N,P Ligands

DOI: 10.1002/ange.200601138

Tris(organozinc) Phosphazenates as Templates for Trimeric and Hexameric Zinc Oxide Clusters**

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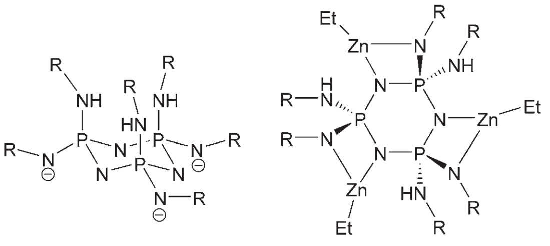
Molecular metal oxide complexes can serve as valuable models in various areas, including surface–substrate interactions in heterogeneous catalysis, metal oxide particles in porous solids, deposition, precipitation, and condensation reactions that lead to M_xO_y framework structures.[1] High oxidation-state metal oxide complexes $[\{R_mM_xO_y\}_n]$ exhibit a variety of frameworks $[\{M_xO_y\}_n]$ that comprise ring or cage structures.[2] While the metal centers are shielded by anionic organic ligands, R, the oxygen centers, as a result of their low basicity, can occupy corner positions of the framework. In contrast, complex oxides of +I and +II metal ions are fairly basic. Hence, their oxide ions are located at interstitial sites surrounded by excess metal ions, and complexes bearing more than two oxide centers are rare.[3] A notable exception is a complex reported by Mulvey and co-workers that contains six oxide ions. It comprises an $\{(MgO)_6\}$ core enclosed by six $NaNR_2$ moieties.[4]

Over the past years, we have studied the coordination behavior of multianionic phosphazenate ligands.[5] The trianionic ligand **A** features three anionic N centers at equatorial positions (N_{eq}) of the chair-shaped $\{P_3N_3\}$ ring and offers three chelating N_{eq}–N_{ring} sites (Scheme 1).[6] Herein, we report that the tris(ethylzinc) complex **B** can act as a template for trimeric and hexameric zinc oxide clusters through the bowl-shaped coordination surface of three Lewis basic N_{eq} functions and three Lewis acidic Zn centers. The *n*-propyl derivative was obtained by deprotonation of the phosphazene $(n\text{PrNH})_6P_3N_3$ (**1**) with three equivalents of Et_2Zn in hexane. The resulting complex **2** shows a singlet at $\delta = 26.4$ ppm in the ^{31}P NMR spectrum. Compound **2** exists as a dimeric complex of molecular D_3 symmetry in the solid state (Figure 1).[7] Two **B** segments are linked through six short Zn–N_{eq} interactions (av: 2.038 Å). Although the Zn–N_{ring} bonds are also short (av: 2.046 Å), the Zn–N_{eq} interactions inside **B** appear to be rather loose (av: 2.390 Å).



A **B**

Scheme 1. Trianionic ligand **A** and tris(ethylzinc) complex **B**.

Recently, we found that phosphazenes $(RNH)_6P_3N_3$ crystallize in the presence of water as distinct hydrates, $(RNH)_6P_3N_3{\cdot}x\,H_2O$, which display hydrogen-bonded networks in the solid state.[8] This behavior suggested to us that we should treat these hydrates with $3 + x$ equivalents of Et_2Zn in anticipation that three equivalents of Et_2Zn deprotonate the phosphazene to form **B**. The ZnO, generated by the in situ hydrolysis of x equivalents of Et_2Zn by x equivalents of water, might then be trapped within the molecular complex. Compound **1**·1.5 H_2O crystallized from a solution of **1** in hexane exposed to moist air. Subsequently, it was treated with 4.5 equivalents of Et_2Zn in hexane, thus giving a singlet at $\delta = 26.1$ ppm in the ^{31}P NMR spectrum. The crystal structure of the product complex **3** shows a planar $\{(ZnO)_3\}$ ring sandwiched between two **B** segments (Figure 1).[7] The cyclohexyl (Cy) derivative $(CyNH)_6P_3N_3$ (**4**) crystallized as the pentahydrate **4**·5 H_2O from THF/water. Proceeding in the same manner as in the synthesis of **3**, we treated **4**·5 H_2O with eight equivalents of Et_2Zn in hexane. The reaction solution was filtered from a small amount of precipitate (presumably excess ZnO). The crystal structure of the product complex **5** comprises a hexagonal $\{(ZnO)_6\}$ prism sandwiched between two **B** segments (Figure 1).[7] To the best of our knowledge, zinc oxide clusters that contain more than two oxide ions have not been reported. There is one example of a planar $\{(ZnO)_3\}$ ring with hydroxide ions,[9] but there are no precedents for $\{(ZnO)_6\}$ prisms.

