Table 2. Consecutive asymmetric autocatalytic reaction[a] shown in Equation (3). The compounds **2a–k** only distinguish in which round the catalyst is used.

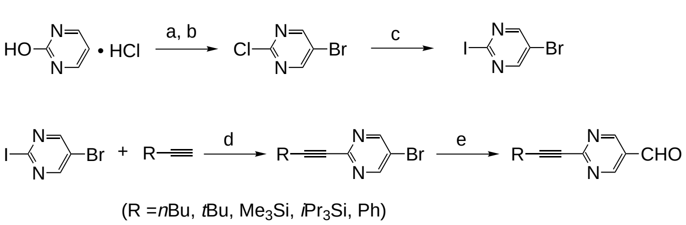
Entry	Asym. Autocat. *ee* [%]	Product yield [%]	Product *ee* [%]	Amplified factor[b]
1	> 99.5 (**2a**)	> 99	> 99.5 (**2b**)	6
2	> 99.5 (**2b**)	> 99	> 99.5 (**2c**)	6^2
3	> 99.5 (**2c**)	> 99	> 99.5 (**2d**)	6^3
4	> 99.5 (**2d**)	> 99	> 99.5 (**2e**)	6^4
5	> 99.5 (**2e**)	> 99	> 99.5 (**2f**)	$6^5 \approx 8 \times 10^3$
6	> 99.5 (**2f**)	> 99	> 99.5 (**2g**)	6^6
7	> 99.5 (**2g**)	> 99	> 99.5 (**2h**)	6^7
8	> 99.5 (**2h**)	> 99	> 99.5 (**2i**)	6^8
9	> 99.5 (**2j**)	> 99	> 99.5 (**2k**)	6^9
10	> 99.5 (**2k**)	> 99	> 99.5 (**2l**)	$6^{10} \approx 6 \times 10^7$

[a] Molar ratio **1**:iPr$_2$Zn (in cumene):catalyst **2** = 1.0:1.7:0.2. [b] The factor by which the amount of **2** has multiplied based on the amount of **2** used as an asymmetric autocatalyst in entry 1.

Experimental Section

Entry 5, Table 1: A solution of **1** (94.2 mg, 0.50 mmol) in cumene (5.0 mL) was added at 0 °C to a mixture of (*S*)-**2** (23.3 mg, 0.10 mmol, > 99.5 % *ee*) in cumene (12.0 mL) and iPr$_2$Zn (0.85 mL of a 1 M solution in cumene, 0.85 mmol) that had been stirred for 15 min at 0 °C. The reaction mixture was stirred for 3 h at 0 °C, then quenched by the addition of 1 M hydrochloric acid (3 mL) and saturated aqueous $NaHCO_3$ (9 mL) at 0 °C. The mixture was filtered through celite and the filtrate was extracted with ethyl acetate (4 × 15 mL). The extract was dried over anhydrous sodium sulfate and evaporated under reduced pressure. Cumene was removed by flash column chromatography (SiO_2, hexane, then hexane/ethyl acetate, 3/1) to give pure **2** (138.8 mg). HPLC analysis of the obtained **2** on a column with a chiral stationary phase (Daicel Chiralcel OD, eluent 3 % 2-propanol in hexane, flow rate 1.0 mL min^{-1}, 254 nm UV detector, retention time 18.1 min for (*S*)-**2**, 26.9 min for (*R*)-**2**) showed that it had an enantiomeric purity of > 99.5 % *ee*. The newly formed (*S*)-alcohol (138.8 − 23.3 = 115.5 mg, 99.2 % yield) had an enantiomeric purity of > 99.5 % *ee*.

Preparation of 2-alkynylpyrimidine-5-carbaldehydes (Scheme 1): Commercially available 2-hydroxypyrimidine hydrochloride was halogenated to form 5-bromo-2-chloropyrimidine by the improved procedure.[7] Halogen exchange occurred at the 2-position by the reaction with hydroiodic acid to give 5-bromo-2-iodopyrimidine, which was then coupled with alkynes to give 2-alkynyl-5-bromopyrimidines in 80–99 %.[8] Lithiation of the bromides by *n*- or *tert*-butyllithium and the subsequent formylation[9] by ethyl formate gave the 2-alkynylpyrimidine-5-carbaldehydes in 25–60 %.



