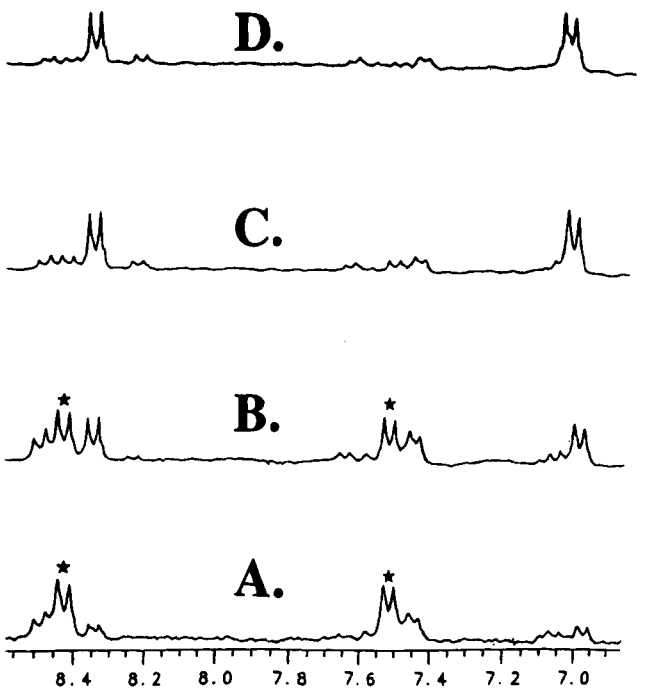
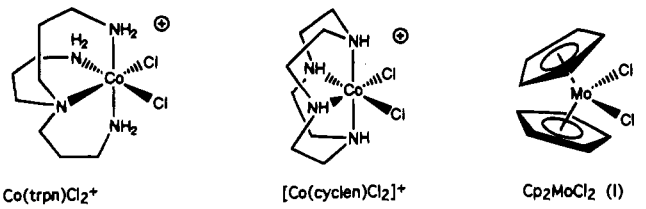


Figure 2. ^1H NMR of NPP (10 mM) after adding I (100 mM) at pD 7.7, 20 °C. Elapsed time: (A) 5 min, (B) 20 min, (C) 40 min, and (D) 1 h. An asterisk represents starting NPP.

nitrophenolate from NPP and BNPP effectively.[2b] The cyclopentadienyl or polyamine ligands maintain the *cis*-MCl_2 configuration(M = Mo or Co) necessary for phosphoester coordination and cleavage.



It was found that **I** (110-fold excess) promotes the release of 1 equiv of 4-nitrophenol from both BNPP and NPP at pH 6 to 9. This discussion outlines the results for the **I**-promoted phosphoester bond cleavage of NPP and BNPP and proposes a mechanism for this chemistry. Figures 2 and 3 show the ^1H and ^{31}P NMR changes that accompany the reaction of **I** with NPP, respectively. The poor solubility of the BNPP/**I** solution at the mM concentrations for NMR studies precluded similar ^{31}P NMR studies with the diester. Finally Table 1 presents a summary of the kinetics for the phosphoester bond cleavage of NPP and BNPP with and without **I**.

Cp_2Mo-Complex Promoted Hydrolysis of NPP. *p*-Nitrophenolate production of NPP by **I** is most rapid at pH 7.9 with a rate constant of 4.5×10^{-3} s^{-1}, and rapidly drops off to negligible activity ($< 10^{-4}$ s^{-1}) below pH 6.0 and above pH 9.0. The absence of hydrolytic activity under strong alkaline conditions may be due to the oligomerization of **I** to inert polymeric species that are known to exist with other metallocenes.[16] Furthermore, when Cp_2MoCl_2(aq) is allowed to oxidize in air (pH 7.0–9.0) for more than 24 h, UV/visible spectroscopy reveals no release of 4-nitrophenol. Titrimetric studies show minimal oligomerization for Cp_2MoCl_2(aq)[10a] and