Complexes **3** and **5** display molecular D_3 and S_6 symmetries, respectively. Both are derived from the insertion of zinc oxide clusters into the dimeric arrangement of two **B** segments. The coordination surface of **B** provides a perfect mold for trimeric and hexameric ZnO clusters that bind Zn ions through N_{eq} centers and oxide ions to the EtZn units. As a result, the $\{(ZnO)_3\}$ ring structure of **3** demands the phosphazenate ligands to be eclipsed, whereas the $\{(ZnO)_6\}$ prism of **5** is supported by a staggered ligand arrangement. The selection of either the ring or prism assembly is largely determined by the steric demand of the R substituents. The cyclohexyl groups are too bulky to maintain the eclipsed conformation, but they are able to interdigitate in the staggered conformation of **5**. When **4**·1.5 H_2O[10] was treated with 4.5 equivalents of Et_2Zn with the aim of producing a $\{(ZnO)_3\}$ ring complex, only an indistinct product mixture was obtained. On the other hand, when the trihydrate of $(i\text{BuNH})_6P_3N_3$ (**6**·3 H_2O),[10] which features the less bulky isobutyl groups, was treated with six equivalents of Et_2Zn to form a $\{(ZnO)_6\}$ complex, the product **7** contained a $\{(ZnO)_3\}$ unit similar to that found in **3**.[7]

The eclipsed ligand arrangement forces the $\{(ZnO)_3\}$ ring of **3** into a planar conformation that shows minimal deviation

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[**] This work was supported by EPSRC.

