# Transformations of Molecules and Secondary Building Units to Materials: A Bottom-Up Approach

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**ABSTRACT**

A variety of complex inorganic solids with open-framework and other fascinating architectures, involving silicate, phosphate, and other anions, have been synthesized under hydrothermal conditions. The past few years have also seen the successful synthesis and characterization of several molecular compounds that can act as precursors to form open-framework and other materials, some of them resembling secondary building units (SBUs). Transformations of rationally synthesized molecular compounds to materials constitute an important new direction in both structural inorganic chemistry and materials chemistry and enable possible pathways for the rational design of materials. In this article, we indicate the potential of such a bottom-up approach, by briefly examining the transformations of molecular silicates and phosphates. We discuss stable organosilanols and silicate secondary building units, phosphorous acids and phosphate secondary building units, di- and triesters of phosphoric acids, and molecular phosphate clusters and polymers. We also examine the transformations of metal dialkyl phosphates and molecular metal phosphates.

## 1. Introduction

In 1756, Cronstedt discovered a class of minerals that on heating produced steam and called them *zeolites* from Greek, meaning *boiling stone*.[1,2] This was followed by the observations of Damour who noticed in 1840 that zeolites could be reversibly dehydrated and of Grandjean (1909) who reported that dehydrated zeolites adsorb small molecules. Weigel and Steinhoff found that the zeolite *chabazite* adsorbs methanol, ethanol, and formic acid but not acetone, ether, and benzene. MacBain interpreted this observation in 1926 in terms of molecular size differentiation at about 5 Å due to dehydration of the zeolites without the loss of the space lattice. Milton produced the first man-made zeolite in 1949.[1,2] Since then, zeolite science has emerged as one of the important areas attracting the attention of chemists, engineers, materials scientists, and physicists. Metal phosphates, on the other hand, exist in nature as minerals or as constituents of living animals and play an important role in energy conversion cycles. From a structural viewpoint, metal phosphates are similar to silicates and for this reason, studies on metal phosphate and related phosphonate materials have received considerable attention.

The search for new zeolite-like structures was initially extended to aluminophosphate-based molecular sieves,[3] and these explorations produced a variety of exotic compounds with open-framework structures, which include besides metal phosphates,[4] carboxylates,[5] sulfates,[6] selenites, and selenates.[7] Growth of this area has been rapid in the past decade necessitating new editions of the *Atlas of Zeolites*.[2] It is noteworthy that metal−organic framework (MOF) solids have been included as zeolite types in the latest edition of the *Atlas of Zeolites*.

While numerous framework structures incorporating a variety of metals and nonmetals have been assembled under laboratory conditions and structurally characterized and their properties have been explored, the present synthetic methodologies available for their preparation (viz., solvothermal and hydrothermal synthesis) do not offer much control over the final products. Typically, a metal source, a ligand, and an organic or inorganic structure-directing template are heated together in a sealed vessel for several days and cooled slowly to crystallize the framework solid. Although some generalizations can be made with regard to these reactions and to predicting the role played by the structure-directing

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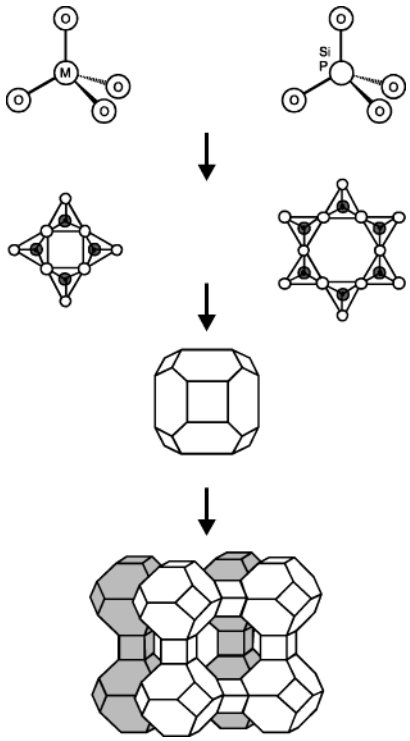
**Chart 1. Schematic Representation of the Formation of Zeolites from $TO_4$ Units**



templates to some extent, it is not yet possible to choose a given set of reactants and reaction conditions and predict *before-hand* the major product that would form in preference to other possible products. In other words, although framework solids and synthetic zeolites are essentially formed by metal ions in association with anions such as $PO_4^{3-}$ and $SiO_4^{4-}$ (Chart 1), it is not yet possible to drive these reactions toward a particular framework solid.

The lack of suitable starting materials, combined with the fact that the reactions are generally carried out in a heterogeneous medium, explains the difficulties faced in designing framework solids. In light of recent developments in the molecular chemistry of siloxanes and phosphates, it is beginning to appear that routes to *designer framework solids* may indeed become possible soon. While there have been numerous literature reports of both hydrothermal synthesis of framework solids and laboratory preparation of model compounds often soluble in organic solvents,[3−8] there have been very few attempts to convert molecular compounds into framework structures through simple chemical transformations. The objective of this Account is to highlight some of the recent developments in the area of molecular compounds that resemble several of the secondary building units (SBUs) identified in extended structures[8] and demonstrate possible strategies and some successes wherein these small molecular units are transformed into framework solids or vice versa. In doing so, it is by no means possible to cover all aspects of this burgeoning area, and we shall therefore refer to pertinent reviews describing materials and structures and limit ourselves solely to the theme relating to molecule/SBU to materials transformations. We have restricted the discussion to silicates and phosphates due to the intense activity on these materials both at the molecular and extended framework levels. For the sake of completeness, a brief discussion on the conversion of the molecular compounds to condensed solids and inorganic−organic hybrid materials with potential use as solid-state catalysts is also included.

**Chart 2. Tetrahedral Primary Building Units**

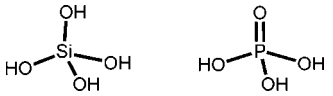
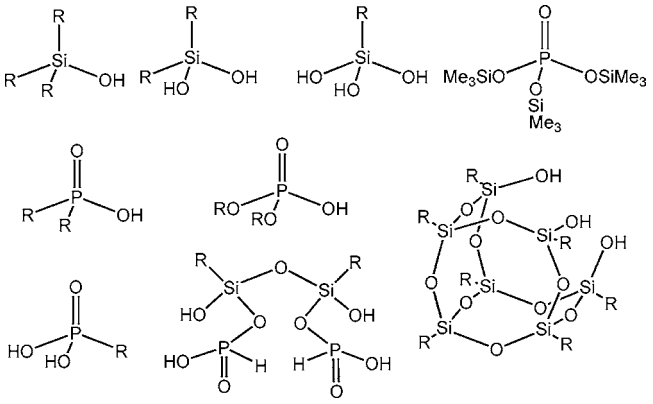


**Chart 3. Silanols and Phosphorous Acids Used as Building Blocks for the Synthesis of Model Compounds**



## 2. Stable Organosilanols and Silicate SBUs

While $Si(OH)_4$ and $P(O)(OH)_3$ could serve as ideal starting materials for the incorporation of $SiO_4^{4-}$ and $PO_4^{3-}$ anions (Chart 2), their use in synthesizing molecular siloxanes and phosphates is somewhat limited since their synthesis is conducted in a homogeneous organic medium. For example, orthosilicic acid is metastable and not available in a free state. Even if $Si(OH)_4$ could be made available, its insoluble nature precludes its chemistry from being explored in solution. Similar problems are encountered in using anhydrous $P(O)(OH)_3$. Synthetic chemists have sought to use alternative starting materials for the incorporation of Si−O and P−O linkages. This has led to the use of a variety of organosilanols,[9] esters of orthosilicic acid, phosphonic acids, and esters of orthophosphoric acid as starting materials (Chart 3).

