(Pyrazolylborate)zinc Organophosphate Complexes Resulting from Hydrolytic Cleavage of Phosphate Esters☆

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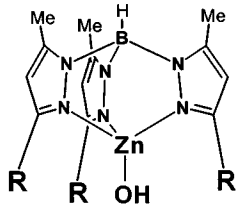
Five different (pyrazolylborate)zinc hydroxide complexes Tp*Zn−OH (**1**) were used as hydrolytic reagents towards esters of various acids of phosphorus. Trimethyl phosphate and trimethyl phosphite could not be cleaved. Dimethyl and diphenyl phosphite yielded $Tp^{tBu,Me}Zn-OPHO(OR)$ (**2**, **3**). Triphenyl phosphate reacted slowly producing moderate yields of $Tp^*Zn-OPO(OPh)_2$ (**4**). Tris(*p*-nitrophenyl) phosphate was cleaved rapidly, forming $Tp^*Zn-OPO(OC_6H_4NO_2)_2$ (**5**) and $Tp^*Zn-OC_6H_4NO_2$ (**6**). Alkylbis(*p*-nitrophenyl) phosphates showed intermediate reactivity, losing *p*-nitrophenolate upon hydrolysis and producing $Tp^*Zn-OPO(OR)(OC_6H_4NO_2)$ (**7**, **8**). When phosphorus acid diesters were employed, condensation between the Zn−OH and P−OH functions occurred. This proved to be the convenient way of preparing the organophosphate complexes $Tp^*Zn-OPO(Ph)_2$ (**9**), $Tp^*Zn-OPO(OPh)_2$ (**4**), and $Tp^*Zn-OPO(OC_6H_4NO_2)_2$ (**5**). Six structure determinations showed the structural variability of the resulting complexes.

One of the largest group of enzymes are those which catalyze phosphate transfer[1]. Many of them are metalloenzymes[2], quite often having two or three metal ions in the active center[3]. Of the metals involved (Mg, Fe, Mn, and Zn) zinc plays an important role, being present for instance in alkaline[4] and acid[5] phosphatases, nucleases[6][7], phospholipases[8], phosphotriesterases[9], and DNA and RNA polymerases[10]. All these latter enzymes are involved in the making and breaking of phosphate ester (P−OR) linkages in their various biological occurrencies.

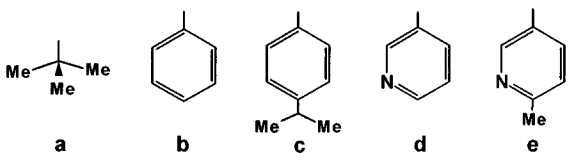
The importance of the subject and the ease of modelling the biological substrates by simple phosphoric acid esters like tris(*p*-nitrophenyl) phosphate has attracted organic chemists and coordination chemists early on. Research groups which have investigated the metal (specifically zinc) ion or complex catalyzed phosphate ester hydrolysis are, among others, those of Breslow[11], Chin[12], Brown[13], Kimura[14], Bianchi[15], and Yashiro[16]. Stoichiometric reactions and structural models for zinc complexes were provided, among others, by Krebs[17], Kitajima[18], Fenton[19], Lippard[20], and ourselves[21]. A typical characteristic of the model mechanisms or structures is the involvement of bidentate phosphate, being coordinated via two of its oxygen atoms to either one or two metal ions. Monodentate coordination is the exception, and to date just one structure of a mononuclear zinc complex bearing a phosphate only as a monodentate ligand has been published[21].

We are interested in exploiting the hydrolytic activity of zinc-bound water molecules or hydroxide groups in an isolated situation, i.e. one where the kind and number of other ligands on zinc leaves just one coordination site for H_2O or OH^-, thereby encapsulating it in an enzyme-like manner. The purpose is to make the reacting zinc complexes strictly monofunctional and allowing only monodentate coordination for the substrate too. We have so far tested it for zinc model complexes of tripodal N,N,N [e.g. tris(benzimidazolylmethyl)amine][22] and N,N,O (e.g. dipicolylglycine)[23] ligands. In our hands the substituted (pyrazolylborate)zinc hydroxides Tp*Zn−OH turned out to be the best nucleophiles, being active in the hydrolysis of esters[24], amides[24], CO_2[25][26] and similar systems with cumulated double bonds[27]. We have also briefly communicated the hydrolytic cleavage of phosphate esters and diphosphates by them[28].

This paper starts a series of publications on the cleavage of phosphate-containing materials by Zn−OH and $Zn-OH_2$ complexes. In order to lay a preparative and structural basis for further work, simple esters of various acids of phosphorus were treated with the five Tp*Zn−OH complexes **1a**−**e**. The reaction conditions were chosen such that one ester group each could be cleaved off, and due to the insolubility of the Tp*Zn−OH complexes in water the reactions were meant to be stoichiometric rather than catalytic.



1a (R = a): $Tp^{tBu,Me}Zn-OH$
1b (R = b): $Tp^{Ph,Me}Zn-OH$
1c (R = c): $Tp^{Cum,Me}Zn-OH$
1d (R = d): $Tp^{Py,Me}Zn-OH$
1e (R = e): $Tp^{Pic,Me}Zn-OH$



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"Small" Phosphates and Phosphites

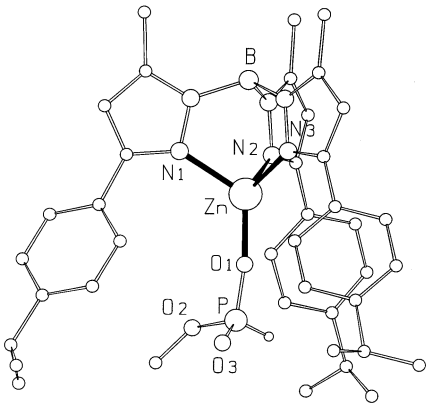
The first attempts at ester cleavage were made with trimethyl phosphite and trimethyl phosphate. Both turned out to be unreactive toward the Tp*Zn−OH reagents. Although, being small molecules, they allow easy access of a nucleophile to phosphorus, their alkyl ester functions seem to be too inert. Making them even smaller led to success, however. Dimethyl phosphite [$HPO(OMe)_2$] reacted with **1a** and **1c**, diphenyl phosphite [$HPO(OPh)_2$] reacted with **1a** producing in very good yields the zinc-phosphate complexes **2a**, **2c**, and **3a** as the products of the hydrolytic removal of one OR group. Both the liberated methanol and phenol did not show up in the form of zinc complexes, in accord with our experience that they don't react with Tp*Zn−OH[29]. One attempt at using an ester of methylphosphonic acid, namely $MePO(OMe)_2$, was also met with failure.

