Zinc Complexes of Condensed Phosphates, 4[‡]

Diphosphate−Zinc Complexes with Encapsulating Tripodal Coligands

Alexandra Müller-Hartmann[a] and Heinrich Vahrenkamp*[a]

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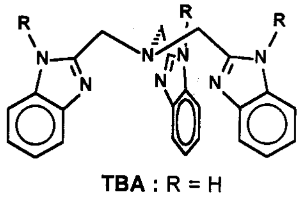
Tris(benzimidazolylmethyl)amine (TBA) and tris(pyrazolyl)borate (Tp) ligands have been used to prepare ternary zinc complexes with triorganodiphosphates (R_3POP^-), triorganomethylenediphosphonates (R_3PCP^-), and diorganodiphosphates (R_2POP^{2-}). The complex types $[(TBA)Zn(R_3POP)]^+$ and $[(TBA)Zn(R_3PCP)]^+$ have been assigned as containing trigonal-bipyramidal zinc with monodentate diphosphate ligands. By X-ray structure determination, the complex type $[(TBA)Zn(R_2POP)]$ has been found to contain the same ZnN_4O coordination pattern, which has also been assigned to the dinuclear complexes $[(TBA)Zn(R_2POP)Zn(TBA)]^{2+}$ incorporating the diphosphates as bis-monodentate bridging ligands. The same monodentate and bis-monodentate attachment of the diphosphates, but with tetrahedral zinc in a ZnN_3O environment, has been identified in the pyrazolylborate complexes $TpZn(R_3POP)$ and $TpZn(R_2POP)ZnTp$.

Introduction

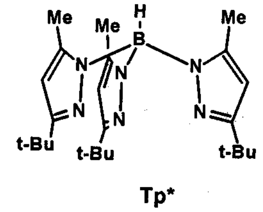
This paper is the fourth and final one in a series on zinc complexes of oligophosphates.[1−3] Our main motivation for this work has stemmed from the importance of metal-containing enzymes in biological phosphate transfer to and from inorganic pyrophosphate, ADP, ATP, and the like, which is among the most frequently observed biological processes. In the first papers of the series,[2,3] we made reference to the biochemical and biostructural background of the work and surveyed the literature on the associated coordination chemistry. While there have been numerous solution studies[4] and structure determinations[5] of metal−ATP species, literature on other metal−oligophosphate compounds is scarce. In the coordination chemistry of zinc, which is of particular interest to us, we are not aware of any studies on soluble complex species other than those of nucleotides.[4,6−8]

Our aim in this field, as before,[9,10] has been to learn about function from structure. We set out to delineate all possible coordination modes between zinc ions and oligophosphate species. In order to avoid typical lattice structures and coordination polymers, which cannot be biorelevant, we reduced the functionality of both the phosphates and the zinc species. The former was achieved by esterification, i.e. rather than pyrophosphate we used diorgano- and triorganodiphosphates. The latter was achieved by reducing the number of available coordination sites at zinc through the use of chelating coligands. We found that bidentate[3] and even tridentate coligands[1] still allow the oligophosphates to become polydentate towards one zinc ion. A further reduction in the functionality at zinc was thus deemed necessary.

In this paper, we describe the use of tripodal coligands for this purpose. As such, we used tris(benzimidazolylmethyl)amine (TBA) and its benzyl derivative TBA*, which we have previously found to be a reliable enforcer of trigonal-bipyramidal coordination in (TBA)Zn−X complexes.[11,12] Likewise, the 3-substituted tris(pyrazolyl)borate (Tp) ligands are known to be tetrahedral enforcers,[13] particularly the *tert*-butyl-substituted Tp*.[14] It thus had to be established whether the enforcing qualities of these tripodal coligands would be sufficiently strong to limit the oligophosphates to monodentate coordination towards one zinc ion.



TBA : R = H
TBA*: R = benzyl



Tp*

The oligophosphates used were the same as those used previously. The methylenediphosphonate PCP and the diphosphates PO^1 and PO^2, both having three organic substituents, were expected to be monofunctional and possibly monodentate. The diorganodiphosphates POP^1−POP^4 were expected to be difunctional, and we know[1,3] that their preferred bonding mode is as OPOPO chelate ligands, which should be unlikely in the presence of the tripodal coligands. Thus, we hoped to limit the oligophosphates to monodentate coordination towards one zinc ion and possibly bis-monodentate coordination as bridging ligands in dinuclear complexes.

[‡] Part 3: Ref.[1]

[a] Institut für Anorganische und Analytische Chemie der Universität Freiburg,
Albertstraße 21, 79104 Freiburg, Germany
Fax: (internat.) + 49-(0)761/203-6001
E-mail: vahrenka@uni-freiburg.de

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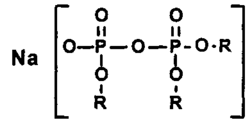
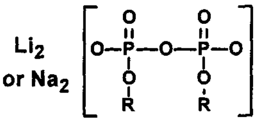
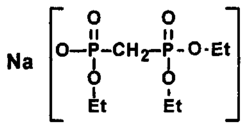


PO¹: R = benzyl
PO²: R = p-Br-benzyl



POP¹: R = benzyl
POP²: R = p-tolyl
POP³: R = p-t-Bu-phenyl
POP⁴: R = p-Cl-phenyl

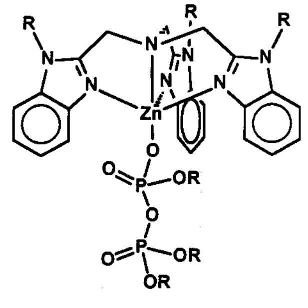


PCP

(TBA)Zn Complexes of Triorganodiphosphates

Both TBA ligands were combined with zinc perchlorate and the three monofunctional phosphates PO^1, PO^2, and PCP. In all six cases, complexes with a 1:1:1 composition, **1−6**, were produced as perchlorate salts. While crystals of **1−6** suitable for X-ray analysis could not be obtained, FAB mass spectra of **1**, **2**, and **5** and an ESI mass spectrum of **3**, each showing the parent ion of the respective cationic complex as the only prominent peak, supported the assignment of the complexes as monomolecular. This makes it likely that the oligophosphates are monodentate and that the coordination geometry is trigonal-bipyramidal as indicated below.