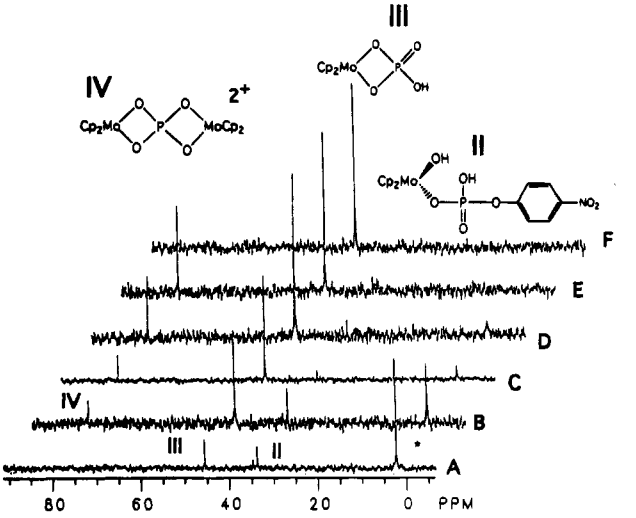


Figure 3. ^{31}P NMR spectra of the NPP (100 mM) after adding **I** (10 mM) at pH 7.8 and 23 °C in H_2O. Elapsed time: (A) 5 min after initial mixing, (B) 20 min, (C) 40 min, (D) 1 h, (E) 2.5 h, (F) 2.5 h + 0.1 M NaOH that shows decomposition of **IV**. An asterisk denotes starting *p*-nitrophenyl phosphate. The spectra were referenced to liquid H_3PO_4 (85%) by the substitution method.

Table 1. Summary of Rate of 4-Nitrophenol Release (k_{obsd}) from NPP and BNPP by Cp_2MoCl_2 (30 °C)

	NPP	BNPP
optimal pH	7.9	7.7
k_{obsd} at optimal pH (s^{-1})[a]	4.5×10^{-3}	5.0×10^{-3}
k_{obsd} at pH 7.0 with **I** (s^{-1})[a]	2.5×10^{-3}	3.3×10^{-3}
k_{obsd} at pH 7.0 without **I** (s^{-1})	6.7×10^{-8} [b]	3.9×10^{-10} [c]
effect in D_2O solution	no effect	no effect
k_{obsd} with 2,4-dinitrophenol leaving group at optimal pH (s^{-1})		1.2×10^{-1}
$\Delta S^{\ddagger}$ (eu)	−16	0.0

[a] All measured k_{obsd} values had less than 10% deviation from one another. [b] Reference 28b: extrapolated from rate measurements at 50 °C with $\Delta S^{\ddagger}$ value of 3.5 eu. [c] Reference 28a; extrapolated from rate measuremed at 100 °C with $\Delta S^{\ddagger}$ value of −25.5 eu.

our kinetic results show a half-order dependence[17] in **I** for *p*-nitrophenolate production. A similar half-order dependence in metal concentration was seen in the phosphate hydrolysis of BNPP by Cu([9]-aneN_3)Cl_2 which was interpreted as a monomeric active metal species.[18] We therefore propose that the reactive agent for **I** is $Cp_2Mo(OH)(OH_2)^+$, which is consistent with the observation that the rate of *p*-nitrophenolate production is most rapid in a pH range between the pK_{a1} (5.5) and pK_{a2} (8.5)[10a] of aqueous **I**.

The absence of any significant solvent isotope effect on the *p*-nitrophenolate production rates (Table 1) suggests a pathway that does not involve a general base mechanism and a transition state with minimal hydrogen bonds with water. This feature was also seen in the phosphoester bond cleavage of $Co(en)_2(OH)O_2PO_2C_6H_4NO_2$ which proceeded via an intramolecular attack of a Co(III)-bound hydroxide at the phosphorus center.[19] The reaction of NPP with **I** can be thought of as having two fundamental steps, phosphate coordination by the Cp_2Mo moiety followed by phosphoester bond cleavage.