$Tp^{R,Me}Zn-OPHO(OMe)$
2a: R = *t*Bu
2c: R = Cum

$Tp^{tBu,Me}Zn-OPHO(OPh)$
3a

The spectroscopic identification of complexes **2a**, **2c**, and **3a** was easy due to their simple ^{1}H-NMR spectra containing the very typical P-H doublet. Confirmation of their constitutional assignment was obtained by a structure determination of **2c** (see Figure 1). The structure shows the expected pseudotetrahedral coordination of zinc with a symmetrical attachment of the $Tp^{Cum,Me}$ ligand and the Zn−O bond very close to the trigonal axis of the Tp*Zn unit. As such it provides no unusual features for a Tp*Zn−OX complex. The bonding situation of its phosphite ligand is discussed below.

Figure 1. Molecular structure of **2c**[a]



[a] Coordination environment of zinc: Zn−O1 1,825(5), Zn−N1 2.016(5), Zn−N2 2.026(5), Zn−N3 2.016(5) A; O1−Zn−N1 123.0(2), O1−Zn−N2 122.0(2), O1−Zn−N3 122.3(2)°. − In the crystal one methanol molecule is attached to O3 by a hydrogen bond.

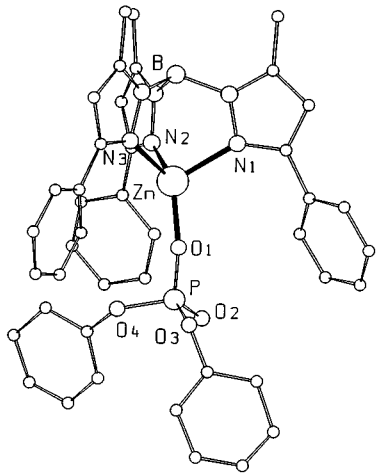
Triphenyl Phosphate

Aryl phosphates are more amenable to hydrolytic cleavage than trialkyl phosphates, yet they are not typically used for model studies for which *p*-nitrophenyl phosphates are the favourites. It turned out that our Tp*Zn−OH reagents are aggressive enough to remove one phenolate ligand from them, especially when applied in large excess for kinetic studies[30]. Stoichiometric reactions were relatively slow and led to product mixtures containing some starting material and side products which were not easy to separate. Thus **1d** and $PO(OPh)_3$ gave only traces of **4d**. Both **1b** and **1c** underwent relatively clean reactions with $PO(OPh)_3$ as evidenced by ^{31}P-NMR spectroscopy. After isolation, the products **4b** and **4c** were of moderate yield. Samples were also obtained of **4b** by condensation (see below) and of **4c** by hydrolytic cleavage of tetraphenyl diphosphate[31].

$Tp^{R,Me}Zn-OPO(OPh)_2$
4a: R = *t*Bu
4b: R = Ph
4c: R = Cum
4d: R = Py

The spectroscopic identification of complexes **4** rests mainly on the ^{1}H-NMR data of their Tp* ligands and the ^{31}P-NMR and υ(P=O) IR data of their phosphate ligands. The assignment was rounded off by a structure determination of **4b** (see Figure 2). It shows a less symmetrical arrangement around the zinc ion as evidenced by the Zn−N bond lengths and the O−Zn−N angles.

Figure 2. Molecular structure of **4b**[a]



[a] Coordination environment of zinc : Zn−O1 1,854(2), Zn−N1 2.009(3), Zn−N2 2.019(2), Zn−N3 2.060(2) A; O1−Zn−N1 114.6(1), O1−Zn−N2 130.8(1), O1−Zn−N3 119.5(1)°.

Tris(*p*-nitrophenyl) Phosphate

As expected, tris(*p*-nitrophenyl) phosphate reacted fast and cleanly with the Tp*Zn−OH reagents. It was, in our hands[30] like in others, the substrate of choice for kinetic measurements. We used it for stoichiometric reactions with **1b** and **1c**. In order to achieve complete consumption of the phosphate, two equivalents of the zinc complex had to be used. The reason for this is fast reaction of the liberated *p*-nitrophenol with the zinc−hydroxide unit in terms of a condensation reaction leading to the *p*-nitrophenolate complexes **6**, as we have described before[29]. Thus the hydrolytic cleavages of the phosphate yielded equimolar mixtures of

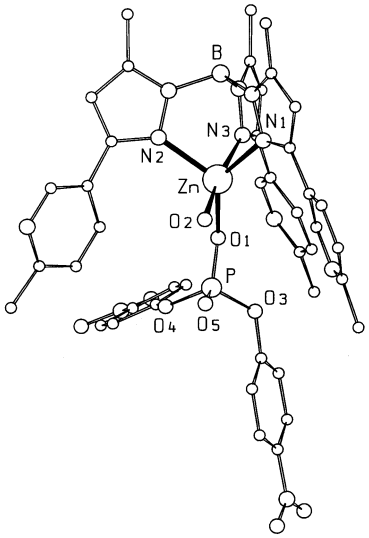
the phosphate complexes **5b**, **c** and the phenolate complexes **6b**, **c** which were separated.

$Tp^{R,Me}Zn-OPO(OC_6H_4-p\text{-}NO_2)_2$
5a: R = *t*Bu
5b: R = Ph
5c: R = Cum
5e: R = Pic

$Tp^{R,Me}Zn-OC_6H_4-p\text{-}NO_2$
6b: R = Ph
6c: R = Cum
6e: R = Pic

The spectroscopic identification of **5b** and **5c** rests on the ^{1}H-NMR data for the Tp* ligands and the υ(P=O) and δ(^{31}P) values again. Compounds **6b** and **6c** which we have described before[29] were identified spectroscopically. Crystals suitable for a structure determination were obtained of **5e** (see below). They turned out to contain hydrated **5e** with five-coordinate zinc (see Figure 3). Five-coordination of zinc seems to be the rule rather than the exception in zinc complexes of tris(3-pyridyl-3′-pyrazolyl)borato ligands[31][32][33]. In **5e** the geometry at zinc is that of a distorted trigonal bipyramid [angle O2−Zn−N3 170.8(1)°, angles between apical and equatorial ligands 85−96°, angles between equatorial ligands 97−139°]. The zinc-bound water molecule is connected via a hydrogen bond to the P=O oxygen (2.69 Å). The phosphate attachment is discussed below.

Figure 3. Molecular structure of **5e** · H_2O[a]



[a] Coordination environment of zinc: Zn−O1 1.996(2), Zn−O2 2.082(2), Zn−N1 2.070(3), Zn−N2 2.072(3), Zn−N3 2.202(3) Å.