$[(TBA)Zn(PO^1)]^+$ **1**
$[(TBA)Zn(PO^2)]^+$ **2**
$[(TBA)Zn(PCP)]^+$ **3**
$[(TBA^*)Zn(PO^1)]^+$ **4**
$[(TBA^*)Zn(PO^2)]^+$ **5**
$[(TBA^*)Zn(PCP)]^+$ **6**



The IR data for the P−O vibrations (Table 1) show a characteristic shift of the 1100 cm^{-1} band, attributable to $\nu_s(PO_2)$, to lower wavenumbers (cf. refs.[1,3]), but yield no structural information. In contrast, the ^{31}P NMR data are quite informative. All the phosphate ligands in **1−6** are unsymmetrical with typical shifts for the ^{31}P nuclei and typical coupling constants. Upon coordination to zinc, one of the two ^{31}P resonances is shifted upfield by 2−5 ppm while the other remains unchanged, and the coupling constants become characteristically smaller. This is in full agreement with the structural assignments. Together with the structure determinations of **8** and **10** (see below), these observations lend support to the statement that in all complexes **1−6** the oligophosphate ligands are monodentate.

Table 1. IR data (KBr, cm^{-1}) and ^{31}P NMR data (DMSO, rel. to H_3PO_4, ppm/Hz) of **1−6** and their phosphate constituents

	ν(PO)	δ/J(^{31}P)
Na[PO^1]	1277 vs, 1136 m	−11.5, −10.9/21.1
Na[PO^2]	1273 vs, 1133 s	−11.6, −11.0/21.1
Na[PCP]	1237 s, 1054 vs	−6.0, +26.5/5.4
[**1**]ClO$_4$	1277 s, 1110 s	−15.0, −11.5/17.0
[**2**]ClO$_4$	1279 s, 1120 vs	−14.8, 11.6/16.6
[**3**]ClO$_4$	1224 s, 1041 vs	−8.1, +24.3/5.1
[**4**]ClO$_4$	1282 s, 1119 s	−15.1, −11.4/16.4
[**5**]ClO$_4$	1285 s, 1122 s	−14.8, −11.5/17.1
[**6**]ClO$_4$	1235 s, 1039 vs	−7.8, +26.1/5.1

(TBA)Zn Complexes of Diorganodiphosphates

Having established that the phosphates can be monodentate in (TBA)Zn complexes, it seemed likely that the bifunctional POP^{2-} ligands would also have this ability, being monodentate in (TBA)Zn(POP) complexes and bis-monodentate in dinuclear $[(TBA)Zn(POP)Zn(TBA)]^{2+}$ complexes. Both alternatives could be realized. Of the eight possibilities in each case, combining the given TBA and POP ligands, four could be realized for the mononuclear complexes and five for the dinuclear complexes. The mononuclear and dinuclear combinations are almost mutually exclusive, i.e. for a given set of TBA and POP only one of the two alternatives seems to be stable.

Mononuclear complexes were isolated only for the unsubstituted coligand TBP, but with all four POP ligands. Compounds **7−10** could be unambiguously identified as mononuclear and molecular entities, e.g. by X-ray structure determinations of **8** and **10** and through the FAB mass spectrum of **9**. Among them, **8** and **10** are the only species for which the dinuclear alternative (**11**, **12**, see below) also exists. However, **8** and **10** could not be prepared in suitably pure form from 1:1:1 mixtures of zinc salts, TBA, and [POP]$^{2-}$. They were obtained from solutions of **11** and **12** when these were left to stand for prolonged periods in attempts to obtain crystals of the latter for structure determinations.

$(TBA)Zn(POP^n)$

7: $n = 1$ **8**: $n = 2$ **9**: $n = 3$ **10**: $n = 4$

In those cases where the syntheses of the dinuclear complexes were successful, they proceeded straightforwardly from 2:2:1 mixtures of zinc perchlorate, the TBA ligand, and the POP salt. Proof of the dinuclear nature of complexes **11−15** and disproof of their existence as coordination polymers was obtained from a FAB mass spectrum of **11** and an ESI mass spectrum of **14**, both of which showed the parent ion of the complex cation as the prominent peak.

Attempts to grow crystals of **11−15** for structure determinations were unsuccessful.

$(TBA)Zn(POP^{n})Zn(TBA)$

11: $n = 2$ **12**: $n = 4$

$(TBA^{*})Zn(POP^{n})Zn(TBA^{*})$

13: $n = 2$ **14**: $n = 3$ **15**: $n = 4$

The IR and ^{31}P NMR spectra of complexes **7−15** (Table 2) yield less information than might have been expected. The strong and characteristic IR bands due to the P−O vibrations are shifted by small amounts, as observed previously.[1,3] A typical feature arising from the coordination of the diphosphates is the pronounced decrease in the intensity of the $\nu_s(PO_2)$ band. The ^{31}P NMR signals undergo the usual upfield shifts of 2−4 ppm upon coordination of the phosphates to zinc. Again,[1,3] in those cases where the diphosphates should be unsymmetrical (complexes **7−10**), there is only one ^{31}P resonance rather than two. As before, the explanation for this must be that in solution the complexes are labile and undergo rapid exchange of their coordinated and uncoordinated P−O donor functions.

