

# Molecular Phosphonate Cages: Model Compounds and Starting Materials for Phosphate Materials<sup>†</sup>

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## Background

Mimicking *nature* or *naturally occurring systems* and suitably modifying them for the human needs has been one of the major fascinations of scientists working in almost any branch of modern science. Depending on the discipline chosen, one can cite a variety of examples to prove this statement. The different major steps in such studies primarily involve (a) identification of a suitable system, (b) close observation and characterization of the system, (c) copying or mapping the system (at least, the essence of the system), and (d) tracing it to get replica or suitably modifying it to get a better replica with added advantages. Our interests in the area of zeolite science and minerals originate with the same intention.

The story of zeolite research began in 1756, when a selection of natural minerals were discovered by Cronestedt which on heating produced steam. Due to this what was then considered to be a strange phenomenon, he called them *zeolites* from the Greek for “*boiling stone*”. Occurring widely in nature, zeolites are a class of microporous materials, which possess pores and channels

of regular dimensions within the crystalline lattice. These *holes* within the structure have proven to be highly useful and continue to be exploited for a wide variety of applications, e.g., ion exchangers, molecular sieves, and stereoselective catalysts. On the other hand, *phosphates* (which have many structural features in common with zeolites) exist in nature largely in the form of minerals or part of living systems (such as bones and data storage and transport molecules such as DNAs/RNAs!).<sup>1</sup> They also play an important role in energy conversion cycles. Owing to their importance in biology, they have been a well-studied class of compounds over a long time.

Unfortunately, the naturally occurring zeolites and phosphates do not meet the complete need of the modern chemical industry in terms of their availability and properties such as larger pore size, high thermal stability, chirality, and size–shape selectivity. For example, *chabazite* was a rare mineral and was available only in laboratory quantities in the early times. In 1949, Milton working at Union Carbide produced the world’s first man-made zeolites, the most important being Linde A and X.<sup>2</sup> Linde A has gone on to become one of the most widely used zeolites. The search of *new zeolite-like structures* saw the extension of the work beyond the traditional aluminosilicate materials to aluminophosphate-based molecular sieves,<sup>3</sup> followed by the exploration of more exotic structures such as berrylo- and zincophosphate and arsonate molecular sieves.<sup>4</sup> Zirconium phosphates were known even before 1925, and were first used in the quantitative determination of zirconium.<sup>5</sup> A wide range of elements (e.g., Be, Sn, Ti, Zr, V, Cr, Mo, Fe, and Zn) have been incorporated into phosphates, and many new framework structure types have been realized.<sup>6,7</sup>

The purpose of this Account is not to dwell much upon the chemistry of the above-described mineral phosphates or synthetic framework phosphates. Several interesting and comprehensive reviews are already available on this subject.<sup>8</sup> The chemistry we have chosen to present here deals with the means by which chemists can mimic the local structures of the complex metal-containing phosphate materials and understand them better.

## Simple Model Compounds

Metal-containing synthetic silicates and phosphates are traditionally synthesized using the well-known hydrothermal pathway. This essentially involves heating a gel of the appropriate starting materials for a set period of time and then allowing it to cool (not too unlike casserole cooking!). As the gel cools, the desired material appears as a microcrystalline powder. The exact product that is so synthesized is very sensitive to the precise reaction conditions, composition, etc. The actual mechanism by which they crystallize is also not well understood, but it is assumed that hydrated metal cations or organic agents present in the reaction mixture are highly influential

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<sup>†</sup> This paper is dedicated to Professor Robert W. Parry.

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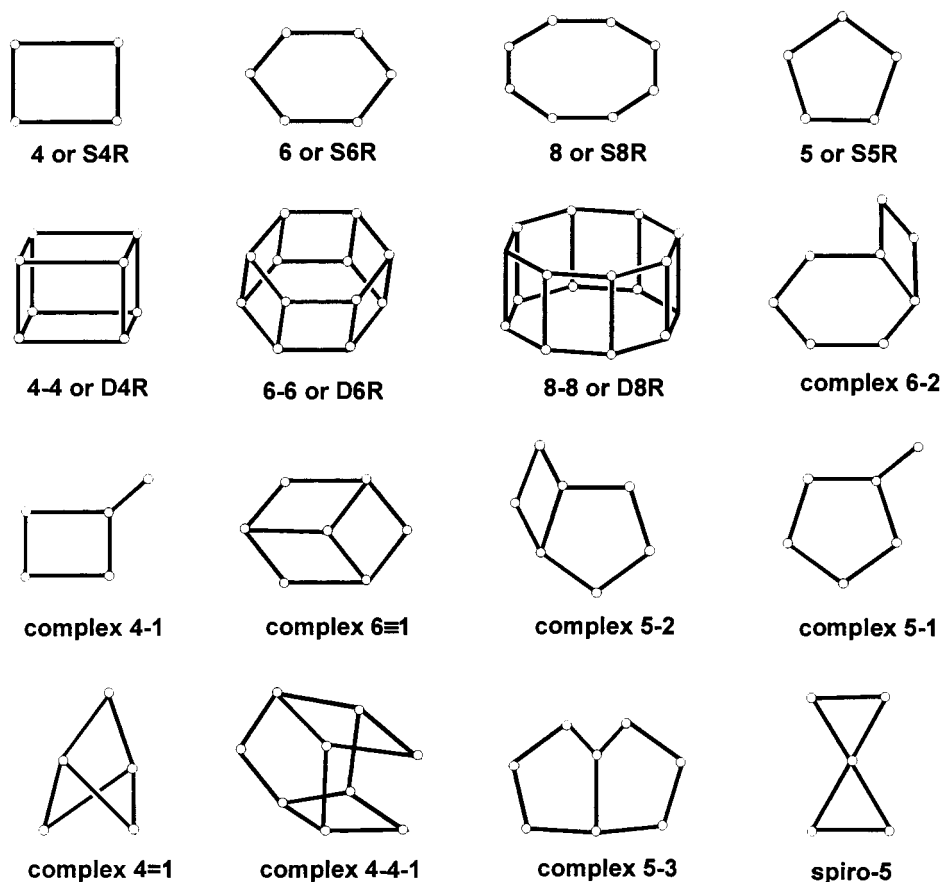


FIGURE 1.

components, behaving as templating agents to direct the formation of the framework about them.<sup>9</sup>

Significant progress has recently been made toward the development of mechanisms of formation of zeolites and aluminophosphate molecular sieves. In this regard, there have been reports on thermochemical calculations of the dense and the microporous phases.<sup>10</sup> There have also been studies on the role of template in the formation of a particular structure.<sup>11</sup> Some models account for the final framework structures by postulating various building blocks, known as secondary building units (SBUs).<sup>12</sup> Several SBUs have been so far identified in the zeolites and in the natural and synthetic aluminum and gallium phosphate molecular sieves (Figure 1).