Scheme 1. Synthesis of 2-alkynylpyrimidine-5-carbaldehydes. a) Br_2, H_2O; b) $POCl_3$, $PhNMe_2$, 55 % over two steps; c) 57 % HI, CH_2Cl_2, 93 %; d) 1–2 mol % [Pd(PPh_3)$_4$], 2–4 mol % CuI, iPr$_2$NH, 80–99 %; e) *n*BuLi or *t*BuLi then HCO_2Et, THF or Et_2O, 25–60%.

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A Functionalized Heterocubane with Extensive Intermolecular Hydrogen Bonds[**]

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*Dedicated to Professor Alan H. Cowley
on the occasion of his 65th birthday*

The use of inorganic cage compounds as molecular building blocks for the rational design of materials is an attractive and challenging avenue for the materials chemist. One example is the silicate cage compounds (RSiO$_{1.5}$)$_n$ (R = organic or inorganic group), which are potentially a very useful class of compounds.[1–6] They have been used as three-dimensional building block units for the synthesis of new materials, such as precursors for ceramics and models in various fields.[1, 3, 4] In addition, an exciting structural organization of the cubic silicate species $[Si_8O_{20}]^{8-}$ was achieved recently with various

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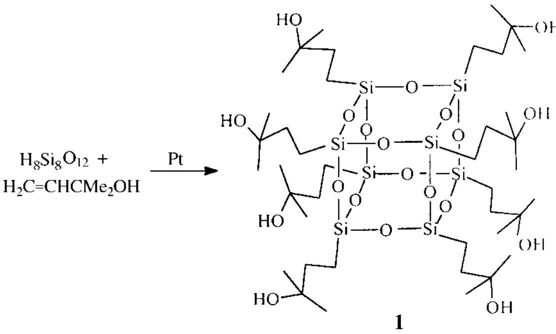
cationic surfactants.[7, 8] This procedure has potential applications as highly ordered mesoporous solids, as organic–inorganic nanocomposites, and as models in the area of biomimetics.[8]

With an eye towards developing a general methodology for the synthesis of soluble metal-containing siloxane derivatives[9, 10] and highly functionalized silsesquioxanes to assist the study of silica, we report herein a facile synthesis of $(Si_8O_{12})(CH_2CH_2CMe_2OH)_8$ (**1**). Such completely condensed oligosilsesquioxanes (POSS) are quite attractive since they retain reactive $SiCH_2CH_2CMe_2$-OH functionalities, which allows their exploitation as ligands in a wide variety of complexations with main group and transition metals. Moreover the conventional hydrogen bond is expected to play an essential role in the construction of a new supramolecular network through intermolecular hydrogen bonds. Endo et al. have shown the self-assembly in porous organic structures through formation of hydrogen bonds.[11] In addition, from a crystal engineering perspective, **1** is a novel solid since the key to the production of materials with predictable crystal structures lies in the engineering of complementary crystal building blocks with hydrogen bond donor/acceptor abilities.[12]



(1)

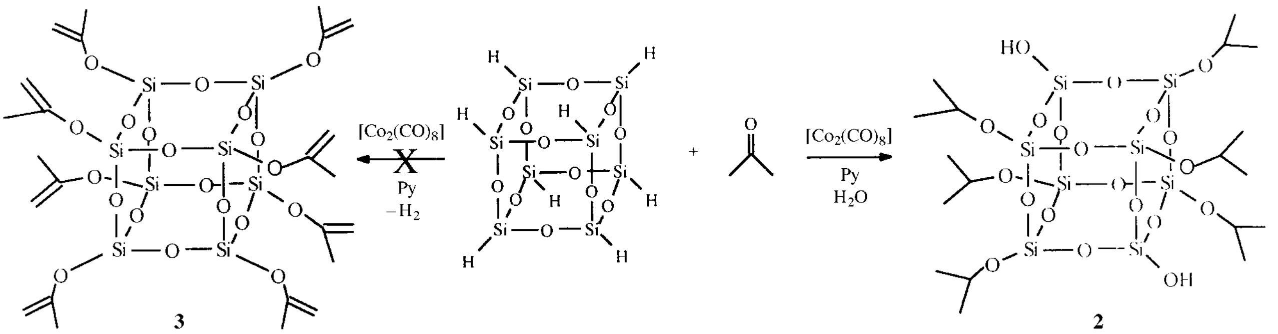
Despite the fact that a variety of functionalized oligosilsesquioxanes are known, their chemistry has remained undeveloped because of the lack of facile methods for their synthesis in useful quantities in a conveniently short period of time.[1, 13] The synthesis of **1** has been accomplished in a one-pot reaction in high yield from the readily available hydrosilsesquioxane $H_8Si_8O_{12}$ and an excess of H_2C=$CHCMe_2OH$ in the presence of a platinum catalyst [Eq. (1)].