Alkylbis(*p*-nitrophenyl) Phosphates

The alkylbis(*p*-nitrophenyl) phosphates contain two ester functions of quite different lability. It could therefore be predicted that they would lose only one *p*-nitrophenolate unit upon hydrolysis by Tp*Zn−OH. This was verified for ethylbis(*p*-nitrophenyl) phosphate with **1b**, **1c**, and **1e** as well as for cyclohexylbis(*p*-nitrophenyl) phosphate with **1e**. Reaction products were the zinc phosphate complexes **7b**, **7c**, **7e**, and **8e** together with the *p*-nitrophenolate complexes **6b**, **6c**, and **6e**, some of which were again difficult to separate. The various steps of the workup procedure resulted in partial hydrolytic destruction in case of **7b** and **7e**, liberating the free pyrazole which was then coordinated to zinc giving the addition products **7b′** and **7e′**. The presence of the additional pyrazole ligands in these complexes was found by ^{1}H-NMR spectroscopy. Otherwise the spectroscopic data of complexes **7** and **8** are in accord with their constitutions and quite similar to those of the related complexes with other phosphate ligands.

$Tp^{R,Me}Zn-OPO(OEt)(OC_6H_4-p\text{-}NO_2)$
7b: R = Ph
7c: R = Cum
7e: R = Pic

7b · 3-methyl-5-phenylpyrazole **7b′**

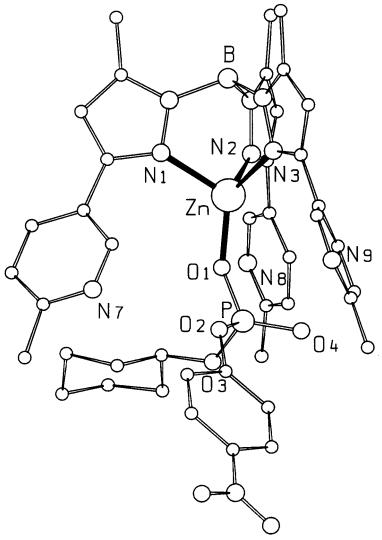
7e · 3-methyl-5-picolylpyrazole **7e′**

$Tp^{Pic,Me}Zn-OPO(OCy)(OC_6H_4-p\text{-}NO_2)$
8e

Of these complexes, one each with fourfold (**8e**) and fivefold (**7b′**) coordination at zinc was chosen for a structure determination. An unusual feature of all complexes **7** and **8** is the presence of phosphorus atoms with four different substituents. The crystals of **8e** and **7b′** are, however, not enantiomerically pure but belong to the centrosymmetric space group P−1.

Complex **8e** (see Figure 4) shares with complex **2c** the symmetrical attachment of the Tp* ligand to zinc. However, unlike the situation in **2c** the Zn−O bond is bent away significantly from the trigonal axis of the Tp* ligand, making the phosphate attachment in **8e** more like that in **4b**.

Figure 4. Molecular structure of **8e**[a]

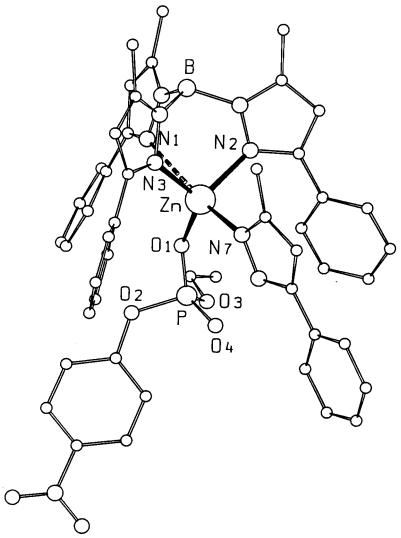


[a] Coordination environment of zinc: Zn−O1 1,854(2), Zn−N1 2.028(3), Zn−N2 2.030(2), Zn−N3 2.033(2) Å; O1−Zn−N1 118.8(1), O1−Zn−N2 116.4(1), O1−Zn−N3 131.8(1)°.

The coordination of zinc in complex **7b′** (see Figure 5) is quite unusual. The attachment of the free pyrazole molecule exerts a kind of a trans effect, pushing one of the Tp* pyrazole donors away on the opposite side of the zinc ion. The result is a very unsymmetrical coordination of the Tp* ligand to zinc, with the Zn−N1 distance (2.90 Å) practically outside a bonding range. The symmetry about the zinc ion can, however, best be described as trigonal-bipyramidal

with N7 and N1 in the apical positions (angle 172°). The angles between the axial and equatorial donors range from 77 to 105°, those between the equatorial donors between 101 and 125°. On the other hand all angles between N7 and the equatorial donors are much larger than 90° (maximum N7−Zn−O1 with 105°), indicating that the four donors O1, N2, N3, and N7 also define a flattened tetrahedron. It seems that electronic preferences favour tetrahedral coordination for **7b′** but the geometrical restraints of the Tp* ligand don′t allow to completely remove the fifth donor, resulting in the observed intermediate type of coordination.

Figure 5. Molecular structure of **7b′**[a]



[a] Coordination environment of zinc: Zn−O1 1.912(3), Zn−N1 2.897(4), Zn−N2 2.022(3), Zn−N3 2.003(3), Zn−N7 2.082(4) Å.

Condensation Reactions

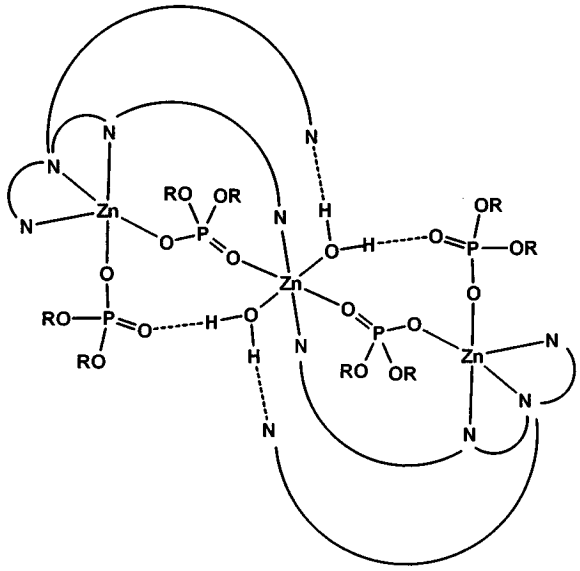
In addition to the phosphoric acid triesters we also tried to find out about the hydrolytic cleavage of phosphoric acid diesters. These are of course acids themselves and as such capable of destroying the pyrazolylborate ligands hydrolytically. To our surprise, however, their main reactivity towards the Tp*Zn−OH complexes consisted in a condensation reaction producing the corresponding diesterphosphate complexes. We then learnt that every $X_2P(O)OH$ compound undergoes this reaction yielding Tp*Zn−O-$P(O)X_2$.

In the context of this paper we applied the condensation reaction to **1a** and diphenylphosphinic acid, giving a good yield of **9a**. Similarly, **1a** with diphenyl phosphate and bis(*p*-nitrophenyl) phosphate yielded **4a** and **5a**, **1b** with both reagents yielded **4b**, **5b**, and **1e** with bis(*p*-nitrophenyl) phosphate yielded **5e** (which was used for the structure determination, see above).