Table 2. IR data (KBr, cm^{-1}) and ^{31}P NMR data (DMSO, rel. to H_3PO_4, ppm) of **7−15** and their phosphate constituents

	$\nu_{as}(PO_2)$	$\nu_s(PO_2)$	$\delta(^{31}P)$
$Na_2[POP^1]$	1270/1239	1141	−8.5
$Li_2[POP^2]$	1270/1230	1140	−15.3
$Li_2[POP^3]$	1249/1220	1138	−15.5
$Li_2[POP^4]$	1254/1223	1155	−16.0
7	1279/1223		−11.0
8	1278/1225	1123	−17.1
9	1263/1230		−16.8
10	1257/1235		−17.6
[**11**]$(ClO_4)_2$	1279/1258		−17.8
[**12**]$(ClO_4)_2$	1279/1265		−19.1
[**13**]$(ClO_4)_2$	1280/1224	1160	−17.8
[**14**]$(ClO_4)_2$	1277		−17.9
[**15**]$(ClO_4)_2$	1282/1236	1161	−19.1

Structure determinations of **8** and **10** were necessary to eliminate any doubts concerning the structural assignments of the complexes in this class. They verified the monodentate coordination of the diphosphates in the 1:1:1 complexes **7−10**. By analogy and spectroscopic similarity, they furthermore supported the assignment of bis-monodentate coordination in the 2:2:1 complex cations **11−15**. The molecular structures of **8** (Figure 1) and **10** (Figure 2) are quite similar in terms of the environment of the zinc ions. However, they show conformational differences, specifically in the orientation of the phenyl rings at the phosphates. Moreover, in **8** there are two independent complex molecules in the asymmetric unit, which again differ conformationally, most notably in their non-bonding Zn···O(P) distances.

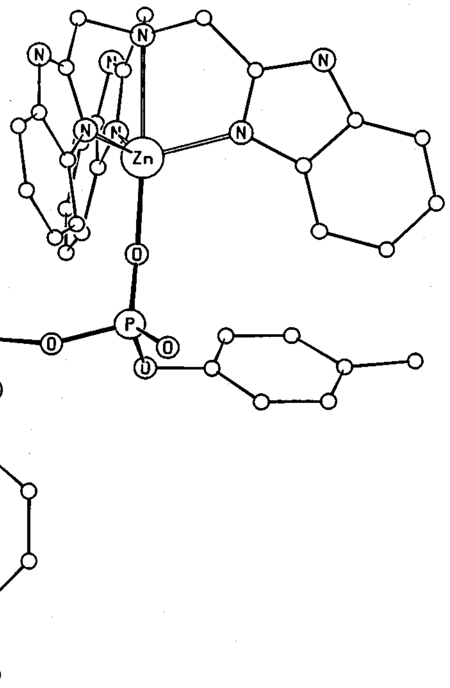


Figure 1. Molecular structure of **8**; selected bond lengths [Å] and angles [°] for both independent molecules: Zn−N(ax) 2.490(4), 2.474(4), Zn−N(eq) 2.030−2.039(4), 2.030−2.044(4), Zn−O 1.969(4), 1.979(4), Zn···O 4.109(4), 3.550(4), P−O(Zn) 1.485(4), 1.480(4), P=O 1.474−1.479(4), 1.475−1.484(4), P−O(P) 1.595−1.617(4), 1.591−1.619(4); Zn−O−P 164.0(3), 156.7(2), P−O−P 136.2(3), 135.7(2)

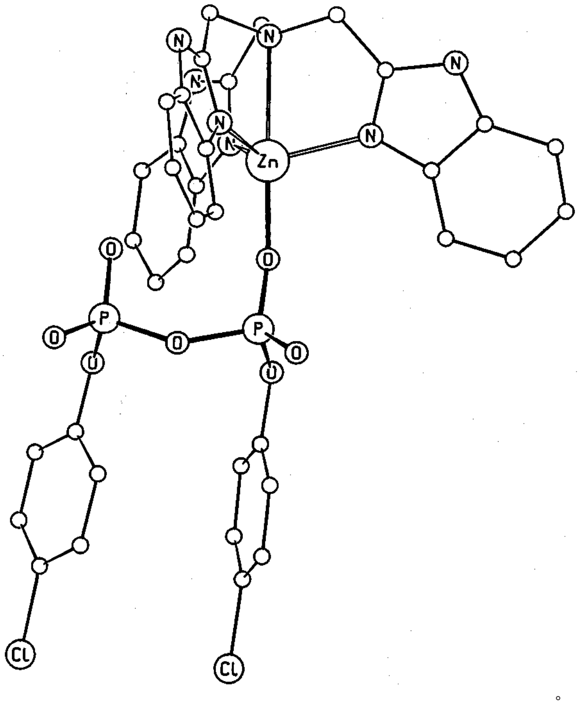


Figure 2. Molecular structure of **10**; selected bond lengths [Å] and angles [°]: Zn−N(ax) 2.49(2), Zn−N(eq) 2.01−2.03(2), Zn−O 1.97(1), Zn···O 3.48(1), P−O(Zn) 1.48(2), P=O 1.44−1.47(2), P−O(P) 1.60, 1.62(2); Zn−O−P 165(1), P−O−P 136(1)