Our entry into this area stems from our long-standing interest in the chemistry of inorganic ring systems. In the early 1980s, we developed routes for the successful synthesis of metallacyclophosphazenes.<sup>13</sup> Subsequently we were interested in several other inorganic ring systems, and we very recently documented the use of organic-soluble silanetriols in the systematic buildup of large inorganic Si–O–M cages.<sup>14</sup> Since SiO<sub>2</sub> is isoelectronic to AlPO<sub>4</sub>, we thought it would be logical to probe into the chemistry of organophosphonates to generate smaller organic-soluble molecules whose core structure would resemble one or more of these SBUs of phosphate materials. Our results along with those of others<sup>15</sup> in this exciting and emerging area are outlined below.

## Neutral Group 13 Phosphonates

**(a) Cubic Group 13 Phosphonates.** While Al-, Ga-, and In-containing layered phosphates have been well studied, the corresponding boron-containing compounds have received very little attention. A few of the mixed-metal phosphates which contain small quantities of boron are known as good catalysts in organic transformations. Similarly, in the case of indium phosphates, only the dense phases are known. Very recently there have been efforts to synthesize indium phosphates with open structures.<sup>7c</sup> Noticeable among the work on gallophosphates is the synthesis of two new materials, namely, the Linde type A and Cloverite type molecular sieves.<sup>16</sup> Interestingly, in the structures of both the materials D4R building units are found.

Hence, to begin with, we were interested in studying suitable group 13 molecular phosphonate model compounds having the structural feature of the D4R and D6R secondary building units. It has been shown earlier by us that the alkane elimination reaction involving metal alkyls and organosilanetriols is the most facile way for high-yield synthesis of polyhedral metallasiloxanes.<sup>14</sup> A similar synthetic strategy has been adopted for the preparation of 20 cubic group 13 phosphonates (Scheme 1).<sup>17–19</sup> While the general reaction depicted in Scheme 1 is normally very facile for group 13 alkyls with polar M–C bonds (M = Al, Ga, In), the alkane elimination reactions of BR<sub>3</sub> require longer reaction periods and reflux condi-

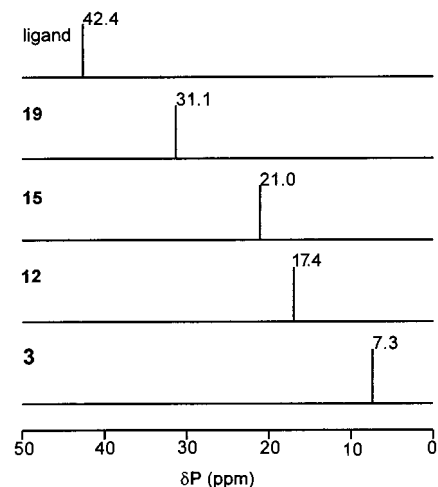
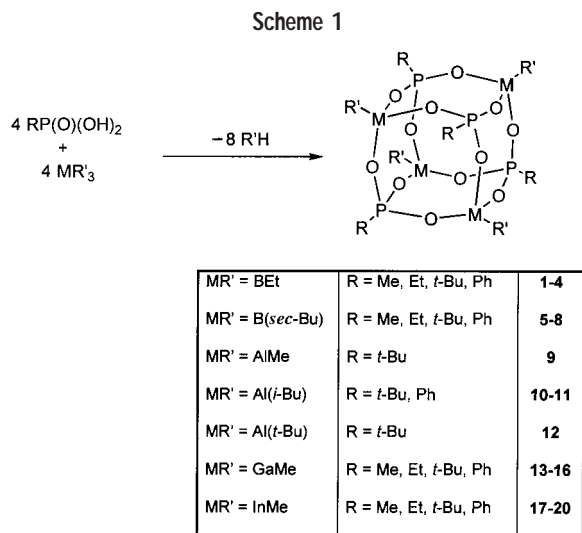


FIGURE 2.

tions owing to the high covalency of the B–C bonds. Cubic phosphonates **1–20** were isolated in moderate to high yields by using this simple alkane elimination reaction. The compounds that contain bulky alkyl groups either on phosphorus (e.g., *t*-Bu) or on group 13 metals (e.g., B-*sec*-Bu, Al-*i*-Bu, or Al-*t*-Bu) yield phosphonates that are completely soluble in all common organic solvents. Further, all the cubic phosphonates are thermally stable, and most compounds were found to either melt or decompose only above 280 °C.<sup>19</sup> It is also of interest to note that, under electron impact mass spectral conditions (70 eV), the cubic core in these molecules remains intact. The peak due to the M<sup>+</sup>–R' fragment is observed as the most prominent peak in all cases. Further, the <sup>31</sup>P NMR chemical shifts of these compounds show a periodic trend. The comparison of <sup>31</sup>P chemical shift data obtained for the *tert*-butylphosphonic acid derived metallaphosphonates indicate that the chemical shifts of all the metal derivatives are high-field-shifted compared to free acid ( $\delta$  42.4 ppm) (Figure 2). The highest shift was observed in the case of borophosphonate **3** ( $\delta$  7.3 ppm,  $\Delta\delta$  = 35.1 ppm), while the least shift was observed for the indium compound **19** ( $\delta$  31.1 ppm,  $\Delta\delta$  = 11.3 ppm). In the case of [*t*-BuPO<sub>3</sub>BEt]<sub>4</sub> and [*t*-BuPO<sub>3</sub>B-*sec*-Bu]<sub>4</sub>, the observed chemical shifts compare well with that reported for [*t*-BuPO<sub>3</sub>BPh]<sub>4</sub> (**21**) ( $\delta$  6.7 ppm).<sup>20</sup>

