Zinc Complexes of Condensed Phosphates, 3[‡]

Diphosphate−Zinc Complexes with Tridentate Coligands

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Keywords: Zinc / Phosphates / Organic pyrophosphates / Methylene diphosphonates / Phosphatases

Diorganodiphosphates (POP^{2-}) and a triorgano-methylenediphosphonate (PCP^{-}) have been combined with zinc salts and the tridentate ligands L [L = bis(benzimidazolylmethyl)amine, bis(2-pyridylmethyl)amine, triazacyclononane, trimethyltriazacyclononane, and (dimethylaminoethyl)(2-pyridylmethyl)amine]. The resulting ternary complexes have been found to contain four-, five-, or six-coordinate zinc. Four-coordinate zinc has been identified in the complex types [L·Zn(PCP)]$^{+}$ and [L·Zn(POP)Zn·L]$^{2+}$, containing monodentate phosphate ligands. Five-coordinate zinc has been found in the complexes [L·Zn(POP)] with chelating diphosphate ligands. Six-coordinate zinc has been observed in the complex type [L·Zn(POP)·H_2O] containing chelating diphosphates and in the complex type [L·Zn(POP)]$_2$ in which the diphosphates act as tridentate bridging ligands. In a few cases, hydrolytic cleavage of the diphosphates resulted in the isolation of the trinuclear complexes [(L·Zn)$_3$(ROPO$_3$)$_2$] HPO$_4$ containing triply-bridging monophosphates.

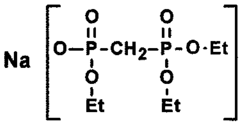
Introduction

In the preceding paper[1] we outlined our motivation for studying the coordination chemistry of zinc with condensed phosphates and the associated scientific background. The main impetus is the importance of metal-containing systems (catalysts, enzymes) in the hydrolytic cleavage of oligophosphates, which is of relevance in the technical as well as in the biological world. Metal catalysis involves coordination of the substrates to the metals, and hence bonding modes of oligophosphates toward metals should provide an insight into possible catalytic pathways for their hydrolysis.

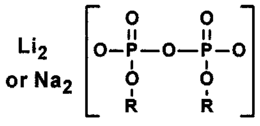
The literature on metal−oligophosphate complexes[1] is largely confined to studies of ATP and inorganic pyrophosphates. Specifically for the biologically important metal zinc, there have been only a few reports and even less structure determinations.[1] We have started to close this gap by carrying out a systematic study, in which the number of available coordination sites at zinc as well as the number of available donor functions on the phosphates have been varied. So far, we have reported on oligophosphate complexes of zinc without coligands[2] and with bidentate coligands.[1] In this paper, we present our results for zinc complexes with tridentate coligands. The succeeding paper[3] will report on systems with encapsulating tripodal coligands.

Phosphates and Coligands

Diphosphates with both P−C−P and P−O−P linkages have been employed. The triethyl methylenediphosphonate PCP[4] was chosen to represent minimal donor qualities since it possesses only one P−O function with a formal negative charge. The diorganodiphosphates POP^1−POP^5 [2,5,6] have two negative charges. They have already[1] been shown to act as chelating bidentate as well as chelating plus bridging tridentate ligands. They could furthermore be expected to act as monodentate or bis-monodentate bridging ligands.

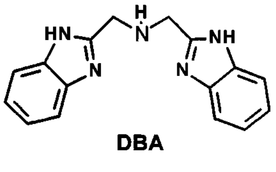


PCP

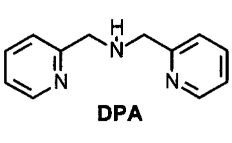


POP^1: R = benzyl
POP^2: R = phenyl
POP^3: R = p-tolyl
POP^4: R = p-t-Bu-phenyl
POP^5: R = p-Cl-phenyl

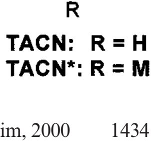
As coligands, we chose tridentate systems containing only nitrogen donors, all of which can be derived from ethylenediamine. DBA,[7] DPA,[8] TACN,[9] and TACN*[10] are well established in coordination chemistry. PDEA was newly prepared by NaBH$_4$ reduction of the corresponding Schiff base.



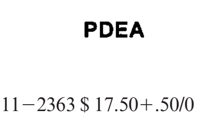
DBA



DPA



TACN: R = H
TACN*: R = Me



PDEA

[‡] Part 2: Ref.[1]

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As in the previous paper,[1] we sort the resulting zinc complexes according to product types rather than according to phosphates or coligands. We observed three different product types and one class of decomposition products.

Four-Coordinate Complexes

It was anticipated that the PCP ligand might only bind in a monodentate fashion. Its combination with the coligands DBA and DPA seems to verify this. With zinc perchlorate, the products **1** and **2** were obtained. While the spectroscopic data (see below) of these and all the other complexes yield no other information than the compositions of the products, support for the mononuclear nature of **1** and **2** was obtained from the ESI mass spectrum of **1**, which showed the parent ion.

[(DBA)Zn(PCP)]ClO_4 [(DPA)Zn(PCP)]ClO_4

1 **2**

Likewise, a presumably bis-monodentate coordination was found for the POP ligands in three cases. All three involved the pyridine-containing coligands DPA or PDEA. The resulting complexes were **3**, **4**, and **5**. The main evidence for their constitutions was again provided by ESI-MS. The MS of compound **4** showed the parent ion of the dinuclear complex cation.

[(L)Zn(POP)Zn(L)]$(ClO_4)_2$

3: L = DPA, POP = POP^3
4: L = DPA, POP = POP^4
5: L = PDEA, POP = POP^1

As none of the compounds proved to be suitable for X-ray structure determination, the structural assignments of **1−5** as tetrahedral complexes with ZnN_3O coordination are not unambiguous. As seen before,[1] the diphosphate ligands can be chelating, leading to five-coordinate zinc. They may also be bridging,[1] giving the same result. While there is some likelihood that the PCP ligand in **1** and **2** is indeed bridging, this should not be the case in **3−5**. The latter would require that the one POP ligand uses four of its P−O functions to generate two chelate rings. Although we have discussed this previously, it is unrealistic and would produce noticeable ^{31}P NMR shifts. The ^{31}P NMR data of **3−5** (see below) are, however, normal, showing the typical small shifts for the attachment of one zinc ion.