Although the chemistry of metal-containing molecular silicates (*metallosiloxanes*) is more than a century old,[10] their use as model compounds for zeolites and as precursors for the preparation of metallosilicate materials has gained importance only in the past decade.[11] While the early work on metallosiloxanes provided insights into the nature of Si−O−M linkages, its direct application to zeolites was somewhat remote since monosilanols, $[R_3Si(OH)]$, produce metallosiloxanes, $[M(OSiR_3)_n]$, that barely resemble any of the SBUs of zeolites.[12] It is no wonder that these compounds have often been referred to as a special class of alkoxides rather than molecular silicates. During the 1970s and 1980s, the synthesis of cyclic metallosiloxanes was reported starting from silanediols of

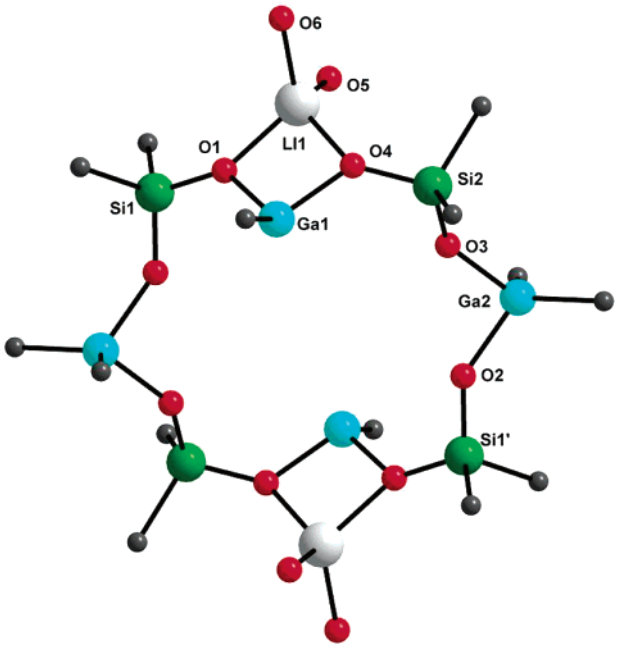



**FIGURE 1.** Molecular structure of the core of the lithium gallium siloxane showing the S8R.

the type $[R_2Si(OH)_2]$ and $[HOSiR_2{-}O{-}SiR_2OH]$.[13] We recently demonstrated that even a simple silanediol such as $Ph_2Si(OH)_2$ could be used for the preparation of the only known soluble compound with a single-8-ring (S8R) motif from its reaction with $LiGaMe_4$ (Figure 1). Interestingly, the cavity formed inside the 8-ring is large enough in this case to accommodate a $(LiOH)_2$ unit.[14]

Modern metallosiloxane chemistry *mainly* deals with three types of silanols: silanetriols,[11] incompletely condensed silasesquioxanes,[15] and tri(*tert*-butyl) ester of orthosilicic acid.[16] Research on these compounds has contributed to the development of model compounds for zeolites, new homogeneous catalysts, and low-temperature pathways to metal−silica materials.

**Silanetriols.** A major break-through in silanol research occurred in the 1990s with reports appearing on the high yield synthesis of silanetriols, $[RSi(OH)_3]$.[17] Silanetriols were traditionally considered to be highly unstable due to the well-known self-condensation reactions through which they form condensed siloxanes. However, the use of a sterically demanding and kinetically stabilizing substituent on silicon allowed the isolation of silanetriols in multigram quantities. For example, the silanetriol $[(2,6\text{-}i\text{Pr}_2C_6H_3)(SiMe_3)NSi(OH)_3]$, is a unique material that is stable in air for at least 3 years![11] It is lipophilic and soluble in a variety of organic solvents. While the bulky 2,6-diisopropylphenyl group no doubt provides the kinetic impedance to Si−OH condensation, the role played by the $SiMe_3$ group in stabilizing this silanetriol is also crucial. This silanetriol has served as a versatile starting material for the synthesis of more than 100 metallosiloxanes, highlighting the use of these compounds as models for metal-embedded silica surfaces and single-source precursors for new catalytic materials. It is interesting that the reactions can often be fine-tuned by paying careful

**Chart 4. Organic Soluble Molecular Silicates Derived from $RSi(OH)_3$**

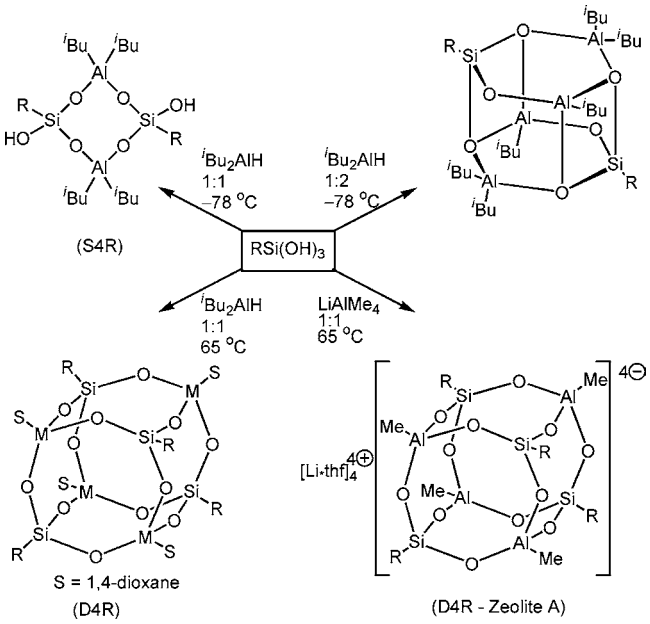
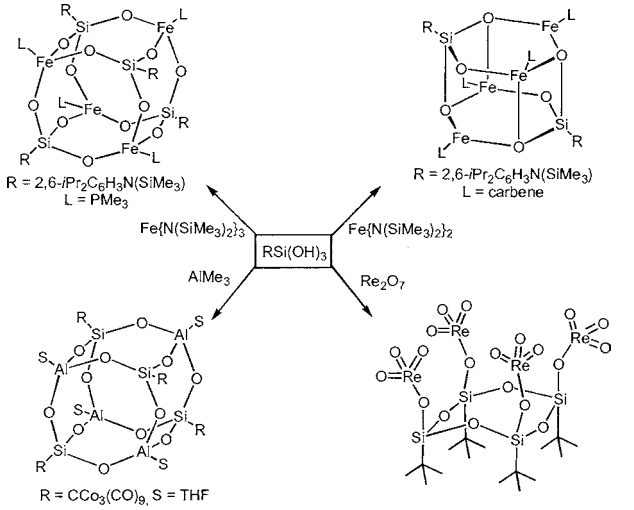



**Chart 5. Interesting Metallosiloxanes Derived from $RSi(OH)_3$**




attention to the nature of the metal precursor, the reaction temperature, and the polarity of the medium. For example, the reactions of $RSi(OH)_3$ with organoaluminum reagents proceed at temperatures between −78 and 80 °C and produce cyclic and cage-soluble aluminosiloxanes, which model zeolites (Chart 4).[18] The structural varieties that can result from silanetriol and metal precursor reactions are shown in Chart 5.[19]

The successful preparation of exceptionally stable and soluble organosilicon trihydroxides has led to the development of exciting new chemistry, and clearly there are several opportunities for further work, especially in the synthesis of framework structures starting from the SBUs shown in Charts 4 and 5.