The solid-state structures of representative phosphonates, viz., [*t*-BuPO<sub>3</sub>BEt]<sub>4</sub> (**3**),<sup>18</sup> [*t*-BuPO<sub>3</sub>B-*sec*-Bu]<sub>4</sub> (**7**),<sup>19</sup> and [*t*-BuPO<sub>3</sub>Al-*i*-Bu]<sub>4</sub> (**10**)<sup>17</sup> have been unambiguously determined by single-crystal X-ray diffraction methods (Figure 3). The core of these molecules as well as those of the recently reported [*t*-BuPO<sub>3</sub>BPh]<sub>4</sub> (**21**)<sup>20</sup> and [PhPO<sub>3</sub>-Ga-*t*-Bu]<sub>4</sub> (**22**)<sup>21</sup> analogues show the presence of a M<sub>4</sub>O<sub>12</sub>P<sub>4</sub> core made up of six eight-membered M<sub>2</sub>O<sub>4</sub>P<sub>2</sub> rings which constitute the faces of the cubic polyhedron. These eight-membered rings have an approximate C<sub>4</sub> crown conformation. The formation of a large number of these compounds clearly indicates that the “cube” is the most favored and stable structure for the neutral group 13 phosphonates. The most important and interesting structural feature of these compounds is the resemblance of the central M<sub>4</sub>O<sub>12</sub>P<sub>4</sub> core to the D4R SBUs of phosphate

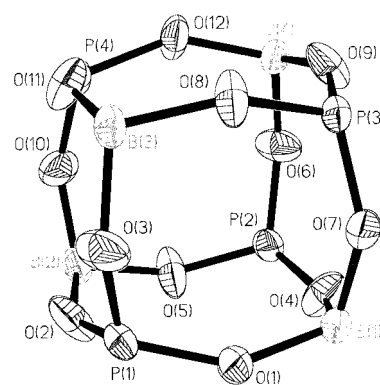


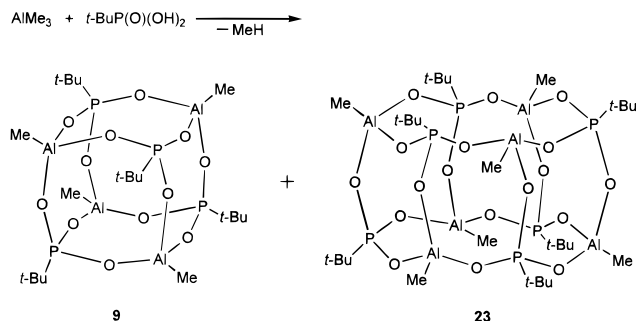
FIGURE 3.

molecular sieves (e.g., cloverite, ULM-5, and gallophosphate-A).<sup>22</sup> Very recently the molecular structures of [MePO<sub>3</sub>AlMe]<sub>4</sub>, [MePO<sub>3</sub>Al-*t*-Bu]<sub>4</sub>, and [PhPO<sub>3</sub>Al-*t*-Bu]<sub>4</sub> have been mentioned in a review by Mason.<sup>15</sup> Cassidy et al. reported the cubic aluminophosphate [Al(PO<sub>4</sub>)(HCl)(EtOH)<sub>4</sub>]<sub>4</sub> as early as in 1975.<sup>23</sup>

A structural comparison of a few of these group 13 cubic phosphonates is presented in Table 1. Unfortunately, the data remain incomplete without a structure determination for any of the cubic indium phosphonates. Our attempts to crystallize any indium compound have so far been unsuccessful. As is evident from Table 1, the size of the central cubic core increases on going from borophosphonates to gallophosphonates. For example, while the average length of the B···P edge of the cube is 2.85 Å in **3** and **7**, the Ga···P distance in [PhPO<sub>3</sub>Ga-*t*-Bu]<sub>4</sub> is 3.22 Å. Similarly, the average lengths of the face diagonals in the M···M and P···P directions increase on going from B to Ga. The body diagonal in the cage of Ga compound is ca. 0.63 Å longer than the corresponding values observed in borophosphonates. However, there is very little change in the M···P, M···M, P···P, and body diagonal distances between the aluminum and gallium derivatives [*t*-BuPO<sub>3</sub>Al-*i*-Bu]<sub>4</sub> and [PhPO<sub>3</sub>Ga-*t*-Bu]<sub>4</sub>. In short, the changes observed in the size of the cubic core on going from B to Al is more pronounced than the corresponding changes observed on going from Al to Ga.

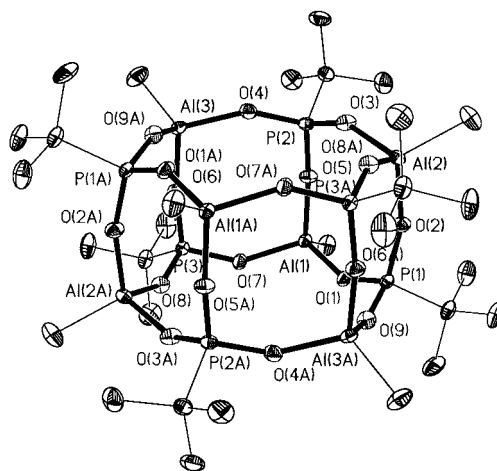
**Table 1. Comparison of the Molecular Structural Parameters of Cubic Group 13 Phosphonates**

structural feature	[ <i>t</i> -BuPO <sub>3</sub> BET] <sub>4</sub>	[ <i>t</i> -BuPO <sub>3</sub> B- <i>sec</i> -Bu] <sub>4</sub>	[ <i>t</i> -BuPO <sub>3</sub> BPh] <sub>4</sub>	[ <i>t</i> -BuPO <sub>3</sub> Al- <i>t</i> -Bu] <sub>4</sub>	[PhPO <sub>3</sub> Ga- <i>t</i> -Bu] <sub>4</sub>
space group	<i>I</i> <sub>4</sub> <i>1</i> / <i>a</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>I</i> <sub>4</sub> <i>1</i> / <i>a</i>	<i>P</i> $\bar{1}$
polyhedral shape	cubic	cubic	cubic	cubic	cubic
M <sub>2</sub> O <sub>4</sub> P <sub>2</sub> ring conformation	<i>C</i> <sub>4</sub> -crown	<i>C</i> <sub>4</sub> -crown	<i>C</i> <sub>4</sub> -crown	<i>C</i> <sub>4</sub> -crown	<i>C</i> <sub>4</sub> -crown
P–O length (average), Å	1.50	1.50	1.50	1.52	1.51
M–O length (average), Å	1.47	1.47	1.46	1.76	1.85
P⋯M length (average), Å	2.85	2.85	2.84	3.17	3.22
P⋯P length (average), Å	3.92	3.93	3.93	4.42	4.42
M⋯M length (average), Å	4.12	4.13	4.15	4.56	4.69
body diagonal (average), Å	4.93	4.94	4.92	5.50	5.57
P–O–M angle (range), deg	146.1–149.3	146.2–148.9	140.7–154.0	147.5–154.9	135.6–175.2
P–O–M angle (average), deg	147.8	147.5	146.8	150.5	150
ref	20	21	23	19	24