$Tp^{tBu,Me}Zn-OP(O)Ph_2$
9a

The destructive power of the acidic phosphoric acid diesters came to effect in only one case, the reaction between **1d** and bis(*p*-nitrophenyl) phosphate. In the course of this reaction one of three Tp*Zn units was lost liberating zinc ions in a way which is unclear as yet. The combination of two Tp*Zn units, one zinc ion, four phosphate anions, and two water molecules then resulted in the formation of complex **10d**, the constitution of which became only clear by a structure determination. The schematic drawing of **10d** (see Figure 6) shows a octahedral zinc ion in the center and two five-coordinate zinc ions in the periphery. On both sides one phosphate each is bridging the zinc ions while the other is terminal. One pyridyl substituent of each $Tp^{Py,Me}$ ligand is used as a donor toward the central zinc ion as observed before in $[(Tp^{Py,Me}Zn)_2(\mu\text{-}H_3O_2)]^+$ [32]. Hydrogen bridging stabilizes the structure which is unique as a whole but comprised of established structural units.

Figure 6. Schematic drawing of complex **10d**[a]



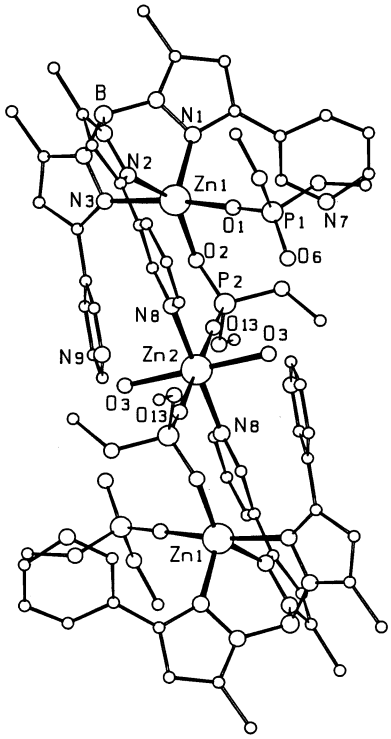
[a] R = *p*-nitrophenyl, the three interconnected N atoms bound to the outer Zn ions represent $Tp^{Py,Me}$ ligands, the four long curves represent one pyridyl substituent each of $Tp^{Py,Me}$.

Figure 7 displays the molecular structure of **10d**, with all atoms except the α-C of the *p*-nitrophenolate units omitted for clarity. The molecule is centrosymmetric. The central zinc ion is in a nearly ideal octahedral ZnN_2O_4 environment with Zn−O and Zn−N distances (2.12−2.14 Å) typically longer than those in all other zinc complexes of this paper. The peripheral zinc ions have a distorted trigonal-bipyramidal ZnN_3O_2 environment comparable to that in **5e** (*trans* angle O1−Zn1−N3 168°, *cis* angles 81−100°, equatorial angles 98−141°). The double-bridged linkage between Zn1 and Zn2 via one phosphate and one pyridylpyrazole unit represents a 10-membered heterocyclic ring.

Discussion of the Zinc−Phosphate Interactions

All the phosphite and phosphate complexes obtained here are molecular compounds soluble in nonpolar organic solvents. This implies that their zinc−phosphate interactions are covalent, as is also evidenced by the structure determinations. We became aware that this may be a questionable statement when observing that the Zn−O−P angles

Figure 7. Molecular structure of **10d**[a]



[a] Coordination environments of the zinc ions: Zn1−N1 2.034(5), Zn1−N2 2.070(5), Zn1−N3 2.224(5), Zn1−O1 2.067(4), Zn1−O2 1.960(4), Å Zn2−N8 2.140(7), Zn2−O3 2.125(6), Zn2−O13 2.128(5) Å.

are never close to the tetrahedral angle to be expected for covalent oxygen and that the formal single bonds P−O(Zn) are almost as short as the formal double bonds P=O. The data related to this are assembled in Table 1 which also includes values from two complexes in the accompanying paper[31].

Table 1 Bonding parameters for the zinc−phosphate interactions

complex	Zn−O	O−P	P=O	Zn−O−P	O−P=O
complexes with four-coordinate zinc					
2c	1.83	1.46	1.45	172	115
4b	1.85	1.48	1.46	155	121
8e	1.85	1.50	1.46	149	119
complexes with intermediate coordination					
7b′	1.91	1.49	1.47	142	120
4c′[a]	1.91	1.49	1.47	147	120
complexes with five-coordinate zinc					
5e·H_2O	2.00	1.50	1.47	136	121
10d[b]	2.07	1.46	1.46	178	123
4e·H_2O[a]	1.95	1.50	1.46	139	118

[a] Structures described in ref.[31]. − [b] Only the terminal phosphate is considered.

The table shows that in all cases there is an almost complete equalization of the formal single and double P−O bonds. Although the "double" bonds are shorter throughout, their shortening amounts to a maximum of 0.04 Å. When referenced against the P−O(R) bond lengths of truely single bonds in the same compounds (1.57−1.60 Å) or the standard value for a true P=O double bond (ca. 1.45 Å[34]) it becomes clear that both P−O bonds in the phosphate complexes described here have close to double bond character as is also observed in various ionic phosphates[34]. This relation to ionic phosphate is underlined by the quite constant and normal values of the O−P=O angles.

The Zn−O bond lengths cannot be used as a measure of the zinc−phosphate interactions. They simply reflect the coordination number of zinc, as made visible by the grouping of compounds in the table. For each of the three groups the range of Zn−O bond lengths is typical, increasing with the coordination number, and all of them are shorter than the value for octahedral zinc (2.15−2.20 Å). Conversely the bond lengths and angles of the P−O entities under consideration do not reflect the coordination number of zinc.

The most variable structural detail in this context is the Zn−O−P angle, showing a spread from 136 to 178°. As the individual values of this angle cannot be related to other bond lengths or angles in the corresponding complexes, they cannot reflect electronic situations, i.e. they must be determined by geometric constraints. This is, however, only obvious for **2c** where the phosphite ligand is "compressed" by the *tert*-butyl substituents of the Tp* ligand. In the other cases it must reflect a combination of intramolecular forces. Altogether the softness of the Zn−O−P angle is the second strong indicater for the rather polar nature of the zinc−phosphate interactions. As such it is reminiscent of the Si−O−Si linkage in silicates and siloxanes which has been discussed in similar terms in the light of modern MO theory[35].

Conclusions

The nucleophilic strength of the "enzyme models" Tp* Zn−OH has been demonstrated for a wide range of esters of phosphorus acids as well as for Tp* ligands of varying polarity and steric bulk. In a favourable case even an alkyl ester could be cleaved. Phenyl esters were of moderate, *p*-nitrophenyl esters of high reactivity. This work has lain the preparative basis for kinetic studies aimed at elucidating mechanistic details of the cleavage reactions.