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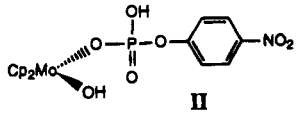
In this connection, ^{31}P NMR techniques were used to look for potential intermediates in the phosphoester cleavage reaction of NPP by **I**. ^{1}H NMR techniques (10 mM of NPP and 100 mM of **I**) showed that 1 equiv of 4-nitrophenol was released with a half-life of about 20 min. The ^{1}H NMR spectra (Figure 2) also show the presence of at least one intermediate in this reaction. Attempts to increase the ratio of **I** to NPP (>50:1) for pseudo-first-order conditions resulted in precipitation due to the poor solubility of **I** at such high concentrations. According to Figure 3, the addition of NPP (10 mM) to **I** (100 mM) at pH 7.5 results in two new species with ^{31}P chemical shifts at 33 and 44 ppm followed by the appearance of a third new signal at 77 ppm sometime later. From the ^{31}P NMR spectra, it is noteworthy that the formation of the species at 33 and 44 ppm is more rapid compared to the final conversion to the 77 ppm species. Furthermore, the series of spectra imply that the starting material and the 33 ppm signal are converted to the final signals at 44 and 77 ppm.

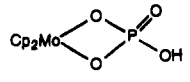
On the basis of previous crystallograhic and ^{31}P NMR studies of Cp_2Mo coordination to phosphomonoesters, we assign the signal at 33 ppm as the monodentate Cp_2Mo-phenyl phosphate complex **II**. These studies have shown that monodentate Cp_2-



II

Mo coordination to the 5′-monophosphate esters of nucleotides results in a 30 ppm displacement of the ^{31}P NMR signal.[10a] In addition, we conducted titration studies of **I** with phenyl phosphate which served as a suitable model for Cp_2Mo coordination to NPP, for phenyl phosphate has a similar ^{31}P chemical shift and a poorer leaving group than NPP. The titration (pH 7.7) of phenyl phosphate with 0.5 and 1.0 equiv of **I** yielded primarily one new ^{31}P signal with a chemical shift of 33 ppm. This particular chemical shift, which is identical to that of **II**, clearly reflects a 30 ppm downfield displacement from the starting phenyl phosphate resulting from monodentate Cp_2Mo coordination.

The ^{31}P NMR signal (Figure 3) at 44 ppm is a Cp_2Mo–phosphate complex without a phenolate ring since both ^{1}H NMR and UV/visible techniques clearly show that 1 equiv of 4-nitrophenol is released when NPP is treated with **I**. We propose that this signal is due to a bidentate $Cp_2Mo(O_2PO_2H)$ complex (**III**) that results from the phosphoester bond cleavage of **II**. The assignment of **III** as the 44 ppm signal comes about

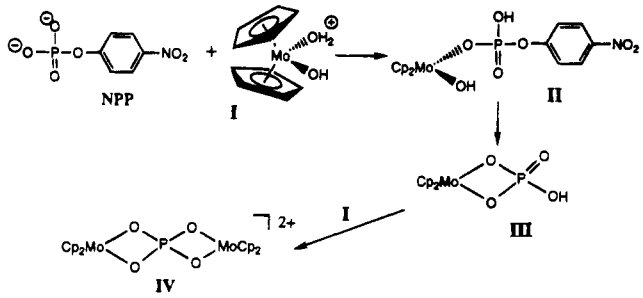


III

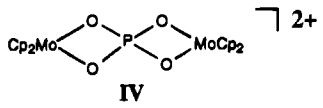
from the observation that the titration of **I** with 1.0 and 0.5 equiv $NaHPO_4$ (pH 7.7) results in only one new species with a signal at 45 ppm. In addition, at 1.0 equiv of $NaHPO_4$, no residual starting phosphate signal was observed which is suggestive of a 1:1 complex with the Cp_2Mo^{2+} moiety. The presence of only one ^{31}P NMR signal that is 40 ppm downfield from the starting phosphate suggests a Cp_2Mo–phosphate complex with both oxygens bound to the Cp_2Mo moiety. Indeed, many chelated Cp_2Mo complexes are known[20] and bidentate Co(III)–phosphate compounds are intermediates in phosphoester bond cleavage reactions.[21] However, attempts to crystallize **III** for X-ray studies have thus far been unsuccessful.