**Scheme 2**

**(b) Larger Group 13 Molecular Phosphonates.** Preparation of a large number of D4R phosphonates made us initially believe that it would be impossible to synthesize larger group 13 phosphonates using this synthetic strategy. However, our subsequent reactions gave us the clue that attendant changes on the steric requirements of the R group of the group 13 trialkyl would probably hold the key to overcome this problem. For example, the EI mass spectral analysis of the crude product of the reaction between AlMe<sub>3</sub> and *t*-BuP(O)(OH)<sub>2</sub> showed the presence of a peak corresponding to the M<sup>+</sup> ion of [*t*-BuPO<sub>3</sub>AlMe]<sub>6</sub> (**23**) along with the expected tetrameric product [*t*-BuPO<sub>3</sub>-AlMe]<sub>4</sub> (**9**) (Scheme 2).<sup>24</sup> Isolation of analytically pure hexameric product **23** in useful yields was subsequently achieved by optimization of the reaction conditions and repetitive recrystallization. The M<sub>6</sub>O<sub>18</sub>P<sub>6</sub> core of **23** (Figure 4) resembles the D6R SBU of phosphate materials such as AlPO<sub>4</sub>-18, AlPO<sub>4</sub>-52 SAPO-34, and SAPO-37.<sup>25</sup>

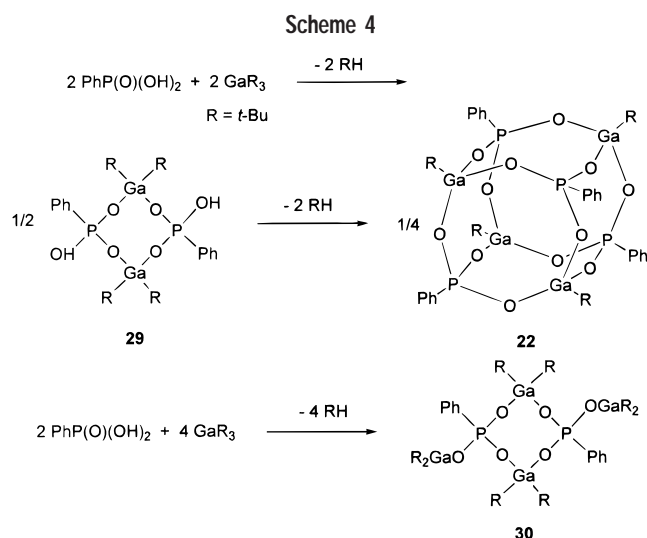
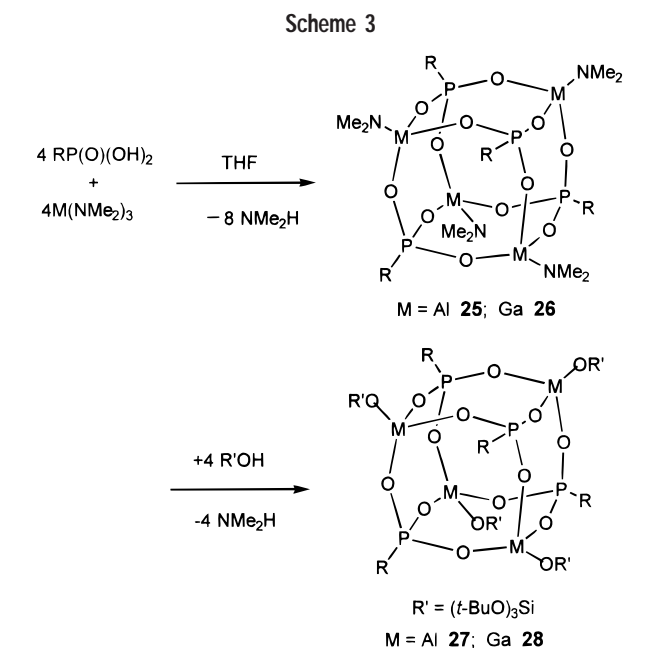
**(c) Functionalized Group 13 Molecular Phosphonates.** The presence of reactive M–C bonds at each of the corners of the cubic polyhedron in principle offers scope for using these compounds as ideal starting materials for the preparation of open framework phosphate materials through cage-fusion reactions or low-temperature sol-gel processes. However, all these compounds despite the presence of these hydrolyzable bonds are stable toward air and moisture and can be left on the benchtop for several weeks without any appreciable decomposition. Hence, reactivity studies were carried out by reacting the B–C bonds in [*t*-BuPO<sub>3</sub>BET]<sub>4</sub> (**3**), and the results reveal that these compounds are stable toward H<sub>2</sub>O, O<sub>2</sub>, ROH, RNH<sub>2</sub>, R<sub>2</sub>NH, etc. However, when **3** was reacted with phenol using diglyme as the solvent (or in the absence of any solvent), a very small amount of reactivity at one of the corner B–C bonds was observed. The resultant monophosphate

**FIGURE 4.**

noxy derivative [*t*-BuPO<sub>3</sub>BET]<sub>3</sub>[*t*-BuPO<sub>3</sub>B(OPh)] (**24**) was formed in less than 5% yield.<sup>19</sup> These experiments clearly demonstrate that although by the virtue of the presence of M–C bonds **1–23** look like functionalized molecules, they are in fact inert under normal conditions.

To obtain really functionalized cubic phosphonates, we reacted the *tert*-butylphosphonic acid with trisamido derivatives Al(NMe<sub>2</sub>)<sub>3</sub> and Ga(NMe<sub>2</sub>)<sub>3</sub> (Scheme 3). The cubic products [*t*-BuPO<sub>3</sub>M(NMe<sub>2</sub>)<sub>4</sub>] (M = Al, **25**; Ga, **26**) obtained by this procedure are highly reactive toward compounds containing acidic hydrogen atoms.<sup>26</sup> For example, they react smoothly with (*t*-BuO)<sub>3</sub>Si(OH) and yield [*t*-BuPO<sub>3</sub>MOSi(O-*t*-Bu)<sub>3</sub>]<sub>4</sub> (**27**, **28**). These compounds would prove very useful starting materials for the preparation of dense-phase silico Al/Ga phosphates under mild conditions through facile elimination of isobutene gas.