Five-Coordinate Complexes

The most typical coordination mode for the POP ligands seems to be the chelating one with six-membered Zn(O-POPO) chelate rings.[1] In combination with the tridentate coligands, this would lead to five-coordinate complexes, a very common coordination motif in zinc chemistry. Surprisingly, this could only be verified for the coligand DBA. In combination with the five POP ligands, it produced the complexes **6−10**. Otherwise, only DPA and POP^1 could be combined in this fashion to yield **11**. Proof of the nature of **6−11** as monomolecular species in solution and in the gas phase was obtained from the ESI mass spectrum of **10**, which showed a prominent peak attributable to the [**10**Na]$^+$ ion.

(DBA)Zn(POP^n) (DPA)Zn(POP^1)

6–10: $n = 1–5$ **11**

Proof of the monomolecular nature in the solid state was obtained by a structure determination of **8** (see Figure 1). The coordination of zinc in **8** is, to a good approximation, trigonal-bipyramidal; the central N atom of DBA and one O atom occupy the axial positions. While the axial Zn−N distance is typically long, the equatorial and axial Zn−O distances differ by just 0.015 Å. The essentially ionic nature of the Zn−O interactions can again[1] be derived from the fact that the P−O bond lengths for the coordinated and uncoordinated P−O functions are virtually identical. The geometrical parameters of the chelating POP ligand compare well with those in other zinc complexes (see below and ref.[1]). Otherwise, structures of trigonal-bipyramidal complexes of DBA or POP ligands are rare, two examples being the $CuCl_2$ complex of DBA[11] and a Cu complex of thiamine pyrophosphate.[12]

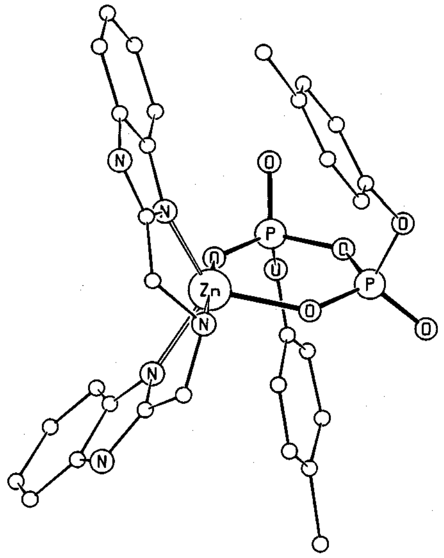

Figure 1. Molecular structure of **8**; selected bond lengths [Å] and angles [°]: Zn−O 2.020(3), 1.987(3), Zn−N 2.018(3), 2.373(3), 2.007(3), P−O(Zn) 1.473(3), 1.494(3), P=O 1.484(4), 1.473(3), P−O(P) 1.602(3), 1.590(3), P−O(C) 1.526(4), 1.594(4); Zn−O−P 134.0(2), 133.1(2), P−O−P 136.5(2), O−Zn−N(axial) 178.4(1)

Six-Coordinate Complexes

The triazacyclononane ligands are well known to form octahedral metal complexes. In this study, they were found to do so without exception. The TACN* coligand could be combined with POP^1, POP^2, and POP^3 in the 1:1:1 zinc complexes **12−14**. These were found to be hydrates like **6** and **7**. However, in contrast to these cases, where the water molecules are co-crystallized solvent, the complexes **12−14** contain coordinated water. This was shown by an X-ray structure determination of **12**. In addition, on the basis of slightly different ^{1}H NMR patterns for the POP ligands, complexes **6–8** and complexes **12–14** can be divided into two separate groups.

(TACN*)Zn(POP^n) · H_2O

12–14: $n = 1–3$

The structure of **12** (Figure 2) contains zinc in a slightly distorted octahedral environment. The diphosphate ligand adopts the chelating mode, and all the salient structural details correspond to those discussed already (see above and ref.[1]). The features of the Zn–TACN* coordination correspond to those in the cationic complex [(TACN*)$_2$Zn$_2$(μ-OAc)$_2$(μ-OH)].[13]

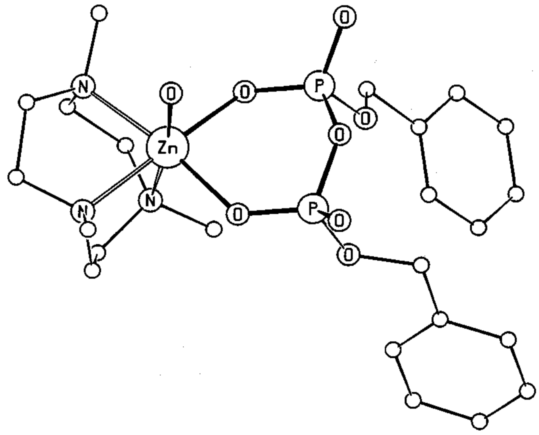

Figure 2. Molecular structure of **12**; selected bond lengths [Å] and angles [°]: Zn–N 2.206, 2.190, 2.178(2), Zn–O(P) 2.055, 2.059(2), Zn–O(H_2O) 2.115(2), P–O(Zn) 1.491, 1.490(2), P=O 1.492, 1.482(2), P–O(P) 1.599, 1.625(2), P–O(C) 1.590, 1.589(2); Zn–O–P 130.4, 131.5(1), P–O–P 131.0(1)

Two other complexes of 1:1:1 composition isolated as hydrates were **15** and **16**. On the basis of their spectral data, these might have been grouped with **12–14**. However, their structure determinations showed that in these cases the water molecules are not coordinated to zinc. Instead, the metal achieves octahedral coordination by using a third P–O function of each diphosphate as a bridging donor, thereby linking two molecular units to a dinuclear complex. We have observed this bonding mode before in dinuclear complexes with five-coordinate zinc.[1] It is difficult to explain why the two alternatives of octahedral coordination (coordinated water or diphosphate bridging), both of which exist in the presence of water, are preferred in specific examples.