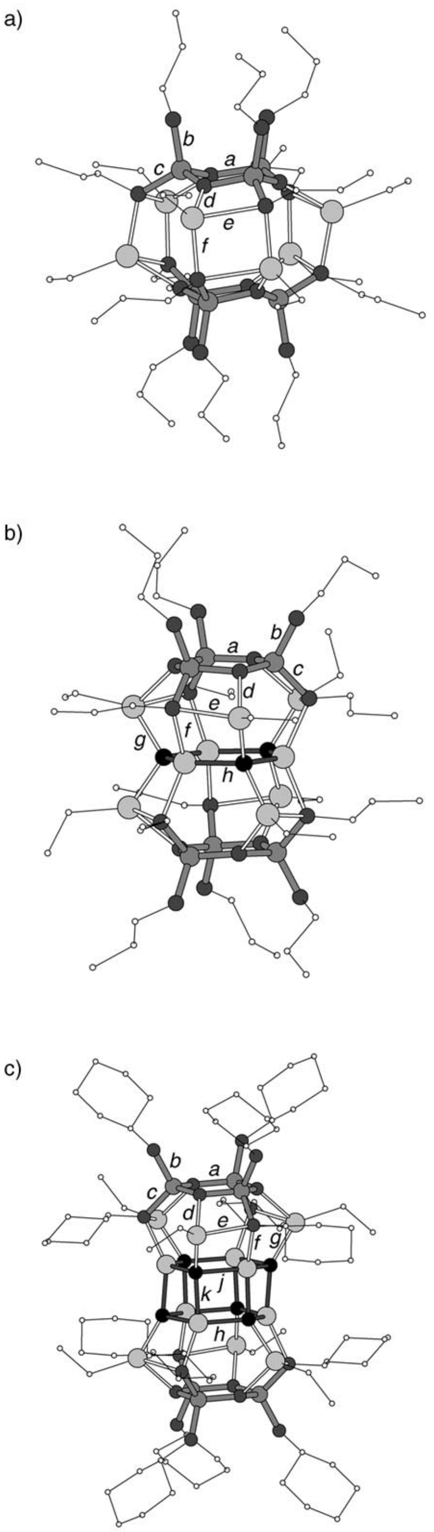

Figure 1. Crystal structures of a) **2**, b) **3**, and c) **5**. Zn light gray, P medium gray, N dark gray, O black, C white. H atoms are omitted for clarity. Selected bond lengths [Å] averaged over topologically equivalent bonds: **2**: P-N(*a*) 1.629, P-N(*b*) 1.654, P-N(*c*) 1.626, Zn-N(*d*) 2.046, Zn-N(*e*) 2.390, Zn-N(*f*) 2.038; **3**: P-N(*a*) 1.623, P-N(*b*) 1.647, P-N(*c*) 1.636, Zn-N(*d*) 2.115, Zn-N(*e*) 2.292, Zn-N(*f*) 2.067, Zn-O(*g*) 1.966, Zn-O(*h*) 1.968; **5**: P-N(*a*) 1.622, P-N(*b*) 1.650, P-N(*c*) 1.641, Zn-N(*d*) 2.176, Zn-N(*e*) 2.290, Zn-N(*f*) 2.021, Zn-O(*g*) 1.949, Zn-O(*h*) 1.963, Zn-O(*j*) 1.984, Zn-O(*k*) 2.034.

from the mean plane (0.007(1) Å), whereas the staggered arrangement in **5** enables the six-membered rings of the $\{(\mathrm{ZnO})_6\}$ prisms to pucker slightly into a chair-conformation (0.054(1) Å). The $\{(\mathrm{PN})_3\}$ rings of **3** and **5** show very little puckering (0.052(2) and 0.063(1) Å, respectively), whereas those of **2** exhibit a more pronounced chair-conformation (0.162(1) Å). This behavior suggests that there is some flexibility within the ligand to adapt to the host structure by tightening or widening its grip. The average distance between the $\mathrm{N_{eq}}$ sites within **B** provides a useful ligand grip parameter that measures 5.22 Å in **2** and that tightens upon coordination of zinc oxide to 4.77 and 4.80 Å in **3** and **5**, respectively.

The bond lengths of the $\{(\mathrm{ZnO})_3\}$ ring in **3** fall within a narrow range of 1.962(2)–1.974(2) Å. The bond angles in the $\{(\mathrm{ZnO})_3\}$ ring are much wider at the Zn (av: 126.4°) than at the O center (av: 113.6°). The $\{(\mathrm{ZnO})_6\}$ cage of **5** contains three types of topologically unique Zn–O bonds (labeled *h*, *j*, and *k* in Figure 1c). Bonds *h* and *k* alternate around both six-membered Zn–O rings. The slightly longer bonds *h* are parallel to $\mathrm{EtZn{-}N_{eq}}$ bonds of the adjacent **B** segment. Bulk ZnO (zincite) exhibits the hexagonal wurtzite structure,[11] whereas its high pressure phase (*hp*ZnO) adapts the cubic structure of rock salt.[12] Zn–O bond lengths in zincite compare well with those found in **3** and **5**. Figure 2 illustrates how the $\{(\mathrm{ZnO})_6\}$ prism of **5** relates to the open $\{(\mathrm{ZnO})_6\}$ segment of zincite and also to the corresponding $\{(\mathrm{ZnO})_6\}$ segment of *hp*ZnO. The prism can be regarded as an intermediate along the pathway of a hypothetical transformation: Compression of the open zincite-type segment along the *z* axis gives the prism, which furnishes the cubic arrangement of *hp*ZnO when squashed along the *x* axis.

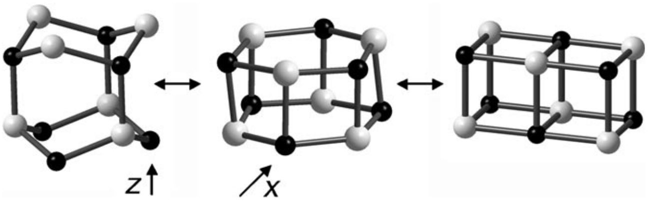

Figure 2. The $\{(\mathrm{ZnO})_6\}$ segments of **5** (center), zincite (left), and *hp*ZnO (right).