While our work was in progress, a few interesting papers related to the synthesis of molecular boron and gallium phosphonates involving bulkier *tert*-butyl groups appeared in the literature. Mason et al. have shown that owing to the bulkiness of the *t*-Bu substituent, it is possible to isolate and structurally characterize the cyclic gallium phosphonate **29** (Scheme 4).<sup>24</sup> Compound **29**, however, on heating in diglyme converts into the cubic phosphonate **22**. Barron et al. have shown that, by doubling the amount of Ga(*t*-Bu)<sub>3</sub>, it is possible to prepare the eight-membered gallium phosphonate ring **30** which contains three-coordinate exocyclic gallium atoms.<sup>27</sup> Kuchen et al.

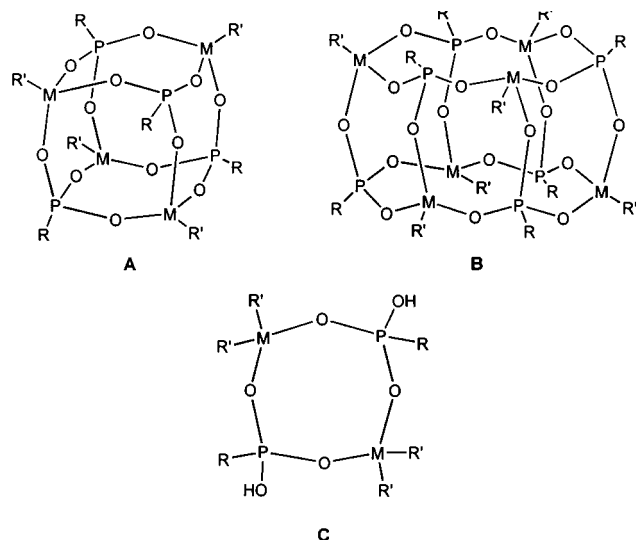


have reported the preparation of  $[\text{t-BuPO}_3\text{BPh}]_4$  (**21**) starting from  $\text{PhBCl}_2$  and  $\text{t-BuP(O)(OSiMe}_3)_2$ .<sup>20</sup>

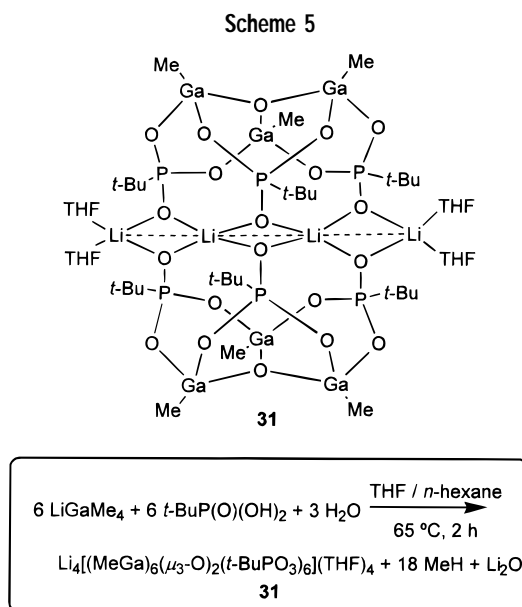
This section can be summarized by stating that the work so far carried out on group 13 phosphonates has resulted in the synthesis of soluble molecular compounds whose polyhedral cores resemble the (i) double-four-ring (D4R or 4-4, **A**), (ii) double-six-ring (D6R or 6-6, **B**), or (iii) single-four-ring (S4R or 4, **C**) SBUs found in zeolites and phosphate molecular sieves (Figure 5). However, it should be noted that, while the D4R SBUs are common among the molecular phosphonates described here, in many 3D framework structures D6R units are more prevalent.

## Group 13 Phosphonates with Alkali Metal Ions

After the success in preparing a multitude of neutral group 13 phosphonates, we wondered about the feasibility of generating anionic group 13 phosphonates which also incorporate different cations within the molecule. We were particularly interested in such molecules because of



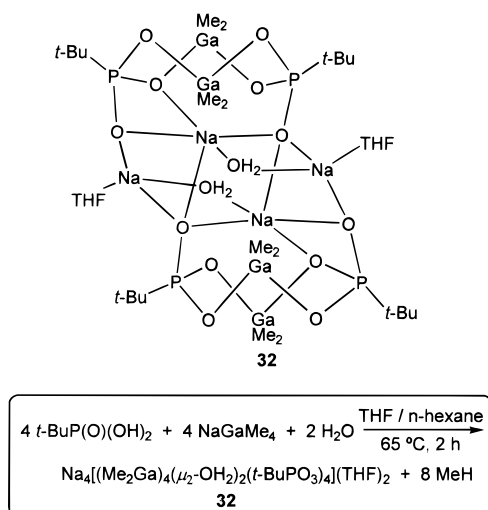
**FIGURE 5.**



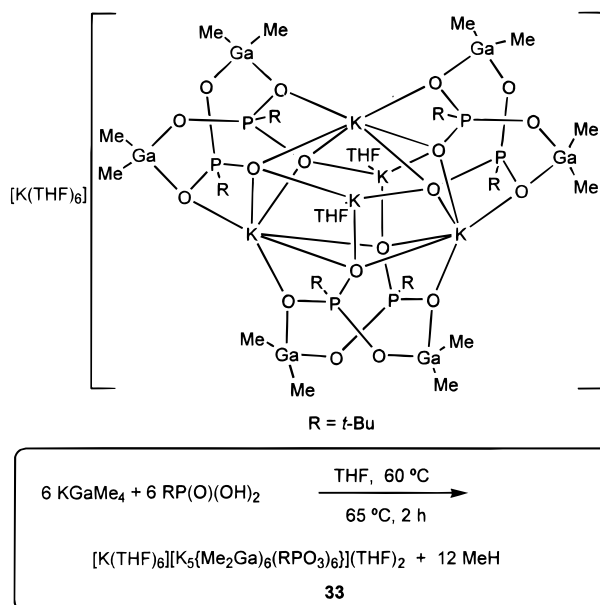
the recent intriguing developments in the area of materials science in the preparation of conductive polymeric materials or metal ions trapped within the channels of zeolites.<sup>28</sup> Alkali metal cations were chosen for these studies because of their monovalency and highly ionic nature which results in weakest covalent bonding interactions with other elements in the periodic table.