(TACN)Zn(POP^1) (PDEA)Zn(POP^2)

15 **16**

The basic structural features of **15** (Figure 3) and **16** (Figure 4) are very similar, and they also resemble those of the previously reported complexes of this type with five-coordinate zinc.[1] The bridging makes the diphosphates tridentate ligands. The dinuclear entities have inversion centers, hence the zinc–diphosphate chelate rings are arranged in a parallel fashion, and the eight-membered rings created by the dimerization are in the chair conformation. In both cases, the Zn–O bond to the bridging oxygen is significantly shorter than the two Zn–O bonds in the chelate ring. For the diphosphate ligands, there is no noticeable change in their geometrical parameters or bond lengths as compared to the purely chelating mode. The distortion of the ZnO_3N_3 octahedra is comparably small in both the hydrate **12** and the dimers **15** and **16**. Compared to the related five-coordinate zinc complexes (see above and ref.[1]), all the Zn–O and Zn–N bonds are elongated.

Trinuclear Monophosphate Complexes

Although the pyrophosphates used in this study were found to be quite inert towards hydrolytic cleavage, in the presence of zinc salts they sometimes underwent hydrolysis.

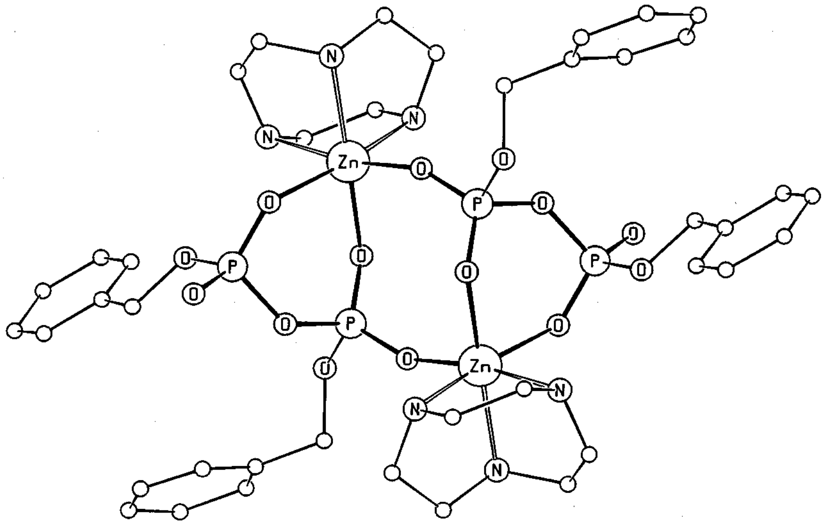

Figure 3. Molecular structure of **15**; selected bond lengths [Å] and angles [°]: Zn–N 2.201, 2.165, 2.169(3), Zn–O(br) 2.027(3), Zn–O(ch) 2.114, 2.099(3), P–O(Zn) 1.476, 1.473, 1.490(3), P=O 1.484(3), P–O(P) 1.612, 1.597(3), P–O(C) 1.600, 1.581(3); Zn–O–P 131.0, 127.8(2), P–O–P 131.5(2)

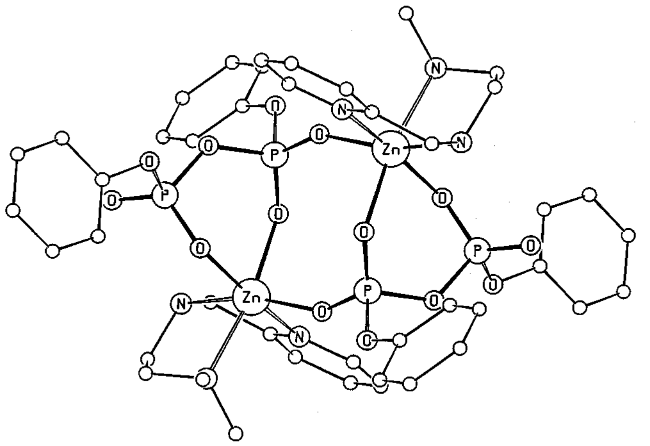

Figure 4. Molecular structure of **16**; selected bond lengths [Å] and angles [°]: Zn−N 2.171, 2.184, 2.221(2), Zn−O(br) 2.016(2), Zn−O(ch) 2.144, 2.112(2), P−O(Zn) 1.485, 1.487, 1.472(2), P=O 1.463(2), P−O(P) 1.609, 1.611(2), P−O(C) 1.603, 1.605(2); Zn−O−P 130.4, 126.1(1), P−O−P 126.8(1)

This normally meant that work-up of the reaction mixtures failed, which is the reason why the series of compounds presented here is incomplete. In two cases, however, the hydrolysis products were isolated as zinc complexes, the trinuclear nature of which was established by structure determinations. Both these complexes, **17** and **18**, were derived from the coligand DPA. They have $HPO_4{}^{2-}$ counterions, as was verified by ^{31}P NMR spectroscopy.

$[(\mathbf{D}PA\cdot Zn)_3(TolOPO_3)_2]\ HPO_4$ $[(\mathbf{D}PA\cdot Zn)_3(ClC_6H_4OPO_3)_2]\ HPO_4$

17 **18**

Figure 5 depicts the structure of the trinuclear cation of complex **17**. The structure of **18** is quite similar, but will not be discussed here because of its mediocre quality. The $Zn_3(ROPO_3)_2$ units give rise to a structural motif that is seemingly unknown in the coordination chemistry of phosphates. The $P_2(OZnO)_3$ framework, having roughly trigonal symmetry and roughly planar POZnOP wings, is that of bicyclo[3.3.3]undecane. In contrast, the coordination of three metal−ligand units to one phosphate is not uncommon, as exemplified by the zinc complex $\{[(12\text{-ane-}N_4)Zn]_3(ROPO_3)\}^{4+}$.[14] The zinc ions in **17** and **18** are in a severely distorted trigonal-bipyramidal environment. Their Zn−O and Zn−N bond lengths fall in the characteristic ranges for ZnO_2N_3 complexes. The P−O bonds of the P−O−Zn linkages are somewhat longer than in those cases where there is only one zinc ion per phosphate unit (see above). The $HPO_4{}^{2-}$ ions in the lattice lie beyond the range for coordination to zinc.

Spectroscopy

The ^1H NMR spectra (see Experimental Section) identify the coligands in the complexes and indicate that the POP ligands are bound in a symmetrical fashion in all cases. This does not conform with the solid-state structures of **15** and **16** and suggests that these complexes exist as solvated monomers or are fluxional in solution.