Platinum-catalysed hydrosilylations of $H_8Si_8O_{12}$ provide a variety of functionalized silsesquioxanes.[6, 14, 15, 16] However, in most cases the products are mixtures of isomers as a consequence of α and β additions to the alkene. Therefore, increasing the steric bulk at the β position is a useful tool to reduce the number of side products.[14, 15] In our case, we could suppress the β addition by using a 3,3-substituted α-alkene. Hence treatment of $H_8Si_8O_{12}$ with H_2C=$CHCMe_2OH$ afforded a high yield of **1**, which spontaneously crystallized from the solution as colorless crystals. The reaction described above could be scaled up to provide much larger quantities of **1**. The easy access of **1** should make it possible to synthesize a wide variety of new hybrid materials.

Herein we also report on the synthesis of $(Si_8O_{12})(OCHMe_2)_6(OH)_2$ (**2**), which was obtained by treatment of $H_8Si_8O_{12}$ with acetone in the presence of a cobalt catalyst and subsequently crystallized in open air from *n*-hexane by slow evaporation (75%) of the solvent over six weeks [Eq. (2)]. In fact we were planning to synthesise cage compound **3**, which is useful as a tailor-made molecular building block, but compound **2** was formed in a 35% pure yield. It is important to note that POSS molecules with one or two reactive functionalities are more desirable for the preparation of linear POSS-based polymers.[17] The slow and total evaporation of the mother liquor of **2** resulted in the formation of a few more crystals along with an oily material. The crystals were identified by elemental analysis as $(i\text{PrO})_8Si_8O_{12}$. Clearly complete hydrolysis had not occured over the six weeks period to give a better yield of **2** from $(i\text{PrO})_8Si_8O_{12}$.

Characterization of **1** and **2** was accomplished by ^1H and ^{29}Si NMR spectroscopy as well as IR spectroscopy and elemental analysis. One signal at $\delta = -64.9$ was observed in the ^{29}Si NMR spectrum of **1**, whereas the spectrum of **2** showed two signals at $\delta = -103.3$ and -103.0. These results are in good agreement with the determined solid state structures. The molecular structures of these two compounds are shown in Figures 1 and 2. The main feature of interest of the octameric cluster **1** is the presence of the hydrogen bonds, which result in the formation of new supramolecular assemblies (Figure 3). The clusters are linked together at each of the vertices to form cavities. As a consequence intramolecular interactions of the $CH_2CH_2CMe_2OH$ groups of **1** are negligible. In addition, the compensation for the steric demand of the eight $CH_2CH_2CMe_2OH$ substituents reflects the flexibility of the Si_8O_{12} framework.

Some more of the chemical peculiarities of the structure of **1** should also be emphasized. Two water molecules are introduced from the catalyst $(H_2[PtCl_6]\cdot 6H_2O)$ during the crystallization from a mixture of tetrahydrofuran and *n*-



(2)