**(a) Synthesis and Structure.** To synthesize group 13 phosphonates containing additional metal ions in the framework, previously characterized alkali metal containing precursors  $\text{MGaMe}_4$  ( $\text{M} = \text{Li, Na, or K}$ ) proved to be ideal starting materials. Gallium phosphonate superstructures **31–33** (Schemes 5–7) have been synthesized by simple alkane elimination reactions between  $\text{MGaMe}_4$  and  $\text{t-BuP(O)(OH)}_2$ .<sup>29,30</sup> Compounds **31–33** are air and moisture stable in the solid state. It is of interest to compare some of the structural features and properties of these alkali metal containing gallium phosphonates. In the structures of **31** and **32** there are no cationic or anionic parts, and the molecules are sufficiently covalent. On the

Scheme 6



Scheme 7



contrary, the structure of **33** is highly ionic and contains discrete cationic and anionic parts. Since all three compounds have been synthesized starting from a similar type of gallium source and the same phosphonic acid and under similar reaction conditions, the large variations in the structures of the resultant products could be largely attributed to the relative size of the different alkali metal ions. The presence of smaller four-coordinate lithium ions which form covalent bonds more readily than the sodium and potassium ions results in the formation of larger twelve-membered gallium phosphonate rings with a somewhat open and linear arrangement of the lithium ions in **31** (Figure 6). On the other hand, the larger sodium and potassium cations, which have the ability to extend their coordination sphere, tend to aggregate themselves and form a closed core in **32** and **33**. The more ionic nature of the latter compounds is also reflected in their mass spectra.<sup>30</sup>

**(b) Alkali Metal Ion Abstraction Studies.** The presence

of exposed lithium ions in **31** (Figure 6) prompted us to explore the possibility of abstracting and/or exchanging them with other metal ions. To test the ease of abstracting lithium ions, a benzene-*d*<sub>6</sub> solution of **31** was treated with an excess 12-crown-4 and D<sub>2</sub>O and the changes were followed by NMR spectroscopy (Scheme 8, experiment 1).<sup>29</sup> While the <sup>1</sup>H NMR spectrum indicated that the methyl groups and *tert*-butyl groups on gallium and phosphorus centers remain intact, the single line observed at 33.4 ppm in the <sup>31</sup>P NMR spectrum for pure **31** has completely disappeared with the appearance of a new resonance at  $\delta$  21.9 ppm. Similarly, in the <sup>7</sup>Li NMR the original singlet observed at  $-0.03$  ppm for **31** has completely shifted to 0.33 ppm, revealing that the coordination environment around lithium ions has considerably changed. These multinuclear NMR observations indicate that the lithium ions could have moved out of the molecular framework of **1**, leaving behind a Li-free gallium phosphonate species. Further characterization of this species by EI MS revealed the presence of a cluster ion at *m/e* 869 with an isotope pattern corresponding to a Ga<sub>4</sub>P<sub>4</sub> unit rather than a Ga<sub>3</sub>P<sub>3</sub> unit arising from one of the bowls of **31**. Although this observation was initially puzzling, additional sets of independent experiments showed that the observed peak arises from the loss of a methyl group from the neutral gallium phosphonate [*t*-BuPO<sub>3</sub>GaMe]<sub>4</sub> (**15**).

In the absence of 12-crown-4, a pure sample of **31** was treated with excess D<sub>2</sub>O at 70 °C (Scheme 8, experiment 2). As expected, the <sup>31</sup>P NMR spectrum showed that the conversion of **31** was less than 10%. Subsequent addition of 12-crown-4 showed no change in the conversion pattern. The reduced rate of conversion in this case could be ascribed to the aggregation of molecules of **31** on the sudden addition of a polar solvent such as water.

The core structures of compounds **32** and **33** (Figure 6) also have implications in their attempted alkali metal ion abstraction reactions with crown ethers. While the lithium gallophosphonate **31** undergoes clean and facile *cage-to-cage* conversion in the presence of 12-crown-4, compound **32** (or **33**) when reacted with 15-crown-5 (or 18-crown-6) under similar reaction conditions does not show any new signals, revealing absence of any cation abstraction reaction.<sup>30</sup> The observance of almost no change in the spectra could be due to the location of the Na<sup>+</sup>/K<sup>+</sup> ions well inside the cage structures. Alternatively, this observation could also be ascribed to the rather strong and extensive coordination of the endocyclic gallium phosphonate ring oxygens in **32** and **33**, as in conventional crown ether complexes.

**(c) Sodium Aluminum Phosphonate.** The reactions leading to alkali metal ions containing phosphonates are not restricted to gallium alone. An equimolar reaction between *t*-BuP(O)(OH)<sub>2</sub> and commercially available NaAl-Et<sub>2</sub>H<sub>2</sub> leads to the isolation of large single crystals of **34** (Scheme 9).<sup>31a</sup> This compound is fairly stable toward moisture and air and can be handled on the benchtop for brief periods. The structure of **34** (Scheme 9) is significantly different from gallophosphonates **31**–**33**. The

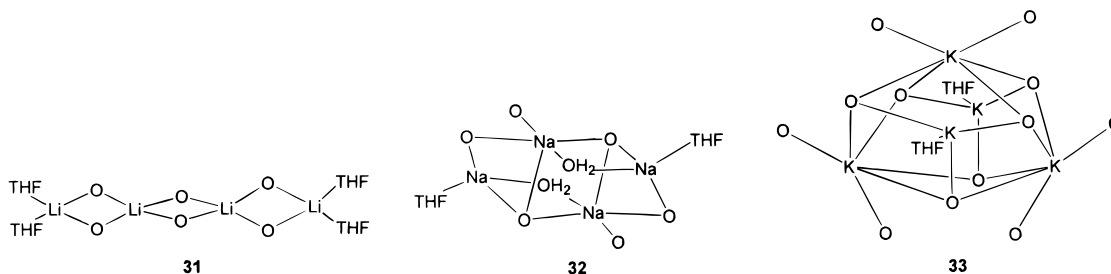


FIGURE 6.