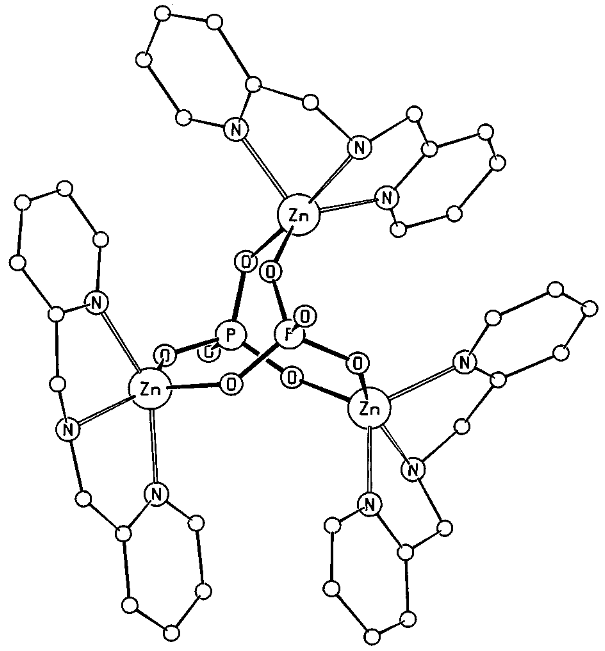

Figure 5. Structure of the zinc complex in **17** (tolyl groups omitted for clarity); important bond lengths [Å] and angles [°]: Zn−O(ax) 1.962−2.002(4), Zn−O(eq) 1.939−1.954(4), Zn−N(ax) 2.148−2.237(6), Zn−N(eq) 2.073−2.149(6), P−O(Zn) 1.493−1.520(4); O−Zn−O 96.8, 105.2, 115.0(2), Zn−O−P 123.5−156.0(3), O−P−O 112.3−114.4(3)

The IR bands in the P−O region show irregular coordination shifts (see Table 1). The $\nu_{as}(PO_2)$ bands are shifted by small amounts to either higher or lower wavenumbers. The $\nu_s(PO_2)$ bands are shifted by 20−30 cm^{-1} to lower wavenumbers. Thus, these bands are only of diagnostic value. More information can be derived from the ^{31}P NMR data. In all cases, an upfield shift is seen upon coordination. Its magnitude is around 1−2 ppm for aryl diphosphates,

Table 1. IR (KBr, cm^{-1}) and ^{31}P NMR (rel. to H_3PO_4) data

	$\nu_{as}(PO_2)$	$\nu_s(PO_2)$	$\delta(^{31}P)$
Na[PCP]	1237	1054	−6.0/26.5 (J = 5.4)
$Na_2[POP^1]$	1270/1239	1141	−8.5
$Li_2[POP^2]$	1256/1226	1155	−15.9
$Li_2[POP^3]$	1270/1230	1140	−15.3
$Li_2[POP^4]$	1249/1220	1138	−15.5
$Li_2[POP^5]$	1254/1223	1155	−16.0
1 (PCP)	1230	1043	9.6/27.7 (J = 5.0)
2 (PCP)	1233	1048	12.2/26.7 (J = 10.1)
3 (POP^3)	1261/1223	1121	−15.8
4 (POP^4)	1258/1230	1119	−15.9
5 (POP^1)	1254/1222	1121	−10.6
6 (POP^1)	1246/1215	1122	−11.4
7 (POP^2)	1247/1224	1115	−17.5
8 (POP^3)	1253/1222	1112	−17.4
9 (POP^4)	1255/1227	1121	−17.3
10 (POP^5)	1259/1219	1115	−17.8
11 (POP^1)	1256/1224	1121	−10.1
12 (POP^1)	1249/1204	1123	−10.8
13 POP^2)	1263/1224	1126	−16.8
14 (POP^3)	1259/1228	1124	−16.5
15 (POP^1)	1281/1234	1127	−10.4
16 (POP^2)	1289/1247	1120	−16.6
17 ($ROPO_3$)	1155/1096[a]	−	−1.3/−1.0
18 ($ROPO_3$)	1156/1091[a]	−	−1.6/−1.0

[a] PO_3 vibrations.

2−3 ppm for benzyl diphosphate, and 10−15 ppm for triethyl methylenediphosphonate. This proves that the phosphates are coordinated to zinc even in good donor solvents such as DMSO or water.

Conclusions

The reliable tridentate attachment of the coligands in this study and the fact that all the complexes contain just one coligand per zinc ion has allowed the observation of three coordination modes for the diphosphates. Monodentate attachment of PCP and bis-monodentate attachment of the POP ligands seems to yield tetrahedral $ZnON_3$ complexes. The most typical coordination mode of the POP ligands seems to be the chelating one. It has been observed in five- and six-coordinate zinc complexes with the coordination patterns ZnO_2N_3 and ZnO_3N_3. The open-chain tridentate ligands favor five-coordination, while the TACN ligands enforce octahedral coordination.

Two unusual bonding types have been found. In one of these, the POP ligands act as chelators for one zinc ion and as additional donors for the other zinc ion in dinuclear complexes. In the other, organo-monophosphates, which result from hydrolysis, act as triply-bridging ligands in trinuclear $(LZn)_3(\text{phosphate})_2$ complexes.

With regard to the catalytic function of zinc in conventional or biological oligophosphate hydrolyses, the complexes described here and in the preceding papers[1,2] seemingly give no mechanistic information. The chelating mode of the diphosphates seems to provide stabilization rather than activation. Specifically in enzymes, steric restrictions at the active center render a chelating coordination unlikely. We therefore decided to enforce similar steric restrictions through the use of encapsulating ligands for zinc. The succeeding paper[3] describes their application in zinc−diphosphate chemistry.

Experimental Section

General: For general working and measuring procedures, see ref.[15] The lithium and sodium salts of the diphosphates[2,4−6] were stored under anhydrous conditions, as were the hygroscopic coligands.[7−10] 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.