The coordination of the zinc ions in **8** and **10** can be described as trigonal-bipyramidal. As usual for TBA complexes,[11,12] the elongation of the axial Zn−N bond is so pronounced and the equatorial Zn−N bonds are so clearly bent away from the Zn−O bond (102−107°) that a tetrahedral description (ignoring the axial Zn−N interaction) is also appropriate. Accordingly, the Zn−O bond is almost as short as in tetrahedral zinc−phosphate complexes.[15,16] The diphosphates are coordinated to zinc in a clearly monodentate fashion. Although one P−O donor function on the second phosphorus atom is oriented towards the zinc ion, its Zn−O distance (3.5−4.1 Å) is outside the range for bonding. Monodentate coordination of oligophosphates to zinc is unprecedented. There are, however, examples in $(NH_3)_5Co^{III}$−oligophosphate chemistry.[17,18] All bonding parameters of the diphosphates in **8** and **10** correspond to those of the same phosphates in the chelating mode and have been discussed in the preceding papers.[1,3] The most important observation in this respect concerns the formal P=O bond lengths, which do not change when one, two, or three of these P=O units are coordinated to zinc, thus indicating that the Zn−O interactions are quite ionic.

(Tp)Zn Complexes

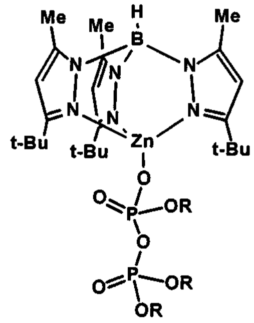
The pyrazolylborate ligand Tp* could be expected to confine the zinc ion to a tetrahedral coordination. The products obtained following condensation reactions of Tp*Zn−OH with the diphosphoric acids $HP_2O_4(OR)_3$ and $H_2P_2O_5(OR)_2$ seemed to confirm this. The monofunctional triorganodiphosphates H[PO^1] and H[PO^2] yielded the mononuclear complexes **16** and **17**, while 2:1 reactions of Tp*Zn−OH with the difunctional diorganodiphosphates led to the dinuclear complexes **18** and **19**.

Tp*Zn(PO^1)	Tp*Zn(PO^2)
16	**17**
Tp*Zn(POP^1)ZnTp*	Tp*Zn(POP^2)ZnTp*
18	**19**

The molecular nature of **16−19** is evident from their solubilities in non-polar solvents. Their nuclearity was confirmed by a FAB mass spectrum of **17** and an ESI mass spectrum of **18**. The IR bands due to the P−O vibrations (Table 3) show little variation as compared to those of the anionic diphosphates (cf. Tables 1 and 2). The most significant information is provided by the ^{31}P NMR spectra recorded in non-polar solvents (Table 3). In all four cases, a considerable upfield shift (7−8 ppm) of the ^{31}P resonance of the zinc-coordinated phosphate unit to higher field is seen, while that of the uncoordinated phosphate unit in **16** and **17** remains practically unchanged. Thus, there is good evidence that the phosphates in **16** and **17** are indeed monodentate and that those in **18** and **19** are bis-monodentate. Together with the evidence from the structure determinations of **8** and **10**, the structural assignments given below for **16** and **17** seem appropriate.

Table 3. IR data (KBr, cm^{-1}) and ^{31}P NMR data ($CDCl_3$, rel. to H_3PO_4, ppm/Hz) of **16−19**

	ν(PO)	δ/*J*(^{31}P)
16	1290, 1187, 1137	−11.8, −18.3/11.2
17	1279, 1185, 1136	−11.6, −18.3/10.0
18	1278, 1186	−15.3
19	1292, 1187, 1123	−23.6



Conclusions

This paper concludes the series of investigations on the coordination of condensed phosphates to zinc. Throughout the series, phosphates with organic substituents have been employed, such that they have some relation to the most important biological oligophosphates, i.e. nucleotides. The available coordination sites at zinc have been controlled by using “naked” zinc ions,[2] bidentate,[3] tridentate,[1] and encapsulating tripodal coligands (this paper). The oligophosphates have been found to be mono-, di-, tri-, and possibly tetradentate. Three coordination sites at zinc had to be blocked in order to prevent the formation of coordination polymers. Furthermore, considerable steric hindrance had to be enforced to ensure purely monodentate coordination. The most commonly encountered coordination mode is that of an OPOPO chelate ligand.

In terms of the catalytic activation of the oligophosphates by zinc for hydrolytic reactions, the monodentate and chelating bidentate coordination modes seem to be relevant. Both provide one point of attachment per phosphate unit, thereby activating the P−O function, and leave coordination sites at the zinc or space in the coordination sphere for the hydrolytic nucleophile. We favor the monodentate attachment, as we have already presented preparative[15,16] and mechanistic[9,10] evidence in support of it. This paper has proved its existence in the environment of encapsulating ligands, which resembles most closely that in enzymes.

An aim of this series of investigations (refs.[1−3] and this paper) was to provide structural information related to catalytic events. Accordingly, conditions favoring stoichiometric or catalytic hydrolyses of the oligophosphates were carefully avoided. Nevertheless, some hydrolytic decomposition was observed, underlining the reactivity of the intermediate zinc−aqua and zinc−hydroxide species in this respect.

Thus, the natural extension of this work will be catalytic studies, in continuation of our previous work on the hydrolyses of pyrophosphates and sulfonatophosphates.[15]

Experimental Section

General: For general working and measuring procedures, see ref.[19] The lithium and sodium salts and the free acids of the triorgano-[20,21] and diorganodiphosphates,[2,20,22] as well as the TBP[11] coligands and Tp*Zn−OH,[23] were stored under inert conditions. During the course of the reactions no precautions were taken to prevent the access of moisture. All organic phosphates are potentially toxic and were handled accordingly.