In conclusion, we have shown that tris(ethylzinc) phosphazenates can act as templates for the construction of novel zinc oxide clusters. Their bowl-shaped coordination surface of three Lewis acidic and three Lewis basic sites provides a perfect mold for planar $\{(\mathrm{ZnO})_3\}$ rings and hexagonal $\{(\mathrm{ZnO})_6\}$ prisms. The availability of well-defined phosphazene hydrates $(\mathrm{RNH})_6\mathrm{P_3N_3}\cdot x\,\mathrm{H_2O}$ offers a convenient route for reactions of reactive metal reagents with stoichiometric amounts of water in situ. In principle, other small substrates that form distinct adducts $(\mathrm{RNH})_6\mathrm{P_3N_3}\cdot y\,\mathrm{H}_z\mathrm{X}$ could react in a similar fashion, thus producing small molecular frameworks that are trapped inside organometal phosphazenate complexes.

Experimental Section

All operations were performed in an inert-gas atmosphere. Compounds **1**, **4**, and **6** were prepared as described previously.[13] Et_2Zn was applied as a 1.0 M solution in hexane. NMR spectra were taken from $[D_8]$toluene solutions.

2: Et_2Zn (6.2 mmol) in hexane (6.2 mL) was added to a solution of **1** (1 g, 2.07 mmol) in hexane (20 mL). The reaction mixture was stirred for 12 h, filtered, and concentrated. Colorless crystals formed after 3 days at 5 °C (1.32 g, 84 %). M.p. > 275 °C (decomp); ^1H NMR (400 MHz): $\delta = 0.66$ (q, $ZnCH_2$), 1.58 (t, $ZnCH_2CH_3$), 0.8–2.3 (m, *n*Pr-H), 3.2–3.4 ppm (m, NCH_2); ^{13}C NMR (100 MHz): $\delta = 12.9$, 21.7, 24.4, 25.0, 30.7, 35.5, 48.7, 61.50 ppm; ^{31}P NMR (162 MHz): $\delta = 26.4$ ppm; IR (Nujol): $\tilde{\nu} = 3393$ w, 1256 s, 1084 vs, 1021 vs, 948 w, 862 w, 799 s cm^{-1}.

3: Et_2Zn (3.5 mmol) in hexane (3.5 mL) was added to a suspension of $\mathbf{1}\cdot 1.5\,H_2O$ (0.40 g, 0.78 mmol) in hexane (10 mL). The reaction mixture was stirred for 12 h, filtered, and concentrated. Colorless crystals formed after 2 days at −20 °C (0.46 g, 67 %). M.p. > 162 °C (decomp); ^1H NMR (400 MHz): $\delta = 0.73$ (q, CH_2Zn), 0.84 (t, $NHCH_2CH_2CH_3$), 1.68 (t, CH_3CH_2Zn), 1.03 (t, $NCH_2CH_2CH_3$), 1.34 (q, $NHCH_2CH_2$), 1.87 (m, NCH_2CH_2), 2.08 (m, NH), 2.86 (m, $NHCH_2$), 3.06 (m, NCH_2); ^{13}C NMR (100 MHz): $\delta = 1.1$, 11.1, 11.9, 13.7, 25.4, 31.6, 43.1, 50.5 ppm; ^{31}P NMR (162 MHz): $\delta = 26.1$ ppm; IR (Nujol): $\tilde{\nu} = 1286$ w, 1261 w, 1227 s, 1112 vs, 1051 s, 888 w, 800 s cm^{-1}.

5: Et_2Zn (4.9 mmol) in hexane (4.9 mL) was added to a suspension of $\mathbf{4}\cdot 5\,H_2O$ (0.25 g, 0.31 mmol) in hexane (10 mL). The reaction mixture was stirred for 12 h, filtered, and concentrated. Colorless crystals formed after 5 days at −20 °C (0.27 g, 71 %). M.p. > 240 °C (decomp); ^1H NMR (400 MHz): $\delta = 0.68$ (q, CH_2Zn), 1.63 (t, CH_3CH_2Zn), 0.8–1.95 (m, CH_2), 2.09 (m, NH), 3.1–3.4 ppm (m, NCH); ^{13}C NMR (100 MHz): $\delta = 1.3$, 12.9, 21.7, 24.0, 21.4, 24.9, 25.9, 30.7, 35.4 ppm; ^{31}P NMR (162 MHz): $\delta = 21.6$ ppm; IR (Nujol): $\tilde{\nu} = 3411$ w (N–H), 1405 w, 1291 m, 1291 m, 1261 m, 1229 s, 1186 w, 1146 m, 1078 vs, 915 s, 888 m, 846 m, 805 s cm^{-1}.