**Silsesquioxanes.** At the same time as silanetriols were stabilized, another significant observation was made in the hydrolysis of silyl trihalides. Incompletely condensed silsesquioxanes, $R_7Si_7O_9(OH)_3$ (Chart 6) are formed along with other products during the hydrolysis of $RSiCl_3$ (R =

**Chart 6. Silasesquioxanes Derived from $(cy)_7Si_7O_9(OH)_3$**

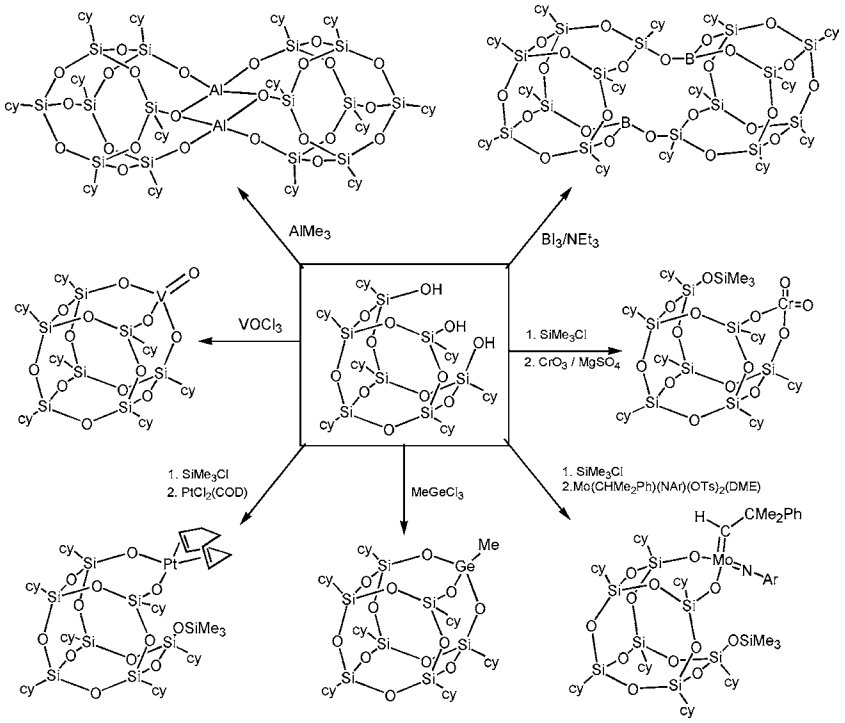
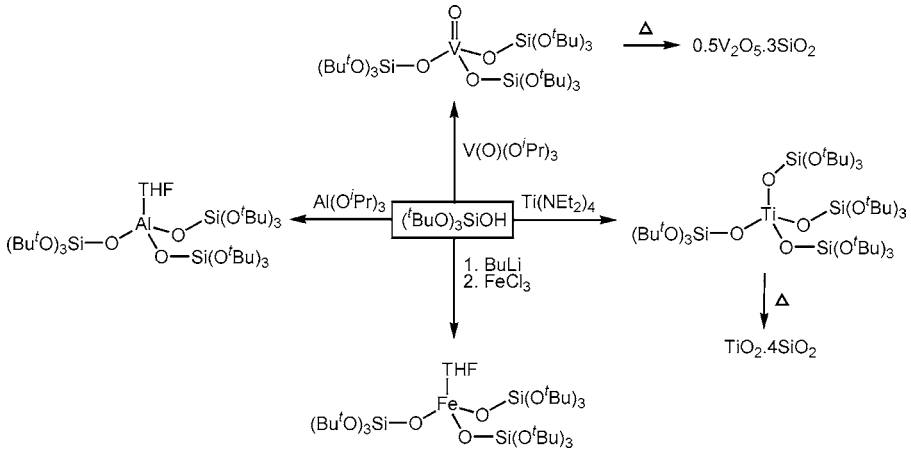



**Chart 7. Thermally Unstable Metal Siloxides Derived from Tri(*tert*-butoxy)silanol**

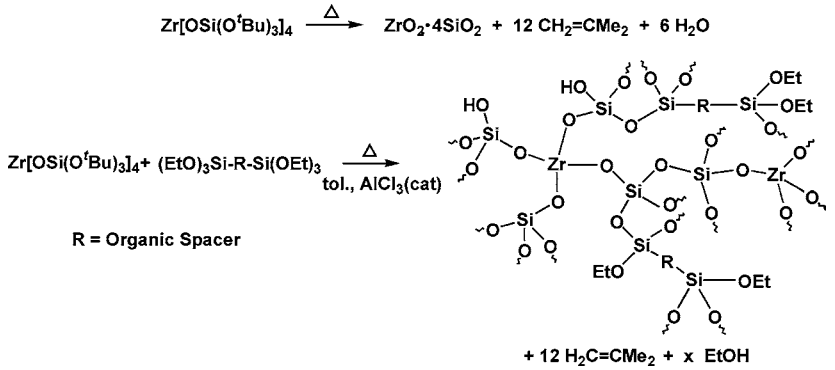



cyclohexyl) in commercial acetone.[20] Silsesquioxanes, $R_7Si_7O_9(OH)_3$, by the virtue of having three Si−OH hydroxyl groups pointing toward an open corner of a cube, are very important as model compounds for silica surfaces and also as starting materials for the preparation of metallasiloxanes through corner-capping reactions (Chart 6).[15] Some of these metallasilsesquioxanes are found to be useful as catalysts in organic transformations.[21] These aspects have been discussed elsewhere[15,21] and will not be elaborated here.