Ligand PDEA: The Schiff base PDEI (derived from pyridine-2-carbaldehyde and *N*,*N*-dimethylethylenediamine[16]) (1.50 g, 8.40 mmol) was dissolved in methanol (15 mL). $NaBH_4$ (1.60 g, 42.3 mmol) was then slowly added with stirring. After stirring for 20 h, 2 N HCl (20 mL) was added. The resulting mixture was extracted with dichloromethane (3 × 20 mL). After drying with Na_2SO_4, the combined extracts were concentrated to dryness. Chromatography of the residue on a 2 × 20 cm silica gel column (0.063−0.20 mm) eluting with cyclohexane/ethyl acetate/triethylamine (8:2:1) yielded the product PDEA; $R_f = 0.29$. 1.02 g (68%) of PDEA was obtained as an orange oil, which was not analytically pure. − $C_{10}H_{17}N_3$ (179.3): calcd. C 67.00, H 9.56, N 23.44; found C 64.22, H 9.30, N 21.88. − ^1H NMR (CD_3OD): δ = 2.21 (s, 6 H, Me), 2.39 (t, *J* = 6.7 Hz, 2 H, CH_2), 2.63 (t, *J* = 6.7 Hz, 2 H, CH_2), 3.79 (s, 2 H, py-CH_2), 7.19 (m, 1 H, py), 7.36 (d, *J* = 7.7 Hz, 1 H, py), 7.70 (m, 1 H, py), 8.40 (d, *J* = 4.9 Hz, 1 H, py).

1: Na[PCP] (70 mg, 0.25 mmol) in boiling ethanol (5 mL) was added to a solution of DBA·H_2O (73 mg, 0.25 mmol) and $Zn(ClO_4)_2 \cdot 6H_2O$ (92 mg, 0.25 mmol) in boiling ethanol (20 mL). After refluxing for 15 min., the mixture was filtered while hot, cooled to room temp., and then slowly concentrated to one third of its original volume. 97 mg (55%) of **1** was precipitated as a colorless powder; m.p. 186 °C. − $C_{23}H_{32}ClN_5O_{10}P_2Zn$ (701.3): calcd. C 39.39, H 4.60, N 9.99, Zn 9.32; found C 38.72, H 4.58, N 9.57, Zn 8.99. − ^1H NMR ([D_6]DMSO): δ = 1.05 (m, 9 H, CH_3), 2.36 (t, *J* = 19.8 Hz, 2 H, PCH_2P), 3.84 (m, 6 H, CH_2), 4.27 (s, 1 H, NH), 4.36 (s, 4 H, NCH_2), 7.31 (m, 4 H, Ph), 7.58 (m, 2 H, Ph), 8.07 (m, 2 H, Ph), 13.31 (s, 2 H, NH).

2: Prepared in the same manner as **1** from Na[PCP] (108 mg, 0.37 mmol) in methanol (20 mL) and $Zn(ClO_4)_2 \cdot 6H_2O$ (140 mg, 0.37 mmol) and DPA (75 mg, 0.37 mmol) in methanol (20 mL). Yield 117 mg (50%) of **2** as a colorless powder; m.p. 186 °C. − $C_{19}H_{30}ClN_3O_{10}P_2Zn$ (623.2): calcd. C 36.62, H 4.85, N 6.74, Zn 10.49; found C 35.95, H 4.71, N 6.63, Zn 10.72. − ^1H NMR (D_2O): δ = 1.20 (m, 9 H, CH_3), 2.33 (t, *J* = 20.2 Hz, 2 H, PCH_2P), 3.86 (dq, *J* = 7.2, 7.3 Hz, 2 H, OCH_2), 4.15 (d, *J* = 16.6 Hz, 2 H, NCH_2), 4.25 (dq, *J* = 7.0, 7.1 Hz, 4 H, OCH_2), 4.53 (d, *J* = 16.6 Hz, 2 H, NCH_2), 7.49 (m, 4 H, Ph), 7.93 (dd, *J* = 8.5, 8.5 Hz, 2 H, Ph), 8.54 (d, *J* = 4.6 Hz, 2 H, Ph).

3: DPA (60 mg, 0.30 mmol) and $Zn(ClO_4)_2 \cdot 6H_2O$ (112 mg, 0.30 mmol) were combined in methanol (12 mL). $Li_2[POP^3]$ (55 mg, 0.15 mmol) in methanol (10 mL) was then added with stirring. After stirring for 15 h, the solvent was removed in vacuo and the residue was taken up in dichloromethane (25 mL). After filtering, *n*-heptane was carefully added to the filtrate until precipitation commenced. Subsequent slow evaporation of the solvent yielded 73 mg (45%) of **3** as colorless microcrystals; m.p. 195 °C. − $C_{38}H_{40}Cl_2N_6O_{15}P_2Zn_2$ (1084.4): calcd. C 42.09, H 3.72, N 7.75, Zn 12.06; found C 40.95, H 3.71, N 7.71, Zn 11.15. − ^1H NMR (CD_3OD): δ = 2.14 (s, 6 H, CH_3), 3.81 (d, *J* = 16.5 Hz, 4 H, NCH_2), 4.34 (d, *J* = 16.5 Hz, 4 H, NCH_2), 6.88 (s, 8 H, Ph), 7.38 (m, 4 H, py), 7.48 (d, *J* = 7.9 Hz, 4 H, py), 7.98 (m, 4 H, py), 8.42 (d, *J* = 4.6 Hz, 4 H, py).

4: Prepared in the same manner as **3** from DPA (29 mg, 0.15 mmol), $Zn(ClO_4)_2 \cdot 6H_2O$ (54 mg, 0.15 mmol), and $Li_2[POP^4]$ (34 mg, 0.073 mmol) in methanol (total volume 15 mL). Yield 50 mg (59%) of **4** as a colorless powder; m.p. 150−155 °C. − $C_{44}H_{52}Cl_2N_6O_{15}P_2Zn_2$ (1168.5): calcd. C 45.23, H 4.49, N 7.19, Zn 11.19; found C 44.65, H 4.40, N 7.07, Zn 11.03. − ^1H NMR (CD_3OD): δ = 1.25 (s, 18 H, *t*Bu), 3.92 (d, *J* = 16.7 Hz, 4 H, NCH_2), 4.43 (d, *J* = 16.7 Hz, 4 H, NCH_2), 6.99 (d, *J* = 8.7 Hz, 4 H, Ph), 7.21 (d, *J* = 8.7 Hz, 4 H, Ph), 7.49 (m, 8 H, py), 7.99 (m, 4 H, py), 8.62 (d, *J* = 3.9 Hz, 4 H, py).