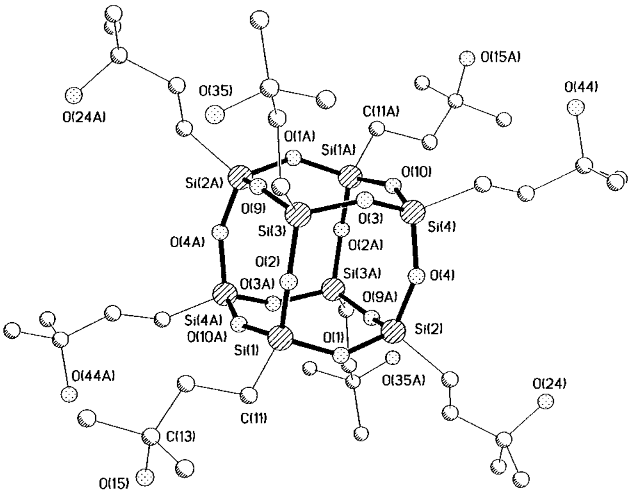


Figure 1. Structure of $1\cdot THF\cdot 2H_2O$ in the crystal.[21a] Selected bond lengths [Å] and angles [°]: Si(1)–O(1) 1.626(2), Si(1)–O(2) 1.626(2), O(1)–Si(2) 1.628(2), Si(2)–O(4) 1.621(2), O(2)–Si(3) 1.619(2), Si(3)–O(3) 1.625(2), O(3)–Si(4) 1.625(2), Si(4)–O(4) 1.622(2), Si(1)–C(11) 1.838(2), C(13)–O(15) 1.439(3); Si(1)-O(1)-Si(2) 142.32(10), O(1)-Si(1)-O(2) 109.45(8), O(2)-Si(1)-C(11) 109.84(9). Hydrogen atoms, tetahydrofuran, and water molecules have been omitted for clarity.

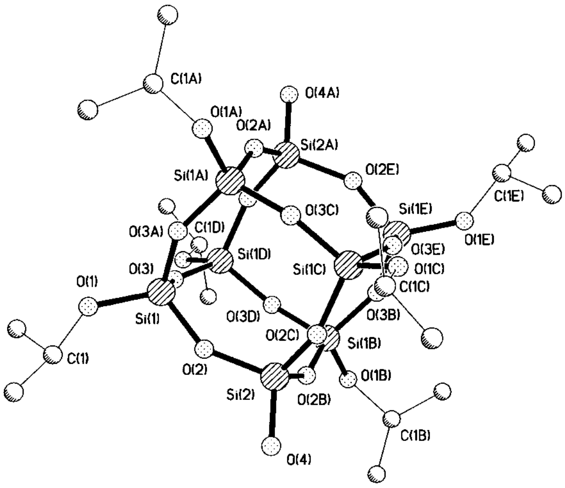


Figure 2. Structure of **2** in the crystal.[21b] Selected bond lengths [Å] and angles [°]: Si(1)–O(1) 1.599(8), Si(1)–O(3) 1.586(7), Si(1)–O(2) 1.607(7), Si(2)–O(4) 1.553(14), O(1)–C(1) 1.370(2); O(3)-Si(1)-O(2) 107.9(4), C(1)-O(1)-Si(1) 129.0(9), Si(2)-O(2)-Si(1) 148.5(5), O(4)-Si(2)-O(2) 109.6(3). Hydrogen atoms have been omitted for clarity.

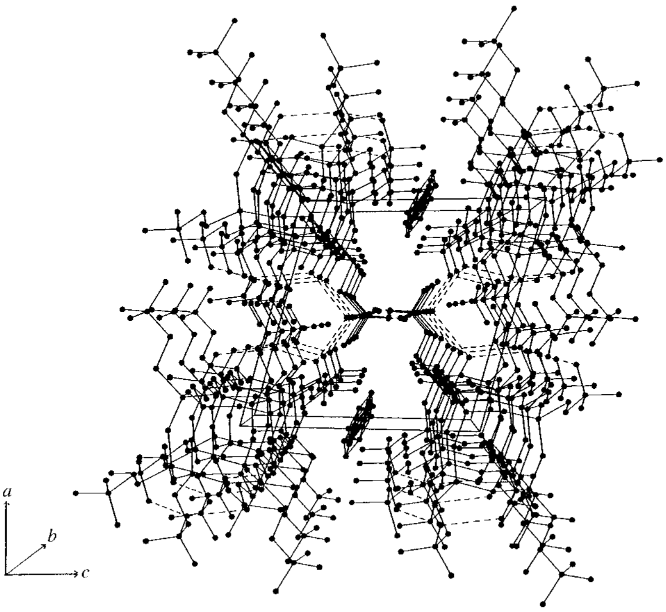


Figure 3. Packing diagram of **1** in the crystal. The O–H···O hydrogen bonds in the crystal of **1** are indicated as dashed lines. Disordered THF molecules are also shown.