**Silicate and Hybrid Materials through Molecular Siloxanes.** Renewed interest in monosilanols and silanediols is primarily because compounds obtained from $[(t\text{BuO})_3\text{SiOH}]$ and $[(t\text{BuO})_2\text{Si(OH)}_2]$ serve as better single-source precursors for ceramic materials. A number of metallasiloxanes have been synthesized starting from $[(t\text{BuO})_3\text{SiOH}]$, and a selection of these compounds is shown in Chart 7. Most of these metallosiloxanes serve as excellent precursors for the preparation of condensed-phase metallosilicate materials (or metal oxide/silica composites) with precise stoichiometries.[16,22,23] For example, direct thermolysis of the titanosiloxane $[\text{Ti}\{(\text{OSi}(\text{O}t\text{Bu})_3\}_4]$ results in the removal of organic material through $\beta$-hydride elimination and condensation of hydroxyl groups to result in $TiO_2{:}4SiO_2$. Using similar strategies, oxides of vanadium, chromium, molybdenum, tungsten, zinc, manganese, and several other metals have been stabilized in a silica matrix.[23] Aluminosilicates have been synthesized using this methodology starting from $[\text{Al}\{(\text{OSi}(\text{O}t\text{Bu})_3\}_3]$. Several of the metallosilicate materials prepared through this pathway are useful catalysts in organic transformations.[24]

An interesting variant of metal−tri(*tert*-butoxy)siloxide chemistry was described recently. Thus, the thermal

**Chart 8. Conversion of $Zr[OSi(O^tBu)_3]_4$ into Ceramic and Inorganic/Organic Hybrid Materials**

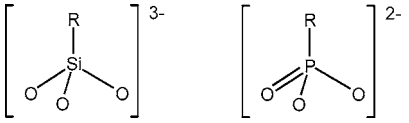



decomposition of $Zr[OSi(OtBu)_3]_4$ occurs in toluene or in the solid state under mild conditions (150 °C) to give ($ZrO_2$·$4SiO_2$) with all of the component elements originating from a single molecular species (Chart 8). On the other hand, the cothermolytic synthesis of the hybrid network materials can be carried out in toluene at 155 °C in the presence of $AlCl_3$ catalyst.[25] It is postulated that the condensation of $Zr[OSi(OtBu)_3]_4$ with $(EtO)_3Si-R-Si(OEt)_3$ proceeds through the initial thermal decompositon of $Zr[OSi(OtBu)_3]_4$ to give $Zr[OSi(OH)_3]_4$. The reactive Si−OH groups then self-condense or condense with Si−OEt groups from $(EtO)_3Si-R-Si(OEt)_3$ to form an inorganic/organic network material via the concomitant elimination of ethanol. Gel formation occurs rapidly within ca. 10 min and affords high-surface-area xerogels upon drying. The as-synthesized materials are highly functionalized with surface OH groups up to 4.8 sites $nm^{-2}$. This method offers an opportunity to synthesize a wide variety of hybrid materials that combine transition metals with diverse organic spacers in an organic medium excluding water.

## 3. Phosphorus Acids and Phosphate SBUs

Unlike the silanols, alkyl phosphorus acids, such as phosphinic acids $[R_2P(O)(OH)]$ and phosphonic acids $[RP(O)(OH)_2]$ (Chart 2), are easier to prepare and handle under laboratory conditions.[26] Metal phosphates derived from these acids are similarly more stable than the corresponding metallasiloxanes. This has resulted in an outburst of activity in building molecular phosphinates and phosphonates that often resemble the smaller secondary building units of zeolites and other framework solids, apart from the synthesis of a large number of layered inorganic phosphonates. The chemistry of hundreds of layered metal phosphonates synthesized from phenylphosphonic acid, alkyl and aryl diphosphonic acids, and phosphonic acids containing additional carboxylic acid functional groups has been documented well in the literature in the last three decades.[26] Structures of these phosphonates do not resemble the SBUs of framework phosphates, nor are they soluble in organic solvents for further reaction chemistry. We will focus our attention here on soluble cyclic and cage-like organic phosphinates and phosphonate molecules, which resemble SBUs of framework solids.

**Chart 9. Silanetriolate Anion vs Phosphonate Anion**

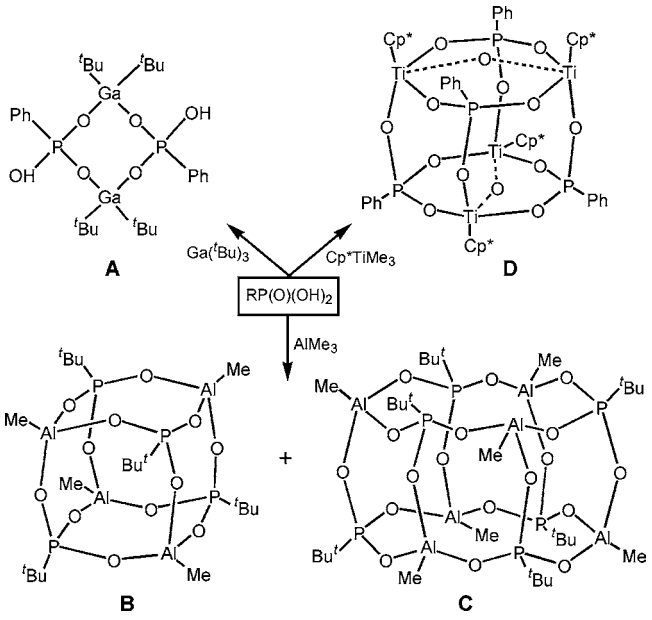



**Phosphonic Acids.** Phosphonic acids, $RP(O)(OH)_2$, when deprotonated afford $RPO_3^{2-}$ which, in principle, should behave similarly to the silanetriols, $RSi(OH)_3$ (Note that $SiO_2$ is isoelectronic to $AlPO_4$) (Chart 9).[26] For reasons of solubility, most of the efforts to generate SBUs have been carried out with *tert*-butylphosphonic acid, although reactions with phenyl- and methylphosphonic acid have also been examined. Thus, the reaction of *t*-$BuP(O)(OH)_2$ with any group 13 trialkyl leads to a three-dimensional cage with a double-4-ring (D4R) core (cf. Chart 4)[27] as in the case of reactions of silanetriols with triaalkylalumnium. While in compounds derived from the phosphonic acids one alkyl group is intact on each heteroatom, the fourth coordination site is a solvent molecule around the heteroelement in the analogous siloxane cubes.

There appears to be a steric control in determining whether a cubic cage (D4R) is always formed in these. A report by Mason suggests that in the reaction of bulky *t*-$Bu_3Ga$ with phenylphosphonic acid, it is possible to obtain both an eight-membered ring compound (single-4-ring, S4R; Chart 10, structure **A**) and a cubic cage (D4R).[28] The reaction of $Me_3Al$ with *tert*-butylphosphonic acid underscores such steric control.[29] In this reaction, apart from the cubic tetrameric aluminophosphonate **B** (D4R), a hexameric drum-like product with a double-6-ring (D6R) core (Chart 10, structure **C**) is obtained in considerable yields. While in the former case the bulkiness of the *tert*-butyl group on gallium is responsible for the formation of the S4R structure, in the latter the rather small size of the methyl group on aluminum is the main cause of the ready assembly of the D6R structure. The reactions of $Cp^*TiMe_3$ with alkyl and aryl phosphonic acids offer easy access to novel oxygen bicapped distorted D4R structures (Chart 10, structure **D**).[30]