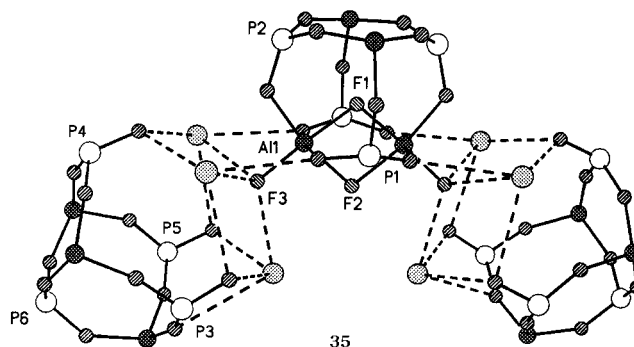
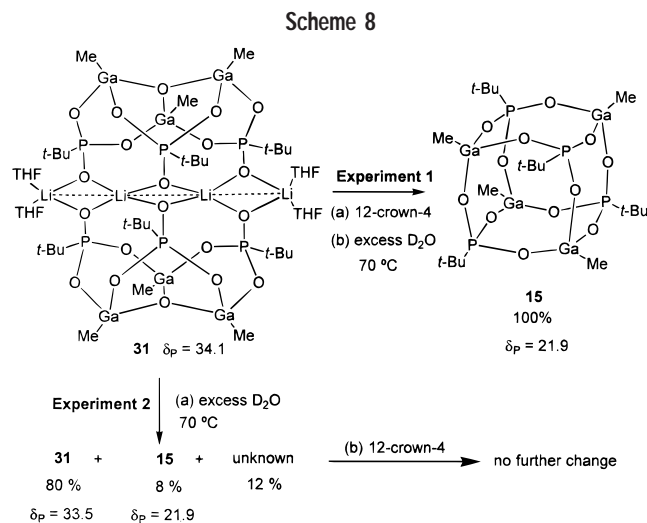


FIGURE 7.

show any interaction with the exocyclic P–O atoms and interact exclusively with the endocyclic oxygen atoms and a solvent THF molecule to result in a heptacoordination with a hexagonal-pyramidal geometry. As a result of the extensive coordination characteristics of exocyclic and endocyclic oxygen atoms, there are two exocyclic  $\mu_4$ -O, four exocyclic  $\mu_3$ -O, two endocyclic  $\mu_4$ -O, and ten endocyclic  $\mu_3$ -O atoms in the molecule. This varied coordination behavior is also reflected in a variety of X–O (X = P, Al, or Na) distances in the molecule.

**(d) Cesium Aluminum Phosphonate.** The initial limitations in finding suitable starting materials for the preparation of heavier alkali metal ion containing group 13 phosphonates have been overcome by the use of fluoride-stabilized binary aluminum alkyl compound Cs-[*i*-Bu<sub>3</sub>AlF]. An equimolar reaction between Cs-[*i*-Bu<sub>3</sub>AlF] and *t*-BuP(O)(OH)<sub>2</sub> results in the formation of [Cs<sub>3</sub>-(THF)<sub>3</sub>F(*i*-BuAl)<sub>3</sub>(*t*-BuPO<sub>3</sub>)<sub>4</sub>]<sub>2</sub>[(*i*-BuAl)<sub>2</sub>Al<sub>2</sub>F<sub>2</sub>(*t*-BuPO<sub>3</sub>)<sub>4</sub>] (**35**) (Figure 7), which contains two tricyclic capped six-ring SBUs (C6R or 6≡1) and a central cube type unit incorporating terminal and bridging fluorides.<sup>31</sup>

## Titanophosphonates

Efforts to incorporate titanium centers inside zeolite matrixes have been of paramount importance owing to the proven utility of Ti-doped zeolite materials as catalysts in many commercially important organic transformations. In the past few years, several workers have succeeded in stabilizing titanium centers in different coordination and site environments inside zeolite-like matrixes and used them as catalysts.<sup>32</sup> Our principal interest in this area is to synthesize molecular and soluble titanosilicates/titano-

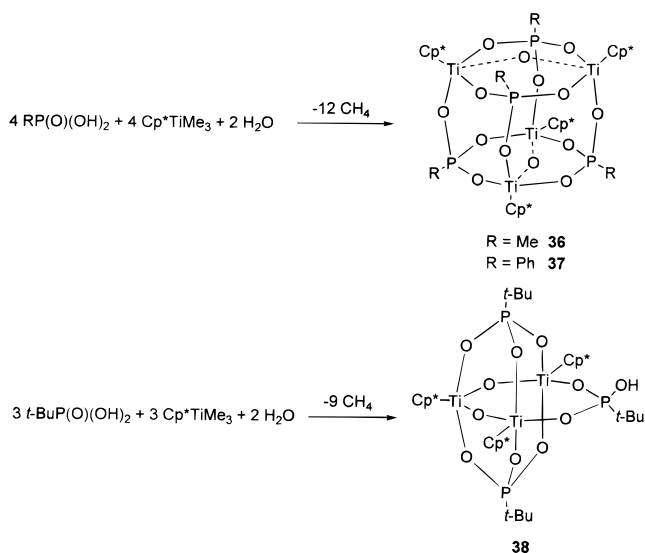
34

**Scheme 9**

$6 \text{ NaAlEt}_2\text{H}_2 + 6 \text{ } t\text{-BuP(O)(OH)}_2 \longrightarrow 34$

molecule contains two twelve-membered rings in the form of trinegatively charged aluminophosphonate crowns [(*t*-BuPO<sub>3</sub>AlEt<sub>2</sub>)<sub>3</sub>]<sup>3-</sup> which bind to six Na<sup>+</sup> ions through varied modes of P–O coordination. The six Na<sup>+</sup> ions in the molecule can be classified in three types: (a) The two central tetracoordinated Na<sup>+</sup> ions which are bound to the aluminum phosphonate rings only through the exocyclic P–O bonds and show no interaction to the endocyclic oxygen atoms. (b) The two Na<sup>+</sup> ions which exist in the proximity of the first type of ions which are also tetracoordinated. However, apart from the three exocyclic P–O coordination bonds, these atoms are also bound to the aluminophosphonate rings through an additional Na–O bond to the one of the endocyclic oxygen atoms. (c) The two peripheral Na<sup>+</sup> ions show a completely different and novel type of coordination behavior. These ions do not

Scheme 10



phosphonates which could serve as models for many of the heterogeneous Ti-doped catalytic materials. Our recent experience in the synthesis of a multitude of soluble titanosilicate molecules<sup>33</sup> prompted us to explore the possibility of synthesizing molecular titanophosphonates which would model many Ti-containing zeolite-like materials.