1: A solution of TBA (100 mg, 0.245 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (91 mg, 0.25 mmol) in ethanol (10 mL) was added to a solution of Na[PO^1] (115 mg, 0.245 mmol) in boiling ethanol (30 mL). After stirring for 15 min., the precipitate was filtered off and recrystallized from hot ethanol to yield 151 mg (58%) of [**1**]·ClO_4, m.p. 170 °C. − $C_{45}H_{42}ClN_7O_{11}P_2Zn{\cdot}2H_2O$ (1019.5 + 36.0): calcd. C 51.20, H 4.39, N 9.29, Zn 6.19; found C 51.51, H 3.97, N 9.17, Zn 5.68. − ^1H NMR ([D$_6$]DMSO): δ = 3.32 (s, 4 H, H_2O), 4.53 (s, 6 H, CH_2), 5.08 (d, *J* = 7.4 Hz, 4 H, CH_2), 5.25 (d, *J* = 6.4 Hz, 2 H, CH_2), 7.12 (t, *J* = 8.0 Hz, 3 H, Ph), 7.28 (m, 15 H, Ph), 7.40 (m, 3 H, Ph), 7.56 (d, *J* = 8.4 Hz, 3 H, Ph), 8.43 (d, *J* = 8.4 Hz, 3 H, Ph), 14.12 (s, 3 H, NH).

2: Prepared in the same manner as **1** from TBA (58 mg, 0.14 mmol), $Zn(ClO_4)_2{\cdot}6H_2O$ (53 mg, 0.14 mmol), and Na[PO^2] (100 mg, 0.14 mmol). Yield 107 mg (60%) of [**2**]·ClO_4; m.p. 142 °C. − $C_{45}H_{39}Br_3ClN_7O_{11}P_2Zn$ (1256.3): calcd. C 43.02, H 3.13, N 7.80, Zn 5.20; found C 42.76, H 3.17, N 7.30, Zn 5.30. − ^1H NMR ([D$_6$]DMSO): δ = 4.53 (s, 6 H, CH_2), 5.05 (d, *J* = 7.9 Hz, 4 H, CH_2), 5.18 (d, *J* = 7.3 Hz, 2 H, CH_2), 7.1−7.5 (m, 18 H, Ph), 7.56 (d, *J* = 8.1 Hz, 3 H, Ph), 8.38 (d, *J* = 7.9 Hz, 3 H, Ph), 13.53 (s, 3 H, NH).

3: Prepared in the same manner as **1** from TBA (79 mg, 0.19 mmol), $Zn(ClO_4)_2{\cdot}6H_2O$ (72 mg, 0.19 mmol), and Na[PCP] (55 mg, 0.19 mmol). Yield 114 mg (72%) of [**3**]·ClO_4; m.p. 156 °C. − $C_{31}H_{38}ClN_7O_{10}P_2Zn$ (831.5): calcd. C 44.78, H 4.61, N 11.79, Zn 7.86; found C 42.90, H 4.57, N 11.02, Zn 6.29. − ^1H NMR ([D$_6$]DMSO): δ = 1.13 (m, 9 H, CH_3), 2.47 (m, 2 H, PCH_2P), 3.95 (q, *J* = 7.2 Hz, 4 H, OCH_2), 4.14 (q, *J* = 7.2 Hz, 2 H, OCH_2), 4.53 (s, 6 H, CH_2), 7.32 (m, 6 H, Ph), 7.56 (m, 3 H, Ph), 8.52 (m, 3 H, Ph), 13.42 (s, 3 H, NH).

4: Prepared in the same manner as **1** from Na[PO^1] (69 mg, 0.15 mmol), $Zn(ClO_4)_2{\cdot}6H_2O$ (54 mg, 0.15 mmol), and TBA* (100 mg, 0.15 mmol). Yield 92 mg (48%) of [**4**]·ClO_4; m.p. 110 °C. − $C_{66}H_{60}ClN_7O_{11}P_2Zn{\cdot}H_2O$ (1290.1 + 18.0): calcd. C 60.60, H 4.78, N 7.50, Zn 5.00; found C 60.13, H 4.31, N 8.16, Zn 4.23. − ^1H NMR ([D$_6$]DMSO): δ = 3.31 (s, 2 H, H_2O), 4.61 (s, 6 H, CH_2), 5.06 (d, *J* = 7.4 Hz, 4 H, OCH_2), 5.27 (d, *J* = 8.0 Hz, 2 H, OCH_2), 5.53 (s, 6 H, CH_2), 7.30 (m, 36 H, Ph), 7.61 (d, *J* = 8.8 Hz, 3 H, Ph), 8.46 (d, *J* = 8.8 Hz, 3 H, Ph).

5: Prepared in the same manner as **1** from Na[PO^2] (104 mg, 0.15 mmol), $Zn(ClO_4)_2{\cdot}6H_2O$ (55 mg, 0.15 mmol), and TBA* (100 mg, 0.15 mmol). Yield 114 mg (51%) of [**5**]·ClO_4; m.p. 116 °C. − $C_{66}H_{57}Br_3ClN_7O_{11}P_2Zn$ (1526.7): calcd. C 51.92, H 3.76, N 6.42, Zn 4.28; found C 51.49, H 3.87, N 6.39, Zn 4.00. − ^1H NMR ([D$_6$]DMSO): δ = 4.60 (s, 6 H, CH_2), 5.03 (d, *J* = 8.1 Hz, 4 H, OCH_2), 5.18 (d, *J* = 6.9 Hz, 2 H, OCH_2), 5.51 (s, 6 H, CH_2), 7.1−7.5 (m, 33 H, Ph), 7.60 (d, *J* = 8.3 Hz, 3 H, Ph), 8.45 (m, 3 H, Ph).