In terms of enzyme modelling the reactions of the alkyl esters are the only ones of relevance. Phosphate transfer from mononucleotides or phospholipids involves the cleavage of aliphatic phosphate esters, i.e. those which are most difficult to hydrolyze. We have shown that this is in principle possible with Tp*Zn−OH. When an alkyl and a *p*-nitrophenyl ester group are present in a phosphoric acid ester, it is exclusively the latter which is cleaved off. Cleavage reactions of this kind have led here to the new class of metal phosphate complexes containing chiral phosphorus centers.

All cleavage reactions by Tp*Zn−OH have shown that a single zinc ion (or Zn−OH, or Zn−OH_2 unit) is sufficient to perform the hydrolysis. The rates of the cleavage reactions observed here are also not smaller than those reported for some dinuclear model complexes, irrespective of the fact that our reactions are stoichiometric rather than catalytic. All reactions end with the formation of phosphate complexes, allowing the mechanistic conclusion that the metal

ion and the phosphate are in contact during the ester cleavage.

The structure determinations of the zinc phosphate complexes have yielded two important pieces of information. Firstly they indicate that the bonding between zinc and phosphate is quite polar in nature. Secondly they show a variety of coordination geometries and ligand arrangements around zinc which is puzzling at first glance. We are optimistic, however, that a systematic analysis of the structures of all odd-shaped Tp*Zn(X)(Y) complexes will allow a superposition yielding a reaction trajectory for the nucleophilic transformation of substrates by Tp*Zn−OH. We are in the course of further structural and basic kinetic work with the aim of finding this trajectory.

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Experimental Section

General experimental methods and measuring techniques see ref.[36]. The Tp*Zn−OH complexes[25][27][33][37] and the alkylbis(*p*-nitrophenyl) phosphates[38] were prepared according to published procedures. All other reagents were obtained commercially. Solvents were air- and water-free. − IR data (cm^{-1}) were recorded from KBr pellets. − ^{1}H- and ^{31}P-NMR data (δ in ppm, int. TMS, ext. H_3PO_4) were recorded from $CDCl_3$ solutions. All compounds are characterized in Table 2.

2a: 200 mg (0.395 mmol) of **1a** and 43.5 mg (0.395 mmol) of dimethylphosphite in 20 ml of dichloromethane were stirred for 16 h. The solvent was removed in vacuo and the residue crystallized from methanol. Yield 210 mg (90%) of **2a**. − IR: 2554m (BH), 1252vs (P=O). − ^{1}H NMR: 1.41 [s, 27 H, *t*Bu], 2.39 [s, 9 H, Me(pz)], 3.72 [d, J = 12.1 Hz, 3 H, OMe], 5.84 [s, 3 H, H(pz)], 7.10 [d, J = 647 Hz, 1 H, PH]. − ^{31}P NMR: −0.6.

2c: 1.00g (1.44 mmol) of **1c** and 1.20 g (10.9 mmol) of dimethyl phosphite in 30 ml of toluene were stirred for 2 h. The solvent was removed in vacuo, the residue washed with 2 ml of cold methanol and then crystallized from methanol. Yield 0.92 g (81%) of **2c**. − IR: 2537m (BH), 1246s (P=O). − ^{1}H NMR: 1.23 [d, J = 6.9 Hz, 18 H, Me(*i*Pr)], 2.50 [s, 9 H, Me], 2.94 [sept, J = 6.9 Hz, 3 H, CH(*i*Pr)], 3.19 [d, J = 11.8 Hz, 3 H, OMe], 6.21 [s, 3 H, CH(pz)], 6.27 [d, J = 654 Hz, 1 H, PH], 7.31 [d, J = 8.2 Hz, 6 H, Ph(3,5)], 7.60 [d, J = 8.2 Hz, 6 H, Ph(2,6)]. − ^{31}P NMR: 1.0.

3a: As before from 500 mg (0.988 mmol) of **1a** and 231 mg (0.988 mmol) of diphenylphosphite. Repeated crystallization from acetonitrile yielded 430 mg (67%) **3a**. − IR: 2558m (BH), 1259s (P=O). − ^{1}H NMR: 1.41 [s, 27 H, *t*Bu], 2.40 [s, 9 H, Me(pz)], 5.86 [s, 3 H, H(pz)], 7.09 [m, 1 H, Ph], 7.30 [m, 4 H, Ph], 7.38 [d, J = 664 Hz, 1 H, PH]. − ^{31}P NMR: −5.0.

General Procedure for the Cleavage of Aryl Phosphates: Two equivalents of the Tp*Zn−OH complex and one equivalent of the aryl phosphate were stirred in a solvent at room temp. All volatiles were removed in vacuo. Treatment of the residue with acetonitrile or ethanol yielded a solution of the phosphate complex and a residue of the phenolate complex. When already known, the phenolate complex was discarded. Otherwise it was recrystallized and characterized (see below). The solution of the phosphate complex was evaporated to dryness in vacuo and the product recrystallized.

4b: From 300 mg (0.530 mmol) of **1b** and 86.5 mg (0.265 mmol) of triphenyl phosphate in 20 ml of CH_2Cl_2 for 3 d. Crystallization from acetonitrile yielded 73.5 mg (36%) of **4b**. − IR: 2549m (BH), 1230s (P=O). − ^{1}H NMR: 2.52 [s, 9 H, Me(pz)], 6.25 [s, 3 H, H(pz)], 6.86 [d, J = 7.3 Hz, 4 H, Ph(phos(2,6))], 6.89−7.27 [m, 9 H, Ph], 7.24 [m, 6 H, Ph(3,5)], 7.64 [d, J = 7.4 Hz, 6 H, Ph(2,6)]. − ^{31}P NMR: −16.6.

4c: From 300 mg (0.433 mmol) of **1c** and 70.7 mg (0.217 mmol) of triphenyl phosphate in 20 ml of CH_2Cl_2 for 4 d. Crystallization from acetonitrile yielded 91 mg (45%) of **4c**. − IR: 2552m (BH), 1282s (P=O). − ^{1}H NMR: 1.04 [d, ^3J = 6.9 Hz, 18 H, Me(*i*Pr)], 2.53 [s, 9 H, Me(pz)], 2.70 [sept, ^3J = 6.9 Hz, 3 H, H(*i*Pr)], 6.26 [s, 3 H, H(pz)], 6.68 [d, ^3J = 7.5 Hz, 4 H, Ph(phos(2,6))], 6.95 [m, ^3J = 7.5 Hz, 6 H, Ph(phos(3,4,5))], 7.13 [d, ^3J = 8.1 Hz, 6 H, Ph(3,5)], 7.62 [d, ^3J = 8.1 Hz, 6 H, Ph(2,6)]. − ^{31}P NMR: −16.6.