Ionic phosphonates, which contain loosely bound alkali metal ions, are of interest from the point of view of modeling zeolites containing dissolved metal ions displaying conductive hyperlattices. Reactions of *t*-$BuP(O)(OH)_2$ with alkali metal salts of tetraalkylgallates provide a convenient route to ionic phosphates (Chart 11).[31] A

**Chart 10. Neutral Phosphonates Mimicking S4R, D4R, D6R, and Bicapped D4R SBUs**




notable feature is that the size of the alkali metal ions regulates the final structure. Thus, the lithium compound is made of two 12-membered gallophosphonate bowls, which sandwich four lithium ions arranged in the form of a one-dimensional wire.[31a] The gallophosphonates derived from both $NaGaMe_4$ and $KGaMe_4$ are essentially made up of an eight-membered gallophosphonate bowl, which surrounds an ensemble of Na or K ions. Because of the larger size of Na and K ions, they can accommodate higher coordination numbers and form agglomerates rather than the linear wire as in the lithium case.[31b]

**Nanosized Metal Phosphonate Aggregates.** Several phosphonate clusters of a very large size have been synthesized in recent years. For example, the use of the organometallic precursor $Cs[Al\textit{i}Bu_3F]$ has allowed the synthesis of a new supercluster $[Cs_3(THF)_3F(\textit{i}BuAl)_3(\textit{t}BuPO_3)_4]_2[(\textit{i}BuAl)_2Al_2(\mu\text{-}F)_2(\textit{t}BuPO_3)_4]$,[32] which contains several structural features closely related to the motifs present in layered and three-dimensional alumino- and gallophosphates (C6R or 6≡1 found in BPH and AFS types of layered aluminophosphates). The reaction of $Et_2Zn$ with $\textit{t}BuP(O)(OH)_2$ leads to a rugby-ball shaped dodecanuclear Zn-cluster, $[Zn_4(\mu_4\text{-}O)(Zn{\cdot}THF)_2(ZnEt)_6(\textit{t}BuPO_3)_8]$.[26] The reaction of $Me_2Cd$ with $\textit{t}BuP(O)(OH)_2$ solution yields a still larger aggregate, $[(MeCd)_{10}((THF)Cd)_4Cd_6(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_2(\textit{t}BuPO_3)_{12}]$, which contains 68 heteroatoms arranged in the form of a hollow sphere (Figure 2).[33] This cluster contains a skeleton made up of 20 cadmium atoms and 12 phosphorus atoms held together by 36 surface oxygen atoms along with a pair of oxo and hydroxo groups in the interior of the sphere (Figure 2). The inorganic core is embedded in the organic sheath made up of 10 methyl groups, four THF, and 12 *tert*-butyl groups. Within the inorganic core, the diagonally opposite Cd−Cd and P−P distances are 10.9 and 9.8 Å, respectively. This giant molecule can encapsulate three $C_{60}$ molecules.

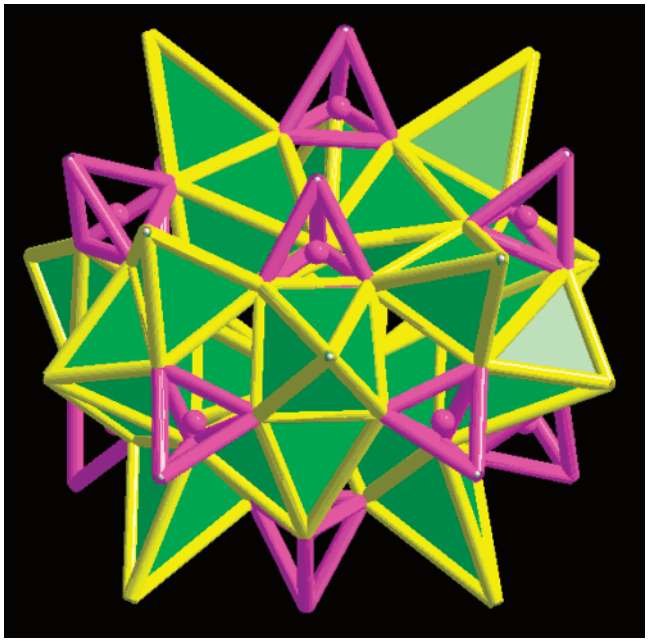


**FIGURE 2.** Polyhedral arrangement in $[(MeCd)_{10}((THF)Cd)_4Cd_6(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_2(\textit{t}BuPO_3)_{12}]$ showing cadmium (closed polyhedra with green interior and yellow edges) and phosphorus (open polyhedra in pink) atoms.

It is possible to use ancillary ligands in addition to phosphonic acids in building up nanosized cluster compounds of late transition metal ions. Thus, the reaction of $CuCl_2$ with *tert*-butylphosphonic acid in the presence of 3,5-dimethylpyrazole affords a dodecanuclear copper phosphonate with an interesting cage structure.[34] Similarly, large vanadium phosphonate clusters with up to 18 vanadium atoms have been assembled from phosphonic acids.[35]

## 4. Phosphoric Acid Esters as Primary Building Units

Much of the work on the use of phosphate esters for building up molecular metallaphosphates has emerged only in the past decade. While di(*tert*-butyl) phosphate (dtbp-H) has been the most widely used,[36,37] studies have also been carried out with the tris(trimethylsilyl) ester, $(Me_3SiO)_3P{=}O$.[38] Compared to phosphonic acid chemistry, the chemistry of phosphate esters assumes importance, because of the presence of the reactive/thermally labile P−OR linkages relative to the stable P−C linkages in the phosphonic acids. Although phosphonic acids provide model compounds that can act as SBUs of zeolite structures and nanoscopic clusters, expansion of these SBUs and clusters to framework solids would require further functionalization of the alkyl groups on phosphorus. Conversely, the generation of P−OH groups on the surface of the molecular cluster formed by phosphorus esters is a relatively easier task and is achieved either by $\beta$-hydride elimination of P−O*t*Bu groups or by the facile hydrolysis of P−$OSiMe_3$ groups in solution. Several metal phosphate molecules have been synthesized starting from these two