The synthesis of titanophosphonates **36–38** has been achieved by the reactions between  $\text{Cp}^*\text{TiMe}_3$  and phosphonic acids  $\text{RP(O)(OH)}_2$  ( $\text{R} = \text{Me, Ph, or } t\text{-Bu}$ , Scheme 10).<sup>34,35</sup> While compounds **36** and **37** are made up of a bicapped cubic  $\text{Ti-O-P}$  framework, compound **38** contains a basket-shaped core structure. The observed difference in the structures of these products could largely be attributed to the bulkiness of the organic substituent on the phosphorus atom. In the structure of **36** and **37**, a  $\text{Ti}_4\text{O}_{12}\text{P}_4$  polyhedron can be defined as the central core which is best described as a highly distorted bicapped cube.<sup>34</sup> The periphery of this polyhedron is surrounded by hydrophobic pentamethylcyclopentadienyl and methyl/phenyl groups. A striking feature in the molecular structure of **36** and **37** is the presence of the Ti centers in a distorted square-pyramidal coordination geometry. The occurrence of square-pyramidal geometry around the titanium centers in titanosilicates and -phosphates is a rare phenomenon. The only structurally characterized synthetic titanosilicate with Ti centers in square-pyramidal geometry was recently reported by Thomas et al.<sup>36</sup> To our knowledge, these compounds represent the first examples of soluble titanophosphonates that contain distorted square-pyramidal Ti centers. Compound **38** is made up of a central  $\text{Ti}_3\text{O}_{10}\text{P}_3$  unit which displays a basket-shaped polyhedron. Although the Ti atoms in **38** are pentacoordinated as in **36**, the coordination geometry around all Ti centers is trigonal-bipyramidal.

Thus, the use of organometallic precursor  $\text{Cp}^*\text{TiMe}_3$  and phosphonic acids as starting materials yields titanophosphonates with different polyhedral frameworks, complementing our results in titanosilicate chemistry. These molecules can be considered as SBUs for the

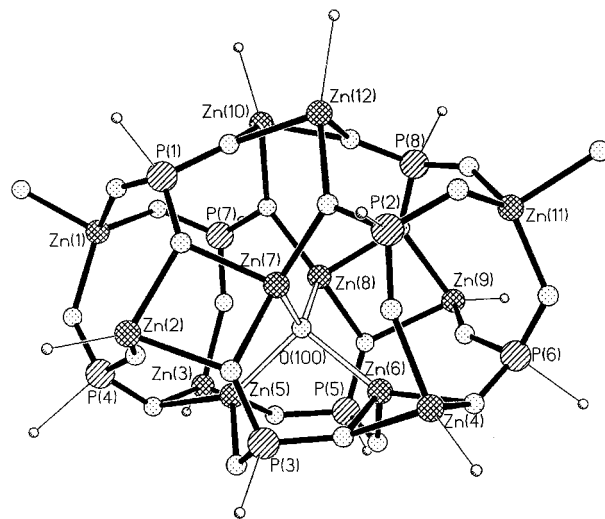
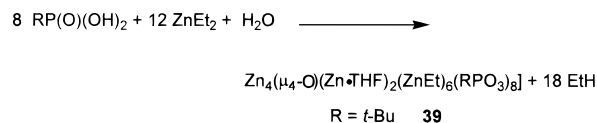


FIGURE 8.

Scheme 11



eventual preparation of solid-state titanophosphate materials by hydrothermal or sol-gel routes.

## Other Soluble Phosphonates

The alkane elimination reaction can in principle be extended to group 12 alkyls. For example, a facile  $\text{C}_2\text{H}_6$  elimination reaction between  $\text{ZnEt}_2$  and  $t\text{-BuP(O)(OH)}_2$  results in well isolated yields of the organozinc phosphonate  $[\text{Zn}_4(\mu_4\text{-O})(\text{Zn}\cdot\text{THF})_2(\text{ZnEt})_6(t\text{-BuPO}_3)_8]$  (**39**) (Scheme 11).<sup>26</sup> Compound **39**, one of the largest molecular organometallophosphonates so far synthesized, contains an oval (or rugby ball) shaped core which is made up of 12 zinc atoms, eight  $t\text{-BuPO}_3$  moieties, and a quadruply bridging  $\text{O}^{2-}$  ion (Figure 8). This core is covered by a sheet of hydrophobic groups such as ethyl and *tert*-butyl groups and THF molecules.

In a closely related work, Tilley and co-workers have reported the synthesis of new and interesting organozinc phosphates  $[\text{Zn}_4(\mu_4\text{-O})\{\text{O}_2\text{P}(\text{O}i\text{-Bu})_2\}_6]$  (**40**) and  $[\text{Zn}\{\text{O}_2\text{P}(\text{O}i\text{-Bu})_2\}_2]_n$  (**41**) starting from  $\text{ZnEt}_2$  and  $[(t\text{-BuO})_2\text{P(O)}(\text{OH})]$ .<sup>37</sup> Compound **40** is found to be thermally labile due to the presence of *tert*-butoxy groups and eliminates isobutene at low temperatures to convert into ceramic materials  $\alpha\text{-Zn}_2\text{P}_2\text{O}_7$  and  $\beta\text{-Zn}(\text{PO}_3)_2$ .<sup>37</sup> Similarly the polymer **41** can be pyrolytically converted into  $\beta\text{-Zn}(\text{PO}_3)_2$ . Several vanadium phosph(on)ate cages have been synthesized by the groups of Zubieta<sup>8a</sup> and Thorn,<sup>38</sup> and a few of these compounds have been found useful in oxidation reactions of dienes. Mention also should be made of the work of Holmes on the phosphinate clusters of tin.<sup>39</sup>



## Outlook

The focus of the work reported herein has been on the synthesis of model compounds for phosphate materials starting from commercially available phosphonic acids and simple organometallic precursors. A more general extension of this work would be using the synthetic approach demonstrated here in the synthesis of phosphonates/phosphates involving late transition metals and rare earths. Especially interesting would be the synthesis of more soluble models for vanadium phosph(on)ates in light of their use as oxidation catalysts. Further modification of the alkyl substituents on the metal precursors could give rise to a variety of model compounds as well as SBUs in the synthesis of silicates and phosphate-based zeolites.

It is expected that there will be more reports in the coming years on soluble models for silicate and phosphate materials by using simple organometallic reactions. We hope that this Account will kindle the interest in this area among other researchers and contribute to the better understanding of metal phosphate chemistry in the future.

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