hexane. The cavity created through O–H···O bonds acts as a host for two water molecules and a THF molecule, which are kept at different positions by some weak interactions. The guest molecules are not interconnected; the two water molecules are separated from each other by 4 Å, but they are connected to the cage by hydrogen bonds. The cross diameter of the cavities is in the range of 8–9 Å and the effective dimensions are approximately 3 × 3 × 8 Å^3. Powder X-ray diffraction investigations showed that heating a sample of compound **1** (130 °C and 0.01 Torr) over a 6 h period resulted in a structural change. Surprisingly such hydrogen bonding is not observed in **2** even though it has two hydroxyl groups at opposite corners of the cube. The orientation of the hydroxyl groups of **2** is such that each hydroxyl group points toward an isopropyl group of the adjacent cluster. The Si–O and Si–C bond lengths as well as O-Si-O, Si-O-Si, and O-Si-C angles are in accord with values observed for well characterized octameric silsesquioxanes for both the compounds **1** and **2**.[18–20]

In summary we have developed a straightforward procedure for the synthesis of a hydroxy-substituted silsesquioxane framework. Moreover we have demonstrated the influence of hydrogen bonds in building up new supramolecular assemblies. This result represents an important progress in the development of silsesquioxanes as models for functionalized silica.

Experimental Section

1: The hydrosilsesquioxane O_h-$H_8Si_8O_{12}$ (0.50 g, 1.18 mmol), 2-methyl-3-buten-2-ol (3 mL, 28.70 mmol), $H_2[PtCl_6]\cdot 6H_2O$ (10 mg), and *n*-hexane (20 mL) were added to a glass pressure reactor and heated at 120 °C for 3 h, during which time a white precipitate formed. The reaction mixture was allowed to cool to room temperature and filtered to yield 0.95 g (72 %) of analytically pure **1**. Further purification was achieved by crystallization from a mixture of tetrahydrofuran and *n*-hexane (10:1) to yield 0.80 g (62 %) of **1** as colorless crystals. (Compound **1** can also be obtained from a mixture of acetone and *n*-hexane (1:5) in a similar yield. However the crystals that were grown from this mixture of solvents were not suitable for X-ray diffraction.) M.p. 275 °C; ^{1}H NMR (200 MHz,$(CD_3)_2CO$): $\delta = 0.721$ (m, 16H; $CH_2CH_2C(CH_3)_2OH$), 1.14 (s, 48H; $CH_2CH_2C(CH_3)_2OH$), 1.57 (m, 16H; $CH_2CH_2C(CH_3)_2OH$), 3.22 (br, 8H; $CH_2CH_2C(CH_3)_2OH$); ^{29}Si NMR (50 MHz, $(CD_3)_2CO$): $\delta = -64.9$; IR (KBr, Nujol): $\tilde{\nu} = 3384$, 1115.9 cm^{-1}; elemental analysis (after drying in vacuo overnight at 50 °C) calcd for $C_{40}H_{88}O_{20}Si_8$: C 43.14, H 7.96, Si 20.17; found: C 43.10, H 7.80, Si 19.55.

2: Pyridine (0.012 g, 0.16 mmol) followed by dry acetone (5 mL) was added to O_h-$H_8Si_8O_{12}$ (0.30 g, 0.71 mmol) and dicobaltoctacarbonyl (0.037 g, 0.11 mmol) in a glass pressure reactor. The mixture was heated at 40 °C for 5 h and finally at 70 °C overnight. The reaction mixture was allowed to cool to room temperature and filtered. Subsequent removal of all volatiles in vacuo gave a residue that was treated with *n*-hexane (15 mL). Compound **2** precipitated as colorless crystals in 35 % yield (0.22 g) over a period of six weeks. M.p. 250 °C; ^{1}H NMR (200 MHz, C_6D_6) $\delta = 1.15$ (q, 36H; $CH(CH_3)_2$), 4.28 (sept, 8H; $CH(CH_3)_2$ and OH); ^{29}Si NMR (50 MHz,

C_6D_6): $\delta = -103.3$ (s, 6 Si, *Si*OCHMe$_2$), -103.0 (s, 2 Si, *Si*OH); IR (KBr, Nujol): $\tilde{\nu} = 3411.3$ cm^{-1}; elemental analysis calcd for $C_{18}H_{44}O_{20}Si_8$: C 26.84, H 5.47, Si 27.93; found C 26.47, H 5.32, Si 27.85.