4d: From 500 mg (0.879 mmol) of **1d** and 143 mg (0.438 mmol) of triphenyl phosphate in 40 ml of CH_2Cl_2 for 16 h. Several recrystallizations from acetonitrile were necessary to yield 35 mg (5%) of **4d**. − IR: 2553m (BH), 1261s (P=O). − ^{1}H NMR: 2.57 [s, 9 H, Me(pz)], 6.27 [s, 3 H, H(pz)], 6.56 [d, ^3J = 8.1 Hz, 4 H, Ph(2,6)], 7.05 [m, 6 H, Ph(3,4,5)], 7.05 [dd, ^3J = 7.9 Hz, ^3J = 4.6 Hz, 3 H, Py(5)], 8.11 [d, ^3J = 7.9 Hz, 3 H, Py(6)], 8.21 [d, ^3J = 4.6 Hz, 3 H, Py(4)], 8.67 [s, 3 H, Py(2)]. − ^{31}P NMR: −14.9.

5b: From 300 mg (0.530 mmol) of **1b** and 122 mg (0.265 mmol) of tris(*p*-nitrophenyl)phosphate in 5 ml of CH_2Cl_2 for 24 h. Two recrystallizations from acetonitrile yielded 37.3 mg (16%) of **5b**. − IR: 2554m (BH), 1548s, 1344s (NO), 1256s (P=O). − ^{1}H NMR: 2.56 [s, 9 H, Me(pz)], 6.27 [s, 3 H, H(pz)], 6.71 [d, ^3J = 7.3 Hz, 4 H, Nitr(2,6)], 7.20 [m, 3 H, Ph(4)], 7.35 [m, 6 H, Ph(3,5)], 7.63 [d,

Table 2 Characterization of the new complexes

no.	m.p. [°C]	formula mol. mass	analyses calcd./found C	H	N
2a	142	$C_{25}H_{45}BN_6O_3PZn$ 584.9	51.43 51.92	7.60 7.50	14.40 13.73
2c7	182	$C_{40}H_{50}BN_6O_3PZn$ 770.1	62.39 61.93	6.54 6.51	10.91 10.58
3a	235	$C_{30}H_{46}BN_6O_3PZn \cdot H_2O$ 663.9	54.27 54.32	7.29 7.16	12.66 12.71
4a	256	$C_{36}H_{50}BN_6O_4PZn$ 738.0	58.59 58.36	6.83 6.76	11.39 11.34
4b	166	$C_{42}H_{38}BN_6O_4PZn$ 798.0	63.22 63.99	4.80 4.86	10.53 11.16
4c	197	$C_{51}H_{56}BN_6O_4PZn$ 924.2	66.28 65.55	6.11 6.07	9.10 8.93
4d	179	$C_{39}H_{35}BN_9O_4PZn$ 801.0	47.83 47.26	3.38 3.28	14.22 14.79
5a	246	$C_{36}H_{48}BN_8O_8PZn$ 828.0	52.22 51.62	5.84 5.87	13.59 13.47
5b	179	$C_{42}H_{36}BN_8O_8PZn \cdot CH_3CN$ 888.0 + 41.1	56.89 56.76	4.23 4.18	13.57 13.62
5c	199	$C_{51}H_{54}BN_8O_6PZn \cdot H_2O$ 1014.2 + 18.0	59.34 58.46	5.47 5.56	10.86 10.91
5e	159	$C_{42}H_{41}BN_{11}O_9PZn$ $\cdot 1/2\,CH_2Cl_2$ ($\cdot H_2O$) 951.1 + 42.5	51.38 51.69	4.26 4.10	15.51 15.83
6e	239	$C_{36}H_{35}BN_{10}O_3Zn \cdot CH_2Cl_2$ 731.9 + 84.9	56.51 56.08	4.69 4.78	18.09 18.03
7b′	153	$C_{48}H_{47}BN_9O_6PZn$ 953.1	60.49 60.88	4.97 4.95	13.23 13.32
7c	181	$C_{47}H_{55}BN_7O_6PZn$ 921.2	61.28 61.12	6.02 5.94	10.64 10.54
7e′	178	$C_{48}H_{51}BN_{13}O_6PZn$ 1013.2	56.90 55.14	5.07 4.92	17.97 17.38
8e	171	$C_{42}H_{46}BN_{10}O_6PZn \cdot CH_2Cl_2$ 894.1 + 84.9	52.76 52.50	4.94 5.01	14.31 14.59
10d	120	$C_{102}H_{86}B_2N_{26}O_{34}P_4Zn_3$ 2561.6	47.83 47.26	3.38 3.28	14.22 14.79

^3J = 7.3 Hz, 6 H, Ph(2,6)], 7.89 [d, ^3J = 7.3 Hz, 4 H, Nitr(3,5)]. − ^{31}P NMR: −18.9.

5c: From 300 mg (0.433 mmol) of **1c** and 70.7 mg (0.217 mmol) of tris(*p*-nitrophenyl)phosphate in 10 ml of CH_2Cl_2 for 2 d. Two recrystallizations from acetonitrile yielded 22 mg (10%) of **5c**. − IR: 3130w (H_2O), 2561m (BH), 1553m, 1344s (NO), 1258m (P=O). − ^{1}H NMR: 1.06 [d, ^3J = 6.8 Hz, 18 H, Me(*i*Pr)], 2.55 [s, 9 H, Me(pz)], 2.73 [sept, ^3J = 6.9 Hz, 3 H, H(*i*Pr)], 6.24 [s, 3 H, H(pz)], 6.69 [d, ^3J = 8.2 Hz, 4 H, Nitr(3,5)], 7.21 [d, ^3J = 8.2 Hz, 6 H, Ph(3,5)], 7.57 [d, ^3J = 8.2 Hz, 6 H, Ph(2,6)], 7.87 [d, ^3J = 8.2 Hz, 4 H, Nitr(2,6)]. − ^{31}P NMR: −19.4.

7b′: From 500 mg (0.884 mmol) of **1b** and 168 mg (0.442 mmol) of ethylbis(*p*-nitrophenyl) phosphate in 10 ml of $CHCl_3$ for 24 h. Recrystallization from methanol/acetonitrile (1:1). Yield 129 mg (31%) of **7b′**. − IR: 2551m (BH), 1544s, 1343s (NO), 1251s (P=O). − ^{1}H NMR: 0.99 [t, ^3J = 7.1 Hz, 3 H, Me(OEt)], 2.49 [s, 12 H, Me(py), Me(pz(a))], 3.65 [dq, ^3J = 7.1 Hz, ^3J = 7.1 Hz, 2 H, CH_2(OEt)], 5.82 [s, 1 H, H(pz(a))], 6.26 [s, 3 H, H(pz)], 7.04−7.57 [m, 16 H, Ph], 7.59 [d, ^3J = 7.3 Hz, 6 H, Ph(2,6)], 8.00 [d, ^3J = 7.2 Hz, 2 H, Nitr(3,5)]. − ^{31}P NMR: −8.2.