5: Prepared in the same manner as **3** from PDEA (54 mg, 0.30 mmol), $Zn(ClO_4)_2 \cdot 6H_2O$ (112 mg, 0.30 mmol), and $Na_2[POP^1]$ (60 mg, 0.15 mmol) in methanol (total volume 25 mL); reflux for 2 h. Yield 80 mg (51%) of **5** as a colorless powder; m.p. 95 °C. − $C_{34}H_{48}Cl_2N_6O_{15}P_2Zn_2$ (1044.4): calcd. C 39.10, H 4.63, N 8.05, Zn 12.52; found C 39.75, H 4.65, N 7.77, Zn 11.81. − ^1H NMR (CD_3OD): δ = 2.27 (s, 12 H, NMe_2), 2.68 (m, 8 H, C_2H_4), 3.87 (d, *J* = 17.3 Hz, 2 H, NCH_2), 4.20 (d, *J* = 17.3 Hz, 2 H, NCH_2), 4.91 (d, *J* = 7.4 Hz, 4 H, OCH_2), 7.20 (s, 10 H, Ph), 7.38 (m, 4 H, py), 7.93 (m, 2 H, py), 8.62 (d, *J* = 4.4 Hz, 2 H, py).

6: $Na_2[POP^1]$ (272 mg, 0.68 mmol) was dissolved in hot methanol (50 mL) and as much water as necessary to obtain a clear solution. The resulting solution was added to a solution of DBA (200 mg, 0.68 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (252 mg, 0.68 mmol) in hot methanol (50 mL). The mixture was refluxed for 8 h and then stirred at room temp. for 48 h. During this time, 310 mg (65%) of **6** was precipitated as a colorless powder; m.p. 230 °C. − $C_{30}H_{29}N_5O_7P_2Zn{\cdot}H_2O$ (689.9 + 18.0): calcd. C 50.26, H 4.36, N 9.77, Zn 9.12; found C 50.88, H 4.30, N 9.70, Zn 8.67. − ^1H NMR ([D$_6$]DMSO): δ = 4.27 (d, J = 4.8 Hz, 4 H, NCH_2), 4.83 (dd, J = 2.7, 2.7 Hz, 4 H, OCH_2), 7.25 (m, 14 H, Ph + Bz), 7.54 (d, J = 8.0 Hz, 2 H, Ph), 8.43 (d, J = 8.0 Hz, 2 H, Ph).

7: $Li_2[POP^2]$ (116 mg, 0.34 mmol) in hot methanol (15 mL) was added to a solution of DBA (100 mg, 0.34 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (126 mg, 0.34 mmol) in boiling methanol (15 mL). On cooling, 99 mg (42%) of **7** was precipitated as a colorless powder; m.p. 270 °C. − $C_{28}H_{25}N_5O_7P_2Zn{\cdot}H_2O$ (670.9 + 18.0): calcd. C 48.82, H 3.95, N 10.17, Zn 9.49; found C 48.32, H 3.79, N 9.74, Zn 9.99. − ^1H NMR ([D$_6$]DMSO): δ = 4.23 (s, 4 H, NCH_2), 4.91 (s, 1 H, NH), 6.91 (m, 2 H, Ph), 7.08 (m, 8 H, Ph), 7.28 (m, 4 H, Ph), 7.56 (d, J = 7.4 Hz, 2 H, Ph), 8.34 (d, J = 7.4 Hz, 2 H, Ph), 13.27 (s, 2 H, NH).

8: Prepared in the same manner as **6** from $Li_2[POP^3]$ (94 mg, 0.21 mmol), DBA (62 mg, 0.21 mmol), and $Zn(ClO_4)_2{\cdot}6H_2O$ (78 mg, 0.21 mmol) in methanol (total volume 50 mL). Slow crystallization by evaporation of the solvent yielded 44 mg (30%) of **8** as colorless crystals; m.p. 300 °C. − $C_{30}H_{29}N_5O_7P_2Zn$ (689.9): calcd. C 51.56, H 4.18, N 10.02, Zn 9.35; found C 51.18, H 4.07, N 11.16, Zn 9.37. − ^1H NMR ([D$_6$]DMSO): δ = 2.13 (s, 6 H, CH_3), 4.22 (d, J = 4.9 Hz, 4 H, NCH_2), 6.82 (d, J = 8.5 Hz, 4 H, Ph), 6.94 (d, J = 8.5 Hz, 4 H, Ph), 7.26 (m, 4 H, Ph), 7.54 (d, J = 7.1 Hz, 2 H, Ph), 8.31 (d, J = 7.3 Hz, 2 H, Ph), 13.21 (s, 2 H, NH).

9: Prepared in the same manner as **6** from $Li_2[POP^4]$ (100 mg, 0.21 mmol), DBA (62 mg, 0.21 mmol), and $Zn(ClO_4)_2{\cdot}6H_2O$ (78 mg, 0.21 mmol) in methanol (total volume 20 mL). Yield 156 mg (95%) of **9** as colorless crystals; m.p. 260 °C. − $C_{36}H_{41}N_5O_7P_2Zn$ (783.1): calcd. C 55.22, H 5.28, N 8.94, Zn 8.35; found C 54.22, H 5.23, N 8.60, Zn 8.55. − ^1H NMR ([D$_6$]DMSO): δ = 1.19 (s, 18 H, *t*Bu), 4.24 (d, J = 4.2 Hz, 4 H, NCH_2), 6.98 (d, J = 8.8 Hz, 4 H, Ph), 7.08 (d, J = 8.8 Hz, 4 H, Ph), 7.25 (m, 4 H, Ph), 7.54 (d, J = 7.2 Hz, 2 H, Ph), 8.38 (d, J = 7.2 Hz, 2 H, Ph), 13.27 (s, 2 H, NH).

10: Prepared in the same manner as **6** from $Li_2[POP^5]$ (100 mg, 0.23 mmol), DBA (69 mg, 0.23 mmol), and $Zn(ClO_4)_2{\cdot}6H_2O$ (87 mg, 0.23 mmol) in methanol (total volume 65 mL). Slow crystallization by evaporation of the solvent yielded 76 mg (44%) of **10** as colorless crystals; m.p. 320 °C. − $C_{28}H_{23}Cl_2N_5O_7P_2Zn$ (739.8): calcd. C 45.46, H 3.13, N 9.47, Zn 8.84; found C 44.99, H 3.15, N 9.49, Zn 8.75. − ^1H NMR ([D$_6$]DMSO): δ = 4.27 (s, 4 H, NCH_2), 7.06 (m, 8 H, Ph), 7.26 (m, 4 H, Ph), 7.45 (d, J = 7.0 Hz, 2 H, Ph), 8.26 (d, J = 7.2 Hz, 2 H, Ph), 13.27 (s, 2 H, NH).