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[21] a) Crystal structure analysis of **1** · THF · 2 H$_2$O: $C_{44}H_{100}O_{23}Si_8$, $M_r = 1221.96$, triclinic, space group $P\bar{1}$, $a = 11.865(2)$, $b = 12.251(2)$, $c = 12.322(2)$ Å, $\alpha = 70.471(0)$, $\beta = 74.136$ (13), $\gamma = 81.244(8)°$, $V = 1.6201(5)$ nm^3, $Z = 1$, $\rho_{calcd} = 1.252$ Mg m^{-3}, $\mu = 0.234$ mm^{-1}, $F(000) = 660$; total number of reflections measured 6191, of which 5723 were unique ($R_{int} = 0.0307$)and 5714 observed, 1 restraint, 341 parameters. Data collection range: $3.54 \leq 2\theta \leq 25.08°$. Final R indices: $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0428$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2} = 0.1174$ for data with $I > 2\sigma(I)$ and $R1 = 0.0470$, $wR2 = 0.1263$ for all data; GOF $= [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(n-p)]^{1/2} = 1.071$; max./min. residual electron density 933/ − 690 e nm^{-3}. b) Crystal structure analysis of **2**: $C_{24}H_{56}O_{20}Si_8$, $M_r = 889.41$, rhombohedral, space group $R\bar{3}$, $a = 15.444(2)$, $b = 15.444(2)$, $c = 16.749(3)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 120°$, $V = 3.459.8(10)$ nm^3, $Z = 3$, $\rho_{calcd} = 1.281$ Mg m^{-3}, $\mu = 0.298$ mm^{-1}, $F(000) = 1416$; total number of reflections measured 1926, of which 711 were unique ($R_{int} = 0.0617$) and 709 observed, 0 restraints, 76 parameters. Data collection range: $3.65 \leq 2\theta \leq 19.94°$. Final R indices: $R1 = 0.1014$, $wR2 = 0.2790$ for data with $I > 2\sigma(I)$ and $R1 = 0.1234$, $wR2 = 0.3502$ for all data; GOF $= 1.022$; max/min. residual electron density 645/ − 455 e nm^{-3}. c) Colorless single crystals suitable for X-ray diffraction studies were grown from tetrahydrofuran and *n*-hexane for **1** and *n*-hexane for **2**. A suitable crystal of each compound was mounted on a glass fiber and coated with paraffin oil. Diffraction data were collected on a Siemens–Stoe AED2 four-circle instrument (at −150 °C for both compounds), with graphite-monochromated Mo$_{K\alpha}$ radiation (0.71073 Å). The structures were solved by direct methods with SHELXS-90[22] and refined against F^2 on all data by full-matrix least-squares with SHELXL-93.[23] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically calculated positions and refined using a riding model. 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-102246 and 102247. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[$Zn_2(thf)_2(EtZn)_6Zn_4(\mu_4\text{-}O)(t\text{Bu}PO_3)_8$]: A Dodecanuclear Zincophosphonate Aggregate with a $Zn_4(\mu_4\text{-}O)$ Core[**]

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*Dedicated to Professor Helmut Werner
on the occasion of his 65th birthday*

Zincophosphates and phosphonates are among the targets of current vigorous research activity aimed at the preparation of novel types of porous structures. These materials could serve as molecular sieves, size/shape selective catalysts, adsorbents, ion exchangers, and matrices for electronic and optical devices. Zincophosphates display a large structural variety and in most cases, they form three-dimensional networks.[1] Importantly, chiral structures[2] and large-pore structures with low densities[3] have also been demonstrated in zincophosphates. Recently, a new family of $M_3Zn_4O(PO_4)_3$ phases (M = alkali metal) that feature $Zn_4(\mu_4\text{-}O)$ centers was reported.[4] Layered,[5] chain-like,[3d, 5a,b, 6] and, in rare cases, even molecular species are also known. Of the two molecular zincophosphates known one features an eight-membered

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