6: Prepared in the same manner as **1** from Na[PCP] (13 mg, 0.05 mmol), $Zn(ClO_4)_2{\cdot}6H_2O$ (17 mg, 0.05 mmol), and TBP* (31 mg, 0.05 mmol). Yield 40 mg (79%) of [**6**]·ClO_4; m.p. 200 °C. − $C_{52}H_{56}ClN_7O_{10}P_2Zn$ (1101.8): calcd. C 56.68, H 5.12, N 8.90, Zn 5.93; found C 55.72, H 5.58, N 8.62, Zn 5.93. − ^1H NMR ([D$_6$]DMSO): δ = 0.83 (t, *J* = 7.0 Hz, 6 H, CH_3), 1.22 (t, *J* = 7.9 Hz, 3 H, CH_3), 2.33 (t, *J* = 20.0 Hz, 2 H, PCH_2P), 3.65 (q, *J* = 7.2 Hz, 4 H, OCH_2), 4.14 (q, *J* = 7.0 Hz, 2 H, OCH_2), 4.62 (s, 6 H, CH_2), 5.49 (s, 6 H, CH_2), 7.1−7.3 (m, 21 H, Ph), 7.60 (m, 3 H, Ph), 8.51 (m, 3 H, Ph).

7: A solution of Na$_2$[POP^1] (30 mg, 0.075 mmol) in boiling methanol (40 mL) was added to a solution of TBA (30 mg, 0.075 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (28 mg, 0.075 mmol) in boiling methanol (10 mL). The mixture was filtered while hot, slowly allowed to cool to room temp., and kept in a desiccator to allow slow removal of the solvent. 45 mg (71%) of **7**, m.p. 250 °C (dec.), was isolated. − $C_{38}H_{35}N_7O_7P_2Zn{\cdot}CH_3OH$ (829.1 + 32.0): calcd. C 54.40, H 4.56, N 11.39, Zn 7.59; found C 53.47, H 4.45, N 11.26, Zn 7.50. − ^1H NMR ([D$_6$]DMSO): δ = 3.27 (s, 3 H, CH_3OH), 4.40 (s, 6 H, CH_2), 4.90 (m, 4 H, OCH_2), 7.19 (m, 16 H, Ph), 7.50 (d, *J* = 7.2 Hz, 3 H, Ph), 8.18 (d, *J* = 7.0 Hz, 3 H, Ph), 13.16 (s, 3 H, NH).

8: **11** (130 mg, 0.084 mmol) in a mixture of acetonitrile (30 mL), water (5 mL), and toluene (3 mL) was kept in a flask fitted with a solvent-permeable plastic seal for 2 months until most of the solvent had evaporated. A single crystal for structure determination was taken from the resulting crude precipitate. After filtration, washing with a small volume of methanol, and drying in vacuo, 85 mg (27%) of impure **8** remained; m.p. 220 °C (dec.). − $C_{38}H_{35}N_7O_7P_2Zn$ (829.1): calcd. C 55.05, H 4.26, N 11.83, Zn 7.89; found C 48.00, H 3.82, N 10.16, Zn 7.29. − ^1H NMR ([D$_6$]DMSO): δ = 2.12 (s, 6 H, CH_3), 4.33 (s, 6 H, CH_2), 6.84 (d, *J* = 8.3 Hz, 4 H, Ph), 6.99 (d, *J* = 8.3 Hz, 4 H, Ph), 7.22 (m, 6 H, Ph), 7.52 (d, *J* = 6.9 Hz, 3 H, Ph), 8.10 (d, *J* = 6.3 Hz, 3 H, Ph).

9: Prepared in the same manner as **7** from Li$_2$[POP^3] (62 mg, 0.13 mmol), TBA (107 mg, 0.26 mmol), and $Zn(ClO_4)_2{\cdot}6H_2O$ (98 mg, 0.26 mmol). Yield 29 mg (24%) of **9**; m.p. 240 °C (dec.). − $C_{44}H_{47}N_7O_7P_2Zn$ (913.2): calcd. C 57.87, H 5.19, N 10.74, Zn 7.16; found C 54.32, H 4.99, N 9.57, Zn 7.00. − ^1H NMR ([D$_6$]DMSO): δ = 1.15 (s, 18 H, *t*Bu), 4.30 (s, 6 H, CH_2), 7.00 (d, *J* = 8.8 Hz, 4 H, Ph), 7.08 (d, *J* = 8.8 Hz, 4 H, Ph), 7.25 (m, 6 H, Ph), 7.52 (m, 3 H, Ph), 8.15 (m, 3 H, Ph).

10: Prepared in the same manner as **8** from **12** (39 mg, 0.025 mmol) within 3 months. Yield 7 mg (32%) of **10**, which, according to NMR analysis, was not pure. − ^1H NMR ([D$_6$]DMSO): δ = 4.42 (s, 6 H, CH_2), 7.05 (d, *J* = 9.1 Hz, 4 H, Ph), 7.11 (d, *J* = 9.1 Hz, 4 H, Ph), 7.25 (m, 6 H, Ph), 7.53 (m, 3 H, Ph), 8.10 (m, 3 H, Ph), 13.11 (s, 3 H, NH).