11: A solution of $K_2[POP^1]$ (130 mg, 0.70 mmol) in methanol (8 mL) was added to a solution of DPA (60 mg, 0.30 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (112 mg, 0.30 mmol) in methanol (15 mL). After stirring for 15 h, the mixture was filtered and the filtrate was concentrated to dryness. The residue was taken up in dichloromethane and the resulting solution was filtered. Addition of a few mL of *n*-heptane and slow evaporation of the solvents yielded 81 mg (44%) of **11** as colorless crystals; m.p. 170 °C. − $C_{26}H_{27}N_3O_7P_2Zn$ (620.9): calcd. C 50.30, H 4.38, N 6.77, Zn 10.53; found C 49.96, H 4.57, N 6.26, Zn 10.55. − ^1H NMR (CD_3OD): δ = 4.27 (d, J = 16.6 Hz, 2 H, NCH_2), 4.72 (d, J = 16.6 Hz, 2 H, NCH_2), 4.80 (dd, J = 3.2, 3.3 Hz, 4 H, OCH_2), 7.10 (s, 10 H, Ph), 7.20 (m, 2 H, py), 7.30 (d, J = 7.8 Hz, 2 H, py), 7.79 (m, 2 H, py), 8.68 (d, J = 5.5 Hz, 2 H, py).

12: $ZnCl_2$ (51 mg, 0.37 mmol) in acetonitrile/water (10 mL) was treated with TACN* (64 mg, 0.37 mmol) and $Na_2[POP^1]$ (150 mg, 0.37 mmol) in acetonitrile/water (20 mL). After stirring at 80 °C for 15 h, the mixture was slowly concentrated to a volume of 15 mL at room temp. 90 mg (36%) of **12** was precipitated as colorless crystals; m.p. 200 °C. − $C_{23}H_{35}N_3O_7P_2Zn{\cdot}5H_2O$ (592.9 + 90.1): calcd. C 40.45, H 6.64, N 6.15, Zn 9.57; found C 40.46, H 6.63, N 6.10, Zn 9.52. − ^1H NMR (CD_3OD): δ = 2.63 (s, 9 H, CH_3), 2.73 (s, 12 H, C_2H_4), 5.03 (dd, J = 3.2, 3.2 Hz, 4 H, OCH_2), 7.36 (m, 10 H, Ph).

13: Prepared in the same manner as **11** from $K_2[POP^2]$ (140 mg, 0.30 mmol), TACN* (51 mg, 0.30 mmol), and $Zn(ClO_4)_2{\cdot}6H_2O$ (112 mg, 0.30 mmol). Crystals were obtained by slow evaporation of the solvents from a methanol/water solution. Yield 124 mg (67%) of **13** as colorless crystals; m.p. 185 °C. − $C_{21}H_{31}N_3O_7P_2Zn{\cdot}3H_2O$ (564.8 + 54.0): calcd. C 40.76, H 6.03, N 6.79, Zn 10.57; found C 41.02, H 5.97, N 6.83, Zn 10.19. − ^1H NMR (CD_3OD): δ = 2.60 (s, 9 H, CH_3), 2.72 (s, 12 H, C_2H_4), 7.08 (m, 2 H, Ph), 7.25 (m, 8 H, Ph).

14: Prepared in the same manner as **11** from $Li_2[POP^3]$ (110 mg, 0.30 mmol), TACN* (51 mg, 0.30 mmol), and $Zn(ClO_4)_2{\cdot}6H_2O$ (112 mg, 0.30 mmol). Yield 93 mg (50%) of **14** as colorless crystals; m.p. 145 °C. − $C_{23}H_{35}N_3O_7P_2Zn{\cdot}1.5H_2O$ (592.9 + 27.0) calcd. C 44.56, H 6.18, N 6.75, Zn 10.55; found C 44.59, H 6.13, N 6.73, Zn 10.40. − ^1H NMR (CD_3OD): δ = 2.28 (s, 6 H, CH_3), 2.59 (s, 9 H, CH_3), 2.73 (s, 12 H, C_2H_4), 7.07 (s, 8 H, Ph).

15: Prepared in the same manner as **11** from $K_2[POP^1]$ (109 mg, 0.25 mmol), TACN (32.2 mg, 0.25 mmol), and $Zn(ClO_4)_2{\cdot}6H_2O$ (93 mg, 0.25 mmol). Yield 36 mg (25%) of **15** as colorless crystals. − $C_{20}H_{29}N_3O_7P_2Zn{\cdot}H_2O$ (550.8 + 18.0): calcd. C 42.23, H 5.49, N 7.39, Zn 11.50; found C 41.09, H 5.29, N 6.76, Zn 11.23. − ^1H NMR (CD_3OD): δ = 2.47 (m, 6 H, C_2H_4), 2.97 (m, 6 H, C_2H_4), 5.01 (s, 4 H, OCH_2), 7.34 (m, 10 H, Ph).

16: Prepared in the same manner as **11** from $K_2[POP^2]$ (102 mg, 0.25 mmol), PDEA (45 mg, 0.25 mmol), and $Zn(ClO_4)_2{\cdot}6H_2O$ (93 mg, 0.25 mmol). Yield 51 mg (35%) of **16** as colorless crystals; m.p. 175 °C. − ^1H NMR (CD_3OD): δ = 2.38 (s, 6 H, CH_3), 2.76 (m, 4 H, C_2H_4), 3.91 (d, J = 17.2 Hz, 1 H, NCH_2), 4.17 (d, J = 17.2 Hz, 1 H, NCH_2), 7.02 (m, 2 H, Ph), 7.20 (m, 8 H, Ph), 7.49 (m, 2 H, py), 8.03 (m, 1 H, py), 8.67 (d, J = 5.8 Hz, 1 H, py).