7: Et_2Zn (5.3 mmol) in hexane (5.3 mL) was added to a mixture of **6** (0.50 g, 0.88 mmol) and H_2O (0.048 mL, 2.65 mmol) in hexane (15 mL). The reaction mixture was stirred for 12 h, filtered, and concentrated. Colorless crystals formed after 2 days at −20 °C (0.48 g,56 %). M.p. > 180 °C (decomp); ^1H NMR (400 MHz): $\delta = 0.72$ (q, CH_2Zn), 0.91 (d, $NHCH_2CH(CH_3)_2$), 1.14 (d, $NCH_2CH(CH_3)_2$), 1.63 (t, CH_3CH_2Zn), 1.67–1.89 (m, $CH_2CH(CH_3)_2$), 2.09 (m, NH), 2.84 (m, $NHCH_2$), 3.11 ppm (m, 12 H, NCH_2); ^{13}C NMR (100 MHz): $\delta = 1.3$, 14.1, 14.6, 22.4, 23.4, 30.8, 32.4, 49.8 ppm; ^{31}P NMR (162 MHz): $\delta = 26.8$ ppm; IR (Nujol): $\tilde{\nu} = 3404$ br, 1401 w, 1279 w, 1231 s, 1200 s, 1130 vs, 1089 s cm^{-1}.

Received: March 22, 2006

Keywords: metal oxides · N,P ligands · phosphazenates · phosphazenes · zinc

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[7] Crystal data were measured on a Bruker Apex diffractometer at $T = 100$ K using $Mo_{K\alpha}$ radiation. Crystal structures were refined against F^2 using all data.[14] **2**: $C_{48}H_{120}N_{18}P_6Zn_6$, $M_r = 1527.7$, $C2/c$, $a = 22.0843(11)$, $b = 13.8929(7)$, $c = 23.6468(12)$ Å, $\beta = 95.3500(10)°$, $V = 7223.6(6)$ Å^3, $Z = 4$, $R1$ $(I > 2\sigma(I)) = 0.028$, $wR2$ (all data) = 0.074; **3**: $C_{48}H_{120}N_{18}O_3P_6Zn_9$, $M_r = 1771.8$, $P2_1/c$, $a = 16.5237(9)$, $b = 15.2248(9)$, $c = 29.8265(17)$ Å, $\beta = 91.7800(10)°$, $V = 7499.8(7)$ Å^3, $Z = 4$, $R1$ $(I > 2\sigma(I)) = 0.038$, $wR2$ (all data) = 0.100; $\mathbf{5}\cdot 1.5\,C_6H_{14}$: $C_{93}H_{189}N_{18}O_6P_6Zn_{12}$, $M_r = 2625.9$, $P\bar{1}$, $a = 14.164(2)$, $b = 14.976(2)$, $c = 16.602(2)$ Å, $\alpha = 113.405(2)$, $\beta = 100.528(3)$, $\gamma = 96.041(2)°$, $V = 3115.2(8)$ Å^3, $Z = 1$, $R1$ $(I > 2\sigma(I)) = 0.035$, $wR2$ (all data) = 0.102; **7**: $C_{60}H_{144}N_{18}O_6P_6Zn_6$, $M_r = 1940.1$, $R\bar{3}c$, $a = 18.8839(10)$, $c = 50.977(6)$ Å, $V = 15743(2)$ Å^3, $Z = 6$, $R1$ $(I > 2\sigma(I)) = 0.099$, $wR2$ (all data) = 0.35. Crystals of **7** diffracted very weakly and refined poorly, thus structural parameters are not discussed; however, the data quality was sufficient to confirm the connectivity of **7**. Crystallographic data in CIF format (CCDC-602267 (**2**), -602268 (**3**), -602269 (**5**), -602266 (**7**)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[8] A detailed account on phosphazene hydrates will be reported elsewhere. Selected data for $\mathbf{1}\cdot 1.5\,H_2O$: m.p. 55 °C, $P2_1/n$, $a = 9.3162(5)$, $b = 24.704(1)$, $c = 24.810(1)$ Å, $\beta = 92.460(1)°$; $\mathbf{4}\cdot 5\,H_2O$: m.p. 162 °C, $P2_1/n$, $a = 16.736(3)$, $b = 19.977(2)$, $c = 27.476(3)$ Å, $\beta = 104.46(2)°$.

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