11: A solution of Li$_2$[POP^2] (55 mg, 0.12 mmol) in boiling ethanol (20 mL) was added to a solution of TBA (100 mg, 0.245 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (91 mg, 0.25 mmol) in boiling ethanol (20 mL). After stirring for 10 min, the clear solution was slowly allowed to cool to room temp. 130 mg (70%) of [**11**]·$(ClO_4)_2$ was precipitated, which was washed with cold ethanol and dried in vacuo; m.p. 260 °C (dec.). − $C_{62}H_{56}Cl_2N_{14}O_{15}P_2Zn_2{\cdot}3H_2O$ (1500.8 + 54.1): calcd. C 47.89, H 4.02, N 12.61, Zn 8.41; found C 46.94, H 3.63, N 12.18, Zn 7.77. − ^1H NMR ([D$_6$]DMSO): δ = 2.12 (s, 6 H, CH_3), 3.37 (s, 6 H, H_2O), 4.48 (s, 12 H, CH_2), 6.85 (d, *J* = 8.2 Hz, 4 H, Ph), 7.06 (d, J = 8.2 Hz, 4 H, Ph), 7.21 (t, J = 7.4 Hz, 12 H, Ph), 7.49 (d, J = 7.8 Hz, 6 H, Ph), 8.19 (d, J = 7.2 Hz, 6 H, Ph).

12: Prepared in the same manner as **11** from $Li_2[POP^4]$ (16 mg, 0.064 mmol), TBA (52 mg, 0.13 mmol), and $Zn(ClO_4)_2\cdot 6H_2O$ (48 mg, 0.13 mmol). The precipitate was recrystallized from hot ethanol to yield 39 mg (38%) of [**12**]$\cdot(ClO_4)_2$; m.p. 250 °C (dec.). − $C_{60}H_{50}Cl_4N_{14}O_{15}P_2Zn_2\cdot 3H_2O$ (1541.7 + 54.1): calcd. C 45.16, H 3.54, N 12.29, Zn 8.19; found C 45.05, H 3.27, N 11.28, Zn 7.57. − ^1H NMR ([D$_6$]DMSO): δ = 3.42 (s, 6 H, H_2O), 4.51 (s, 12 H, CH_2), 7.2−6.9 (m, 20 H, Ph), 7.46 (d, J = 8.2 Hz, 6 H, Ph), 8.29 (d, J = 7.4 Hz, 6 H, Ph).

13: Prepared in the same manner as **11** from $Li_2[POP^2]$ (33 mg, 0.074 mmol), TBA* (100 mg, 0.15 mmol), and $Zn(ClO_4)_2\cdot 6H_2O$ (55 mg, 0.15 mmol). The precipitate was recrystallized from hot ethanol to yield 134 mg (87%) of [**13**]$\cdot(ClO_4)_2$; m.p. 161 °C. − $C_{104}H_{92}Cl_2N_{14}O_{15}P_2Zn_2\cdot 2H_2O$ (2041.6 + 36.0): calcd. C 60.12, H 4.66, N 9.44, Zn 6.29; found C 59.71, H 4.43, N 9.53, Zn 6.33. − ^1H NMR ([D$_6$]DMSO): δ = 2.08 (s, 6 H, CH_3), 3.36 (s, 4 H, H_2O), 4.61 (s, 12 H, CH_2), 5.45 (s, 12 H, CH_2), 6.75 (d, J = 7.7 Hz, 4 H, Ph), 6.88 (d, J = 7.7 Hz, 4 H, Ph), 7.11 (m, 12 H, Ph), 7.23 (m, 30 H, Ph), 7.50 (d, J = 7.7 Hz, 6 H, Ph), 8.23 (d, J = 7.7 Hz, 6 H, Ph).

14: Prepared in the same manner as **11** from $Li_2[POP^3]$ (46 mg, 0.097 mmol), TBA* (132 mg, 0.195 mmol), and $Zn(ClO_4)_2\cdot 6H_2O$ (73 mg, 0.19 mmol). Yield 105 mg (51%) of [**14**]$\cdot(ClO_4)_2$; m.p. 174 °C. − $C_{110}H_{104}Cl_2N_{14}O_{15}P_2Zn_2$ (2125.7): calcd. C 62.15, H 4.93, N 9.22, Zn 6.15; found C 60.49, H 4.92, N 8.94, Zn 6.45. − ^1H NMR ([D$_6$]DMSO): δ = 1.22 (s, 18 H, *t*Bu), 4.60 (s, 12 H, CH_2), 5.46 (s, 12 H, CH_2), 6.9−7.2 (m, 50 H, Ph), 7.51 (d, J = 8.1 Hz, 6 H, Ph), 8.27 (d, J = 8.1 Hz, 6 H, Ph).

15: Prepared in the same manner as **11** from $Li_2[POP^4]$ (15 mg, 0.035 mmol), TBA* (47 mg, 0.070 mmol), and $Zn(ClO_4)_2\cdot 6H_2O$ (26 mg, 0.070 mmol). Recrystallization from hot ethanol yielded 64 mg (88%) of [**15**]$\cdot(ClO_4)_2$; m.p. 180 °C (dec.). − $C_{102}H_{86}Cl_4N_{14}O_{15}P_2Zn_2$ (2082.5): calcd. C 58.83, H 4.16, N 9.42, Zn 6.28; found C 58.63, H 4.26, N 9.44, Zn 5.62. − ^1H NMR ([D$_6$]DMSO): δ = 4.67 (s, 12 H, CH_2), 5.54 (s, 12 H, CH_2), 7.17 (m, 50 H, Ph), 7.53 (m, 6 H, Ph), 8.22 (m, 6 H, Ph).