17: A solution of $Li_2[POP^3]$ (180 mg, 0.40 mmol) in hot methanol (40 mL) was added to a solution of BPA (160 mg, 0.80 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (299 mg, 0.80 mmol) in boiling methanol (20 mL). After refluxing for 10 min, the mixture was filtered while hot and the filtrate was cooled to −24 °C. 70 mg (32%) of **17** was precipitated as colorless crystals; m.p. 235 °C. − $C_{50}H_{54}N_9O_{12}P_3Zn_3{\cdot}H_2O$ (1262.1 + 18.0): calcd. C 46.91, H 4.41, N 9.85, Zn 15.32; found C 43.01, H 3.85, N 8.96, Zn 14.55. − ^1H NMR (CD_3OD): δ = 2.28 (s, 6 H, CH_3), 3.78 (d, J = 16.2 Hz, 6 H, NCH_2), 4.33 (d, J = 16.2 Hz, 6 H, NCH_2), 7.05 (m, 14 H, Ph, py), 7.41 (d, J = 7.8 Hz, 6 H, py), 7.83 (dd, J = 7.2, 7.8 Hz, 6 H, py), 8.59 (d, J = 4.8 Hz, 6 H, py). − ^{31}P NMR ([D$_6$]DMSO): δ = −1.3 (3 P), −1.0 (1 P).

18: Prepared in the same manner as **17** from $Li_2[POP^5]$ (106 mg, 0.25 mmol), BPA (99 mg, 0.50 mmol), and $Zn(ClO_4)_2{\cdot}6H_2O$

(185 mg, 0.50 mmol) in boiling methanol (total volume 40 mL). Yield 70 mg (32%) of **18** as colorless crystals; m.p. 235 °C. − $C_{48}H_{48}Cl_2N_9O_{12}P_3Zn\cdot H_2O$ (1302.9 + 18.0): calcd. C 44.25, H 3.71, N 9.68, Zn 15.05; found C 40.32, H 3.30, N 8.83, Zn 13.73. − ^1H NMR (CD_3OD): δ = 3.81 (d, *J* = 16.2 Hz, 6 H, NCH_2), 4.36 (d, *J* = 16.2 Hz, 6 H, NCH_2), 7.04 (dd, *J* = 5.7, 6.1 Hz, 6 H, py), 7.18 (m, 8 H, Ph), 7.43 (d, *J* = 7.8 Hz, 6 H, py), 7.82 (dd, *J* = 7.3, 7.4 Hz, 6 H, py), 8.58 (d, *J* = 4.4 Hz, 6 H, py). − ^{31}P NMR ([D$_6$]DMSO): δ = −1.6 (3 P), −1.0 (1 P).

Structure Determinations:[17] 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 ω/2θ technique on a Nonius CAD4 diffractometer fitted with a molybdenum tube (K_α, λ = 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.[18] 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.[19] The crystallographic data are collected in Table 2.

Table 2. Crystallographic details

	8	**12**	**15**	**16**	**17**	**18**
Empirical formula	$C_{30}H_{29}N_5O_7P_2Zn$	$C_{23}H_{35}N_3O_7P_2Zn\cdot 5H_2O$	$C_{20}H_{29}N_3O_7P_2Zn\cdot H_2O$	$C_{22}H_{27}N_3O_7P_2Zn\cdot 0.5H_2O$	$C_{50}H_{54}N_9O_{12}P_2Zn_3\cdot H_2O$	$C_{48}H_{48}Cl_2N_9O_{12}P_3Zn\cdot H_2O$
Molecular mass	689.9	592.9 + 90.1	550.8 + 18.0	572.8 + 9.0	1262.1 + 18.0	1302.9 + 18.0
Crystal size [mm]	1.1 × 1.1 × 1.1	0.3 × 0.2 × 0.2	0.4 × 0.4 × 0.3	0.4 × 0.3 × 0.3	0.5 × 0.2 × 0.1	0.3 × 0.2 × 0.2
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P4_2/n$	$P4_2/n$
Z	4	2	2	8	8	8
a [Å]	10.152(2)	8.911(1)	8.419(2)	16.611(2)	21.349(3)	21.284(3)
b [Å]	16.232(3)	10.135(1)	10.457(2)	12.503(1)	21.349(3)	21.284(3)
c [Å]	19.707(4)	17.751(2)	14.373(2)	24.954(2)	26.636(5)	26.242(5)
α [°]	90	85.44(2)	79.37(3)	90	90	90
β [°]	99.02(3)	80.36(2)	87.62(3)	100.22(2)	90	90
γ [°]	90	89.14(2)	79.20(3)	90	90	90
V [Å^3]	3207.3(11)	1575.5(4)	1221.6(4)	5100.4(8)	12140(3)	11888
d(calcd) [gcm^{-3}]	1.47	1.44	1.55	1.51	1.39	1.46
μ(Mo-K_α) [mm^{-1}]	0.92	0.94	1.19	1.14	2.67 (Cu)	1.44
hkl range	*h*: 0 to 12	*h*: −11 to 11	*h*: −9 to 9	*h*: −21 to 10	*h*: 0 to 26	*h*: −22 to 0
	k: 0 to 20	*k*: −13 to 12	*k*: −11 to 11	*k*: −16 to 15	*k*: 0 to 26	*k*: −22 to 0
	l: −24 to 24	*l*: −22 to 23	*l*: −15 to 15	*l*: −33 to 31	*l*: 0 to 33	*l*: −28 to 0
Measured reflections	6707	13914	7869	15660	13079	7992
Independent reflections	6341	7055	3494	6035	12399	7429
Observed refl. [$I > 2\sigma(I)$]	4633	5902	2749	4021	8410	3173
Parameters	406	370	307	321	698	698
Refined reflections	6341	7055	3494	6035	12399	7429
R_1 (obsd. refl.)	0.055	0.043	0.044	0.033	0.090	0.110
wR_2 (all refl.)	0.155	0.154	0.132	0.075	0.279	0.378
Residual electron density [e/Å^3]	+1.4 −0.6	+0.7 −0.5	+0.7 −0.5	+0.6 −0.3	+2.3 −0.8	+1.4 −0.6

Acknowledgments

This work was supported by the Fonds der Chemischen Industrie. We are indebted to Drs. W. Deck and A. Trösch for help with the structure determinations.

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[17] 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-141962 (for **8**), -141963 (for **12**), -141964 (for **15**), -141965 (for **16**), -141966 (for **17**), and -141967 (for **18**). 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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Received March 23, 2000
[I00110]