**Chart 11. Anionic Gallium Phosphonates**

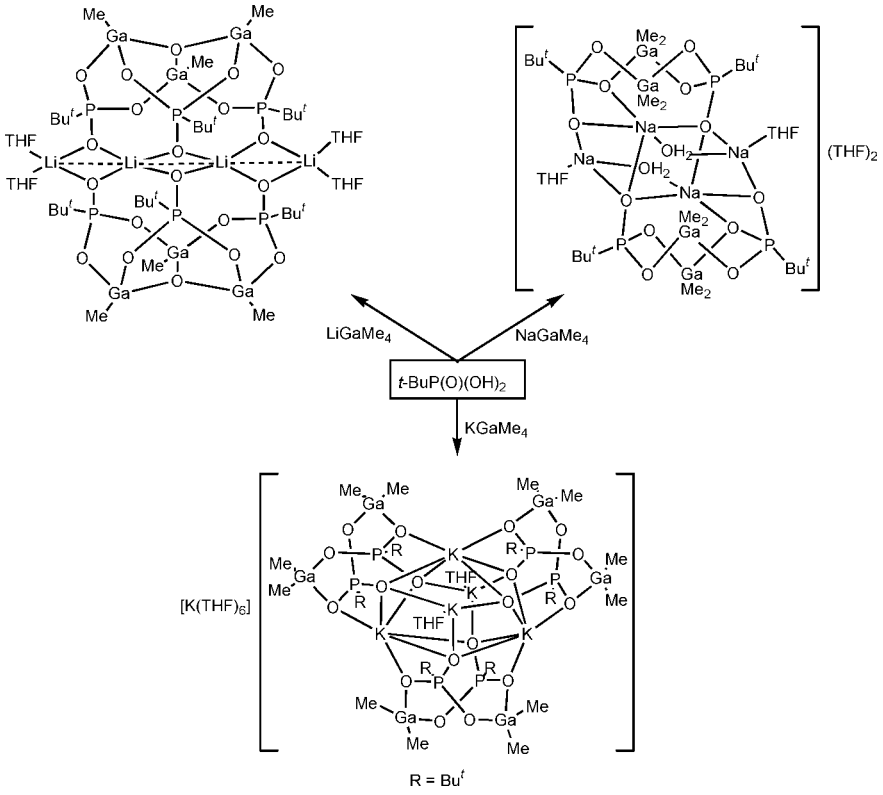



**Chart 12. Complexes of Di(*tert*-butyl) Phosphate with Aluminum**

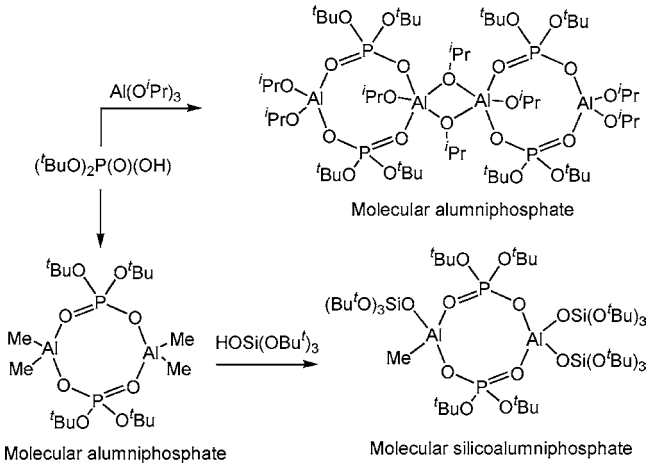
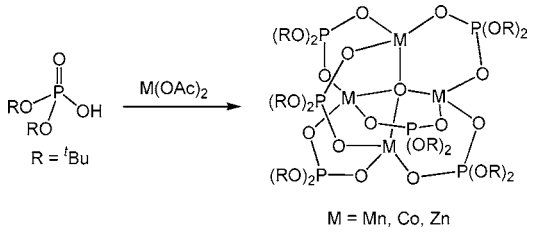



**Chart 13. Synthesis of Tetranuclear Phosphates**




phosphate esters; we shall limit the discussion here to those that can act as precursors for ceramic phosphates or have the potential to act as starting materials for building up framework structures.

The reaction of 2 equiv of dtbp-H with $Al_2Me_6$ affords an eight-membered ring by the loss of 2 equiv of methane.[37c] On the other hand, the reaction with $[Al(OiPr)_3]_4$ yields a centrosymmetric tetramer with two eight-membered rings connected by bridging isopropoxides (Chart 12). The presence of reactive Al−Me, Al−O*i*Pr, and P−O*t*Bu linkages in these S4R products renders them useful as starting materials to build higher structures. For example, the cyclic aluminophosphate with Al−Me groups reacts readily with 3 equiv of $(tBuO)_3SiOH$ to give a molecular silicoaluminophosphate (M-SAPO) (Chart 12), which on further thermal treatment or sol−gel processing is transformed to a SAPO-type material.[39]

## 5. Molecular Phosphate Clusters and Polymers

Tetranuclear clusters of divalent transition metal ions are generated from the direct reaction of a metal acetate with dtbp-H (Chart 13).[36a] Advantages of this reaction over the other reactions described in this article lie in the use of metal acetates instead of the more expensive and moisture-sensitive metal alkyls and the use of methanol as a solvent in aerobic conditions. It is to be noted, however, that organometallic routes can also be used to synthesize these tetrameric compounds.[37a] Small changes in the reaction conditions and the use of mild Lewis bases bring about changes in the structures. For example, polymeric phosphates are formed by the addition of THF or a mild base during the course of the reaction (Chart 14). These one-dimensional polymers are made up of M−O−P inorganic backbones covered with a hydrophobic sheath of *tert*-butyl groups.[36b] Thermal decomposition of the polymers in the 300−400 °C range produces the corresponding metal metaphosphate (Chart 15).[36b]

**Chart 14. Preparation of 1D Polymeric Phosphates**

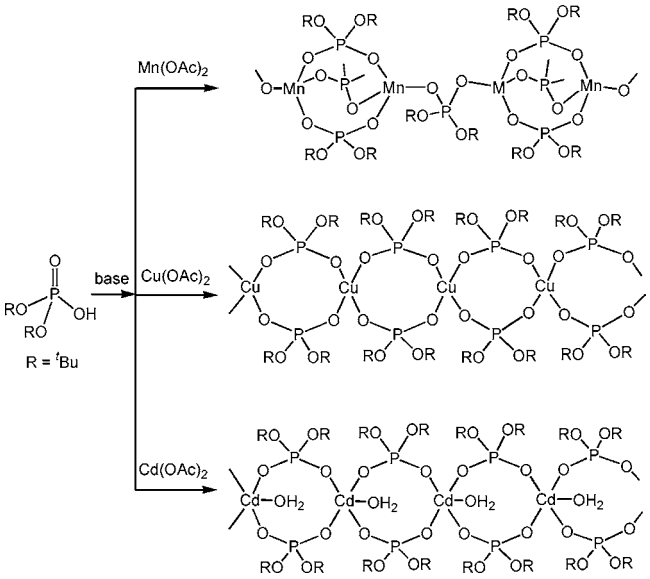



**Chart 15. Preparation of Phosphate Materials from Molecular Complexes**

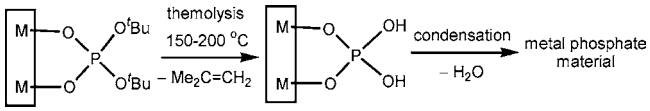
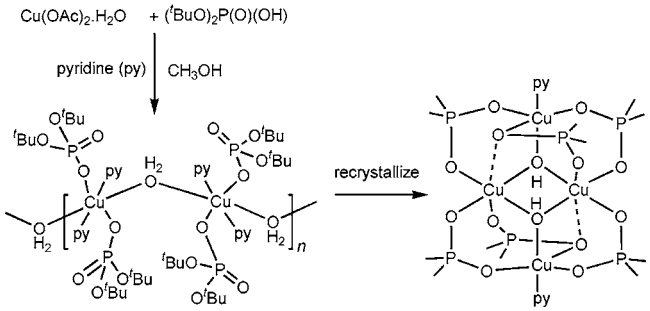



**Chart 16. Linear Polymer and Tetrameric Cage Phosphates from the Same Reaction**




## 6. Structural Transformations in Metal Dialkyl Phosphates

If instead of a mild Lewis base such as THF a strong Lewis base such as pyridine is used in the reaction between copper acetate and dtbp-H, one obtains yet another type of one-dimensional polymeric phosphate (Chart 16).[36c] Recrystallization of this water-bridged polymer in a DMSO/THF/$CH_3OH$ mixture results in the transformation of the polymer to a more stable tetranuclear copper cluster [$Cu_4$-($\mu_3$-OH)$_2$(dtbp)$_6$(py)$_2$] in about 60% yield (Figure 3). This observation demonstrates that even simple recrystallization can bring about an interesting structural transformation at room temperature in such materials.