The signal at 77 ppm is assigned as the binuclear Cp_2MoO_2-PO_2MoCp_2 complex **IV** which results from an additional Cp_2-

Scheme 2



Mo coordination/chelation to **III**. Like the case with Co(III) complexes, a second Cp_2Mo coordination to phosphates results in a further downfield displacement of the ^{31}P signal.[22] This is in accordance with the relative chemical shift of **IV** compared to **III**. The ^{31}P NMR assignment for complex **IV**, which has



IV

been previously characterized by X-ray diffraction,[8] comes from the observation that the addition of two equivalents of **I** to $NaHPO_4$ (pH 7.7) immediately results in only one signal with a chemical shift of 76 ppm. The strained nature of the double four membered chelate in complex **IV** is underscored when 0.1M NaOH is added. As can seen in the ^{31}P NMR spectra in Figure 3F, this results in its immediate decomposition to possibly **III**.

We propose a pathway for the Cp_2MoCl_2-promoted phosphoester bond cleavage of PNPP (Scheme 2) that is consistent with the ^{31}P NMR results. In this scheme, Cp_2Mo coordination, which is rapid, is followed by a phosphoester bond cleavage step to form a Cp_2Mo(phosphate) complex. Furthermore, under a 10-fold excess of **I** over NPP, it is clear that there is no major buildup of the intermediate complex **II** which, to a rough approximation, agrees with the absence of a significant induction period in the *p*-nitrophenolate production as seen with UV/visible experiments. However, it should be noted that conditions (concentration, ratio of NPP and **I**, and temperature) for the ^{31}P NMR and UV/visible studies are not identical, and thus comparisons in kinetics between these two spectroscopic observations are rather tenuous.

In support of an intramolecular pathway are the kinetic data presented in Table 1. It is unlikely that a metaphosphate pathway is present here as such reactions have entropies of activation close to zero,[23] and the cationic Cp_2Mo moiety would

(20) (a) Cp_2MoX_n systems with four-membered chelate rings about the equatorial girdle of the Cp_2Mo framework have been crystallographically characterized. For example, Cp_2Mo(2-aminopyridine),[20b] Cp_2-Mo(2-oxopyridine),[20b] Cp_2Mo(9-methyladenine),[10a] and Cp_2Mo(1-methylcytosine)[10a] are Cp_2MoX_n chelate systems with nitrogen-containing ligands. $Cp_2Mo(SO_4)$[20c] and $Cp_2MoO_2PO_2MoCp_2$[12] are known chelate systems with Cp_2Mo–oxygen coordination. (b) Calhorda, M. J.; di C. T. Carrondo, M. A. A. F.; Da Costa, R. G.; Dias, A. R.; Duarte, M. T. L. S.; Hursthouse, M. B. *J. Organomet. Chem.* **1987**, *320*, 53–62. (c) Calhorda, M. J.; di C. T. Carrondo, M. A. A. F.; Da Costa, R. G.; Dias, A. R.; Domingos, A. M. T. S.; Simoes, J. A. M.; Teixeira, C. *Organometallics* **1986**, *5*, 660–667.

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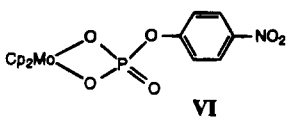
retard the elimination process. It has also been shown that cobalt(III) coordination complexes do not exhibit a metaphosphate intermediate.[27] In the same vein, bimolecular solvolysis reactions commonly have entropies of activation of −25 to −30 e.u.,[24] a k_{H_2O}/k_{D_2O} of 1.5 and are subject to negative salt effects.[13a,25] The absence of these properties with NPP phosphate degradation by **I** suggests an intramolecular pathway.

Cp_2Mo-Complex Promoted Hydrolysis BNPP and Summary of Rate Acceleration. The phosphoester bond cleavage of BNPP by **I** has a negligible deuterium isotope effect, releases 1 equiv of 4-nitrophenol, and has a 20-fold rate enhancement with bis(2,4-dinitrophenyl) phosphate (Table 1). Unfortunately the poor solubility of the BNPP−**I** solution (at mM concentrations) made the detection of putative intermediates with ^{31}P NMR difficult. This makes it problematic to speculate on the mechanism of BNPP hydrolysis by **I** except that the absence of any rate changes in D_2O potentially precludes a bimolecular process. When this information is coupled with the observation that only 1 equiv of 4-nitrophenol was released, it suggests that an intramolecular process is taking place which leaves behind a final Cp_2Mo−phenyl phosphate product. Such a proposed final product could be **VI**, which is the four-membered chelate of **II**. A final product that involves a monodentate complex