7c: From 233 mg (0.336 mmol) of **1c** and 62.0 mg (0.168 mmol) of ethylbis(*p*-nitrophenyl) phosphate in 5 ml of $CHCl_3$ for 48 h. Crystallization from acetonitrile yielded two crystal fractions which had to be sorted manually (**6c** and **7c**). Yield 43 mg (28%) of **7c**. − IR: 2551m (BH), 1550m, 1344s (NO), 1256s (P=O). − ^{1}H NMR: 0.84 [t, ^3J = 7.1 Hz, 3 H, Me(OEt)], 1.15 [d, ^3J = 6.9 Hz, 18 H, Me(*i*Pr)], 2.55 [s, 9 H, Me(pz)], 2.79 [sept, ^3J = 6.9 Hz, 3 H, H (*i*Pr)], 3.46 [dq, ^3J = 7.1 Hz, ^3J = 7.1 Hz, 2 H, CH_2(OEt)], 6.23 [s, 3 H, H(pz)], 6.74 [d, ^3J = 7.2 Hz, 2 H, Nitr(2,6)], 7.29 [d, ^3J = 8.2 Hz, 6 H, Ph(3,5)], 7.61 [d, ^3J = 8.2 Hz, 6 H, Ph(2,6)], 7.84 [d, ^3J = 7.2 Hz, 2 H, Nitr(3,5)]. − ^{31}P NMR: −12.0.

7e′: From 312 mg (0.550 mmol) of **1e** and 101 mg (0.275 mmol) of ethylbis(*p*-nitrophenyl) phosphate in 5 ml of $CHCl_3$ for 48 h. Recrystallization from acetonitrile. Yield 107 mg (46%) of **7e′**. − IR: 2537m (BH), 1545m, 1342s (NO), 1248s (P=O). − ^{1}H NMR: 1.02 [t, ^3J = 7.1 Hz, 3 H, Me(OEt)], 2.34 [s, 12 H, Me(py), Me-(py(a))], 2.55 [s, 12 H, Me(pz)], 3.67 [dq, ^3J = 7.1 Hz, ^3J = 7.1 Hz, 2 H, CH_2(OEt)], 5.91 [s, 1 H, H(pz(a))], 6.29 [s, 3 H, H(pz)], 7.08 [d, ^3J = 8.0 Hz, 3 H, Py(5)], 7.12 [d, 1 H, Py(5(a))], 7.25 [d, ^3J = 7.2 Hz, 2 H, Nitr(2,6)], 7.64 [dd, ^3J = 8.0 Hz, ^4J = 2.2 Hz, 1 H, Py(6(a))], 7.93 [dd, ^3J = 8.0 Hz, ^4J = 2.1 Hz, 3 H, Py(6)], 8.13 [d, ^3J = 7.2 Hz, 2 H, Nitr(3,5)], 8.55 [d, ^4J = 2.1 Hz, 1 H, Py(2(a))], 8.59 [d, ^4J = 2.1 Hz, 3 H, Py(2)]. − ^{31}P NMR: −8.3.

8e: From 500 mg (0.818 mmol) of **1e** and 175 mg (0.414 mmol) of cyclohexylbis(*p*-nitrophenyl) phosphate in 20 ml of CH_2Cl_2 for 16 h. Recrystallization from acetonitrile/dichloromethane (4:1). Yield 278 mg (75%) of **8e**. − IR: 2570m (BH), 1544m, 1340s (NO), 1251s (P=O). − ^{1}H NMR: 0.91 [m, 2 H, Cy(4)], 1.28 [m, 4 H, Cy(3), C(5)], 1.36 [m, 4 H, Cy(2), Cy(6)], 2.44 [s, 9 H, Me(py)], 2.56 [s, 9 H, Me(pz)], 3.61 [m, ^3J = 7.6 Hz, 1 H, Cy(1)], 6.31 [s, 3 H, H(pz)], 7.09 [d, ^3J = 9.1 Hz, 2 H, Nitr(2,6)], 7.27 [d, ^3J = 8.0 Hz, 3 H, Py(5)], 8.03 [dd, ^3J = 8.0 Hz, ^4J = 2.1 Hz, 3 H, Py(6)], 8.09 [d, ^3J = 9.1 Hz, 2 H, Nitr(3,5)], 8.63 [d, ^4J = 2.1 Hz, 3 H, Py(2)]. − ^{31}P NMR: −11.3.

General Procedure for the Condensation Reactions: The reagents were combined in 20 ml of dichloromethane and stirred for one day. The solvent was removed in vacuo and the residue crystallized from acetonitrile.

Table 3 Crystallographic details

	2c	**4b**	**5e**·H_2O	**7b′**	**8e**	**10d**
formula	$C_{40}H_{50}BN_6O_3PZn$ · CH_3OH	$C_{42}H_{38}BN_6O_4PZn$	$C_{42}H_{41}BN_{11}O_9PZn$ · CH_3CN · CH_3CN	$C_{48}H_{47}BN_9O_6PZn$ · H_2O	$C_{42}H_{46}BN_{10}O_6PZn$ · 1/2 CH_2Cl_2	$C_{51}H_{43}BN_{13}O_{17}P_2$-$Zn_{1.5}$ · CH_3CN · 5 · 1/2 CH_3CN
mol. mass	802.1	797.9	1012.6	971.1	936.5	1424.5
cryst. from	methanol	acetonitrile	acetonitrile	dichloromethane/ benzene	dichloromethane/ acetonitrile	acetonitrile
crystal size [mm]	0.6 × 0.4 × 0.2	1.20 × 1.10 × 0.60	0.6 × 0.6 × 0.4	0.80 × 0.60 × 0.60	0.5 × 0.4 × 0.2	0.5 × 0.4 × 0.2
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	4	2	2	2	2	2
a [Å]	17.685(2)	10.988(4)	10.5440(4)	12.8873(6)	12.0108(6)	12.328(2)
b [Å]	14.015(1)	11.324(7)	13.9212(8)	13.4892(12)	12.8637(10)	14.050(6)
c [Å]	18.795(3)	16.255(14)	18.299(3)	17.4426(11)	15.489(2)	20.417(4)
α [°]	90	103.81(5)	101.970(7)	95.04(3)	71.162(7)	108.37(2)
β [°]	114.80(1)	91.51(5)	102.873(6)	91.95(3)	89.353(6)	97.38(2)
γ [°]	90	90.50(4)	101.036(4)	118.44(3)	80.276(5)	104.43(3)
V [Å^3]	4228.8(9)	1963.2(22)	2480.8(4)	2646.0(3)	2230.0(3)	3166.8(16)
d (calc.) [g·cm^{-3}]	1.23	1.35	1.36	1.22	1.40	1.49
d (obs.) [g·cm^{-3}]	1.21	1.31	1.30	1.18	1.35	1.44
temp. (K)	293(2)	293(2)	293(2)	293(2)	293(2)	200(2)
μ (Mo-$K\alpha$) [mm^{-1}]	0.662	0.716	0.593	0.549	0.705	0.707
Θ range [°]	2.5−26.3	3.1−26.0	2.5−26.0	2.8−26.0	2.3−26.0	3.1−26.0
hkl range	$-22\le h\le 19$ $-17\le k\le 0$ $0\le l\le 23$	$-13\le h\le 0$ $-13\le k\le 13$ $-20\le l\le 20$	$0\le h\le 13$ $-17\le k\le 16$ $-22\le l\le 21$	$-15\le h\le 15$ $-16\le k\le 16$ $-21\le l\le 0$	$-14\le h\le 0$ $-15\le k\le 15$ $-19\le l\le 19$	$0\le h\le 14$ $-17\le k\le 16$ $-24\le l\le 24$
refl. measd.	8828	8079	10277	10698	9168	12308
indep. refl.	8564	7663	9726	10342	8726	11729
obs. refl. (I>2σ(I))	4550	6922	6894	7855	6798	7581
parameters	478	496	640	622	578	998
refl. refined	8534	7662	9715	10337	8718	11702
R (obs. refl.): $R1$, $wR2$	0.079, 0.196	0.044, 0.122	0.046, 0.124	0.061, 0.203	0.046, 0.116	0.075, 0.163
R (all refl.): $R1$, $wR2$	0.176, 0.280	0.050, 0.131	0.088, 0.152	0.087, 0.237	0.073, 0.137	0.142, 0.215
residual el. density e/ Å^3	+1.1 −0.7	+0.8 −0.7	+0.6 −0.3	+1.1 −0.3	+0.9 −0.5	+1.2 −2.1