Encouraged by the 1D polymer → tetrameric cage transformation, other possibilities of transforming metal dialkyl phosphates have been investigated. Interesting among the results obtained so far is the transformation of the 1D cobalt-dtbp polymer into a 2D polymeric grid structure by reaction with 2 equiv of 4,4-bipyridine in

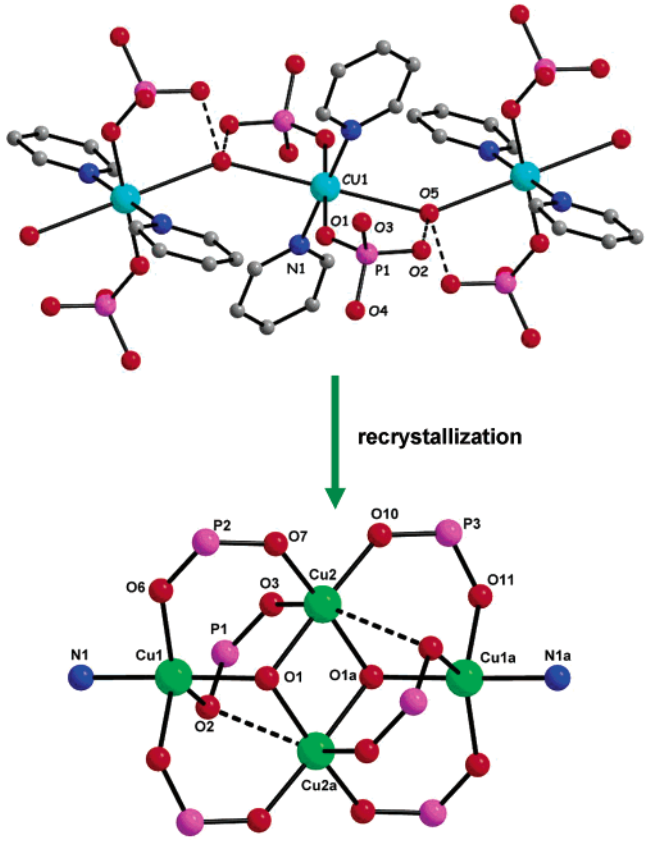
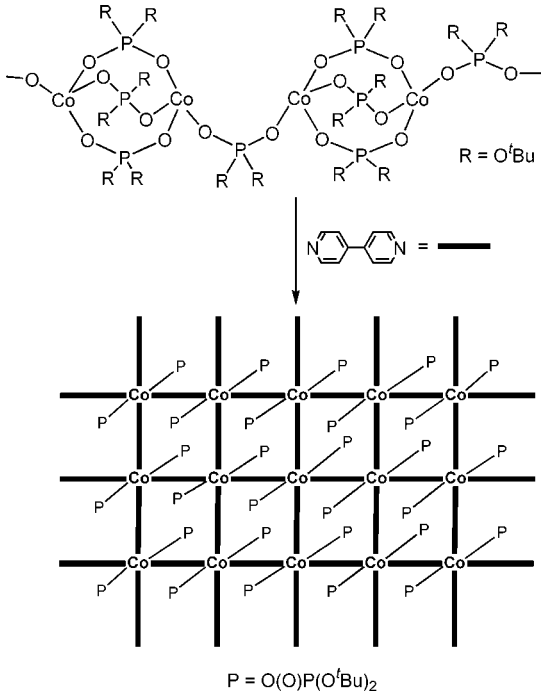



**FIGURE 3.** Conversion of a 1D polymer to a cage structure by simple recrystallization.

**Chart 17. Linear Polymer → 2D Grid Structure Conversion at Room Temperature**




methanol at room temperature as shown in Chart 17.[40] This reaction is quantitative with no side products.

The above two examples are representative of how it is possible to either increase or decrease the dimensional-

ity of a metal dialkyl phosphate, and clearly other possibilities exist in this area. Especially interesting would be the exploitation of the hydrolyzable P−O*t*Bu linkages in the presence of added amines (structure directors) to build up 3D framework phosphates.

## 7. Molecular Metal Phosphates from $P(O)(OH)_3$ and Their Conversion to Higher Dimensional Structures

While all the above molecular phosphates were prepared starting from phosphonic acids and phosphate esters, there are a few examples of molecular phosphates synthesized from phosphoric acid in aqueous medium. Although under hydrothermal conditions the reactions of phosphoric acid with metal ions generally result in extended open framework structures, it has been possible to isolate molecular zero-dimensional metal phosphates.[41,42]

A zero-dimensional tin phosphate comprising a four-membered ring was isolated a few years ago.[41] Similar molecular zinc phosphates were isolated by carrying out the reaction between zinc oxide, phosphoric acid, and an amine at 80 °C.[42a] Another four-membered ring zinc phosphate was obtained by the reaction between a zinc salt, phosphoric acid, and the amine at room temperature over an extended period of time.[42b] This four-membered ring phosphate could also be obtained by the reaction of the amine phosphate with the zinc salt. What is interesting about these four-membered ring metal phosphates is their close resemblance to the S4R secondary building unit. It has been shown recently that the four-membered ring zinc phosphate transforms to one-dimensional, two-dimensional, and three-dimensional structures under relatively mild conditions (Figure 4).[43,44] Interestingly, one-dimensional phosphates with linear chains or ladder structures also transform to two-dimensional and three-dimensional structures, while the layered two-dimensional structures transform to three-dimensional structures.[45,46] These studies show that the formation of complex three-dimensional structures may involve a progressive building up process, as indeed verified by synchrotron studies.[47] Acid degradation of three-dimensional zinc phosphates with channel structures have been found to yield low-dimensional structures, showing thereby the reversibility of the 1D ↔ 2D ↔ 3D transformation process.[48] What is especially noteworthy is the recent observation of the transformation of a four-membered ring zinc phosphate to a linear chain structure at room temperature on reaction with piperazine. The linear chain then transforms to a sodalite-related structure with a $4^6 8^8$ cage at 50 °C (Figure 5).[49] A transformation of metal squarates to sodalite structures has been observed recently,[50] showing thereby that the four-membered ring motif can generally act as a SBU.