16: A freshly prepared solution of $H[PO^1]$ (49 mg, 0.12 mmol) in dichloromethane (6 mL) was added to a solution of Tp*Zn−OH (56 mg, 0.12 mmol) in dichloromethane (12 mL). After stirring for 1 d, the mixture was filtered and the filtrate was concentrated to dryness. The residue was taken up in the minimum volume of dichloromethane and this solution was layered with *n*-hexane (25 mL). After a few days at 0 °C, 38 mg (34%) of **16** had separated, which was washed with cold acetonitrile (1 mL); m.p. 42 °C. − $C_{45}H_{61}BN_6O_7P_2Zn$ (936.2): calcd. C 57.74, H 6.57, N 8.98, Zn 6.98; found C 57.85, H 6.15, N 8.89, Zn 6.52. − ^1H NMR ($CDCl_3$): δ = 1.29 (s, 27 H, *t*Bu), 2.35 (s, 9 H, CH_3), 5.18 (d, J = 6.2 Hz, 4 H, OCH_2), 5.30 (d, J = 6.4 Hz, 2 H, OCH_2), 5.79 (s, 3 H, pz), 7.30 (m, 15 H, Ph).

17: Prepared in the same manner as **16** from $H[PO^2]$ (102 mg, 0.15 mmol) and Tp*Zn−OH (75 mg, 0.15 mmol). Yield 44 mg (25%) of **17**; m.p. 112 °C. − $C_{45}H_{58}BBr_3N_6O_7P_2Zn$ (1172.9): calcd. C 46.08, H 4.98, N 7.17, Zn 5.57; found C 46.16, H 4.97, N 6.99, Zn 5.60. − ^1H NMR ($CDCl_3$): δ = 1.30 (s, 27 H, *t*Bu), 2.38 (s, 9 H, CH_3), 5.12 (m, 4 H, OCH_2), 5.25 (d, J = 6.7 Hz, 2 H, OCH_2), 5.83 (s, 3 H, pz), 7.20 (d, J = 8.5 Hz, 2 H, Ph), 7.26 (d, J = 8.5 Hz, 4 H, Ph), 7.43 (m, 6 H, Ph).

18: Prepared in the same manner as **16** from $H_2[POP^1]$ (36 mg, 0.11 mmol) and Tp*Zn−OH (119 mg, 0.24 mmol). Yield 38 mg (27%) of **18**; m.p. 214 °C. − $C_{62}H_{94}B_2N_{12}O_7P_2Zn_2$ (1333.9): calcd. C 55.83, H 7.10, N 12.60, Zn 9.80; found C 55.99, H 7.05, N 12.17, Zn 9.99. − ^1H NMR ($CDCl_3$): δ = 1.30 (s, 54 H, *t*Bu), 2.37 (s, 18 H, CH_3), 5.64 (m, 4 H, OCH_2), 5.78 (s, 6 H, pz), 7.26 (m, 10 H, Ph).

19: Prepared in the same manner as **16** from $H_2[POP^2]$ (77 mg, 0.20 mmol) and Tp*Zn−OH (218 mg, 0.43 mmol). Yield 150 mg (58%) of **19**; m.p. 235 °C. − $C_{62}H_{94}B_2N_{12}O_7P_2Zn_2$ (1333.9): calcd. C 55.83, H 7.10, N 12.60, Zn 9.80; found C 54.97, H 7.09, N 12.19,

Table 4. Crystallographic details

	8	10
Empirical formula	$C_{38}H_{35}N_7O_7PZn\cdot CH_3CN\cdot 4H_2O$	$C_{36}H_{29}Cl_2N_7O_7P_2Zn\cdot 2C_2H_5OH\cdot 3H_2O$
Molecular mass	829.1 + 82.1 + 72.1	869.9 + 92.1 + 54.1
Crystal size [mm]	0.6 × 0.5 × 0.3	0.3 × 0.3 × 0.3
Space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
a [Å]	13.941(7)	11.560(4)
b [Å]	18.074(6)	13.400(2)
c [Å]	20.522(5)	16.967(4)
α [°]	67.81(2)	72.29(2)
β [°]	73.85(3)	88.00(2)
γ [°]	84.93(4)	67.32(2)
V [Å^3]	4598(3)	2300(1)
d(calcd) [gcm^{-3}]	1.41	1.46
μ(Mo-K_α) [mm^{-1}]	0.67	0.79
hkl range	h: −13 to 0	h: −10 to 9
	k: −17 to 17	k: −12 to 0
	l: −20 to 19	l: −15 to 14
Measured reflections	9473	3477
Independent reflections	8986	3317
Observed refl. [$I > 2\sigma(I)$]	7303	2498
Parameters	722	349
Refined reflections	8980	3317
R_1 (obsd. refl.)	0.049	0.103
wR_2 (all refl.)	0.147	0.374
Residual electron density	+0.7	+0.9
[e/Å^3]	−0.4	−0.9

Zn 10.01. − ^{1}H NMR ($CDCl_3$): δ = 1.34 (s, 54 H, *t*Bu), 2.27 (s, 6 H, CH_3), 2.37 (s, 18 H, CH_3), 5.79 (s, 6 H, pz), 6.99 (d, J = 8.4 Hz, 4 H, Ph), 7.40 (d, J = 8.4 Hz, 4 H, Ph).

Structure Determinations:[24] The selected crystals were taken directly from the reaction solutions and used without drying in vacuo. They were immersed in fluorinated polyether oil and immediately placed in the nitrogen stream of the diffractometer's cooling system. Diffraction data were recorded at ca. −100 °C using the $\omega/2\theta$ technique with a Nonius CAD4 diffractometer fitted with a molybdenum tube (Mo-K_α, $\lambda = 0.7107$ Å) and a graphite monochromator. Empirical absorption corrections based on ψ scans were applied. The structures were solved by direct methods and refined anisotropically with the SHELX program suite.[25] Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.5 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.[26] The crystallographic data are collected in Table 4.

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[24] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-141968 (for **8**) and -141969 (for **10**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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