VI

like **II** would further undergo phosphoester bond cleavage to release a second 4-nitrophenol which was not observed with UV/visible spectroscopy. Indeed, at no time did we see any ^{31}P NMR signal in the suspension (i.e. 33 ppm) corresponding to a monodentate Cp_2Mo complex.[26] Further work on the complete characterization of the final product(s) and putative intermediate(s) in BNPP hydrolysis by **I** is underway.

While the four-member chelates (**VI** and **III**) that are proposed in this phosphate hydrolysis reaction appear to be strained, there are many crystallographic examples in the literature of Cp_2MoX_n systems with such a chelation.[19] Indeed, theoretical and experimental studies have shown[27] that for the d^0, d^1, and d^2 Cp_2MX_2 systems, the d^2 complexes have the smallest X−M−X bond angles (76−82°). This feature adds to the notion that the Cp_2Mo framework can readily accommodate such a four-member chelate ring for complexes **III** and **VI**. One can further speculate that such chelate structures are stable intermediates or final products for Cp_2Mo−phosphate complexes and may in fact be a driving force for the phosphoester bond cleavage reactions.

In terms of the acceleration for the *p*-nitrophenolate production, **I** exhibits significant and impressive enhancements in the observed cleavage of the phosphoester bond. As a benchmark, we used the k_{obsd} (pH 7.0) rates for the hydrolysis of NPP and BNPP without added metals.[28] The observed pseudo-first-order rate (pH 7.0, 30 °C) constants for the phosphoester cleavage of BNPP by **I** is 3.3×10^{-3} s^{-1} which is 10^7 times faster than the hydrolysis of BNPP without added metals (3.9×10^{-10} s^{-1}). For NPP, the k_{obsd} at pH 7.0 is 2.5×10^{-3} s^{-1} which reflects a 10^5-fold acceleration in phosphoester bond cleavage compared to no metal added (6.7×10^{-8} s^{-1}). In comparison with other coordination complexes, the compound $[Co(trpn)Cl_2]Cl$ exhibits a 10^8 increase in the observed rate constant of BNPP degradation relative to neutral water, and $[Co(trien)Cl_2)Cl$ (trien = triethylenetetramine) shows a 10^5 increase in the phosphoester bond cleavage of NPP.[7a] The larger rate acceleration for the **I**-promoted reaction of BNPP vs NPP is due, in part, to the metaphosphate pathway for the hydrolysis of NPP in water which is not available for BNPP hydrolysis.[29]

Conclusion

We have found the first case of an organometallic compound that promotes the phosphoester bond cleavage of activated phosphate diesters and monoesters with rate accelerations of 10^7 and 10^5, respectively. These rate accelerations are comparable to the best Co(III) coordination complexes that promote phosphoester cleavage. The structural and coordination features of this water-stable metallocene compound bear a resemblance to those found in Co(III) polyamine complexes that also degrade phosphoesters. These features, which include a Cp−Mo ligation inert to hydrolysis and isomerization, serve to minimize metal aggregation and preserve the *cis*-Cl−Mo−Cl configuration essential for phosphoester hydrolysis.

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Supporting Information Available: Supplemental Figure 1 showing the hydrolysis of NPP by **I** as observed by UV/visible spectroscopy (1 page). Ordering information is given on any current masthead page.

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(26) Under the same conditions as those described in Figure 3 (100 mM in **I** and 10 mM in BNPP), only one ^{31}P NMR signal with a chemical shift of 44 ppm was observed. This chemical shift is almost 10 ppm downfield of the ^{31}P NMR signal for **II**. This downfield displacement has been seen for bidentate phosphate chelation of cobalt(III) phosphate complexes.[22] Therefore it is probable that this signal is due to the Cp_2Mo bidentate structure proposed for **VI**. Isolation of this final product for further analysis however, has been problematic.
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