In the case of aluminum phosphates, Ozin et al.[3b] have pointed out the possibility of the transformation of a chain structure to other chains or to layered and three-dimensional open-framework structures through a hydrolysis−condensation self-assembly pathway. We have recently carried out a few interesting molecule−material

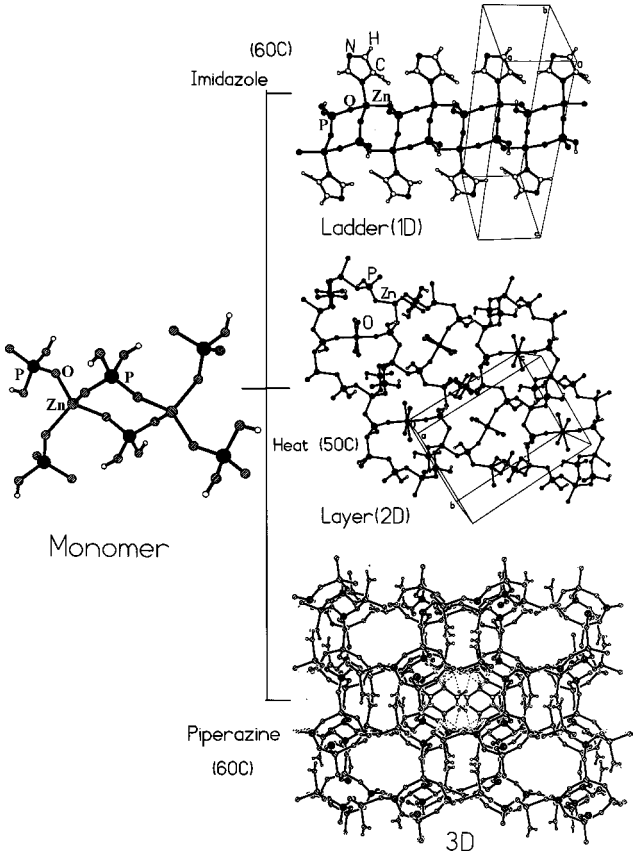



**FIGURE 4.** Transformations of a zero-dimensional monomeric zinc phosphate to 1D (ladder), 2D (layer), and 3D structures.

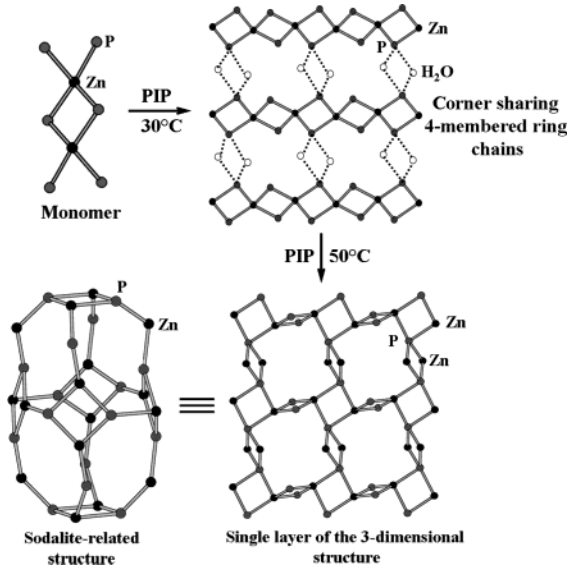



**FIGURE 5.** Transformation of a four-membered ring zinc phosphate (SBU) to a linear chain phosphate and the transformation of the latter to a 3D sodalite-related structure with a $4^6 8^8$ cage.

transformations in aluminophosphates. Thus, we found that the centrosymmetric, tetrameric molecular aluminophosphate (see Chart 12) transforms to a layered structure[51] of composition $[NH_3(CH_2)_2NH_3]^{2+}[Al_2(OH)_2(PO_4)_2(H_2O)]^{2-}\cdot H_2O$ on reaction with ethylenediamine in aqueous medium at 150 °C as shown in Figure 6. Interestingly, this structure can also be obtained as the transformation

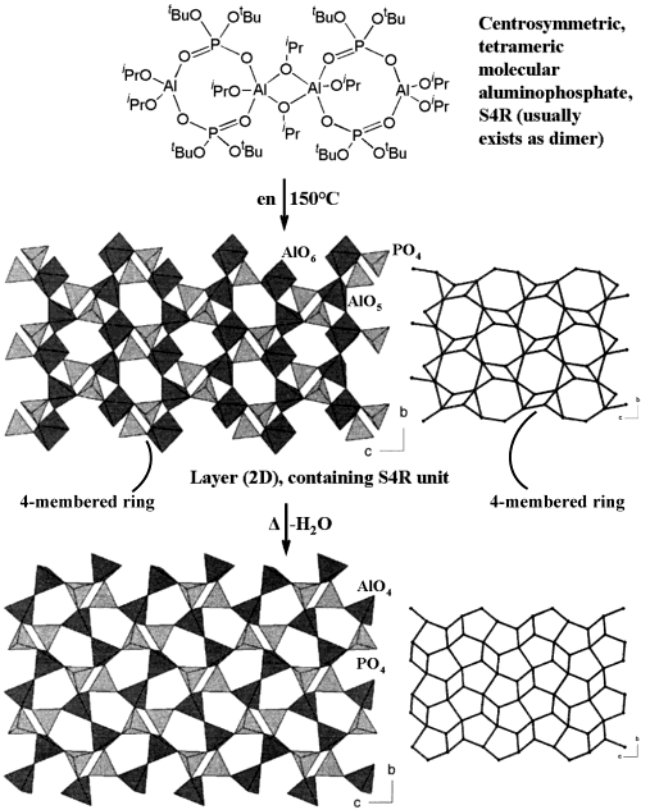



**FIGURE 6.** Transformation of a four-membered ring aluminophosphate (S4R) to a layered phosphate, which then undergoes transformation to another layered structure by the loss of water molecules. Note that the 2D component contains four-membered rings.

product of a one-dimensional ladder compound of composition $[NH_3(CH_2)_2NH_3][AlP_2O_8H]$.[52] This layered structure transforms to another layered structure by loss of water molecules, followed by reorganization of the aluminophosphate layer (Figure 6). The molecular aluminum phosphate compound gives rise to a three-dimensional structure with channels on reacting with piperazine in aqueous medium at 150 °C. We are exploring reactions of this molecular aluminum phosphate precursor and similar compounds in various media.

## 8. Conclusions and Outlook

The discussion in the previous sections should suffice to indicate the importance of the transformations of molecular compounds to materials. Studies of such transformations are only making a beginning, and there appears to be a great future for such investigations. Thus, the recent synthesis of a sodalite-related structure from a molecular zinc phosphate is noteworthy, besides the transformation of the centrosymmetric, tetrameric, molecular aluminophosphate to open-framework structures. Preliminary investigations[53] have shown that interesting transformations also occur in metal carboxylates. Thus, molecular zinc oxalate monomers and dimers are found to transform to chain or three-dimensional structures on heating with piperazine in an aqueous medium. The chain structure transforms to a layer structure. We believe that it would be rewarding to pursue investigations on the transformation of various molecular precursors including those involving aluminophosphate and silicate motifs.

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