9a: From 500 mg (0.988 mmol) of **1a** and 215 mg (0.988 mmol) of diphenylphosphinic acid. Yield 620 mg (88%) of **9a** which was not analytically pure and could not be purified by repeated crystallizations. − IR: 2547m (BH), 1218vs (P=O). − ^{1}H NMR: 1.26 [s, 27 H, *t*Bu], 2.37 [s, 9 H, Me(pz)], 5.81 [s, 3 H, H(pz)], 7.32 [m, 6 H, Ph], 8.05 [m, 4 H, Ph]. − ^{31}P NMR: +17.8.

4a: From 200 mg (0.395 mmol) of **1a** and 98.7 mg (0.395 mmol) of diphenyl phosphate. Yield 260 mg (88%) of **4a**. − IR: 2552m (BH), 1290vs (P=O). − ^{1}H NMR: 1.41 [s, 27 H, *t*Bu], 2.39 [s, 9 H, Me(pz)], 5.84 [s, 3 H, H(pz)], 7.03 [m, 2 H, Ph], 7.19 [m, 8 H, Ph]. − ^{31}P NMR: −17.3.

5a: From 200 mg (0.395 mmol) of **1a** and 134 mg (0.395 mmol) of bis(*p*-nitrophenyl) phosphate. Yield 290 mg (75%) of **5a**. − IR: 252m (BH), 1537s, 1345s (NO), 1302vs (P=O). − ^{1}H NMR: 1.38 [s, 72 H, *t*Bu], 2.41 [s, 9 H, Me(pz)], 5.88 [s, 3 H, H(pz)], 7.42 [d, J = 8.9 Hz, 4 H, Ph], 8.17 [d, J = 8.9 Hz, 4 H, Ph].

4b: From 300 mg (0.530 mmol) of **1b** and 133 mg (0.530 mmol) of diphenyl phosphate. Yield 368 mg (87%).

5b: From 250 mg (0.442 mmol) of **1b** and 150 mg (0.442 mmol) of bis(*p*-nitrophenyl) phosphate. Yield 310 mg (79%).

5e: From 500 mg (0.818 mmol) of **1e** and 278 mg (0.817 mmol) of bis(*p*-nitrophenyl) phosphate. Yield 694 mg (91%) of **5e**. − IR: 3378w (H_2O), 2554m (BH), 1518s, 1344s (NO), 1258m (P=O). − ^{1}H NMR: 2.36 [s, 9 H, Me(py)], 2.58 [s, 9 H, Me(pz)], 6.31 [s, 3 H, H(pz)], 6.92 [d, ^3J = 9.1 Hz, 4 H, Nitr(2,6)], 7.13 [d, ^3J = 8.0 Hz, 3 H, Py(5)], 7.89 [dd, ^3J = 8.0 Hz, ^4J = 2.3 Hz, 3 H, Py(6)], 8.02 [d, ^3J = 9.1 Hz, 4 H, Nitr(3,5)], 8.66 [d, ^4J = 2.3 Hz, 3 H, Py(2)]. − ^{31}P NMR: −17.2.

Preparation of **10d**: 500 mg (0.879 mmol) of **1d** and 299 mg (0.879 mmol) of bis(*p*-nitrophenyl) phosphate in 40 ml of CH_2Cl_2 were stirred for 16 h. The solvent was removed in vacuo, the residue picked up in 50 ml of hot acetonitrile, filtered hot and left to crystallize at room temp.. After 3 days 330 mg (44%) of **10d** had precipitated. − IR: 2551m (BH), 1517s, 1345s (NO), 1257m (P=O). − ^{1}H NMR: 2.55 [s, 18 H, Me(pz)], 6.56 [s, 6 H, H(pz)], 7.35 [d, ^3J = 9.3 Hz, 16 H, Nitr(3,5)], 7.54 [dd, ^3J = 7.9 Hz, ^3J = 4.8 Hz, 6 H, Py(5)], 7.97 [ddd, ^3J = 7.9 Hz, ^4J = 2.2 Hz, ^4J = 1.6 Hz, Py(6)], 8.15 [d, ^3J = 9.3 Hz, 16 H, Nitr(2,6)], 8.64 [dd, ^3J = 4.8 Hz, ^4J = 1.6 Hz, 6 H, Py(4)], 8.79 [d, ^4J = 2.2 Hz, 6 H, Py(2)]. − ^{31}P NMR: −13.4.

Structure Determinations[39]: Diffraction data were recorded with the ω/2θ technique on a Nonius CAD4 diffractometer fitted with a molybdenum tube (K_α, λ = 0.7107 Å) and a graphite monochromator. No absorption corrections were applied. The structures were solved with direct methods and refined anisotropically with the SHELX program suite.[40] Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.2 times those of their attached atoms. Parameters were refined against F^2. The R values are defined as $R_1 = \Sigma F_o - F_c/\Sigma F_o$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$. Drawings were produced with SCHAKAL.[41] Table 3 lists the crystallographic data.

☆ Dedicated to Professor *Achim Müller* on the occasion of his 60th birthday.

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